

**Design Strategy of Planar Azapyrene-
Based Covalent Organic Frameworks:
Exploring the Electronic Properties of 2D
and 1D Structures**

Li Zhuowei

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Preface

Covalent Organic Frameworks (COFs) are crystalline porous polymers made from covalently bonded organic building blocks, providing high chemical stability and a structure that enables dense π -plane stacking. This structure leads to high crystallinity and large crystal domains, reducing vibrational scattering of charge carriers. Two-dimensional (2D) COFs, with their unique π - π stacking and large conjugated domains, exhibit efficient vertical charge transport. However, most COFs show lower-than-expected charge mobility due to defects or small crystal domains. Theoretically, 2D COFs can expand into one-dimensional (1D) nanotube structures, which would enhance charge transport and minimize carrier transport defects.

Therefore, this thesis designs a nitrogen-doped pyrene by replacing the carbon atoms at the 2,7 positions of the pyrene skeleton with nitrogen atoms, limiting the rotational angle of the terminal 4-amino phenyl groups to reduce the interlayer distance and enhance crystallinity and transport capacity. Utilizing this nitrogen-doped pyrene structure, a novel type of intermolecular electron conjugation can be achieved, which differs from traditional π -conjugated systems, enabling electron conjugation through spatial interactions. Furthermore, the tubular nitrogen-doped pyrene obtained by rolling the 2D COF may form stable electronic conduction pathways in air, and stable charge carrier doping can be achieved through the nitrogen centers of the nitrogen-doped pyrene, leading to high electrical conductivity and proton conductivity.

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General Introduction

In the 1990s, researchers first reported the discovery of metal-organic framework materials (MOFs), which sparked widespread interest in the novel concept of "reticular chemistry" in material construction. Building on this concept, Professor Omar M. Yaghi's group at the University of California, Berkeley, synthesized and introduced covalent organic frameworks (COFs) for the first time in 2005. The Yaghi' group designed a two-dimensional (2D) COF material based on boronic acid monomers, named COF-1.^[1]

COF-1 is formed through a dehydration condensation reaction that connects boronic acid and diol molecules into a covalent organic network. In this process, organic molecules are linked together via covalent bonds, resulting in a highly ordered and stable channel structure. As a new class of porous framework materials following metal-organic frameworks, COFs have a framework structure formed by light elements such as carbon (C), boron (B), nitrogen (N), and oxygen (O) that are connected in an ordered manner through strong covalent bonds, creating a periodic network structure. This gives COFs certain advantages over other crystalline materials (such as zeolites, boron nitride, perovskites, and MOFs), including a large specific surface area, low density, regular pore structures, and ease of modification.

Another attractive feature of COFs is their predictable structure. The organic units are arranged in specific spatial directions and extend into three-dimensional space through covalent bonds, allowing for tunable pore sizes and shapes, thereby showcasing a rich structural diversity. Furthermore, the stability of the covalent bonds imparts unique properties to COFs, such as high thermal stability and good chemical stability. These advantages have led to the widespread application of COFs in various fields, such as adsorption,^[2-6] catalysis,^[7-11] energy storage,^[12-17] and biomedical sciences.^[18-23]

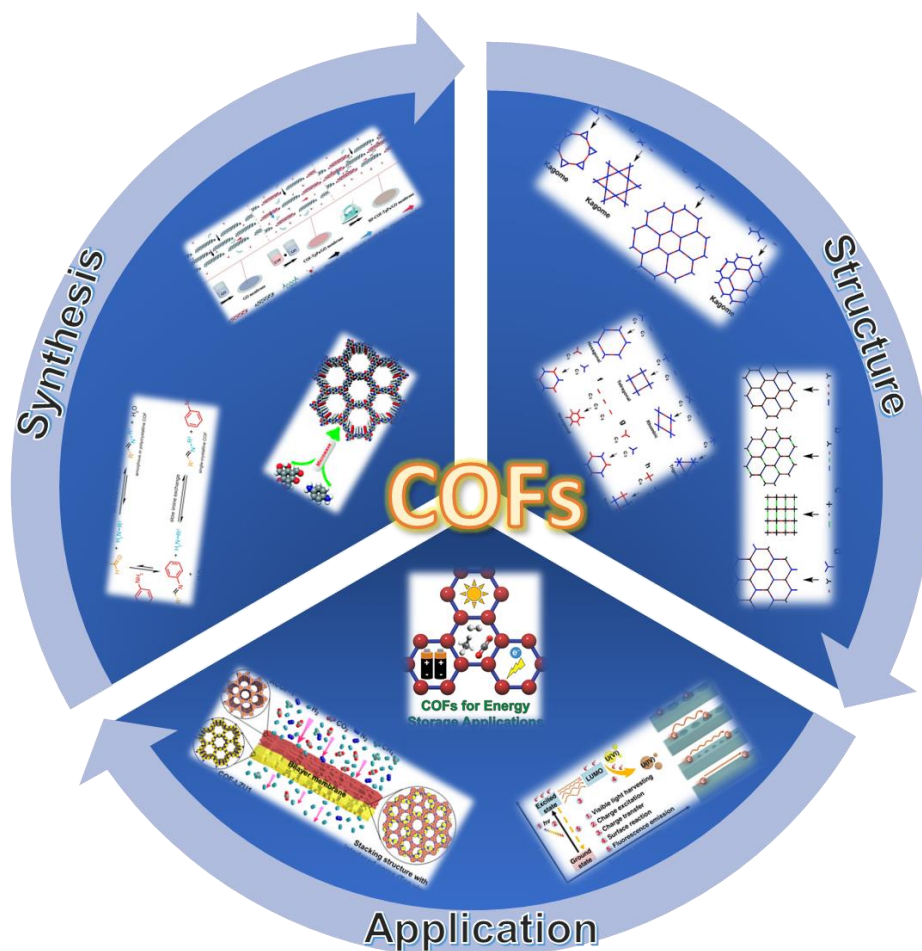


Figure 1. Recent advances in COF-based framework: synthesis^[4, 24, 25], structure^[26], and application.^[6, 9, 13, 27]

1. Development of 2D imine-based COFs

Unlike 1D and 3D COFs, 2D COFs have a unique layered structure that forms periodic columnar π arrays and independent 1D channels. This results in the crystallinity of 2D COFs being governed by covalent bonds in the planar direction, while the interlayer interactions rely on non-covalent forces such as π - π stacking, hydrogen bonds, and van der Waals forces. Yaghi and his collaborators pointed out, “All COFs are 3D materials, but their covalent connectivity can be 3D, 2D, or even 1D. In COFs whose connectivity extends in three dimensions, the crystallinity of the system is almost exclusively a result of the order imposed

by the linkage. In layered materials where covalent connectivity extends only in 2D, however, noncovalent interactions play a key role.”^[28] As a result, 2D COFs offer improved accessibility to reaction sites, and the π -orbital overlap provides additional driving force, making it easier to obtain highly crystalline products.^[29] This gives 2D COFs a synthetic advantage over other dimensional COFs. As a result, most current research focuses on 2D COFs.

Most 2D COFs are synthesized using dynamic covalent chemistry (DCC), where molecular units are connected into extended structures through reversible covalent bonds, as Figure 2 shows. The formation of an ordered framework requires these reversible or rearrangeable bonds to allow for error correction, providing ample opportunities for structural proofreading. Under solvothermal conditions, these reversible covalent reactions offer the necessary flexibility for error correction and have been successfully applied in the synthesis of most 2D COFs reported to date.^[30]

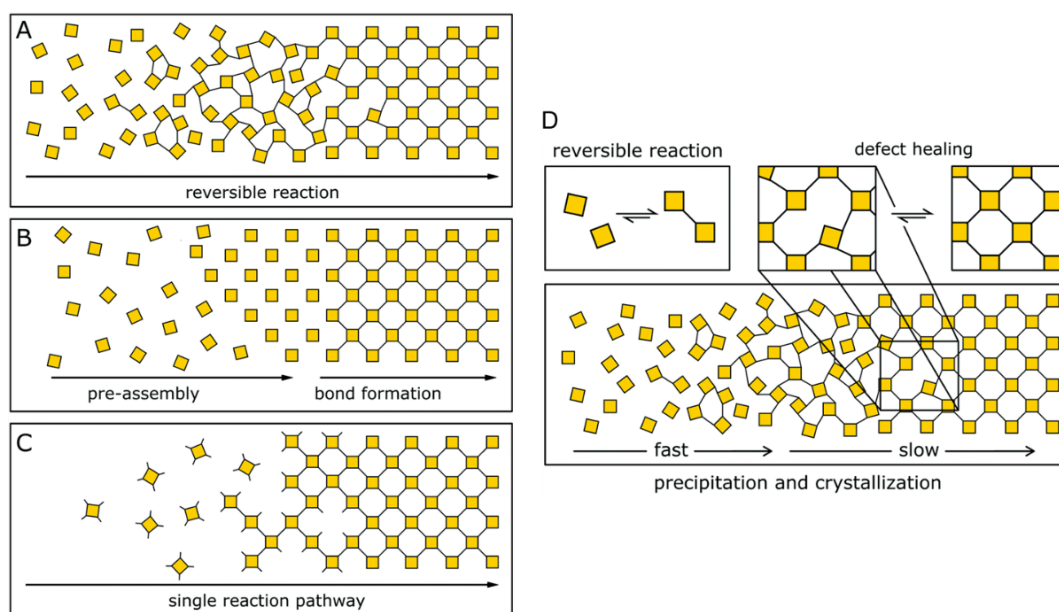


Figure 2. Three approaches to forming a crystalline covalently bound polymer: (A) reversible reactions; (B) pre-orientation; (C) single reaction pathway. (D) Reversible COF formation by slow crystallization. First, an amorphous gel is formed that then slowly crystallizes. This crystallization mechanism corresponds to the formation of imine COFs.^[30]

On the other hand, although COFs exhibit significant thermal stability and structural rigidity in diverse chemical environments, including organic solvents, they are still prone to hydrolysis and decomposition. This susceptibility stems from the production of water as a byproduct during the reversible reactions that create COFs. According to Le Chatelier's principle, an excess of water in the reaction medium favors the reverse reaction resulting in the breakdown of COFs. This is especially relevant for boronate and borate ester COFs, which generally experience structural degradation when they come into direct contact with moisture or water. As a result, stability concerns need to be resolved before COFs can be utilized in many practical applications. In 2011, the Yaghi's group synthesized a high-charge mobility 2D Imine COF (COF-366) using terephthalaldehyde and 5,10,15,20-tetra(4-aminophenyl)porphyrin as monomers through a Schiff base reaction. This COF, which integrates thermal stability, conductivity, high charge mobility, and porosity, marks the major advancement in the COFs field, demonstrating that COFs can be constructed using imine linkages (C=N).^[31]

Due to the ability to create porous crystalline COFs with both thermal stability and chemical stability, imine-based COFs have gradually become the focus of research. Studies have shown that imine COFs are less prone to hydrolytic decomposition because their synthesis requires only a small amount of acid catalysis and is produced through pH-induced reversible reactions. Imine COFs are mainly created through the condensation of aromatic amines and aromatic aldehydes, facilitated by organic acids or Lewis acids as catalysts. Compared to boron-based COFs (which have simple synthesis methods but are easily hydrolyzed) and triazine-based COFs (which have good thermal stability but require harsh synthesis conditions and are limited to ionothermal methods), imine COFs exhibit good chemical and thermal stability, milder synthesis conditions, and diverse synthesis methods (including solvothermal, microwave, mechanical grinding, room temperature, and interfacial synthesis methods). They can also remain stable in commonly used organic solvents, water, and even strong acid or base solutions. Consequently, due to their extremely high surface area, nanoscale pores, high porosity, and excellent physicochemical stability, imine COFs have become one of the most widely studied classes of COFs.

In 2011, the Wang Wei's group reported the synthesis of COF-LZU-1, which is linked by an aldehyde-amine connection derived from the condensation of paraformaldehyde and para-phenylenediamine. They also applied it in the catalysis of the Suzuki-Miyaura coupling reaction. This marked the first time that a porous COF material was used as a catalyst support in heterogeneous catalysis, which is one of the most widely explored fields for COF applications today. [32]

In 2012, Banerjee's group synthesized two highly thermally and alkali-stable 2D Imine COFs—TpPa-1 and TpPa-2 which using para-phenylenediamine, 2,5-dimethyl-1,4-phenylenediamine, and 1,3,5-tris(aldehyde)phenol as monomers based on keto-enol tautomerism. Their unique lamellar structure can serve as a carrier for doping with nanoparticles, enriching the application prospects in the field of catalysis. [8]

In 2016, the Zhao Xin's group synthesized a series of 2D Dual-Pore Imine COFs, SIOC-COF-5, and SIOC-COF-6 with a dual-pore structure, as well as SIOC-COF-1 and SIOC-COF-2 with a tri-pore structure by selecting symmetrical monomers. The development of these porous COFs materials provides greater flexibility and selectivity, creating a platform to accommodate more complex reaction systems. [33] At the same year, the Zhang Fan's group reported the first stable COF connected by carbon-carbon double bonds, namely 2DPPV. The arrangement of the carbon-carbon double bonds with the π - π conjugation of the phenyl rings in the COF backbone provides this material with enticing prospects for applications in the optoelectronic field. Moreover, carbon-carbon double bonds exhibit greater stability compared to the widely used imine-linked COFs, and the remaining cyano groups at the edges provide significant potential for future modifications. This work was published in the specialized journal Polymer Chemistry and undoubtedly marks a significant breakthrough in the connection types of COFs and the history of COF development. [34] In 2016, Rahul Banerjee's group also made the breakthrough by developing high-flux distillation membranes with vertically aligned channels and hydrophilic gradients. Using a simple molecular precursor baking strategy, they successfully fabricated self-supporting COF membranes that demonstrated excellent flexibility, continuity, and long-term stability and were free from internal defects or cracks. Furthermore, these membranes are recyclable. The simplicity of

the fabrication process, combined with the membranes' processability and mechanical stability, marked a major step forward in the practical application of COF materials.^[35]

In 2017, Jiang Donglin's group also reported a similar COF connected by carbon-carbon double bonds: sp^2c -COF. They fully described the basic characteristics of this totally sp^2c conjugated COF about magnetism and free radicals.^[36]

In 2022, Austin M. Evans' research group utilized a nitrile-containing solvent and aniline as a monofunctional modulator for polymerization. Benzoic acid was used in a catalyst to fix structural flaws so that a single-crystalline of imine-linked 2D COF (TAPPy-PD) with a size of 5 minutes could be synthesized using a micron-sized method. The COF was also shown to be more effective because of this development, which also allowed for improved reaction mechanism interpretation.^[37]

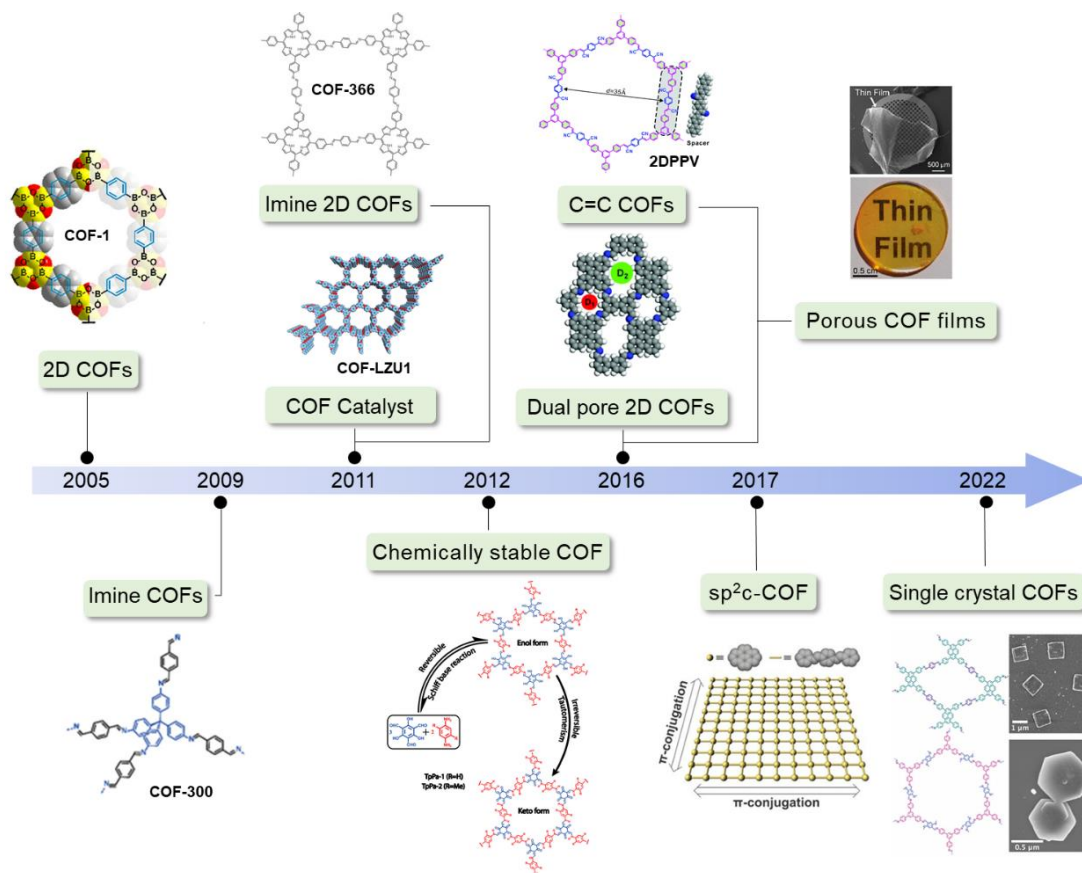


Figure 3. The important evolution of COFs, in particular of 2D imine COFs.^[1, 8, 31-38]

Despite the rapid development of 2D COFs over the past decades and the significant advancements in their structure, morphology, and applications, the electrical performance still lags behind that of organic molecules and polymer-based semiconductors. Future progress is focused on the design of high-mobility building blocks, the optimization of bonding within planar conjugated network structures, and refining the growth dynamics of crystalline structures.

2. Topological design of 2D COFs

COFs are a type of fully pre-designed polymer created through a synthesis process that combines topological diagram-directed polymer growth with geometric matching of monomers. This molecular design principle is fundamentally different from that of linear polymers, allowing us to achieve unprecedented capabilities in the pre-design of both primary and advanced structures.

Moreover, COFs are characterized by unique conformations and morphologies, enabling them to interact with photons, excitons, electrons, holes, spins, ions, and molecules within a limited molecular space and interface. This interaction creates new molecular platforms for structural design and functional development.

2.1 Single pore 2D COFs

2D COFs exhibit a variety of topological structures, which can be categorized into single-pore 2D COFs and hierarchically porous 2D COFs based on pore size. So far, the reported topological structures of 2D COFs mainly encompass hexagonal, triangular, rhombic, and rectangular forms, with the corresponding structural unit symmetries being mainly C_2 , C_3 , C_4 , C_6 , and C_n types.

As Figure 4 shows the hexagonal topology leverages the diversity of C_3 - and C_2 -symmetric monomers, while the tetragonal topology is derived from C_4 - and C_2 -symmetric monomers. The rhombic topology is achieved by lowering the symmetry from C_4 to C_2 . Designing microporous COFs with pore sizes less than 2 nm has long posed a challenge; however, the introduction of triangular topology (as shown in the $[C_6+C_2]$ diagram) has made the predesign of microporous frameworks possible.^[39]

2.2 Hierarchically pore 2D COFs

Furthermore, a dual-porous framework with a Kagome lattice has been developed for the first time by combining C_3 -symmetric macrocyclic nodes with C_2 -symmetric linkers. This structure features a central octagonal mesopore surrounded by six triangular micropores.^[40] In addition to diamond topologies, the $[C_2+C_2]$ arrangement can also form Kagome

frameworks (Figure 4i, j).^[41] Besides, tribranch structures with C_2 or C_3 symmetric units can combine with C_2 symmetric units to construct a Kagome structure characterized by a central hexagon surrounded by six irregular hexagons (Figures 4k, l).^[42, 43]

On the other hand, to overcome the limitation of most COFs being based on a single type of linkage, researchers have explored a dual-stage strategy using C_1 -symmetric monomers. These monomers contain two distinct reactive groups that do not interact with one another. By designing systems such as $[C_3+C_3+C_1]$ ^[44] and $[C_4+C_4+C_1]$ ^[45], a variety of frameworks with different linkages (including hexagonal, tetragonal, and rhombic) can be generated, thereby increasing the complexity and diversity of the structures.

2.3 Multi-component design strategy of 2D COFs

By utilizing a multi-component design approach that integrates C_3 -symmetric knots with C_2 -symmetric linkers, diverse and complex hexagonal and tetragonal frameworks can be constructed, providing a structural basis for specific interactions. The framework displays anisotropic structures within the [1+2] three-component system, resulting in tetragonal frameworks characterized by anisotropic tiling and rectangular pores. The four-component system, designated as [1+3] can be created by combining a C_3 -symmetric knot with three distinct C_2 -symmetric linkers. This four-component system integrates linkers of varying lengths and functions, enabling the further design of complex structures (Figure 4p-s).

Theoretically, one knot and ten linkers can yield 210 different COFs, significantly enhancing the diversity and structural complexity of COFs.^[46]

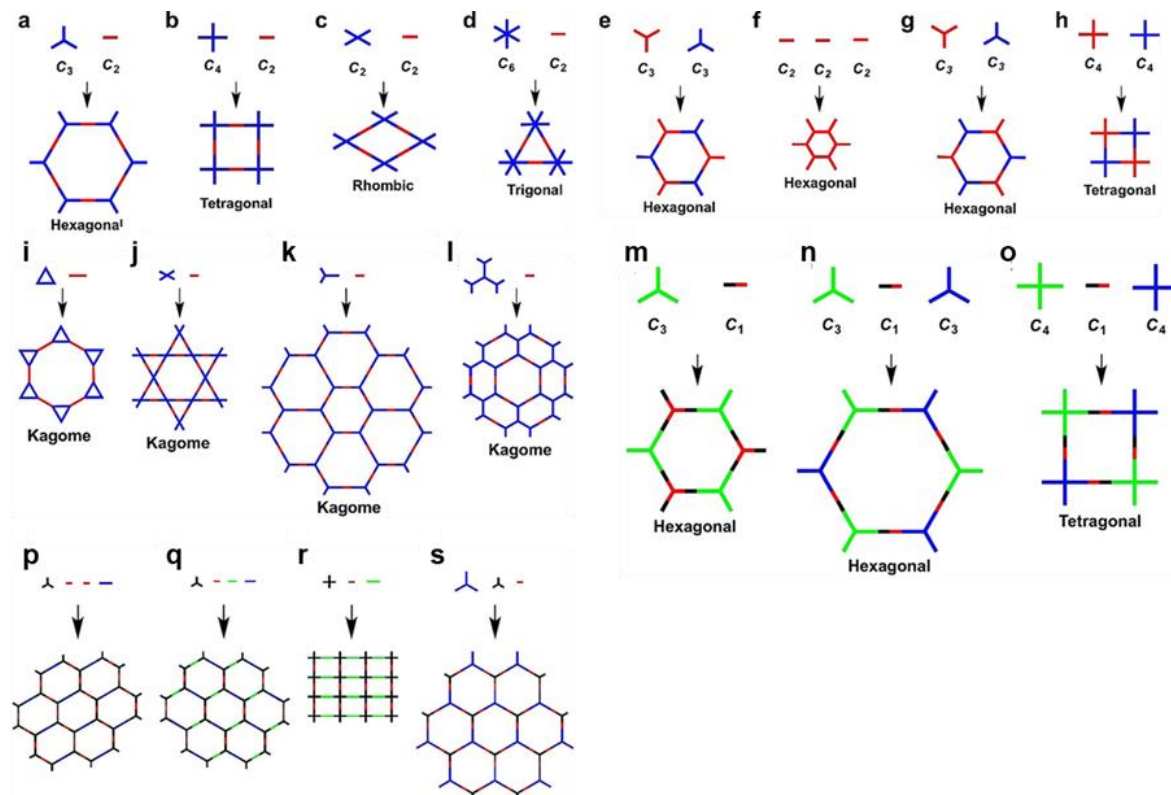


Figure 4. Topological design of 2D COFs.^[26]

2.4 Functionalization of 2D COFs

It is worth noting that, as research into COF structures advances, the functionalization of COF materials has become a key consideration in structural design. One of the main features of COF materials is the presence of various functional groups, which enable different applications based on the specific functionalities of these groups. Currently, two primary strategies for COF functionalization have been reported. The first involves selecting building units with targeted functional groups and directly synthesizing COFs with these groups through covalent bonding—this is known as the direct modification method. The second approach, called post-synthetic functionalization, entails synthesizing COFs with modifiable groups and then introducing the desired functional groups via subsequent modification

reactions (Figure 5). Functionalization is necessary for bringing COF materials closer to practical applications, as it allows for the grafting of specific functional groups onto the COF framework, fully leveraging the advantages of COFs as porous materials.

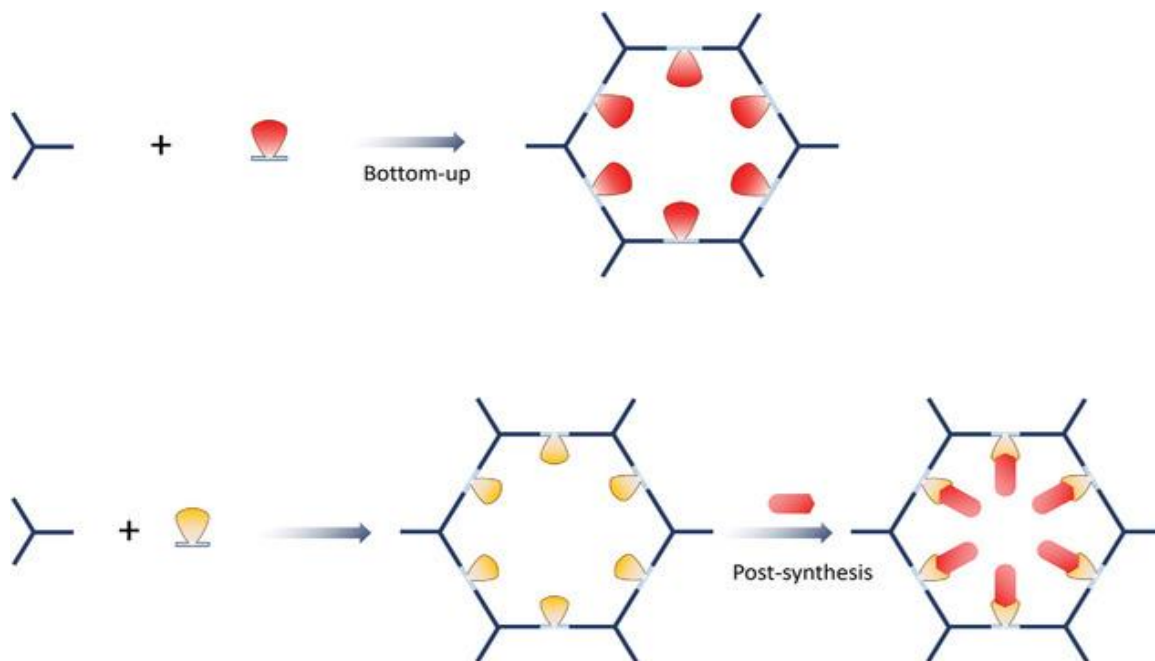


Figure 5. The two strategies for introducing functional groups into COF structures are bottom-up synthesis and post-synthesis modification.^[24]

3. The crystallinity of COFs

One key feature of COFs is their crystalline structure. Highly crystalline COFs possess fewer defects, resulting in a significantly reduced number of trap sites.^[47] High crystallinity in COFs not only aids in the precise determination of structural parameters such as pore size, atomic positions, bond lengths, and angles,^[48] but also significantly enhances their performance in areas like photocatalysis,^[49] energy storage,^[50] and electronics. However, achieving high crystallinity or single-crystal COFs poses a substantial challenge, as the covalent bonds in COFs exhibit lower reversibility, often even irreversibility, compared to the coordination bonds and hydrogen bonds found in metal-organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs).

3.1 Factors affecting crystallinity of COFs

Crystallinity, stability, and functionality are often competing characteristics.^[30] There is an inverse relationship between crystallinity and stability, as the synthesis of high-crystallinity and porous COFs relies on the reversibility of condensation reactions. This reversibility allows structural defects to be repaired during the assembly of building blocks through the continuous formation and cleavage of chemical bonds. However, there exists a trade-off effect between the crystallinity of COFs and bond energy: under thermodynamic control, stronger chemical bonds accelerate the reaction rate, leading to increased structural disorder and making it more difficult to repair defects, ultimately affecting crystallinity and possibly resulting in an amorphous structure. In 2008, Arne Thomas's group produced covalent triazine frameworks (CTFs) by trimerizing nitriles, leading to the creation of CTF-1. Most of these COFs were produced using ZnCl_2 as a catalyst under high temperatures (around 400°C).^[51] While these frameworks exhibit excellent stability, their crystallinity is often poor due to the condensation of nitrile groups, which has limited the development of CTFs. In 2018, Wei Wang's group, in collaboration with Junliang Sun and Omar Yaghi, achieved a breakthrough by growing large, single crystals of three-dimensional COFs with imine linkages and successfully determining their structure via single-crystal X-ray diffraction (SXRD).^[48] While previous studies had reported single crystals with nitroso linkages^[52] and structures determined through electron diffraction,^[53] this work introduced a more versatile and practical approach by adding competitive modulators and nucleation inhibitors. Given that imine-linked COFs are among the most widely used COFs, the successful construction of single-crystal imine COFs marks a significant advancement, establishing a strong basis for the practical use of highly crystalline COFs.

Furthermore, crystallinity and stability may compete with functionality. Stability needs to be assessed in the context of the operating temperature and conditions of the target application. If the working conditions of a material are significantly milder than those applied during its synthesis, then the impact of reversibility during synthesis on stability is minimized. However, synthesizing stable COFs through reactions that are only reversible at higher temperatures or under harsher conditions restricts the range of functional groups and

functionalities that can be included in the COFs, as these groups may undergo chemical or thermal decomposition during the synthesis process. [30]

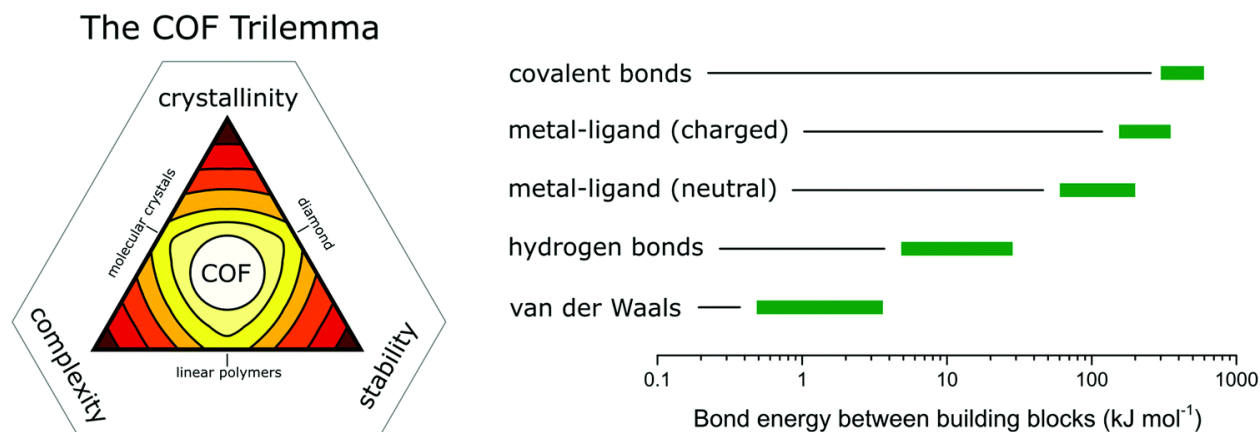


Figure 6. The trilemma of materials design for COF synthesis based on reversible reactions (left). Strengths of bonds that are used for the synthesis of molecularly defined materials (right). [30]

3.2 Design strategies for improving the crystallinity of COFs

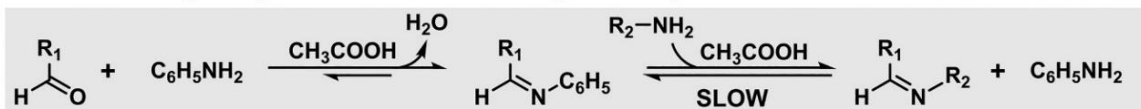
In recent years, researchers have proposed various strategies to enhance the crystallinity of COFs. These strategies can generally be divided into two primary approaches optimizing the polymerization reaction process and improving intermolecular or intramolecular interactions. [54]

In terms of reaction conditions, common methods for enhancing the crystallinity of COFs include acid or base catalysis, the addition of modulators, and controlling the rate of monomer addition. A slow addition of monomers can effectively reduce the nucleation and crystal growth rates, leading to the formation of highly crystalline COFs. For instance, Matsumoto et al. replaced traditional acetic acid catalysts with Lewis acidic metal trifluoromethanesulfonates. Compared to conventional acid-catalyzed methods, which often require high temperatures and extended reaction times, this approach accelerated the formation and exchange of imines, enabling the successful synthesis of highly crystalline TAPB-PDA COF within minutes at room temperature. [55]

Moreover, the introduction of modulators during the condensation reaction can compete with monomers, slowing down the formation rate of COFs and allowing sufficient time for self-healing of defects. Calik et al. selected 4-mercaptopbenzeneboronic acid (MPBA) as a modulator and, under optimized conditions, achieved crystal domains of several hundred nanometers in the boronate ester-linked COF-5.^[56]

Notably, in 2024, Wang Wei's group successfully obtained COF single crystals with dimensions up to 150 micrometers by employing strong acid catalysts alongside compatible modulators within just 1 to 2 days. The quality of these single crystals was exceptionally high, with a structural resolution of 0.79 Å determined using laboratory SXRD. This achievement challenges the conventional notion that the growth of single-crystalline COFs requires prolonged crystallization periods, which typically take at least 15 days for detectable single crystals.^[25]

A Growth of single-crystal COFs in 15–80 days in the previous work



B Fast growth of single-crystal COFs in 1–2 days in this work

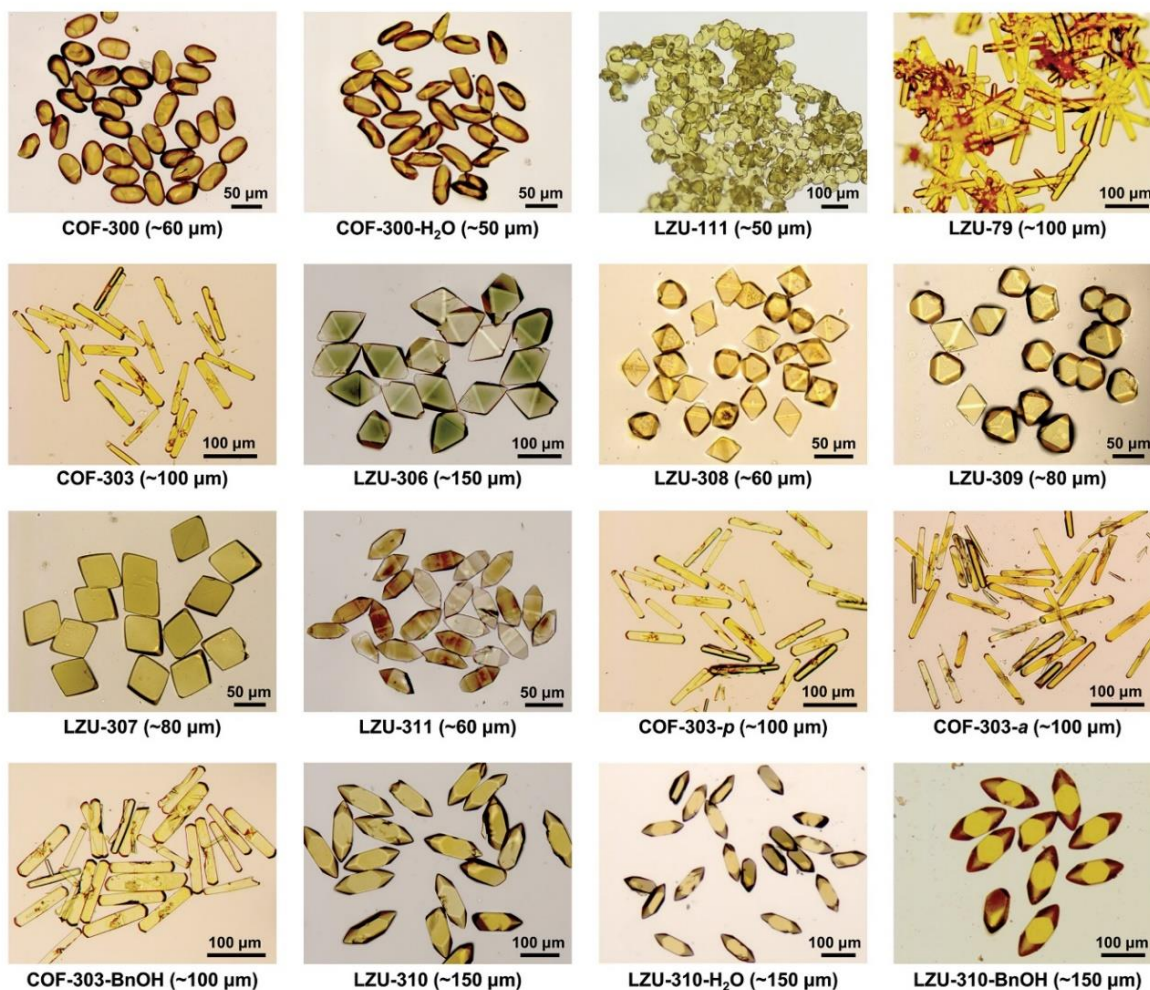
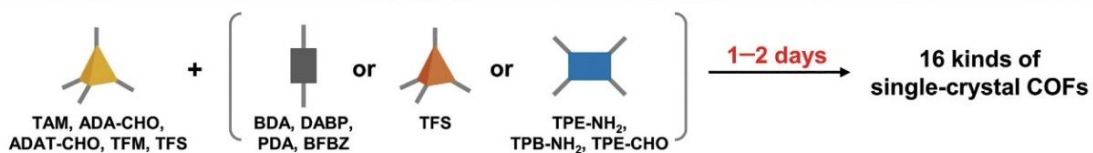
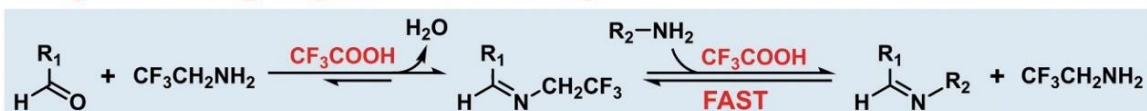


Figure 7. The fast growth of large-sized single-crystal COFs.^[25]

In terms of intermolecular π -stacking interactions in 2D COFs can also be enhanced through hydrogen bonding and fluorine substitution. Banerjee's group created a 2D porphyrin COF (DhaTph) that features --OH units capable of forming intramolecular $\text{O--H}\cdots\text{N=C}$ hydrogen bonds with nearby C=N groups. These $\text{O--H}\cdots\text{N=C}$ hydrogen bonds help to maintain the phenyl units in a coplanar arrangement, enhancing the structural rigidity and thereby improving the crystallinity.^[57] Similarly, Chen et al. employed fluorine substitution to control interlayer interactions based on self-complementary π -electronic forces, leading to enhanced crystallinity in COFs.^[58]

4. Improving the planarity of COFs

The presence of sterically hindered substituents in building blocks not only affects the network structure of 2D COFs but also interferes with the interactions between the layers of the COFs.^[59] Larger functional groups can induce intra- and intermolecular repulsions, resulting in changes to the torsion angles of peripheral units. This alteration disrupts layer stacking and weakens supramolecular interactions (such as π - π stacking and hydrogen bonding) between COF layers, leading to increased interlayer distances.^[60] Such changes are detrimental to the crystallinity and porosity of 2D COFs. Consequently, flat aromatic core structures are often preferred in the synthesis of 2D COFs.

Additionally, there are reports that enhancing planarity can be achieved by introducing nitrogen atoms or removing twisted substituents. For instance, Bettina V. Lotsch demonstrated that replacing C--H units in phenyl rings with nitrogen atoms can reduce steric hindrance, thus enhancing planarity. Using a series of triphenylaldehyde building units containing 0–3 nitrogen atoms in the central aryl rings, she synthesized 2D azine-linked COFs, which showed structural variations reflecting the changes in the triphenylene platform.^[61]

Another example comes from an earlier study by Bein's group, which synthesized a series of pyrene-based 2D COFs. They discovered that the steric repulsions among the hydrogens in the core tetraphenylpyrene unit caused the phenyl rings to rotate relative to the pyrene core. This rotation led to a "chair-like" conformation for the tetraphenylpyrene core,

which facilitated synchronized slipped stacking in the 2D COFs. As a result, offsets were minimized, allowing for tighter packing compared to the "propeller" conformation observed in model compounds. The carefully controlled geometry of the tetraphenylpyrene-derived building block established periodic docking sites, promoting the formation of highly crystalline 2D COFs with domain sizes reaching up to half a micrometer.^[62] Subsequently, Bein, Auras, and their collaborators introduced isoindigo- and thienoisindigo-based monomers as bridging units into highly crystalline imine-linked COFs (Py-pII, Py-pTII, and Py-tTII) with tetraphenylpyrene nodes. In the case of Py-tTII, the steric repulsion was replaced by electrostatic attraction, resulting in a more planar configuration for the bridging units.^[63]

While planar building blocks derived from molecular structure are not commonly used, they represent a highly effective approach. Subtle adjustments at the molecular level can significantly enhance the crystallinity and properties of the resulting COFs, making this strategy particularly appealing.

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Chapter 1

Ultrafine Spatial Modulation of Diazapyrene-Based Two-Dimensional Conjugated Covalent Organic Frameworks

Abstract:

Tailormade bottom-up synthesis of covalent organic frameworks (COFs) from various functional building blocks not only offer tunable topology and pore size, but also multi-dimensional properties. High crystallinity is one of the prerequisite for their structures and associated physico-chemical properties. Among different π -conjugated motifs for constructing COFs, pyrene-based tetragonal structures are effective in achieving highly ordered and crystalline states. In the present research, I demonstrated that the substitution of pyrene with 2,7-diazapyrene produces nearly “flat” structures of two-dimensional (2D) COF layers by controlling the torsional angle of linker molecules. Featuring finite pore diameters and excellent thermodynamic stability to ~ 500 °C, the ordered face-to-face (slipped AA) stacking arrangements were produced. Extended electrical conjugation spanning 2D frames with modest optical bandgaps (E_g) of ~ 2.1 eV, shows the planar character of diazapyrene-based COFs. This study highlights that by varying the in-terlayer distances of pyrene core by substituting the peripheral CH group of the pyrene by nitrogen atom a series

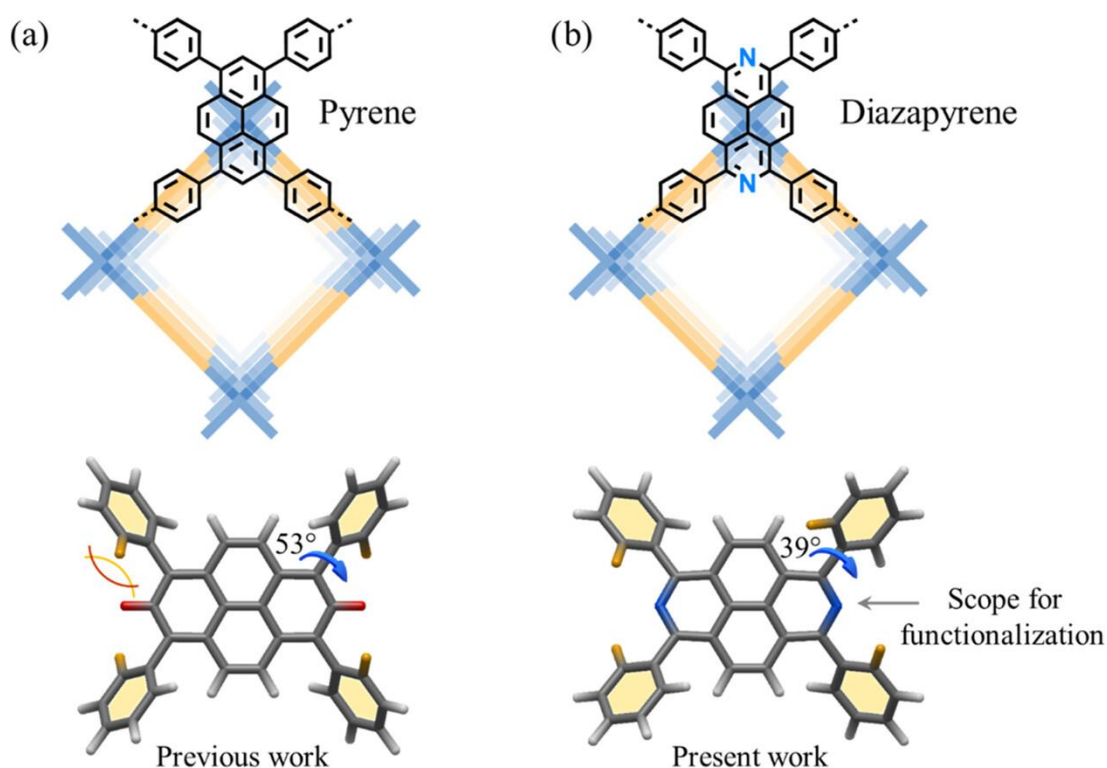
of highly crystalline porous crystalline frameworks can be realized.

Introduction

In recent years, covalent organic frameworks (COFs) have attracted significant attention from researchers due to their unique properties and potential applications across various fields, including gas storage and separation,^{[1][2][3][4]} catalysis,^{[5][6][7]} biomedical sciences^{[8][9][10][11]}, energy storage,^{[12][13][14]} and porous organic semiconductors.^{[15][16][17]} These crystalline porous polymers are synthesized by connecting organic building blocks in a topologically linked manner.^{[18][19][20]} To promote the utilization and diversity of COFs, researchers have explored different building blocks, condensation reactions, and geometries.^{[21][22][23]} The obtained results have substantially expanded the COF capabilities.^{[24][25][26][27][28][29]}

Notably, COFs that incorporate tetraphenylpyrene as a building block have demonstrated high degrees of crystallinity with large crystal domains.^{[30][31][32][33]} In this building block, the steric repulsion between the phenylene protons and protons located at the 2- and 7-positions of the pyrene core causes a twist of four phenylenes against the pyrene structure. As a result, two highly symmetrical configurations can be obtained. The “propeller” configuration is observed for the parent tetraphenylpyrene structure with the slipped stacks of alternating right-handed and left-handed propellers.^[34] Meanwhile, in pyrene-based COFs, the “armchair” configuration, in which the normal vectors of the four phenylenes point to the same direction, allows the cofacial arrangement of both pyrene cores and phenylenes, leading

to strong π - π interactions and close packing.^{[31][35]} These pyrene-based COFs are promising materials for chemical sensors because of their solvatochromism,^{[36][37]} acidochromism,^[38] and good photocatalytic properties.^{[39][40]} However, the presence of the four phenyl rings attached to the core results in a significant rotation degree relative to the pyrene plane. This rotation considerably increases the interlayer distance in COFs, inhibiting the interlayer charge transport and, consequently, limiting their electronic applications.^[41]



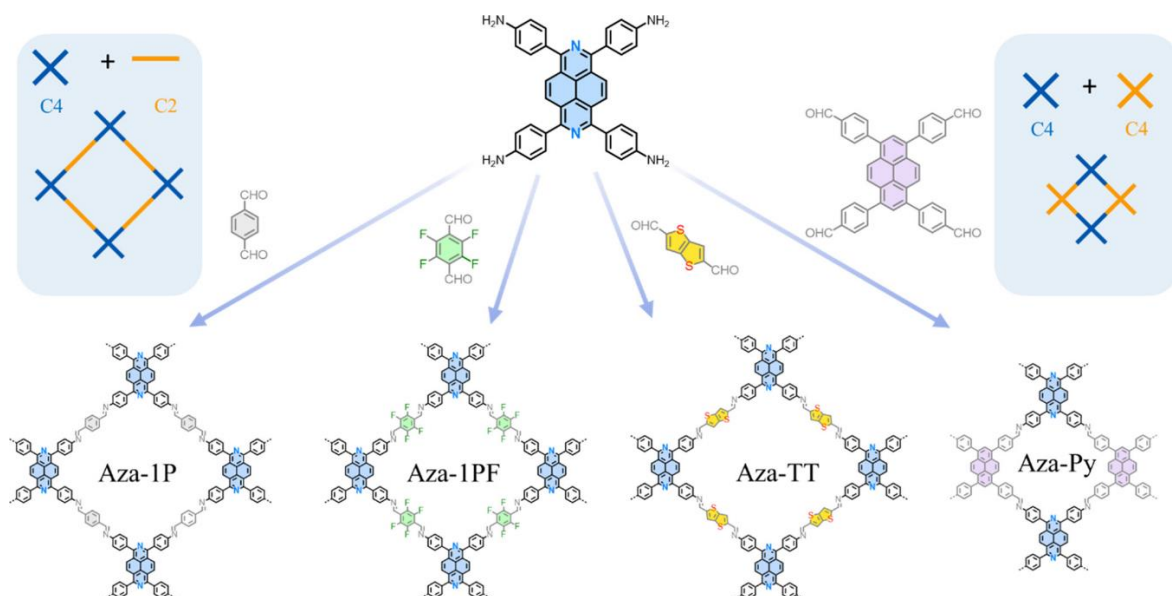
Scheme 1. Design principle of COFs via reducing the steric hindrance.

In general, incorporating heteroatoms into the cores of polycyclic aromatic hydrocarbons, such as pyrene and perylene, significantly alters their conformations as well as the optical and electronic properties.^[42] Herein, I propose the utilization of 2,7-diazapyrene

instead of pyrene as an essential building block of COFs. As shown in Scheme 1, introducing nitrogen atoms into the pyrene core reduces the degree of steric repulsion between the phenyl ring and diazapyrene core, decreasing the rotation angle. This, in turn, leads to smaller π - π distances and stronger interlayer interactions.

Results and discussion

Synthesis



Scheme 2. Synthesis procedure and structures of the 2,7-diazapyrene-based COFs.

I have selected 1,3,6,8-tetrakis(4-aminophenyl)-2,7-diazapyrene **AzaPy(NH₂)₄** as the amine monomer along with four different aldehyde counterparts (**Scheme 2**). According to the topology design strategy,[43] two quadrilateral COFs with different pore sizes can be designed based on "C4+C2" and "C4+C4" compositions. Mesoporous diazapyrene-based COFs in the "C4+C2" configuration were synthesized through the condensation reactions

between **AzaPy(NH₂)₄** and three dialdehydes **1P(CHO)₂**, **1PF(CHO)₂**, and **TT(CHO)₂**. For efficient generation of free charge carriers in 2D COFs, the donor–acceptor (D-A) conjugation strategy has been recently adopted with the realization of formation of segregated D–A stacks with bicontinuous heterojunctions π -columns[44]. This type of D-A structure can significantly increase the mobility and extend the longevity of charge carriers.[45] Here, 1,3,6,8-tetrakis(4-aminophenyl)-2,7-diazapyrene **AzaPy(NH₂)₄**, as the amine monomer act as a donor unit. Combinations of this donor with electron-deficient aldehyde **1PF(CHO)₂** and electron donating **TT(CHO)₂** will produce COFs with tunable energy band structures. On the other hand, combination of the amine with **Py (CHO)₄** linker, will produce COFs with the smallest donor–acceptor contrast and smallest pore size. These types of D-A assembly with tunable pore size, can further improve the charge carrier generation yield after incorporation of suitable dopant. These reactions were performed under solvothermal conditions at 120°C for 7 d, utilizing a 2:1 vol. solvent mixture of mesitylene/1,4-dioxane and 6 M acetic acid.

Furthermore, following the "C4+C4" configuration, a microporous COF (**Aza-Py**) was synthesized through the reaction of **AzaPy(NH₂)₄** with **Py(CHO)₄**. Pyrene, which is structurally similar to 2,7-diazapyrene, serves as a linking unit to further explore the preference of D-A type COF stacking: whether it creates an alternating stacking of D and A units or the same ordered stacking structure of D and D, A and A in the interlayer. The condensation reaction was conducted in a 2:1 solvent mixture of mesitylene/benzyl alcohol

with 6 M acetic acid at 120°C for 5 d. The successful synthesis of these COFs is confirmed by a series of spectroscopic analyses.

Characterization

Figure 1 demonstrates that the Fourier transform infrared (FT-IR) spectra of all the synthesized COFs, which exhibits distinct C=N stretching bands at 1611–1699 cm^{-1} . In addition, the absence of the characteristic C=O and N–H stretching bands at 1657–1706 and 3398–3200 cm^{-1} for the aldehyde-functionalized and amine-functionalized monomers used for COF preparation indicates the complete consumption of the reactants.^[46] To gain further structural insight, solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR measurements were performed and signal peaks are marked in **Figure S18**. The peak (150–160 and 130 ppm) in solid-state CP/MAS ^{13}C NMR reveals the carbon signal of the imine bond (**Figure S18**). Moreover, the peaks due to fluorine-bound carbons in **Aza-1PF** are also shifted to downfield and appear at ~145–155 ppm. These results match well with FT-IR studies and confirm the complete polymerization of the building blocks.

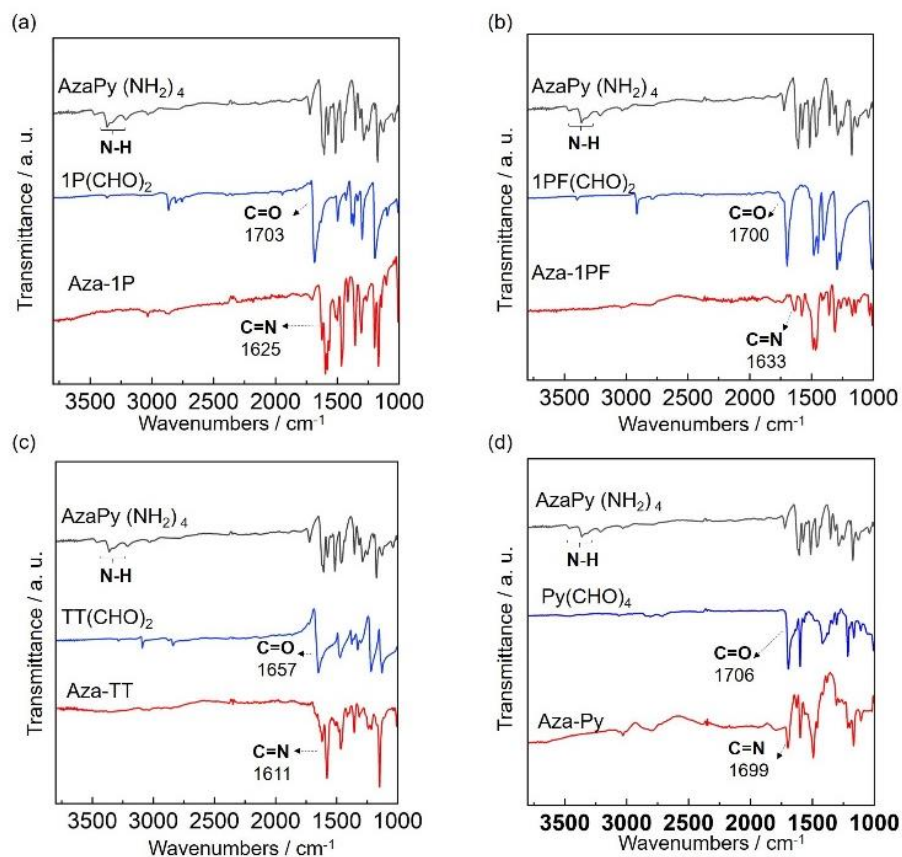


Figure 1. FT-IR spectra of the (a) Aza-1P, (b) Aza-1PF, (c) Aza-TT, and (d) Aza-Py.

To investigate the solid-state packing configuration and crystallinity of the prepared COFs, their powder X-ray diffraction (PXRD) patterns were recorded. As shown in **Figure 2**, the peaks were observed at $2\theta = 3.48^\circ$, 7.04° , and 24.23° , for **Aza-1P**; at $2\theta = 3.71^\circ$, 5.35° , 7.55° , and 24.10° , for **Aza-1PF**; at $2\theta = 3.48^\circ$, 4.96° , 6.99° , and 24.37° , for **Aza-TT**; $2\theta = 3.54^\circ$, 5.12° , 7.10° , and 23.64° , for **Aza-Py** which are assignable to (100), (110), (200), and (001) diffractions, respectively. The crystallinity of the as-synthesized COFs was analyzed via the full width at half-maximum (FWHM) of (100) diffraction. The FWHM₁₀₀ values of **Aza-1P**, **Aza-1PF**, **Aza-TT**, and **Aza-Py** were evaluated as 0.362° , 0.421° , 0.430° , and

0.460°, respectively, suggesting that **Aza-1P** COF had the highest crystallinity among these synthesized COFs. On the other hand, FWHM₁₀₀ values of **Py-1P** COFs 0.592° indicates a lower degree of crystallinity. (**Figure 2**). The last broad peak at 24° in the PXRD patterns is correspond to (001) plane resulting from the interlayer distance of the 2D layers. It is noteworthy that among these, **Aza-TT** has the smallest interlayer distance as 3.65Å. To compare the interlayer characteristics of pyrene- and diazapyrene core; I have further synthesized the pyrene-based COF **Py-1P** and found that the interlayer distance of **Aza-1P** (3.67Å) is shorter than the interlayer distance of **Py-1P** (3.77Å) (**Figure S1**) The calculated diffraction pattern of the sliding AA stack model is in good agreement with the experimental results. Furthermore, the Pawley refinement of the *C2/m* symmetric structural model optimized using density functional theory (DFT) closely matches the experimental data with minimal discrepancies. (**Table S3 and Figure S1**) It is noteworthy that all the aza-based COFs exhibited smaller half-width compared to that of **Py-1P**, indicating greater crystalline domain size. This disparity could arise from the different monomer purities or suboptimal reaction conditions. The experimental PXRD patterns of **Aza-1PF** and **Aza-TT** are also in excellent agreement with the simulated patterns, confirming the presence of a highly crystalline slipped AA stacking structure (**Figure 2a–d**).

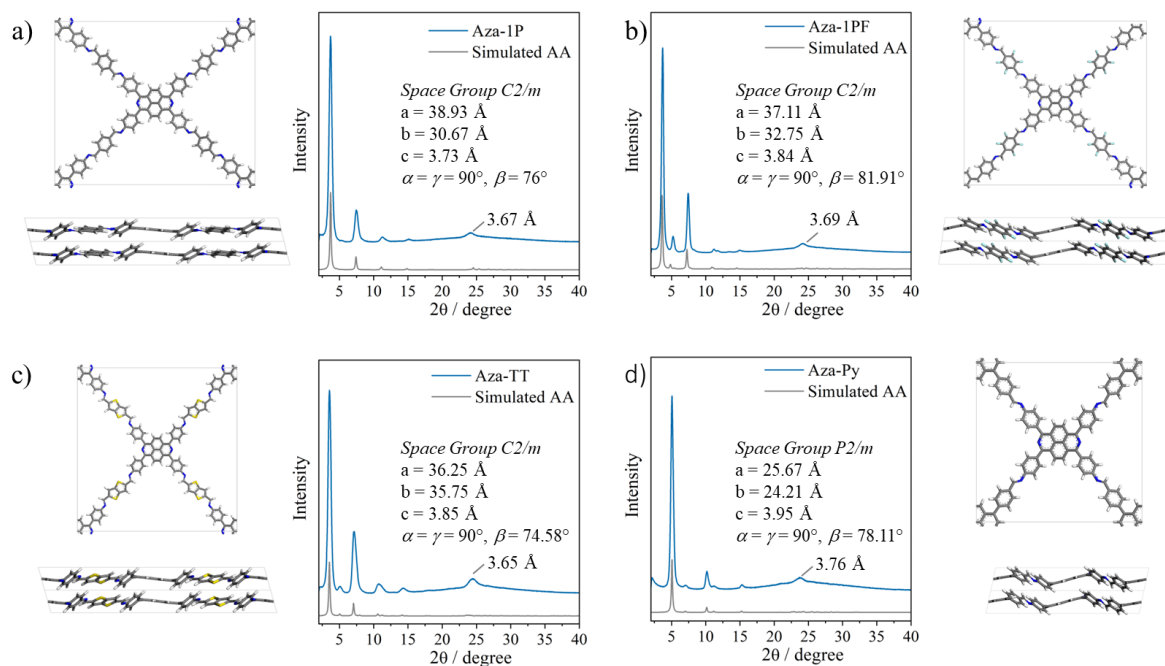


Figure 2. Experimental PXRD profiles (turquoise curves) and PXRD patterns simulated in the slipped AA-stacking mode (gray curves) with corresponding structural models in top and side view: (a) **Aza-1P**, (b) **Aza-1PF**, (c) **Aza-TT**, and (d) **Aza-Py**.

In contrast, **Aza-Py** with the "C4+C4" exhibits high crystallinity and the smallest pore diagonal size (1.6 nm). Owing to the structural similarity between the diazapyrene and pyrene units, two possible stacking modes exist: "diazapyrene on diazapyrene" and "diazapyrene on pyrene". The calculated diffraction patterns using the "diazapyrene on diazapyrene" stacking model are in better agreement with the experimental patterns than those obtained in the "diazapyrene on pyrene" stacking mode (**Figure 2d**). This stacking behavior can be attributed to the various rotation angles of the phenylene rings and π - π interactions between the adjacent layers, as indicated by the corresponding model structures, also supported by

simulated and experimental PXRD patterns (**Figure 2d**). This design approach offers a new avenue for developing COFs, wherein structurally similar units are arranged in an alternating pattern to form different twist angles and, consequently, distinct columnar structures.

Scanning electron microscopy (SEM) observations revealed the microstructures of **Aza-1P**, **Aza-1PF**, **Aza-TT**, and **Aza-Py**, in which **Aza-1P** and **Aza-Py** crystals exhibited rhomboid plate morphologies and micrometer-scale sizes of approximately 20–40 μm (**Figures 3a, 3d, and S2**). Cryo-transmission electron microscopy (Cryo-TEM) images were taken by dispersing the COFs powder into ethanol through sonication. These observations further demonstrated the formation of well-defined periodic frameworks in **Aza-1P**, **Aza-1PF**, **Aza-TT**, and **Aza-Py** with periodic channels that closely match the π - π stacking configurations with the repeated interlayer distances predicted by the structural model and consist with PXRD results. The spacings of **Aza-1P**, **Aza-1PF**, and **Aza-TT** are 2.3 nm, and the spacing of **Aza-Py** is 1.6 nm (**Figures 3b, 3c, 3e, 3f, and S3**): the shortest interlayer distance.

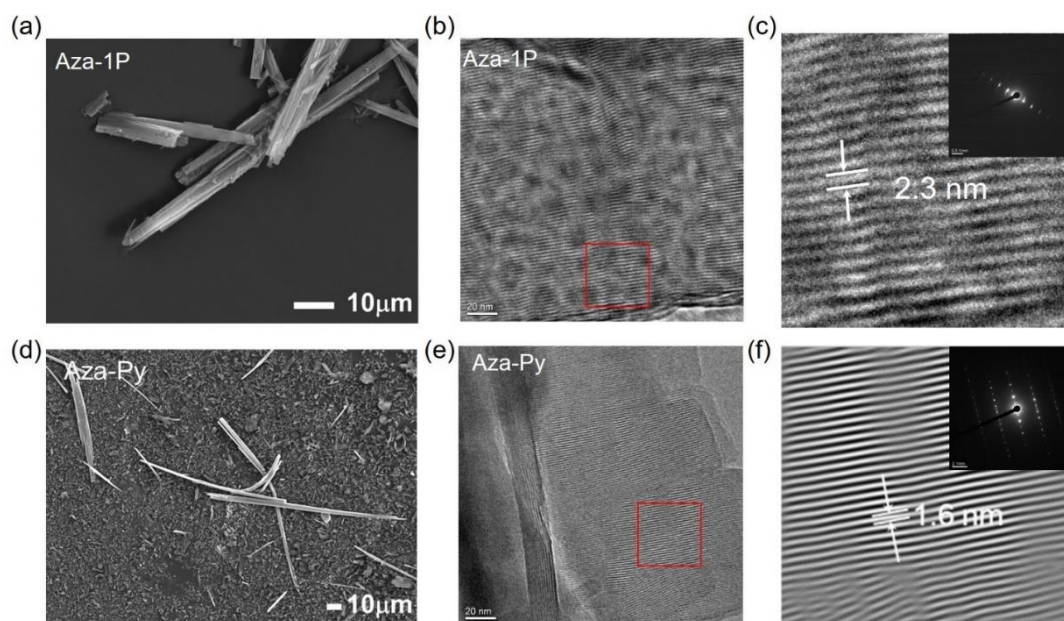


Figure 3. SEM images of the (a) **Aza-1P** and (d) **Aza-Py**. Cryo-TEM images of (b) **Aza-1P** and (e) **Aza-Py**. Fourier transform images of (c) **Aza-1P** and (f) **Aza-Py**. Insets: selected area diffraction patterns.

The pore volumes of the synthesized COFs were determined by conducting nitrogen adsorption–desorption measurements (**Figure 4 and Table S1**). The isotherms of **Aza-1P**, **Aza-1PF**, and **Aza-TT** exhibit fully reversible Type IV isotherm shapes, confirming their mesoporous structures, while **Aza-Py** produces a Type I isotherm, indicating its microporous nature. The Brunauer–Emmett–Teller (BET) surface areas of these COFs were determined as 1908 (**Aza-1P**), 1620 (**Aza-1PF**), 1380 (**Aza-TT**), and 1162 m² g^{−1} (**Aza-Py**). Notably, the BET surface area of these diazapyrene based COFs is larger than

the most previously reported pyrene-based COFs. [47][48][49][50] Non-local density functional theory (NLDFT) calculations revealed remarkably narrow pore size distributions with the maximum values are in close agreement with those obtained using the structural models.

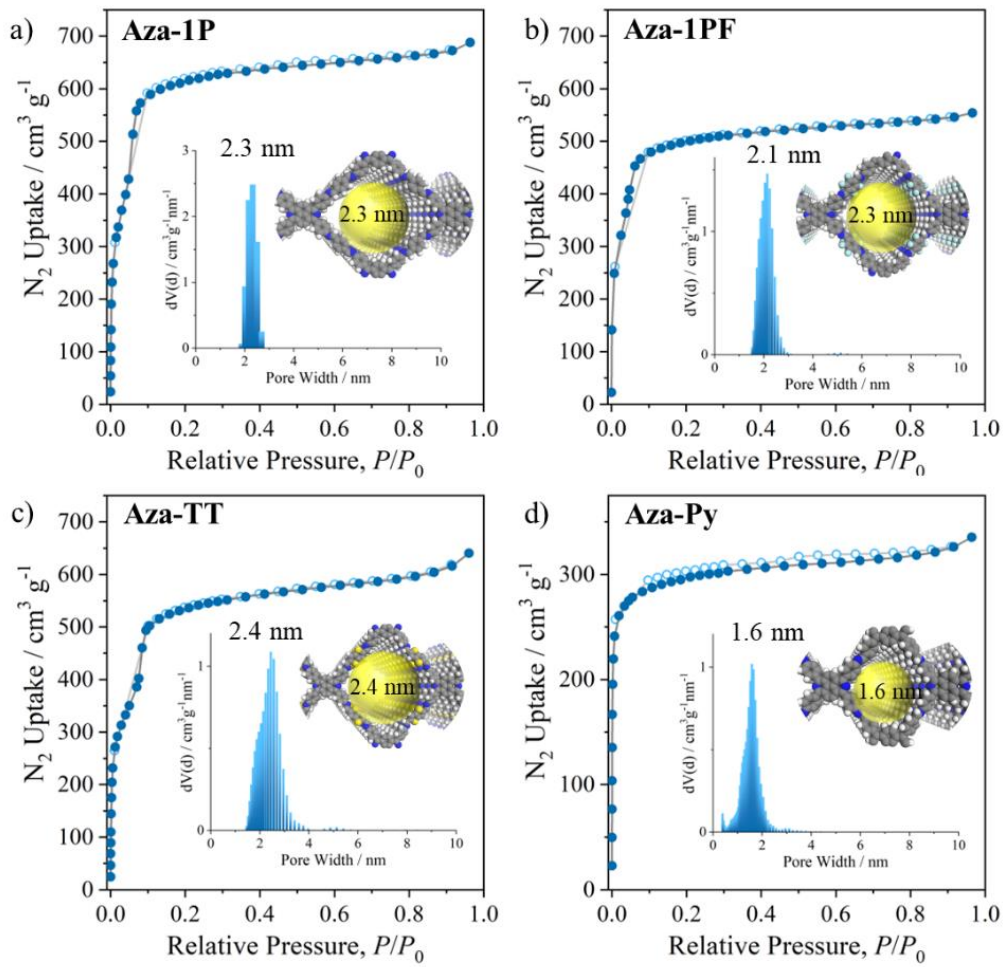


Figure 4. Nitrogen adsorption isotherms of the (a) **Aza-1P**, (b) **Aza-1PF**, (c) **Aza-TT**, and (d) **Aza-Py** recorded at 77 K. Inset: pore size distributions obtained via NLDFT calculations.

The thermal stabilities of the diazapyrene-based COFs were assessed via thermogravimetric analysis (TGA) (**Figure S4**). The obtained TGA curves exhibit two mass loss stages, indicating that the synthesized material possessed relatively high thermal stability at temperatures as high as 500°C. Meanwhile, a mass loss of approximately 25% occurred between 300 K and approximately 500°C owing to the desorption of adsorbed water. Among them, the thermal stability of **Aza-TT** and **Aza-1PF** are slightly lower than that of **Aza-1P** and **Aza-Py**. In studies of COF thermal stability, a complex interplay of multiple parts may cause observed differences in degradation temperature trends. Structural distortions in 2D layers, particularly those caused by entropy, may result in decreasing thermal stability with increased pore size.^[51] Therefore, **Aza-TT** with its larger pore size (2.4 nm), has the lowest thermal stability among the four COFs. On the other hand, although having the same pore diameters, **Aza-1PF** has worse thermal stability than **Aza-1P**, which is most likely due to differences in the thermal stability of their respective units.

Electronic Properties

The optical properties of the COFs were evaluated using ultraviolet (UV)–visible diffuse reflectance spectroscopy, and their bandgaps were estimated by constructing Tauc

plots (**Figure 5**). **Aza-1P** exhibits a significant redshift with respect to **Py-1P** (dashed line), which can be attributed to the synergistic effect of the relatively planar structure of the COF and extended π -conjugation induced by the electronegative nitrogen atom, resulting in a lowest unoccupied molecular orbital (LUMO) energy level.

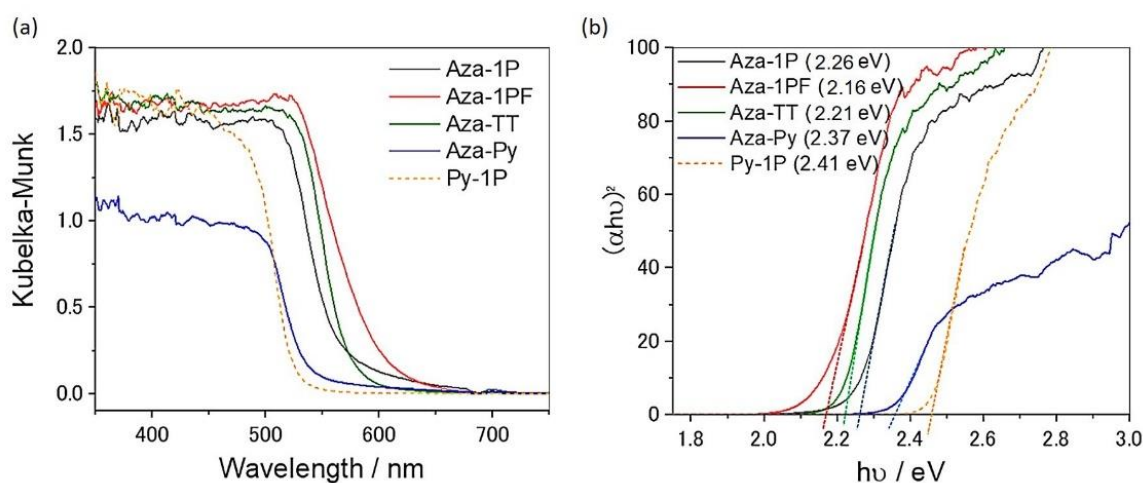


Figure 5. (a) UV-vis diffuse reflectance spectra of the COFs and (b) the corresponding Tauc plots.

The frontier orbitals were calculated using the DFT method with the DMol3 basis set, the GGA functional, and the PBE exchange-correlation functional at the Gamma point (**Figure S5**). The obtained results indicate that the COFs are semiconductors with bandgaps larger than 2.1 eV, albeit smaller than the experimental values because traditional DFT methods tend to underestimate the bandgap size. In **Aza-1P** and **Aza-1PF**, the highest occupied molecular orbital (HOMO) was localized on the diazapyrene

unit, while the LUMO was localized on the phenylene and tetrafluorophenylene bridges, confirming the formation of the D–A system.

Conclusion

In summary, I have successfully synthesized four 2,7-diazapyrene-based COFs with high crystallinity and porosity. The reduced rotation angle of phenylenes contributed to the shorter interlayer distance and denser packing of the produced materials. The combined effect of the extended conjugation due to the relatively planar structure of **Aza-1P** and electronegative nitrogen atom was confirmed via PXRD and diffuse reflectance spectroscopy. Notably, **Aza-Py** exhibited a unique structural arrangement, in which structurally similar units alternated to form distinctive columnar structures. This introduced a novel design guideline for COFs using subtle differences in the rotation angle to achieve distinct stacking patterns.

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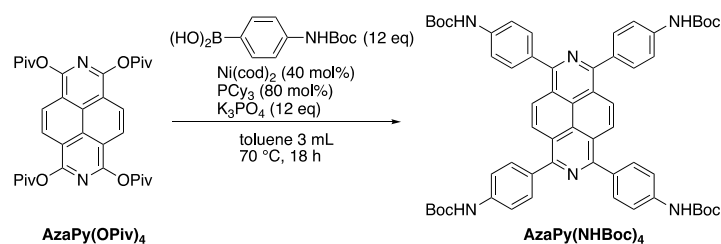
Chapter 1 Appendix

1. Building block syntheses

A Bruker AVANCE III HD analyzer or JEOL JNM-ECZ600R spectrometer was used to record ^1H NMR (400 MHz) or ^{13}C NMR (150 MHz) spectra. Only a ^{13}C -NMR spectrum of AzaPy(NH₂)₄ was recorded with Bruker Avance III (150 MHz). In the case of ^1H NMR, chemical changes were shown on the delta scale in ppm compared to CDCl₃ (δ = 7.260 ppm) and DMSO-*d*₆ (δ = 2.50 ppm). In the case of ^{13}C NMR, chemical changes were shown on the delta scale in ppm compared to DMSO-*d*₆ (δ = 39.52 ppm). I collected high-resolution atmospheric pressure chemical ionization time-of-flight APCI-TOF and high-resolution electrospray ionization time-of-flight ESI-TOF mass spectra on a Bruker microTOF device in a positive ionization mode.

All reagents were purchased from Tokyo Chemical Industry (TCI) and FUJIFILM Wako Chemicals, sourced from FUJIFILM Wako Chemicals and Tokyo Chemical Industry Co., Ltd. AzaPy(OPiv)₄ was prepared following the literature method [1]. Unless specified otherwise, materials obtained from commercial suppliers were used without additional purification.

1.1 Synthesis of Boc-protected aminophenyl-2,7-diazapyrene, AzaPy(NHBoc)₄



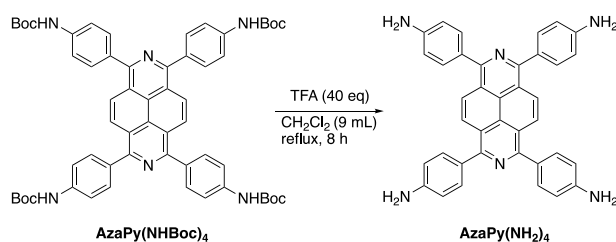
The K₃PO₄ (509 mg, 2.44 mmol) was put in a 50 mL J-Young tube and heated under low pressure (120 °C, 1.0 Torr) for one hour. Once K₃PO₄ was dry, 121 mg of AzaPy(OPiv)₄ and 570 mg of 4-[(tert-butoxycarbonyl)-amino]phenylboronic acid was added to the tube.

In total, they weighed 0.20 mmol. After that, toluene (6 mL), tricyclohexylphosphine (45.0 mg, 0.16 mmol), and Ni(cod)₂ (22.2 mg, 0.080 mmol) were put in the reaction bottle inside the glove box. The reaction mix was mixed at 70 °C for 18 hours. The reaction mixture was mixed with 6 mL of a 10% water solution of ethylenediamine. The solution that was left over was extracted with 50 mL of CHCl₃. The organic layer that was mixed was dried over Na₂SO₄ and gathered in a vacuum. The residue was cleaned using column chromatography (SiO₂) with CH₂Cl₂/EtOAc (30/1) and then separated again from CH₂Cl₂/hexane. This gave us AzaPy(NHBoc)₄ (57.9 mg, 0.060 mmol, 30% yield).

Chemical formula: C₅₈H₆₀N₆O₈: ¹H NMR (400 MHz, CDCl₃): 8.29 (s, 4H), 7.89 (d, *J* = 11 Hz, 8H), 7.58 (d, *J* = 11 Hz, 8H), 6.64 (br s, 4H), 1.57 (s, 36H). ¹³C NMR (150 MHz, DMSO-*d*₆): 152.8, 152.2, 140.2, 132.8, 131.2, 128.9, 125.8, 121.4, 117.9, 79.4, 28.2.

HRMS (APCI) Calcd. For C₅₈H₆₀N₆O₈[M]⁺: 969.4545. Found: 969.4589.

1.2 Synthesis of 1,3,6,8-tetrakis(4-aminophenyl)2,7-diazapyrene, AzaPy(NH₂)₄



The AzaPy(NHBoc)₄ (116 mg, 0.12 mmol) was mixed with 9 mL of CH₂Cl₂ in a 50 mL Schlenk flask. Trifluoroacetic acid (TFA) (0.37 mL, 4.8 mmol) was then added at 0 °C. It took 8 hours to heat the reaction mixture back up. An aqueous solution of saturated NaHCO₃ was used to stop the process. It was then extracted with 50 mL of CH₂Cl₂ and 50 mL of EtOAc. The mixed organic layer was dried over Na₂SO₄ and drained until it was completely dry. It was cleaned up using column chromatography (with amino-coated SiO₂) and CH₂Cl₂/EtOAc (2/1) and then washed with CH₂Cl₂ to get AzaPy(NH₂)₄ (43.8 mg, 0.077 mmol, 65% yield). Chemical formula: C₃₈H₂₈N₆: ¹H NMR (400 MHz, DMSO-*d*₆): 8.21 (s, 4H), 7.62 (d, *J* = 11 Hz, 8H), 6.78 (d, *J* = 11 Hz, 8H), 5.49 (br s, 8H). ¹³C NMR (150 MHz, DMSO-*d*₆): 152.4, 149.4, 131.6, 129.6, 126.8, 125.1, 120.3, 113.5. HRMS (APCI) Calcd. For C₃₈H₂₈N₆ [M]⁺: 568.2370. Found: 568.2347.

1.3 1,3,6,8-tetrakis(4-formylphenyl)pyrene, Py(CHO)₄

This compound was synthesized according to the literature. 1,3,6,8-tetrabromopyrene (1.00 g, 1.93 mmol), 4-formylphenylboronic acid (1.74 g, 11.6 mmol), K₂CO₃ (2.1 g, 15

mmol) and $\text{Pd(PPh}_3)_4$ (0.12 g, 0.10 mmol) were refluxed at 100 °C in 30 mL dry 1,4-dioxane for 3 days. After cooling to room temperature, the precipitate was collected by filtration. The crude product was purified by column chromatography on silica gel using acetone and hexane as eluent. Chemical formula: $\text{C}_{44}\text{H}_{26}\text{O}_4$: ^1H NMR (400 MHz, CDCl_3): 10.16 (s, 4H), 8.18 (s, 4H), 8.10 (d, $J = 8.20$ Hz, 8H), 8.04 (s, 2H), 7.86 (d, $J = 8.20$ Hz, 8H).

1.4 1,3,6,8-tetrakis(4-aminophenyl)pyrene, $\text{Py(NH}_2)_4$

This compound was synthesized according to the literature. A reaction mixture containing 1,3,6,8-tetrabromopyrene (2.0 g, 3.9 mmol), 4-aminophenylboronic acid pinacol ester (5.07 g, 23 mmol), K_2CO_3 (4.2 g, 30 mmol), and $\text{Pd(PPh}_3)_4$ (0.24 g, 0.20 mmol) in 60 mL 1,4-dioxane was refluxed at 100 °C for 3 days. The resulting precipitate was collected via filtration and purified by column chromatography on silica gel using acetone and hexane as eluent, yielding a bright yellow powder. Chemical formula: $\text{C}_{40}\text{H}_{30}\text{N}_4$
 ^1H NMR (400 MHz, CDCl_3): 8.13 (s, 4H), 7.79 (s, 2H), 7.34 (d, $J = 8.4$ Hz, 8H), 6.77 (d, $J = 8.5$ Hz, 8H), 5.30 (s, 8H).

2. COF syntheses

2.1 Aza-1P COF

AzaPy(NH₂)₄ (14.0 mg, 25 μ mol, 1 eq.) and terephthalaldehyde, 1P(CHO)₂ (6.60 mg, 49 μ mol, 2 eq.) were filled into a reaction tube, followed by the addition of mesitylene (667 μ L), 1,4-dioxane (333 μ L) and 6 M acetic acid (100 μ L). The tube was kept under 120°C for 7 days. After cooling to the room temperature, the precipitate was collected by filtration, washed with acetone and THF, soaked in THF for 1 day, and then dried at 90°C under vacuum, yielding a light orange powder.

2.2 Aza-1PF COF

AzaPy(NH₂)₄ (14.0 mg, 25 μ mol, 1 eq.) and tetrafluoroterephthalaldehyde, 1PF(CHO)₂ (10.1 mg, 49 μ mol, 2 eq.) were filled into a reaction tube, followed by the addition of mesitylene (667 μ L), 1,4-dioxane (333 μ L) and 6M acetic acid (100 μ L). The tube was sealed and the reaction mixture was heated at 120°C for 7 days. After cooling to the room temperature, the precipitate was collected by filtration, washed with acetone and THF, soaked in THF for 1 day, and then dried at 90°C, yielding a red powder.

2.3 Aza-TT COF

AzaPy(NH₂)₄ (14.0 mg, 25 μmol, 1 eq.) and thieno[3,2-*b*]thiophene-2,5-dicarbaldehyde, TT(CHO)₂ (9.66 mg, 49 μmol, 2 eq.) were filled into a reaction tube, followed by the addition of mesitylene (667 μL), benzyl alcohol (333 μL) and 6 M acetic acid (100 μL). The tube was sealed and the reaction mixture was heated at 120°C for 7 days, yielding an orange powder.

2.4 Aza-Py COF

AzaPy(NH₂)₄ (14.0 mg, 25 μmol, 1 eq.) and 1,3,6,8-tetrakis(4-aminophenyl)pyrene, Py(CHO)₄ (15.3 mg, 25 μmol, 1 eq.) were filled into a reaction tube, followed by the addition of mesitylene (667 μL), benzyl alcohol (333 μL) and 6 M acetic acid (100 μL). The tube was sealed and the reaction mixture was heated at 120°C for 5 days, yielding a yellow powder.

2.5 Py-1P COF

Py(NH₂)₄ (14.0 mg, 20 μmol, 1 eq.) and terephthalaldehyde (5.4 mg, 40 μmol, 2 eq.) were filled into a reaction tube, followed by the addition of mesitylene (667 μL), 1,4-dioxane (333 μL), and 6 M acetic acid (100 μL). The tube was sealed and heated at 120°C for 7

days. After cooling to room temperature, the precipitate was collected by filtration, yielding a bright orange powder

3. Structure characterization

Fourier-transform infrared (FT-IR) spectra were recorded on a JASCO FT-IR 4700 instrument. Solid samples were put in place right away and looked at for 64 scans.

Powder X-ray diffraction (PXRD) measurements were carried out using CuK α (λ = 0.15406 nm) for powder diffraction.

Transmission electron microscopy (TEM) was performed on JEM-2200FS equipped with a field emission gun operated at 200 kV.

Diffuse reflectance spectra were measured on the JASCO V-650 UV-Vis. spectrophotometer referenced to BaSO₄ powder as white standard.

Adsorption isotherms of N₂ at 77 K were measured with Bellsorp–mini ^{II} equipment. Before the adsorption measurements, powdered samples were activated under reduced

pressure ($<10^{-5}$ bar) at 120 °C for 12 h. To evaluate the surface area, the BET model was applied in the ranges $0.05 \leq p / p_0 \leq 0.25$. The pore size distribution was analyzed by Nonlocal density function theory (NLDFT).

Scanning Electron Microscope (SEM) was carried out with JEOL JSM-7001F.

Solid-state NMR measurements were conducted on a Bruker AVANCE NEO 600 NMR spectrometer operating under a static magnetic field of 14.1 T (wide-bore) equipped with a ^1H – ^{13}C double resonance 3.2 mm magic angle spinning (MAS) probe. The ^1H field strength of 100 kHz (the 90° pulse length was 2.5 μs) and 16 transients were accumulated. The spectra were externally referenced to adamantane (1.80 ppm, ^1H). For $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization/MAS (CP/MAS) experiments, the 90° pulse length for ^1H was 3 μs , the ^{13}C field strength was 83.3 kHz during the ramped CP process with the contact time of 4.0 ms, and the ^1H field strength was 100 kHz during the SPINAL64 decoupling period. 4096 transients were accumulated. Double quantum filter MAS experiments were performed with 2 rotor cycles of the Back-to-Back (BaBa) recoupling pulse sequence. 16 transients were accumulated. The recycle delays were set to 8 s. The MAS speed was 15 kHz for CP/MAS experiments and 20 kHz for all the other experiments.



Figure S1. (a-b) PXR profile (red) and XRD patterns were simulated with the slipped AA-stacking mode (green) of **Py-1P**. The Pawley refinement of (c) **Py-1P**, (d) **Aza-1P**, (e) **Aza-1PF**, (f) **Aza-TT** and (g) **Aza-Py COF**.

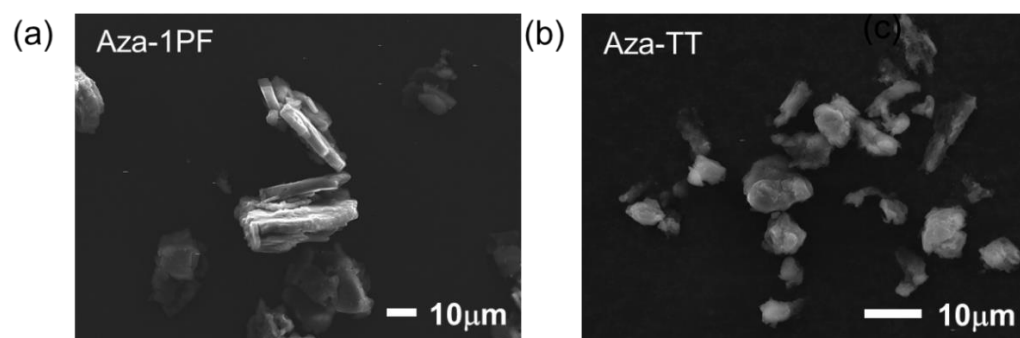


Figure S2. SEM images of (a) **Aza-1PF** and (b) **Aza-TT** COFs.

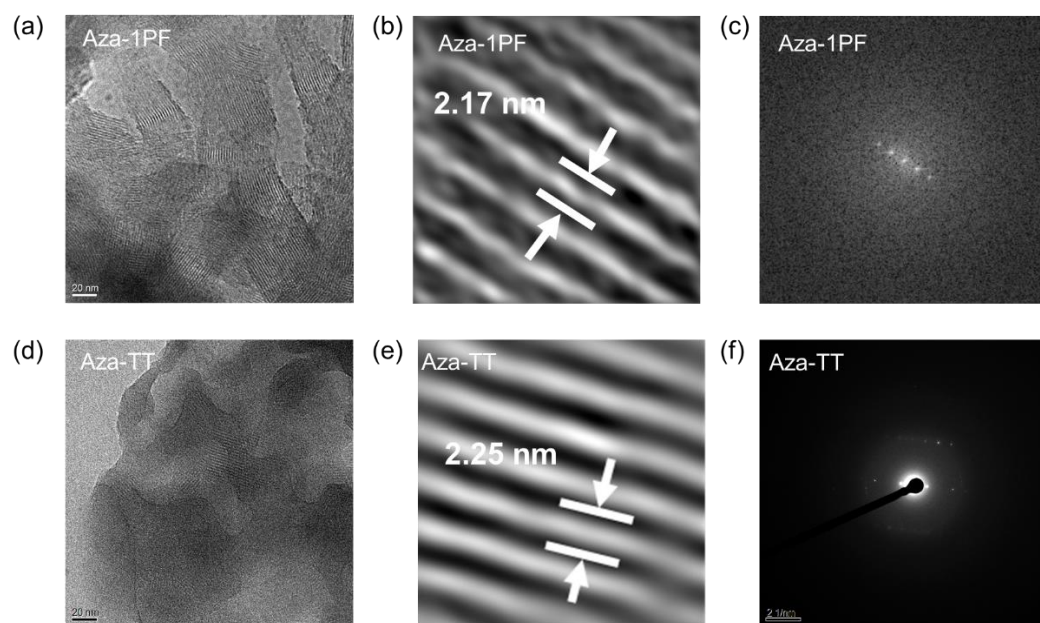


Figure S3. Cryo-TEM images of (a) **Aza-1PF** and (d) **Aza-TT**. The Fourier-filtered images of (b) (c, inversed) **Aza-1PF** and (e) **Aza-TT**. (f) Electron diffraction patterns of **Aza-TT**.

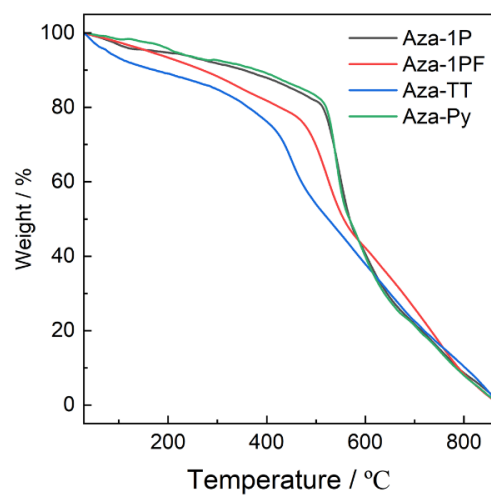


Figure S4. TGA curve of Aza-based COFs.

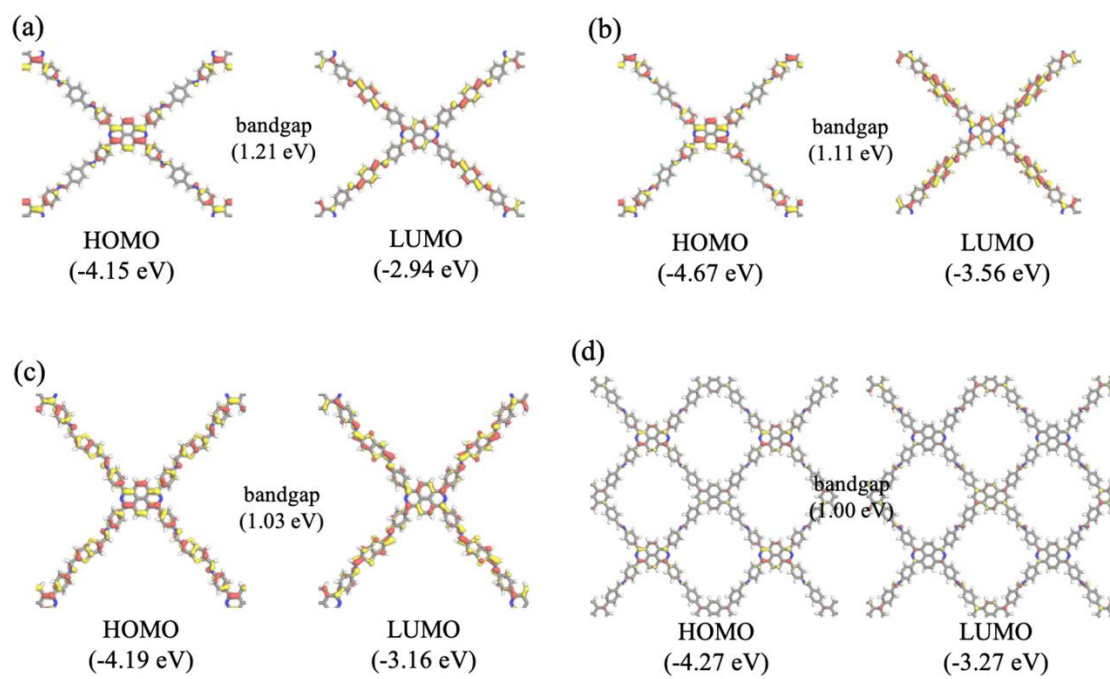


Figure S5. HOMO and LUMO of (a) **Aza-1P**, (b) **Aza-1PF**, (c) **Aza-TT**, (d) **Aza-Py** calculated by DMol3 at Gamma point.

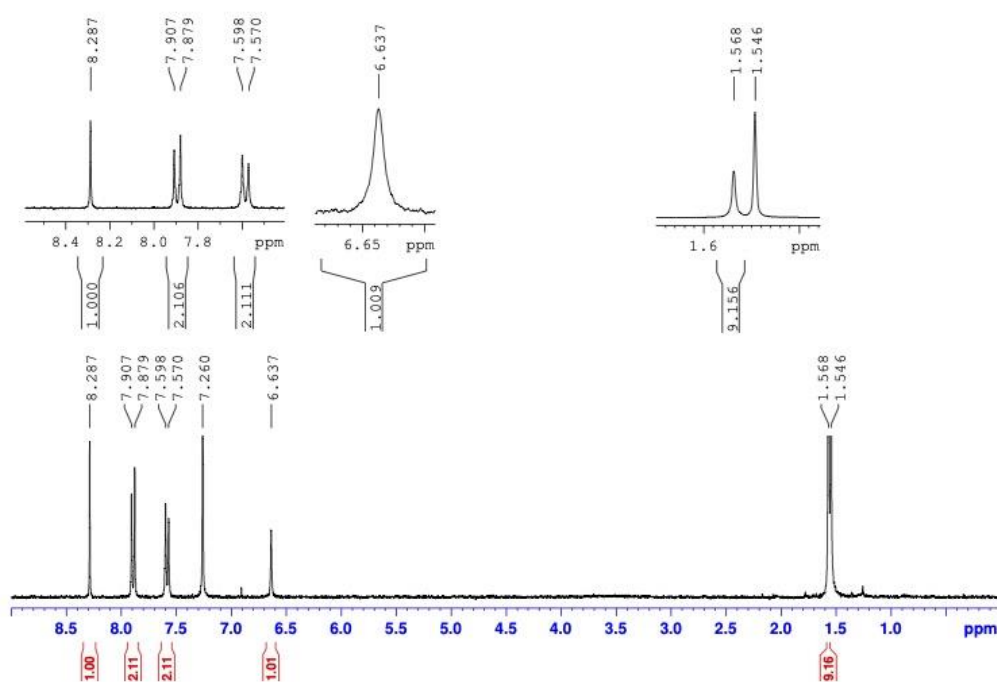


Figure S12. ^1H NMR of AzaPy(NHBoc) $_4$.

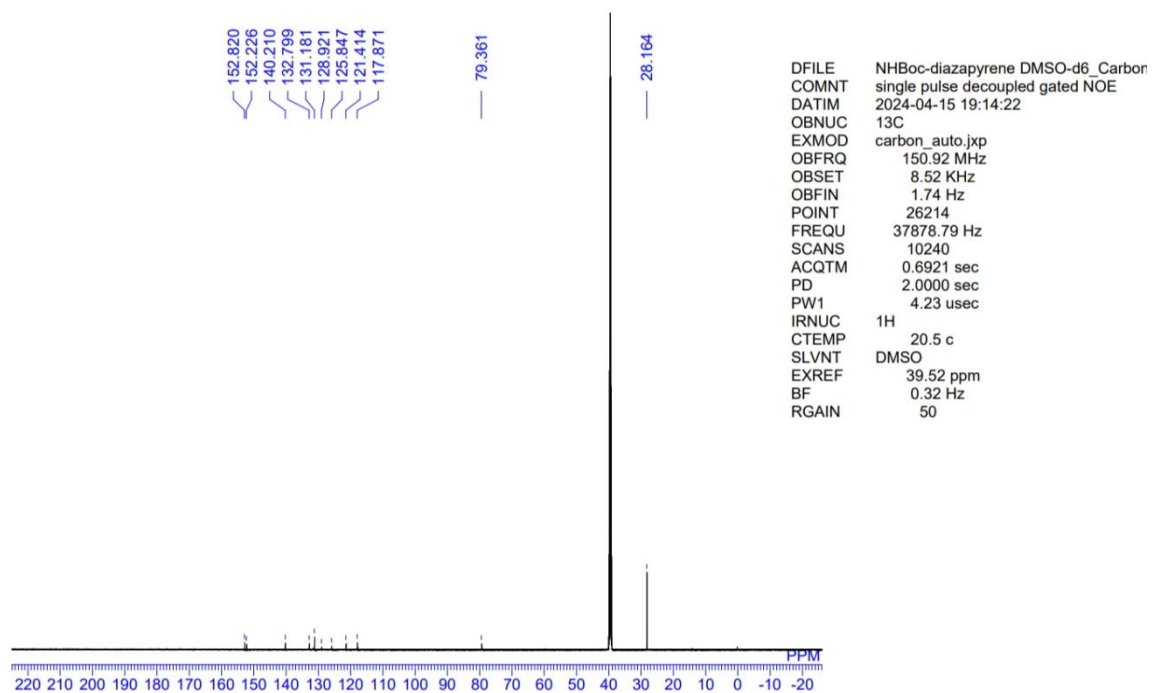


Figure S13. ^{13}C NMR of AzaPy(NHBoc)₄.

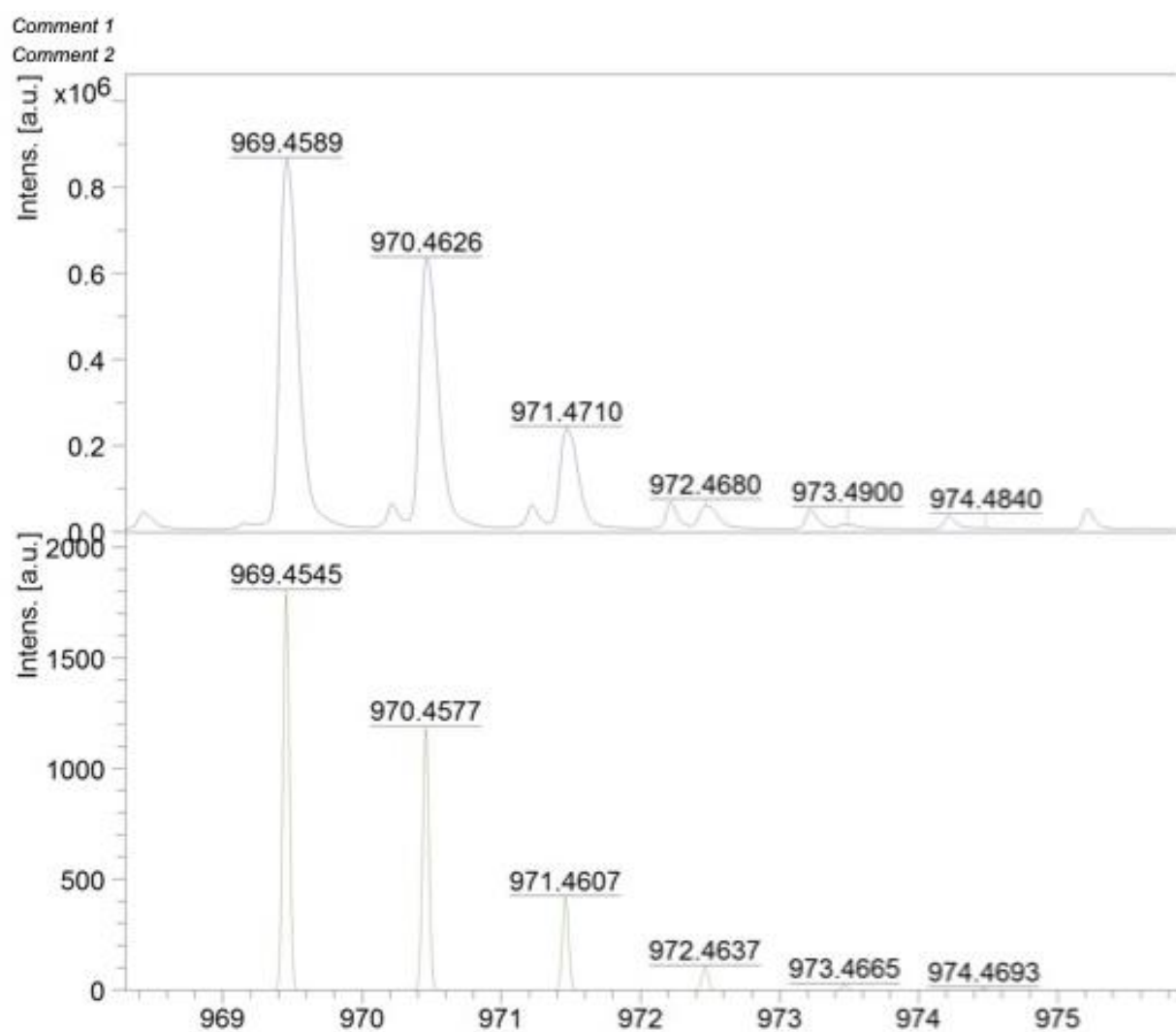


Figure S14. MS spectra of AzaPy(NHBoc)₄.

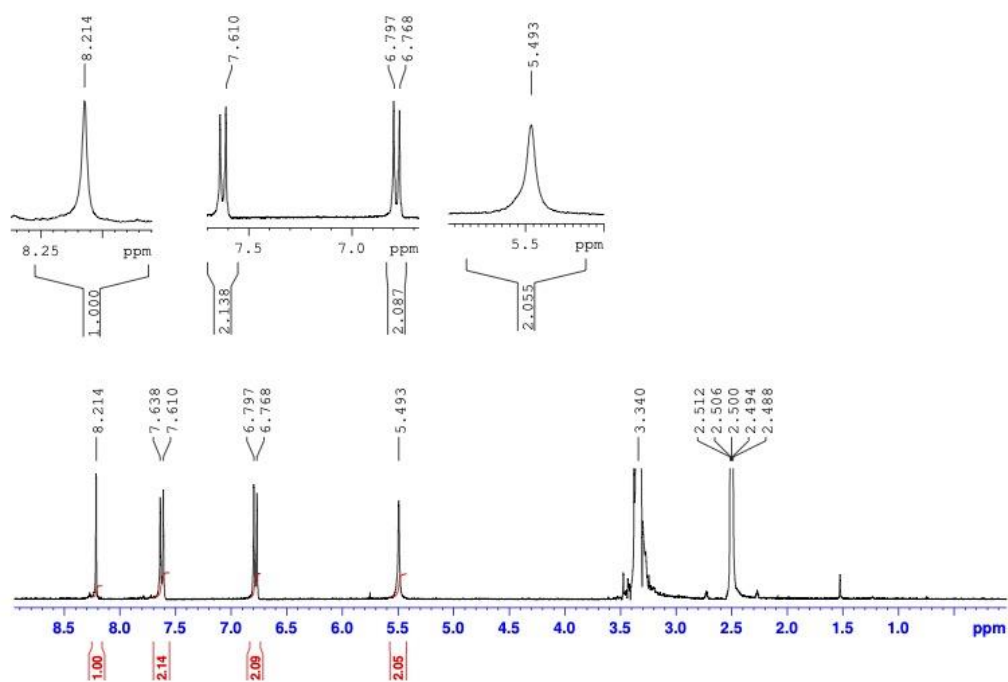


Figure S15. ^1H NMR of AzaPy(NH₂)₄.

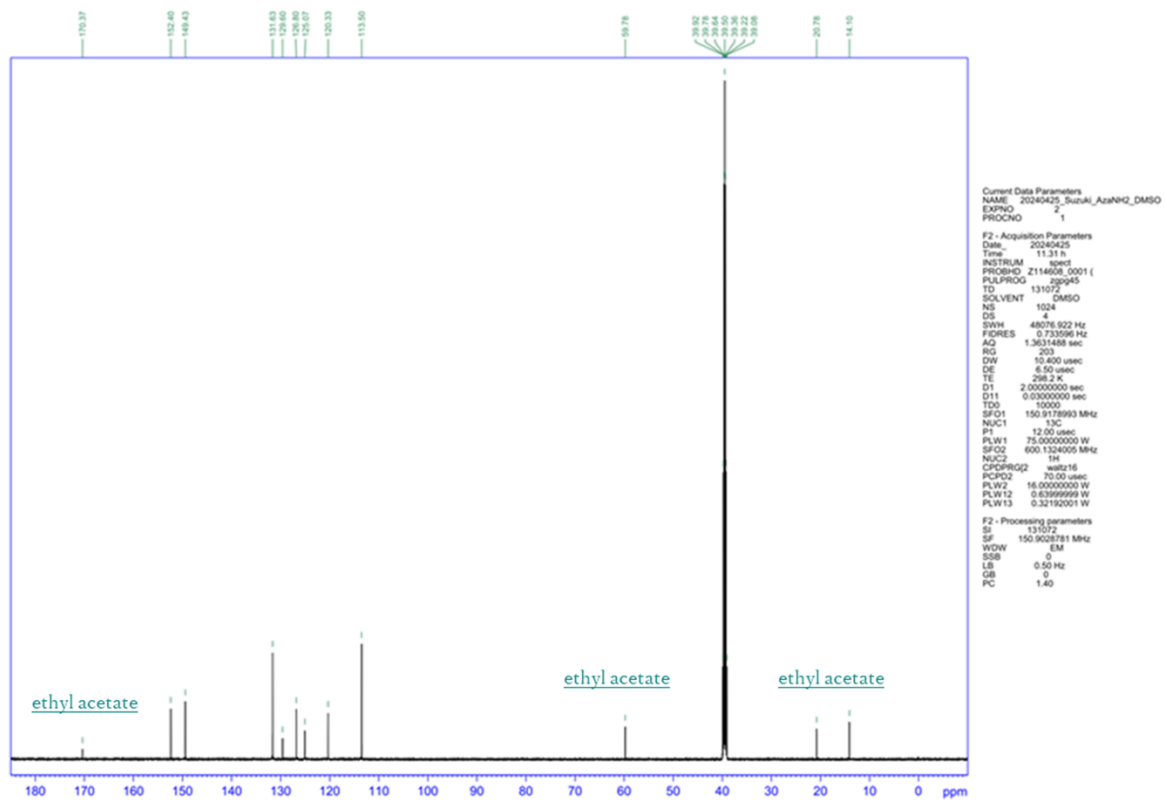


Figure S16. ^{13}C NMR of AzaPy(NH_2) $_4$.

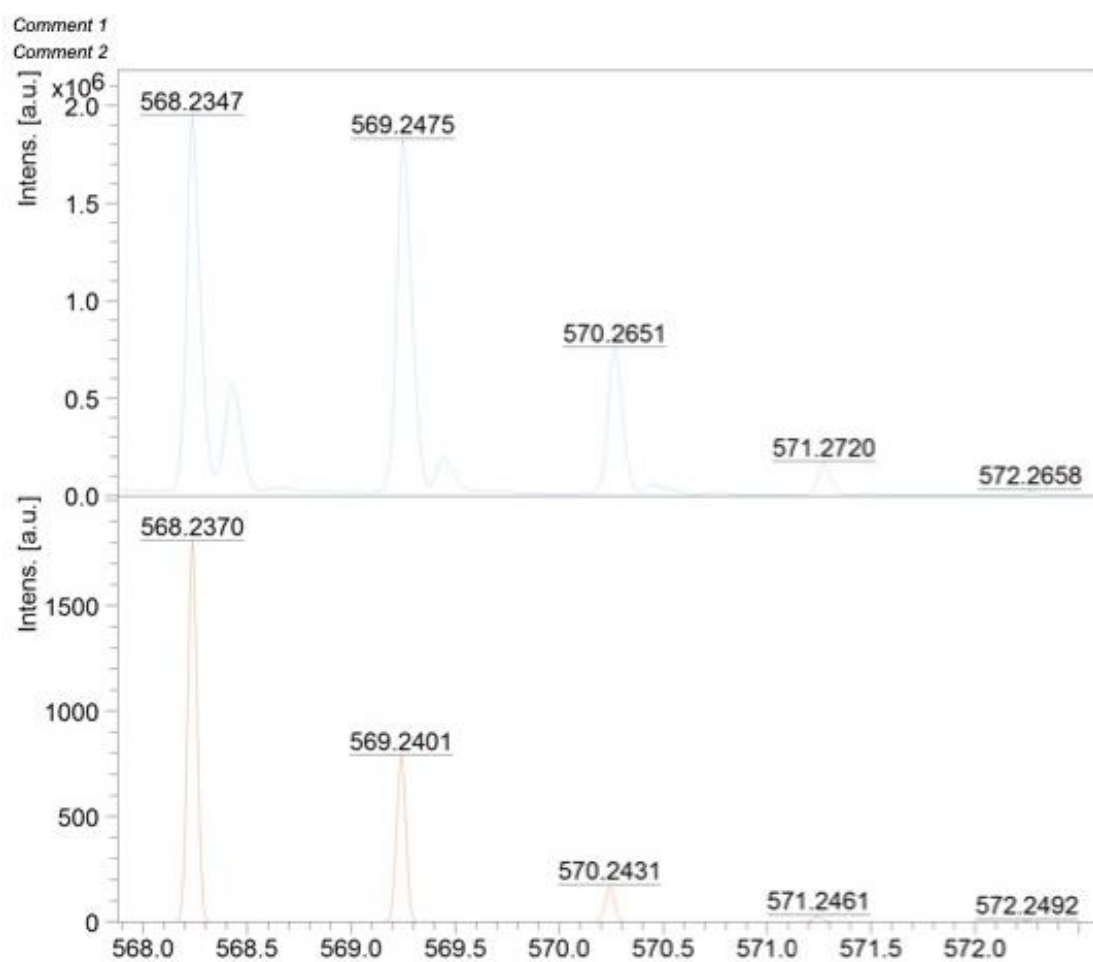


Figure S17. MS spectra of AzaPy(NH₂)₄.

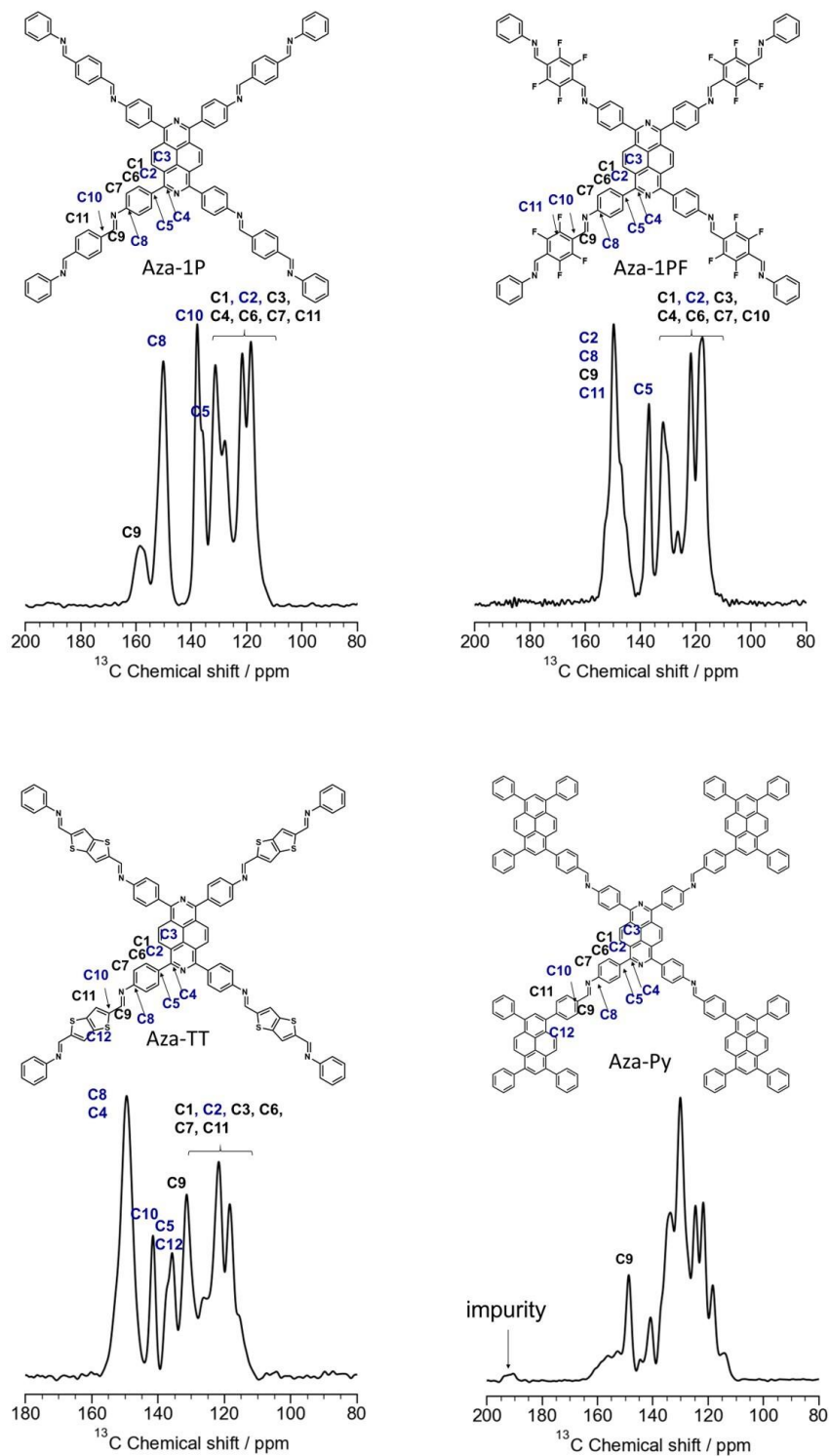


Figure S18. CP/MAS ^{13}C NMR spectra of Aza-1P, Aza-1PF, Aza-TT, and Aza-Py.

Table S1. Summary of nitrogen sorption measurement and NLDFT analysis.

	Aza-1P	Aza-1PF	Aza-TT	Aza-Py
Isotherm type	IV	IV	IV	I
BET surface area / cm ² g ⁻¹	1908	1620	1380	1162
Pore volume / cm ³ g ⁻¹	1.06	0.86	0.99	0.20
Theoretical pore size / nm	2.3	2.3	2.4	1.6
Experimental pore size / nm	2.3	2.1	2.4	1.6

Table S2. Fractional atomic coordinate of COFs.

Aza-1P Triclinic: P 1; a = 38.9310 Å; b = 30.6713 Å; c = 3.7352 Å; $\alpha = 90.0000$; $\beta = 76.0000$; $\gamma = 90.0000$.			
Atom list	x	y	z
C1	0.42785	0.53872	0.43149
C2	0.46391	0.54036	0.46061
C3	0.48291	0.58007	0.48295
C4	0.40376	0.57707	0.43332
C5	0.58621	0.38269	0.74622
C6	0.61041	0.34879	0.7281
C7	0.64628	0.3543	0.54192
C8	0.65683	0.39467	0.3661
C9	0.63219	0.42789	0.3781
N10	0.66968	0.31867	0.52127
C11	0.70146	0.32279	0.56763
C12	0.72599	0.28555	0.53311
C13	0.71572	0.24307	0.45591
C14	0.73925	0.20831	0.42364
H15	0.47023	0.61148	0.4733
H16	0.55935	0.3776	0.91037
H17	0.60193	0.31837	0.87315
H18	0.68413	0.39966	0.21155
H19	0.64079	0.45832	0.23365
H20	0.71176	0.35465	0.6415
H21	0.68909	0.23761	0.42029
H22	0.73072	0.17583	0.36245
C23	0.51799	0.5	0.52067
C24	0.58854	0.5	0.57762

Aza-1PF Triclinic: P 1; a = 36.8621 Å; b = 32.6814 Å; c = 3.8267 Å; $\alpha = 90.0000$; $\beta = 82.0445$; $\gamma = 90.0000$.			
Atom list	x	y	z
C1	0.426	0.536	0.341

C2	0.463	0.538	0.414
C3	0.482	0.575	0.459
C4	0.401	0.572	0.319
C5	0.588	0.39	0.844
C6	0.613	0.358	0.846
C7	0.65	0.362	0.68
C8	0.661	0.4	0.526
C9	0.636	0.432	0.526
N10	0.673	0.327	0.691
C11	0.703	0.323	0.481
C12	0.726	0.286	0.499
C13	0.714	0.25	0.683
C14	0.737	0.215	0.684
H15	0.469	0.605	0.433
H16	0.561	0.386	0.984
H17	0.604	0.329	0.976
H18	0.689	0.405	0.407
H19	0.645	0.461	0.4
H20	0.714	0.345	0.273
F21	0.681	0.247	0.866
F22	0.724	0.182	0.872
C23	0.926	0.036	0.345
C24	0.963	0.038	0.418
C25	0.982	0.075	0.464
C26	0.901	0.073	0.323
C27	0.088	0.89	0.847
C28	0.113	0.858	0.848
C29	0.15	0.862	0.681
C30	0.161	0.9	0.527
C31	0.136	0.932	0.528
N32	0.173	0.827	0.691
C33	0.203	0.822	0.48
C34	0.226	0.786	0.497
C35	0.214	0.749	0.682
C36	0.237	0.715	0.682

H37	0.969	0.105	0.438
H38	0.061	0.886	0.987
H39	0.104	0.829	0.977
H40	0.189	0.905	0.408
H41	0.145	0.961	0.402
H42	0.214	0.845	0.272
F43	0.181	0.747	0.865
F44	0.224	0.682	0.87
C45	0.574	0.536	0.655
C46	0.537	0.538	0.583
C47	0.518	0.575	0.537
C48	0.599	0.573	0.677
C49	0.412	0.39	0.153
C50	0.387	0.358	0.152
C51	0.35	0.362	0.318
C52	0.339	0.4	0.472
C53	0.364	0.432	0.472
N54	0.327	0.327	0.307
C55	0.297	0.323	0.518
C56	0.274	0.286	0.501
C57	0.286	0.249	0.317
C58	0.263	0.215	0.317
H59	0.531	0.605	0.563
H60	0.439	0.386	0.013
H61	0.396	0.329	0.022
H62	0.311	0.405	0.591
H63	0.355	0.461	0.597
H64	0.286	0.345	0.726
F65	0.319	0.247	0.133
F66	0.276	0.182	0.13
C67	0.074	0.036	0.659
C68	0.037	0.038	0.587
C69	0.018	0.075	0.541
C70	0.099	0.072	0.68
C71	0.912	0.89	0.156

C72	0.887	0.858	0.153
C73	0.85	0.862	0.32
C74	0.839	0.9	0.474
C75	0.864	0.932	0.474
N76	0.827	0.827	0.308
C77	0.797	0.823	0.519
C78	0.774	0.786	0.501
C79	0.786	0.75	0.317
C80	0.763	0.715	0.316
H81	0.031	0.105	0.567
H82	0.939	0.886	0.016
H83	0.896	0.829	0.024
H84	0.811	0.905	0.593
H85	0.855	0.961	0.6
H86	0.786	0.845	0.727
F87	0.819	0.747	0.133
F88	0.776	0.682	0.128
C89	0.574	0.464	0.655
C90	0.537	0.462	0.583
C91	0.518	0.425	0.537
C92	0.599	0.428	0.677
C93	0.412	0.61	0.152
C94	0.387	0.642	0.15
C95	0.35	0.638	0.317
C96	0.339	0.6	0.471
C97	0.364	0.568	0.47
N98	0.327	0.673	0.306
C99	0.297	0.677	0.517
C100	0.274	0.714	0.5
C101	0.286	0.751	0.316
C102	0.263	0.785	0.316
H103	0.531	0.395	0.563
H104	0.439	0.614	0.012
H105	0.395	0.671	0.021
H106	0.311	0.595	0.59

H107	0.355	0.539	0.596
H108	0.286	0.655	0.725
F109	0.319	0.753	0.132
F110	0.276	0.818	0.128
C111	0.074	0.964	0.659
C112	0.037	0.962	0.586
C113	0.018	0.925	0.54
C114	0.099	0.927	0.68
C115	0.912	0.11	0.157
C116	0.887	0.142	0.155
C117	0.85	0.138	0.321
C118	0.839	0.1	0.475
C119	0.864	0.068	0.475
N120	0.827	0.173	0.31
C121	0.797	0.178	0.521
C122	0.774	0.214	0.503
C123	0.786	0.251	0.318
C124	0.763	0.285	0.317
H125	0.031	0.895	0.566
H126	0.939	0.114	0.017
H127	0.896	0.171	0.025
H128	0.811	0.095	0.594
H129	0.855	0.039	0.6
H130	0.786	0.155	0.728
F131	0.819	0.253	0.135
F132	0.776	0.318	0.13
C133	0.426	0.464	0.341
C134	0.463	0.462	0.414
C135	0.482	0.425	0.459
C136	0.401	0.427	0.32
C137	0.588	0.61	0.843
C138	0.613	0.642	0.845
C139	0.65	0.638	0.679
C140	0.661	0.6	0.526
C141	0.636	0.568	0.525

N142	0.673	0.673	0.691
C143	0.703	0.678	0.48
C144	0.726	0.714	0.497
C145	0.714	0.751	0.682
C146	0.737	0.785	0.683
H147	0.469	0.395	0.434
H148	0.561	0.614	0.983
H149	0.604	0.671	0.975
H150	0.689	0.595	0.406
H151	0.645	0.539	0.4
H152	0.714	0.655	0.272
F153	0.681	0.753	0.865
F154	0.724	0.818	0.871
C155	0.926	0.964	0.345
C156	0.963	0.962	0.417
C157	0.982	0.925	0.463
C158	0.901	0.928	0.323
C159	0.088	0.11	0.847
C160	0.113	0.142	0.849
C161	0.15	0.138	0.682
C162	0.161	0.1	0.529
C163	0.136	0.068	0.529
N164	0.173	0.173	0.693
C165	0.203	0.177	0.482
C166	0.226	0.214	0.499
C167	0.214	0.251	0.683
C168	0.237	0.285	0.683
H169	0.969	0.895	0.436
H170	0.061	0.114	0.988
H171	0.104	0.171	0.978
H172	0.189	0.095	0.409
H173	0.145	0.039	0.403
H174	0.214	0.155	0.275
F175	0.181	0.253	0.866
F176	0.224	0.318	0.87

C177	0.518	0.5	0.541
N178	0.591	0.5	0.684
C179	0.018	0	0.545
N180	0.091	-3E-05	0.687
C181	0.482	0.5	0.455
N182	0.409	0.5	0.313
C183	0.982	3E-05	0.459
N184	0.909	6E-05	0.317

Aza-TT Triclinic: P 1; a = 36.2541 Å; b = 35.7548 Å; c = 3.8525 Å; $\alpha = 90.0000$; $\beta = 74.5849$; $\gamma = 90.0000$.			
Atom list	x	y	z
C1	0.575	0.534	0.581
C2	0.538	0.535	0.548
C3	0.518	0.568	0.521
C4	0.599	0.568	0.549
C5	0.587	0.6	0.745
C6	0.611	0.631	0.698
C7	0.647	0.63	0.451
C8	0.659	0.597	0.258
C9	0.636	0.566	0.306
N10	0.674	0.658	0.402
C11	0.666	0.692	0.523
C12	0.698	0.716	0.505
S13	0.742	0.696	0.321
C14	0.764	0.736	0.415
C15	0.699	0.752	0.636
H16	0.532	0.595	0.536
H17	0.56	0.601	0.95
H18	0.602	0.656	0.868
H19	0.688	0.597	0.069
H20	0.644	0.541	0.147
H21	0.637	0.703	0.644

H22	0.673	0.768	0.764
C23	0.593	0.5	0.602
C24	0.519	0.5	0.527

Aza-Py Triclinic: P 1; a = 51.3498 Å; b = 48.4242 Å; c = 3.9500 Å; $\alpha = 90.0000$; $\beta = 78.2636$; $\gamma = 90.0000$.			
Atom list	x	y	z
C1	0.199	0.275	0.31
C2	0.225	0.275	0.397
C3	0.238	0.3	0.447
C4	0.182	0.299	0.322
C5	0.19	0.324	0.134
C6	0.174	0.347	0.173
C7	0.149	0.346	0.4
C8	0.14	0.321	0.578
C9	0.157	0.298	0.542
C10	0.447	0.026	0.37
C11	0.473	0.025	0.428
C12	0.487	0.05	0.462
C13	0.431	0.05	0.356
C14	0.405	0.052	0.558
C15	0.39	0.076	0.55
C16	0.401	0.099	0.339
C17	0.426	0.096	0.132
C18	0.441	0.072	0.142
C19	0.387	0.124	0.33
N20	0.365	0.13	0.566
H21	0.23	0.319	0.412
H22	0.208	0.325	-0.03
H23	0.18	0.364	0.036
H24	0.122	0.32	0.737
H25	0.15	0.281	0.683

H26	0.48	0.069	0.438
H27	0.397	0.036	0.718
H28	0.371	0.077	0.7
H29	0.435	0.112	-0.03
H30	0.459	0.072	-0.01
H31	0.395	0.138	0.14
C32	0.301	0.275	0.69
C33	0.275	0.275	0.603
C34	0.262	0.3	0.553
C35	0.318	0.299	0.678
C36	0.31	0.324	0.866
C37	0.326	0.347	0.827
C38	0.351	0.346	0.6
C39	0.36	0.321	0.422
C40	0.343	0.298	0.458
C41	0.053	0.026	0.63
C42	0.027	0.025	0.572
C43	0.013	0.05	0.538
C44	0.069	0.05	0.644
C45	0.095	0.052	0.442
C46	0.11	0.076	0.45
C47	0.099	0.099	0.661
C48	0.074	0.096	0.868
C49	0.059	0.072	0.858
C50	0.113	0.124	0.67
N51	0.135	0.13	0.434
H52	0.27	0.319	0.588
H53	0.292	0.325	1.029
H54	0.32	0.364	0.964
H55	0.378	0.32	0.263
H56	0.35	0.281	0.318
H57	0.02	0.069	0.562
H58	0.103	0.036	0.282
H59	0.129	0.077	0.3

H60	0.065	0.112	1.026
H61	0.041	0.072	1.007
H62	0.105	0.138	0.86
C63	0.301	0.225	0.69
C64	0.275	0.225	0.603
C65	0.262	0.2	0.553
C66	0.318	0.201	0.678
C67	0.31	0.176	0.866
C68	0.326	0.153	0.827
C69	0.351	0.154	0.6
C70	0.36	0.179	0.422
C71	0.343	0.202	0.458
C72	0.053	0.474	0.63
C73	0.027	0.475	0.572
C74	0.013	0.45	0.538
C75	0.069	0.45	0.644
C76	0.095	0.448	0.442
C77	0.11	0.424	0.45
C78	0.099	0.401	0.661
C79	0.074	0.404	0.868
C80	0.059	0.428	0.858
C81	0.113	0.376	0.67
N82	0.135	0.37	0.434
H83	0.27	0.181	0.588
H84	0.292	0.175	1.029
H85	0.32	0.136	0.964
H86	0.378	0.18	0.263
H87	0.35	0.219	0.318
H88	0.02	0.431	0.562
H89	0.103	0.464	0.282
H90	0.129	0.423	0.3
H91	0.065	0.388	1.026
H92	0.041	0.428	1.007
H93	0.105	0.362	0.86

C94	0.199	0.225	0.31
C95	0.225	0.225	0.397
C96	0.238	0.2	0.447
C97	0.182	0.201	0.322
C98	0.19	0.176	0.134
C99	0.174	0.153	0.173
C100	0.149	0.154	0.4
C101	0.14	0.179	0.578
C102	0.157	0.202	0.542
C103	0.447	0.474	0.37
C104	0.473	0.475	0.428
C105	0.487	0.45	0.462
C106	0.431	0.45	0.356
C107	0.405	0.448	0.558
C108	0.39	0.424	0.55
C109	0.401	0.401	0.339
C110	0.426	0.404	0.132
C111	0.441	0.428	0.142
C112	0.387	0.376	0.33
N113	0.365	0.37	0.566
H114	0.23	0.181	0.412
H115	0.208	0.175	-0.03
H116	0.18	0.136	0.036
H117	0.122	0.18	0.737
H118	0.15	0.219	0.683
H119	0.48	0.431	0.438
H120	0.397	0.464	0.718
H121	0.371	0.423	0.7
H122	0.435	0.388	-0.03
H123	0.459	0.428	-0.01
H124	0.395	0.362	0.14
C125	0.237	0.25	0.447
N126	0.188	0.25	0.243
C127	0.263	0.25	0.553

N128	0.312	0.25	0.757
H129	0.084	0	0.727
C130	0.065	0	0.67
C131	0.013	0	0.537
H132	0.416	0	0.273
C133	0.435	0	0.331
C134	0.487	0	0.463
C135	0.699	0.275	0.31
C136	0.725	0.275	0.397
C137	0.738	0.3	0.447
C138	0.682	0.299	0.322
C139	0.69	0.324	0.134
C140	0.674	0.347	0.173
C141	0.649	0.346	0.4
C142	0.64	0.321	0.578
C143	0.657	0.298	0.542
C144	0.947	0.026	0.37
C145	0.973	0.025	0.428
C146	0.987	0.05	0.462
C147	0.931	0.05	0.356
C148	0.905	0.052	0.558
C149	0.89	0.076	0.55
C150	0.901	0.099	0.339
C151	0.926	0.096	0.132
C152	0.941	0.072	0.142
C153	0.887	0.124	0.33
N154	0.865	0.13	0.566
H155	0.73	0.319	0.412
H156	0.708	0.325	-0.03
H157	0.68	0.364	0.036
H158	0.622	0.32	0.737
H159	0.65	0.281	0.683
H160	0.98	0.069	0.438
H161	0.897	0.036	0.718

H162	0.871	0.077	0.7
H163	0.935	0.112	-0.03
H164	0.959	0.072	-0.01
H165	0.895	0.138	0.14
C166	0.801	0.275	0.69
C167	0.775	0.275	0.603
C168	0.762	0.3	0.553
C169	0.818	0.299	0.678
C170	0.81	0.324	0.866
C171	0.826	0.347	0.827
C172	0.851	0.346	0.6
C173	0.86	0.321	0.422
C174	0.843	0.298	0.458
C175	0.553	0.026	0.63
C176	0.527	0.025	0.572
C177	0.513	0.05	0.538
C178	0.569	0.05	0.644
C179	0.595	0.052	0.442
C180	0.61	0.076	0.45
C181	0.599	0.099	0.661
C182	0.574	0.096	0.868
C183	0.559	0.072	0.858
C184	0.613	0.124	0.67
N185	0.635	0.13	0.434
H186	0.77	0.319	0.588
H187	0.792	0.325	1.029
H188	0.82	0.364	0.964
H189	0.878	0.32	0.263
H190	0.85	0.281	0.318
H191	0.52	0.069	0.562
H192	0.603	0.036	0.282
H193	0.629	0.077	0.3
H194	0.565	0.112	1.026
H195	0.541	0.072	1.007

H196	0.605	0.138	0.86
C197	0.801	0.225	0.69
C198	0.775	0.225	0.603
C199	0.762	0.2	0.553
C200	0.818	0.201	0.678
C201	0.81	0.176	0.866
C202	0.826	0.153	0.827
C203	0.851	0.154	0.6
C204	0.86	0.179	0.422
C205	0.843	0.202	0.458
C206	0.553	0.474	0.63
C207	0.527	0.475	0.572
C208	0.513	0.45	0.538
C209	0.569	0.45	0.644
C210	0.595	0.448	0.442
C211	0.61	0.424	0.45
C212	0.599	0.401	0.661
C213	0.574	0.404	0.868
C214	0.559	0.428	0.858
C215	0.613	0.376	0.67
N216	0.635	0.37	0.434
H217	0.77	0.181	0.588
H218	0.792	0.175	1.029
H219	0.82	0.136	0.964
H220	0.878	0.18	0.263
H221	0.85	0.219	0.318
H222	0.52	0.431	0.562
H223	0.603	0.464	0.282
H224	0.629	0.423	0.3
H225	0.565	0.388	1.026
H226	0.541	0.428	1.007
H227	0.605	0.362	0.86
C228	0.699	0.225	0.31
C229	0.725	0.225	0.397

C230	0.738	0.2	0.447
C231	0.682	0.201	0.322
C232	0.69	0.176	0.134
C233	0.674	0.153	0.173
C234	0.649	0.154	0.4
C235	0.64	0.179	0.578
C236	0.657	0.202	0.542
C237	0.947	0.474	0.37
C238	0.973	0.475	0.428
C239	0.987	0.45	0.462
C240	0.931	0.45	0.356
C241	0.905	0.448	0.558
C242	0.89	0.424	0.55
C243	0.901	0.401	0.339
C244	0.926	0.404	0.132
C245	0.941	0.428	0.142
C246	0.887	0.376	0.33
N247	0.865	0.37	0.566
H248	0.73	0.181	0.412
H249	0.708	0.175	-0.03
H250	0.68	0.136	0.036
H251	0.622	0.18	0.737
H252	0.65	0.219	0.683
H253	0.98	0.431	0.438
H254	0.897	0.464	0.718
H255	0.871	0.423	0.7
H256	0.935	0.388	-0.03
H257	0.959	0.428	-0.01
H258	0.895	0.362	0.14
C259	0.737	0.25	0.447
N260	0.688	0.25	0.243
C261	0.763	0.25	0.553
N262	0.812	0.25	0.757
H263	0.584	0	0.727

C264	0.565	0	0.67
C265	0.513	0	0.537
H266	0.916	0	0.273
C267	0.935	0	0.331
C268	0.987	0	0.463
C269	0.199	0.775	0.31
C270	0.225	0.775	0.397
C271	0.238	0.8	0.447
C272	0.182	0.799	0.322
C273	0.19	0.824	0.134
C274	0.174	0.847	0.173
C275	0.149	0.846	0.4
C276	0.14	0.821	0.578
C277	0.157	0.798	0.542
C278	0.447	0.526	0.37
C279	0.473	0.525	0.428
C280	0.487	0.55	0.462
C281	0.431	0.55	0.356
C282	0.405	0.552	0.558
C283	0.39	0.576	0.55
C284	0.401	0.599	0.339
C285	0.426	0.596	0.132
C286	0.441	0.572	0.142
C287	0.387	0.624	0.33
N288	0.365	0.63	0.566
H289	0.23	0.819	0.412
H290	0.208	0.825	-0.03
H291	0.18	0.864	0.036
H292	0.122	0.82	0.737
H293	0.15	0.781	0.683
H294	0.48	0.569	0.438
H295	0.397	0.536	0.718
H296	0.371	0.577	0.7
H297	0.435	0.612	-0.03

H298	0.459	0.572	-0.01
H299	0.395	0.638	0.14
C300	0.301	0.775	0.69
C301	0.275	0.775	0.603
C302	0.262	0.8	0.553
C303	0.318	0.799	0.678
C304	0.31	0.824	0.866
C305	0.326	0.847	0.827
C306	0.351	0.846	0.6
C307	0.36	0.821	0.422
C308	0.343	0.798	0.458
C309	0.053	0.526	0.63
C310	0.027	0.525	0.572
C311	0.013	0.55	0.538
C312	0.069	0.55	0.644
C313	0.095	0.552	0.442
C314	0.11	0.576	0.45
C315	0.099	0.599	0.661
C316	0.074	0.596	0.868
C317	0.059	0.572	0.858
C318	0.113	0.624	0.67
N319	0.135	0.63	0.434
H320	0.27	0.819	0.588
H321	0.292	0.825	1.029
H322	0.32	0.864	0.964
H323	0.378	0.82	0.263
H324	0.35	0.781	0.318
H325	0.02	0.569	0.562
H326	0.103	0.536	0.282
H327	0.129	0.577	0.3
H328	0.065	0.612	1.026
H329	0.041	0.572	1.007
H330	0.105	0.638	0.86
C331	0.301	0.725	0.69

C332	0.275	0.725	0.603
C333	0.262	0.7	0.553
C334	0.318	0.701	0.678
C335	0.31	0.676	0.866
C336	0.326	0.653	0.827
C337	0.351	0.654	0.6
C338	0.36	0.679	0.422
C339	0.343	0.702	0.458
C340	0.053	0.974	0.63
C341	0.027	0.975	0.572
C342	0.013	0.95	0.538
C343	0.069	0.95	0.644
C344	0.095	0.948	0.442
C345	0.11	0.924	0.45
C346	0.099	0.901	0.661
C347	0.074	0.904	0.868
C348	0.059	0.928	0.858
C349	0.113	0.876	0.67
N350	0.135	0.87	0.434
H351	0.27	0.681	0.588
H352	0.292	0.675	1.029
H353	0.32	0.636	0.964
H354	0.378	0.68	0.263
H355	0.35	0.719	0.318
H356	0.02	0.931	0.562
H357	0.103	0.964	0.282
H358	0.129	0.923	0.3
H359	0.065	0.888	1.026
H360	0.041	0.928	1.007
H361	0.105	0.862	0.86
C362	0.199	0.725	0.31
C363	0.225	0.725	0.397
C364	0.238	0.7	0.447
C365	0.182	0.701	0.322

C366	0.19	0.676	0.134
C367	0.174	0.653	0.173
C368	0.149	0.654	0.4
C369	0.14	0.679	0.578
C370	0.157	0.702	0.542
C371	0.447	0.974	0.37
C372	0.473	0.975	0.428
C373	0.487	0.95	0.462
C374	0.431	0.95	0.356
C375	0.405	0.948	0.558
C376	0.39	0.924	0.55
C377	0.401	0.901	0.339
C378	0.426	0.904	0.132
C379	0.441	0.928	0.142
C380	0.387	0.876	0.33
N381	0.365	0.87	0.566
H382	0.23	0.681	0.412
H383	0.208	0.675	-0.03
H384	0.18	0.636	0.036
H385	0.122	0.68	0.737
H386	0.15	0.719	0.683
H387	0.48	0.931	0.438
H388	0.397	0.964	0.718
H389	0.371	0.923	0.7
H390	0.435	0.888	-0.03
H391	0.459	0.928	-0.01
H392	0.395	0.862	0.14
C393	0.237	0.75	0.447
N394	0.188	0.75	0.243
C395	0.263	0.75	0.553
N396	0.312	0.75	0.757
H397	0.084	0.5	0.727
C398	0.065	0.5	0.67
C399	0.013	0.5	0.537

H400	0.416	0.5	0.273
C401	0.435	0.5	0.331
C402	0.487	0.5	0.463
C403	0.699	0.775	0.31
C404	0.725	0.775	0.397
C405	0.738	0.8	0.447
C406	0.682	0.799	0.322
C407	0.69	0.824	0.134
C408	0.674	0.847	0.173
C409	0.649	0.846	0.4
C410	0.64	0.821	0.578
C411	0.657	0.798	0.542
C412	0.947	0.526	0.37
C413	0.973	0.525	0.428
C414	0.987	0.55	0.462
C415	0.931	0.55	0.356
C416	0.905	0.552	0.558
C417	0.89	0.576	0.55
C418	0.901	0.599	0.339
C419	0.926	0.596	0.132
C420	0.941	0.572	0.142
C421	0.887	0.624	0.33
N422	0.865	0.63	0.566
H423	0.73	0.819	0.412
H424	0.708	0.825	-0.03
H425	0.68	0.864	0.036
H426	0.622	0.82	0.737
H427	0.65	0.781	0.683
H428	0.98	0.569	0.438
H429	0.897	0.536	0.718
H430	0.871	0.577	0.7
H431	0.935	0.612	-0.03
H432	0.959	0.572	-0.01
H433	0.895	0.638	0.14

C434	0.801	0.775	0.69
C435	0.775	0.775	0.603
C436	0.762	0.8	0.553
C437	0.818	0.799	0.678
C438	0.81	0.824	0.866
C439	0.826	0.847	0.827
C440	0.851	0.846	0.6
C441	0.86	0.821	0.422
C442	0.843	0.798	0.458
C443	0.553	0.526	0.63
C444	0.527	0.525	0.572
C445	0.513	0.55	0.538
C446	0.569	0.55	0.644
C447	0.595	0.552	0.442
C448	0.61	0.576	0.45
C449	0.599	0.599	0.661
C450	0.574	0.596	0.868
C451	0.559	0.572	0.858
C452	0.613	0.624	0.67
N453	0.635	0.63	0.434
H454	0.77	0.819	0.588
H455	0.792	0.825	1.029
H456	0.82	0.864	0.964
H457	0.878	0.82	0.263
H458	0.85	0.781	0.318
H459	0.52	0.569	0.562
H460	0.603	0.536	0.282
H461	0.629	0.577	0.3
H462	0.565	0.612	1.026
H463	0.541	0.572	1.007
H464	0.605	0.638	0.86
C465	0.801	0.725	0.69
C466	0.775	0.725	0.603
C467	0.762	0.7	0.553

C468	0.818	0.701	0.678
C469	0.81	0.676	0.866
C470	0.826	0.653	0.827
C471	0.851	0.654	0.6
C472	0.86	0.679	0.422
C473	0.843	0.702	0.458
C474	0.553	0.974	0.63
C475	0.527	0.975	0.572
C476	0.513	0.95	0.538
C477	0.569	0.95	0.644
C478	0.595	0.948	0.442
C479	0.61	0.924	0.45
C480	0.599	0.901	0.661
C481	0.574	0.904	0.868
C482	0.559	0.928	0.858
C483	0.613	0.876	0.67
N484	0.635	0.87	0.434
H485	0.77	0.681	0.588
H486	0.792	0.675	1.029
H487	0.82	0.636	0.964
H488	0.878	0.68	0.263
H489	0.85	0.719	0.318
H490	0.52	0.931	0.562
H491	0.603	0.964	0.282
H492	0.629	0.923	0.3
H493	0.565	0.888	1.026
H494	0.541	0.928	1.007
H495	0.605	0.862	0.86
C496	0.699	0.725	0.31
C497	0.725	0.725	0.397
C498	0.738	0.7	0.447
C499	0.682	0.701	0.322
C500	0.69	0.676	0.134
C501	0.674	0.653	0.173

C502	0.649	0.654	0.4
C503	0.64	0.679	0.578
C504	0.657	0.702	0.542
C505	0.947	0.974	0.37
C506	0.973	0.975	0.428
C507	0.987	0.95	0.462
C508	0.931	0.95	0.356
C509	0.905	0.948	0.558
C510	0.89	0.924	0.55
C511	0.901	0.901	0.339
C512	0.926	0.904	0.132
C513	0.941	0.928	0.142
C514	0.887	0.876	0.33
N515	0.865	0.87	0.566
H516	0.73	0.681	0.412
H517	0.708	0.675	-0.03
H518	0.68	0.636	0.036
H519	0.622	0.68	0.737
H520	0.65	0.719	0.683
H521	0.98	0.931	0.438
H522	0.897	0.964	0.718
H523	0.871	0.923	0.7
H524	0.935	0.888	-0.03
H525	0.959	0.928	-0.01
H526	0.895	0.862	0.14
C527	0.737	0.75	0.447
N528	0.688	0.75	0.243
C529	0.763	0.75	0.553
N530	0.812	0.75	0.757
H531	0.584	0.5	0.727
C532	0.565	0.5	0.67
C533	0.513	0.5	0.537
H534	0.916	0.5	0.273
C535	0.935	0.5	0.331

C536	0.987	0.5	0.463
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References

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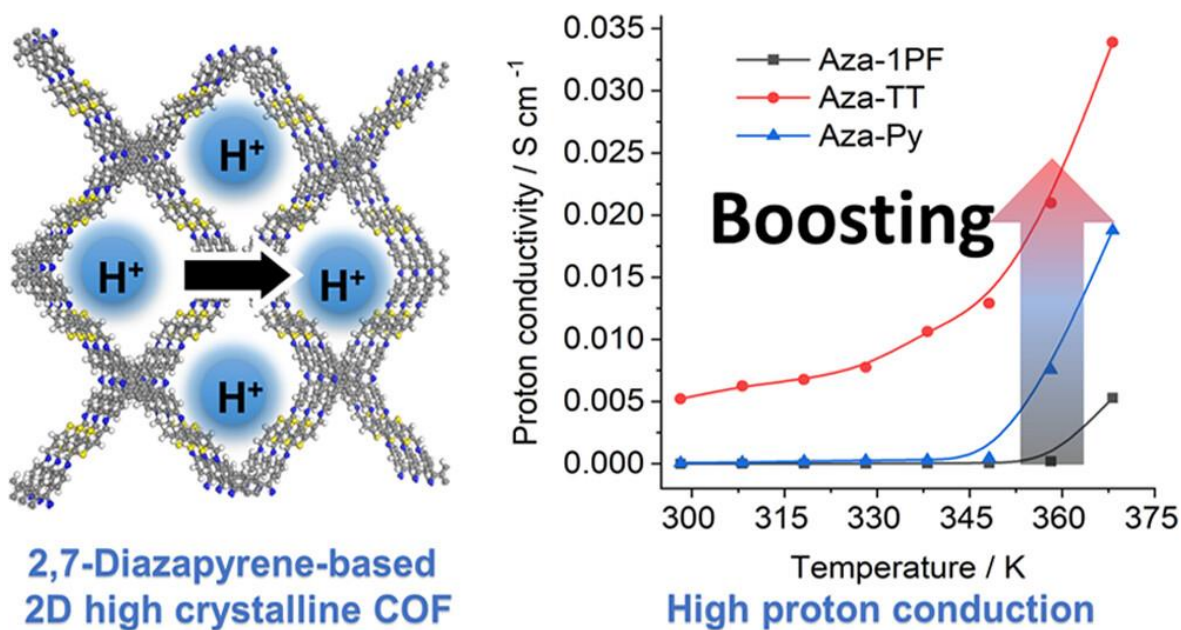
Chapter 2

Efficient Proton Conduction of Diazapyrene-Based Two-Dimensional Conjugated Covalent Organic Frameworks

Abstract:

Due to the stacking of the conjugated 2D Diazapyrene-based COFs frames with small E_g values is also beneficial for the formation of highly stable conducting pathways in the crystalline state, which was confirmed by the results of microwave conductivity measurements. Nitrogen centers in diazapyrene units also play a key role as the active sites for proton transfer, and the maximum proton conductivity of $\sigma = 10^{-2} \text{ S cm}^{-1}$ was achieved along the co-continuous nanopore structures surrounded by the active sites. Results show that tetragonal COFs based on diazapyrene can be used as a highly crystalline two-dimensional material with special electrical and proton conducting capabilities.

This study highlights that that these highly crystalline Diazapyrene-based COFs not only possess stable one-dimensional proton conduction channels, but can also be further used in low-temperature proton conducting membranes by utilizing the nitrogen active centers of the diazopyrene core without any external doping. These COFs can be further used for low temperature proton conducting membranes via utilizing the nitrogen active centers of the diaza-pyrene core, without any external doping.



Scheme 1. 2,7-Diazapyrene-based COFs realized efficient proton conduction via utilizing the nitrogen active centers of the dia-za-pyrene core, without any external doping.

Introduction

Recently, COFs have attracted considerable attention as proton-conducting materials owing to their low density, high thermal stability, and inherent framework structure.^{[57][58][59]} Proton conduction occurs in COFs through protonation–deprotonation reactions between functional groups.^[60] As compared with fluorinated polymer electrolytes and various aromatic polymers, COFs exhibit superior toughness, particularly under harsh conditions.^{[61][62][63][64]} Furthermore, the microporous structure of COFs surpasses that of polymer membranes, promoting the confinement of proton carriers within pores and preventing their leakage.^{[65][66][67][68]}

Currently, two types of proton conductivity are identified: wet proton conductivity^{[69][70][71]} and anhydrous proton conductivity^{[72][73][74]}. However, most COFs exhibit low stability in humid and harsh chemical environments.^[75] In the presence of an acid, an alkali, or water, a reverse reaction may occur, leading to the destruction of the framework structure, transformation into an amorphous state, and loss of the proton transmission channel.^[76] Banerjee *et al.* reported the first proton-conducting COF containing an azo (--N=N--) bond, Tp-Azo COF. Because the N=N (azo) unit of Tp-Azo COF is protonated and forms a hydrogen bonding network with H_2PO_4^- anions, it exhibits high proton conductivity under humid conditions (relative humidity: 98%, $\sigma = 9.9 \times 10^{-4} \text{ S cm}^{-1}$ at 59°C).^[77] However, a higher proton conductivity is often observed for anhydrous COFs containing dopants or acidic groups in their building blocks under high-temperature conditions.^{[65][77][78][79]} Materials that can conduct protons in the presence of water are more suitable for a wide range of practical applications, especially those that can be used under mild conditions and demonstrate high-speed conduction properties and biocompatibility. Many anhydrous proton-conducting materials require elevated temperatures to achieve high proton conductivity. In contrast, water-conducting materials frequently exhibit excellent proton conductivity at lower temperatures. In biomedical

applications, water-containing materials are generally more biocompatible because water is a common component of biological systems, whereas anhydrous conductive materials may exert adverse effects on living organisms.^[80]

To control precisely crystallinity and proton conductivity, I utilized the modular nature of COFs in which various building blocks distribute evenly throughout the COFs. In the structures of diazapyrene-based COFs, each unit contains two pyridine centers with multiple N sites serving as hydrogen bond donors and N–H sites acting as hydrogen bond acceptors. This configuration is advantageous for introducing external proton sources. The tightly stacked one-dimensional channels within the COF structure provide a stable path for proton transport and ample loading sites for proton sources. This atomic arrangement may facilitate fast and smooth proton transport, effectively boosting proton conductivity.

Results and discussion

It is challenging to assess the interlayer conductivity of powdered COF structures using the direct current method. To evaluate the interlayer conductivity of the

diazapyrene-based COFs, flash photolysis time-resolved microwave conductivity (FP-TRMC) measurements were performed.

Upon optical charge injection at an excitation wavelength of 355 nm (3.5 eV), a transient enhancement in photoconductivity is observed for the diazapyrene-based COFs despite the negligible decay in this time regime (**Figures 6a–d**). Inspired by the coexistence of a large surface area and conductive pathways, I subsequently protonated diazapyrene units within the diazapyrene-based COFs using trifluoroacetic acid (TFA). Initial rapid decay was observed for the transients of all the COFs after doping with TFA, which is suggestive of TFA acting as a dopant for the static charge carriers/counter charges to lead the rapid recombination of photogenerated charge carriers. Notably, post-doping with TFA increased the photoconductivity of the diazapyrene-based COFs. In particular, the photoconductivity of the doped COFs is 2–3 times greater than that of the undoped COFs. This confirms the effectiveness of the TFA doping approach, which introduces doping charge carriers into the diazapyrene-based COFs through the protonation of diazapyrene units via vapor diffusion, utilizing TFA as the proton source. According to **Figures 6a–d** and **S1**, all the COFs showed enhancement in photoconductivity signals after the doping with TFA, which is considered as an effective charge carrier generation due to the protonation of the π -moiety. Following doping, the $\Phi\Sigma\mu$ value of **Aza-1P**

increases from 4.4×10^{-5} (undoped) to $7.7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; **Aza-1PF** increases from 8.5×10^{-6} (undoped) to $1.67 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; **Aza-TT** increases from 1.1×10^{-5} (undoped) to $2.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; and **Aza-Py** increases from 1.2×10^{-5} (undoped) to $3.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In contrast, the photoconductivity enhancement of **Py-1P** remains negligible (from 5×10^{-6} to $9 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; see **Figure S6**), which can be attributed to the larger number of protonatable nitrogen active sites within the structure of **Aza-1P** compared with that of **Py-1P**. These results demonstrate that shorter π – π stacking is advantageous in terms of charge carrier injection and the stable covalent bond allows chemical doping without disrupting the conductive pathways.

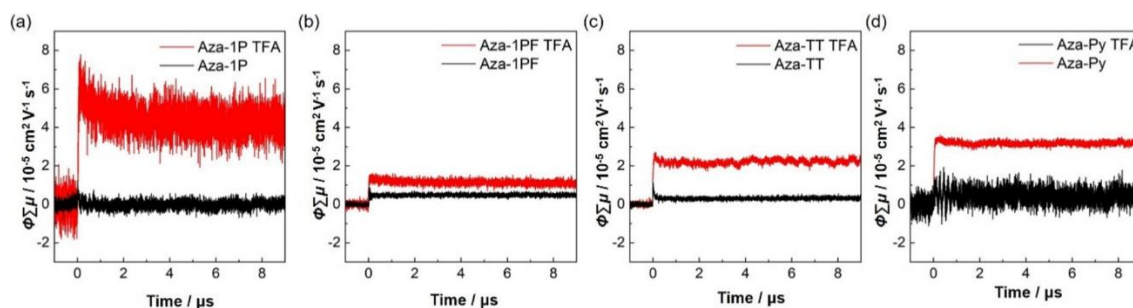


Figure 6. FP-TRMC transient decay profiles of (a) Aza-1P, (b) Aza-1PF, (c) Aza-TT, and (d) Aza-Py.

To investigate the proton conductivity of the diazapyrene-based COFs, I evaluated the proton transport behavior of the corresponding membranes by pressing COF powders into the discs with diameters of 5 mm and thicknesses of 1 mm under controlled humidity

conditions. Electrochemical impedance spectroscopy (EIS) was performed to assess the proton transfer behavior of the diazapyrene-based COF membranes at different temperatures (**Figures 7a** and **S2–S4**). Because the diazapyrene-based COFs do not contain internal proton sources, COF proton conductors are typically prepared through pore impregnation. This method involves the use of a strong acid as a proton carrier within the COF to enhance proton conductivity or water molecules to evaluate the material proton conduction in a humid environment. As expected, diazapyrene-based COF did not show proton conductivity under anhydrous conditions, which is shown in **Figure S5**. Therefore, this experiment was conducted at a relative humidity of 98%. **Figure 7b** indicates that the proton conductivity of the diazapyrene-based COFs increases with temperatures, and **Aza-TT** achieves the highest conductivity value of $3.4 \times 10^{-2} \text{ S cm}^{-1}$ at 95°C (368 K). Compared with the results reported by Li *et al.* for Im@Py-TT-COF-50 ($3.1 \times 10^{-3} \text{ S cm}^{-1}$ at 130°C)^[59], the proton conductivity of **Aza-TT** is higher by an order of magnitude and at a lower temperature without doping. Furthermore, **Aza-TT** exhibits superior proton conduction characteristics among the studied diazapyrene-based and pyrene-based COFs. The introduction of electron-rich thiophene rings effectively enhances the hydrogen-bonding interactions of imine bonds, thereby significantly improving proton conductivity. In addition, structural stacking in cofacial A-A manner

with high crystallinity through π - π stacking would provide effective and homogeneous pathway for proton movement.

Interestingly, **Aza-1PF** and **Aza-Py** exhibited significant differences in proton conductivity with increasing temperature. For **Aza-1PF** its proton conductivity value increased from $2.4 \times 10^{-7} \text{ S cm}^{-1}$ at 25°C (298 K) to $5.3 \times 10^{-3} \text{ S cm}^{-1}$ at 95°C (368 K), while for **Aza-Py** its value increased from $7.1 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C (298 K) to $1.9 \times 10^{-2} \text{ S cm}^{-1}$ at 95°C (368 K). Such a substantial difference in proton conductivity suggests that the **Aza-1PF** and **Aza-Py** COFs can be potentially used as proton-conduction switches. This emphasizes the significant contributions of the proton-donating and proton-accepting functional groups to the intrinsic proton conductivity of COFs. Finally, the activation energies (E_a) of the studied COFs were determined from the EIS data obtained at different temperatures. According to their Arrhenius plots, the E_a values of **Aza-TT**, **Aza-1PF**, and **Aza-Py** are estimated as 0.24, 0.69, and 1.01 eV, respectively. (Figure 7c) The efficient proton transport in the series of COFs has been discussed in terms of theoretical calculation based on Density Functional Theory (DFT) method. All the COFs are expected to have two active sites: lone pair at N in diazapyrene and N atoms in imine linkages. The adsorption/desorption energy of protons at the two active sites in the gas phase were deduced by the calculation (Figure S10), and summarized in the Table S1, suggesting both sites bind strongly protons in all COFs, the energy ranging from 2.9 – 3.8 eV.

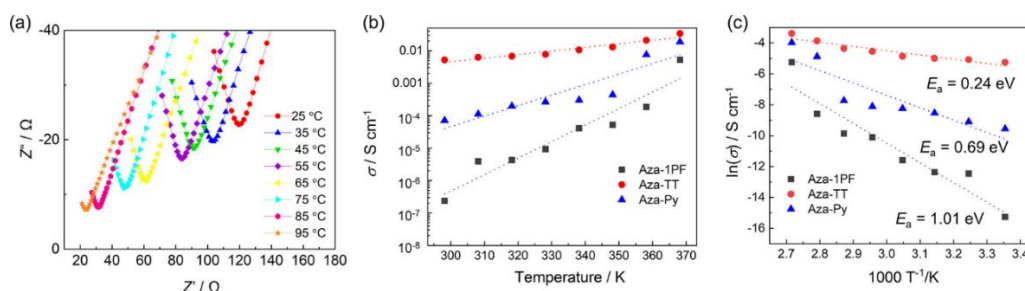


Figure 7. (a) Impedance spectra of **Aza-TT** obtained at different temperatures and a relative humidity of 98%. (b) Proton conductivities of **Aza-1PF**, **Aza-TT**, and **Aza-Py** determined at different temperatures and a relative humidity of 98%. (c) Arrhenius plots constructed for **Aza-1PF**, **Aza-TT**, and **Aza-Py**.

In addition, a proton at N in the diazapyrenes were more stable than that in imine linkages. Therefore, I focused the proton at N in diazapyrene (**Figure 8a**). Detailed calculation results were summarized in the SI (**Figures S8 and S9**). The desorption energy of the proton, however, higher than the experimental activation energy recorded for **Aza-1PF** and **Aza-TT**. Experimentally, proton conductivity in the COFs was assessed under humid conditions at 98% in these porous materials, thus enriched water molecules confined in the pores are presumed to form hydrogen bonding networks. The contribution from the networks was, in turn, taken into account for the theoretical simulation, as represented by the schematic figure (**Figure 8b-c**). The local hydrogen bonding networks significantly reduces the proton binding at N sites (**Figure 8b**), leading to the desorption energy of 1.1 eV for both the **Aza-1PF** and **Aza-TT**, which is in consistent with the activation energy recorded in **Aza-1PF**. In contrast, the developed hydrogen bonding in **Aza-TT** (**Figure 8c**) exhibits the reduction down to 0.3 eV; this is the case giving the very small activation energy of ~ 0.25 eV in **Aza-TT**.^{[52][53][54]} Thus, the calculation results suggested the importance of the developed hydrogen bonding network for proton

conductivity. If the hydrogen bonding network is well-formed around the N site, **Aza-1PF** would exhibit high proton conductivity. However, experiments showed relatively high activation energy, which is probably due to fluorine atoms at the linkages in the **Aza-1PF** hampering the formation of the network.

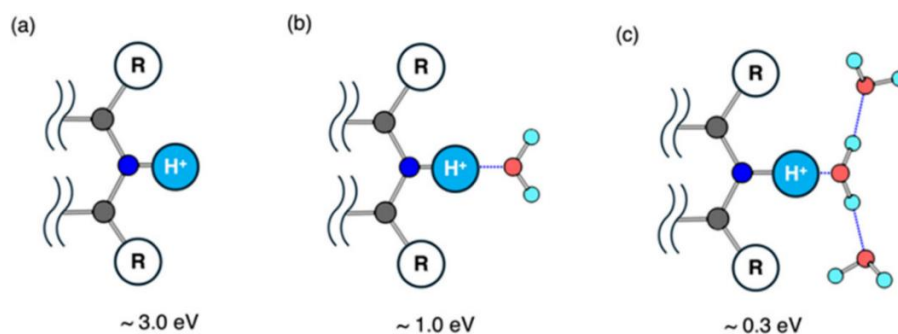


Figure 8. Schematic illustration of model structure of protonated COFs (a) in gas phase, (b) with only one water molecule, (c) in developed hydrogen bonding network. Here, a large quantum-chemical stabilization of the proton is caused by surrounding water molecules. The approximate desorption energies of the proton are also shown below those figures.

Comparison of 1H magic angle spinning (MAS) and double-quantum-filtered (DQF) MAS spectra allows us to distinguish mobile and rigid protons ^[55]. To gain insights into mobile protons in the Aza-based COFs, I performed 1H MAS and 1H DQF measurements as shown in **Figure 9**. For all COFs, 1H MAS NMR spectra showed two major signals; the signals at 5–9 ppm originate from aromatic protons and the signals at around 1.3 ppm can be characterized as protons (probably due to water) captured inside COF. The intensity of signals at 1.3 ppm significantly decreased for the DQF 1H NMR spectra, indicating that the protons were mobile. In addition, the linewidth of these signals has been sharpened with increasing the temperature (**Figure S7**). These results indicate that

the captured protons are highly mobile in nature.

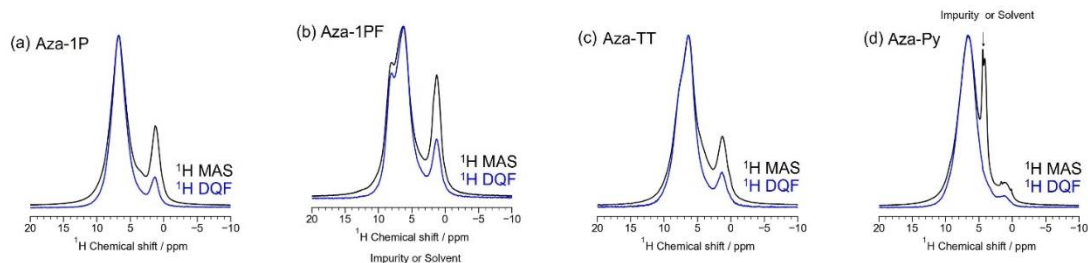


Figure 9. ^1H MAS (black) and ^1H DQF (blue) NMR spectra of (a) **Aza-1P**, (b) **Aza-1PF**, (c) **Aza-TT**, and (d) **Aza-Py**.

To check the stability of these COFs during the EIS measurement I measured the PXRD spectra of these COFs after the EIS studies and compared the data with their pristine samples. I observed that **Aza-TT** retained its crystallinity, however **Aza-1PF** and **Aza-Py** show some additional peaks probably due to the phase change of these materials which may be attributed for the certain jump in proton conductivity in the range of 345 to 355 K (**Figure 7c**). On the other hand, **Aza-1P** exhibited a huge loss of crystallinity after the EIS measurement and thus justified the lowest proton conductivity among all, (**Figure S6**).

Conclusion

In summary, the presence of diazapyrene centers in the synthesized COF can be utilized for proton coordination, and their proton conductivity was temperature-dependent. At a relative humidity of 98%, a four-order increase in the proton conductivity of **Aza-1PF** was observed in the temperature range from 25°C (298 K) to 95°C (368 K). Furthermore, **Aza-TT** exhibited the highest proton conductivity of $3.4 \times 10^{-2} \text{ S cm}^{-1}$ at

95°C (368 K). This finding highlights the potential of these COFs for low temperature proton conducting membranes as well as their implementation in the proton-conduction switches.

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Chapter 2 Appendix

Experimental

Powder X-ray diffraction (PXRD) measurements were carried out using CuK α ($\lambda = 0.15406$ nm) for powder diffraction.

Flash-Photolysis Time-Resolved Microwave Conductivity (FP-TRMC)

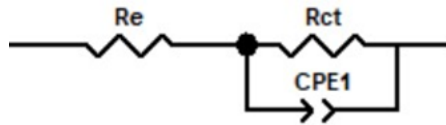
measurements were performed for COF films over a quartz substrate. Before the test at 40°C, the COFs were dried and emptied under a vacuum for 30 minutes. After that, COFs on quartz plates were put inside a TE-102 mode microwave cavity and made sure to be firmly placed at the electric field maximum. An Ophir VEGA power meter with a PE-25 head was used to measure the strength of the excitation light that went through the crystal and quartz. A Schottky diode was used to pick up transient microwave reflections from the cavity ($\Delta P_R(t)$), which were then boosted and looked at with a Tektronics TDS3054 digital oscilloscope. The monitored $\Delta P_R(t)$ is converted immediately into transient photoconductivity $\phi \sum \mu(t)$ by,

$$\phi \sum \mu(t) = A \frac{\Delta P_R(t)}{e I_0 F_L P_R} \quad (1),$$

where, A , e , I_0 , F_L , and P_R are sensitivity factors, elementary charge, incident photon density of the excitation laser, correction factor for overlapping between special distribution of photo-generated charge carriers and electromagnetic field strength of probing microwave in the cavity, and static microwave reflection from the cavity, respectively.

Proton conductivity measurement

Proton conductivity measurements were carried out with ALS760E two-probe AC impedance measurements. The powdered samples were compressed to ~ 0.5 mm in thickness and 5 mm in diameter. The COF pellets were placed between two electrodes in a homemade humidity chamber. The relative humidity (RH) was controlled by saturating salt aqueous solutions at a constant temperature.[1] All of the temperatures were kept for at least one hour so that the sample would achieve the equilibrium. Proton conductivity was measured by the equation $\sigma = L/(R \cdot A)$, where σ , L , R , and A are the proton conductivity (S/cm), thickness of the pellet (cm), resistance of the pellet (Ω), and area of the pellet (cm^2), respectively.



Scheme S1. Equivalent circuit model representation for the proton conduction with COFs. (Re and Rct: Resistance, CPE1: Constant phase element)

The activation energy (E_a) of the samples was calculated from the above conductivity

σ using the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (2),$$

where σ_0 is a preexponential factor conductivity, k is the Boltzmann constant, and T is temperature, respectively.

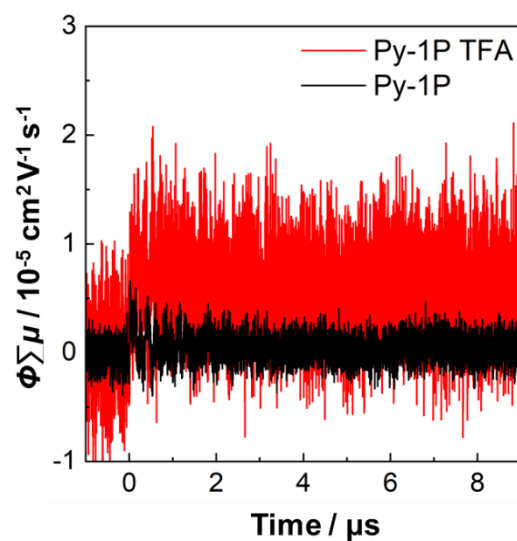


Figure S1. FP-TRMC transient conductivity decay profile of **Py-1P** COF.

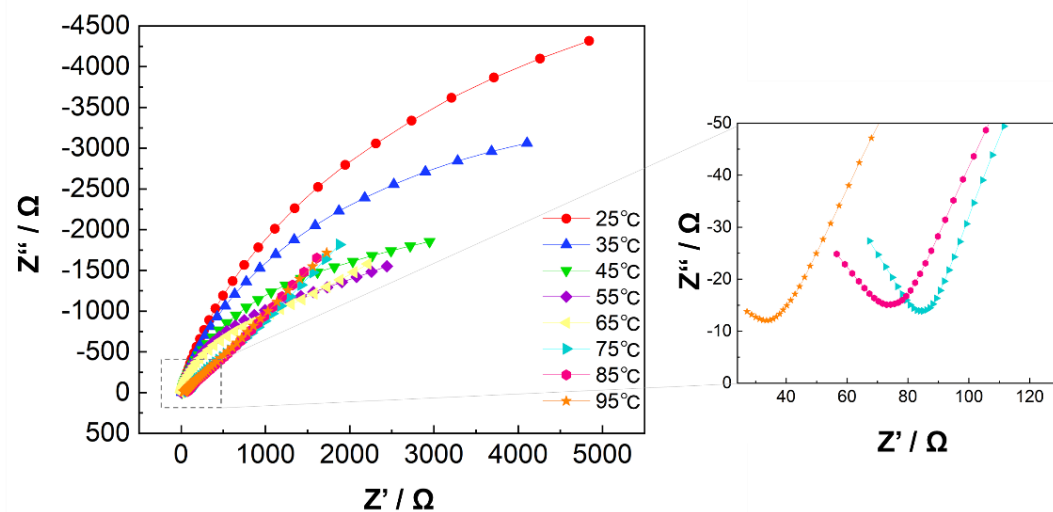


Figure S2. Impedance spectrum of Aza-Py COF at different temperatures under 98% relative humidity.

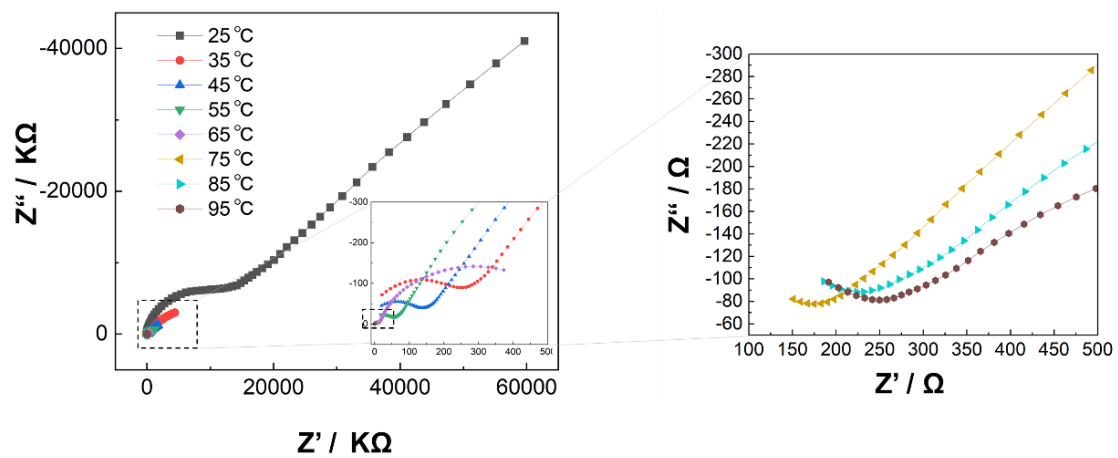


Figure S3. Impedance spectrum of **Aza-1PF** COF at different temperatures under 98% relative humidity.

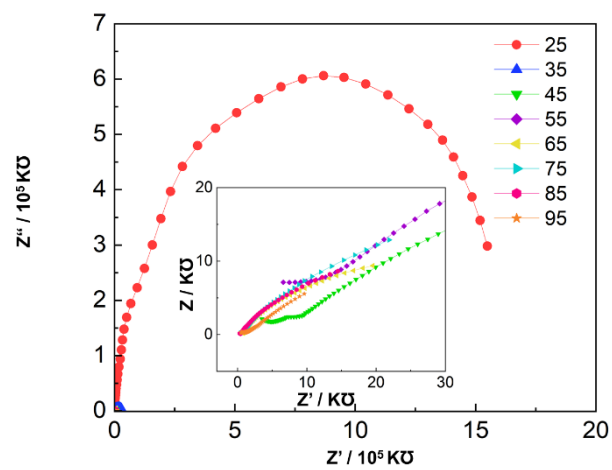


Figure S4. Impedance spectrum of **Aza-1P** COF at different temperatures under 98% relative humidity.

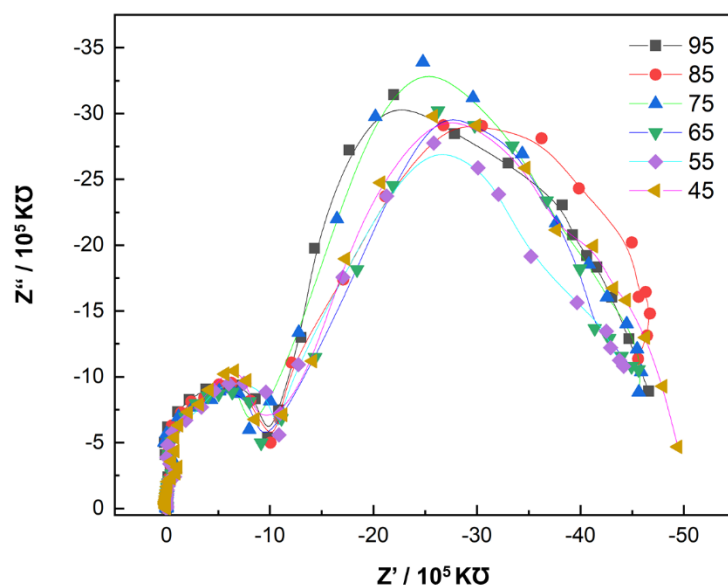


Figure S5. Impedance spectrum of **Aza-1PF** COF at different temperatures under anhydrous conditions.

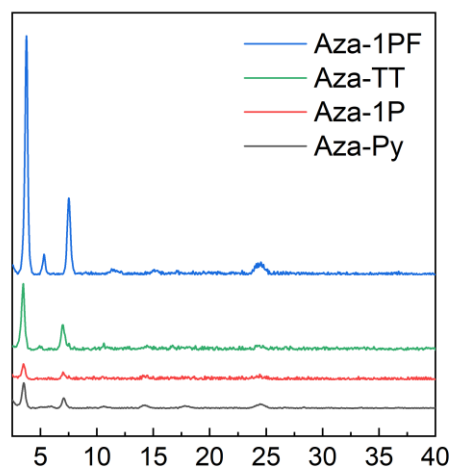


Figure S6. XRD patterns recorded after EIS measurements.

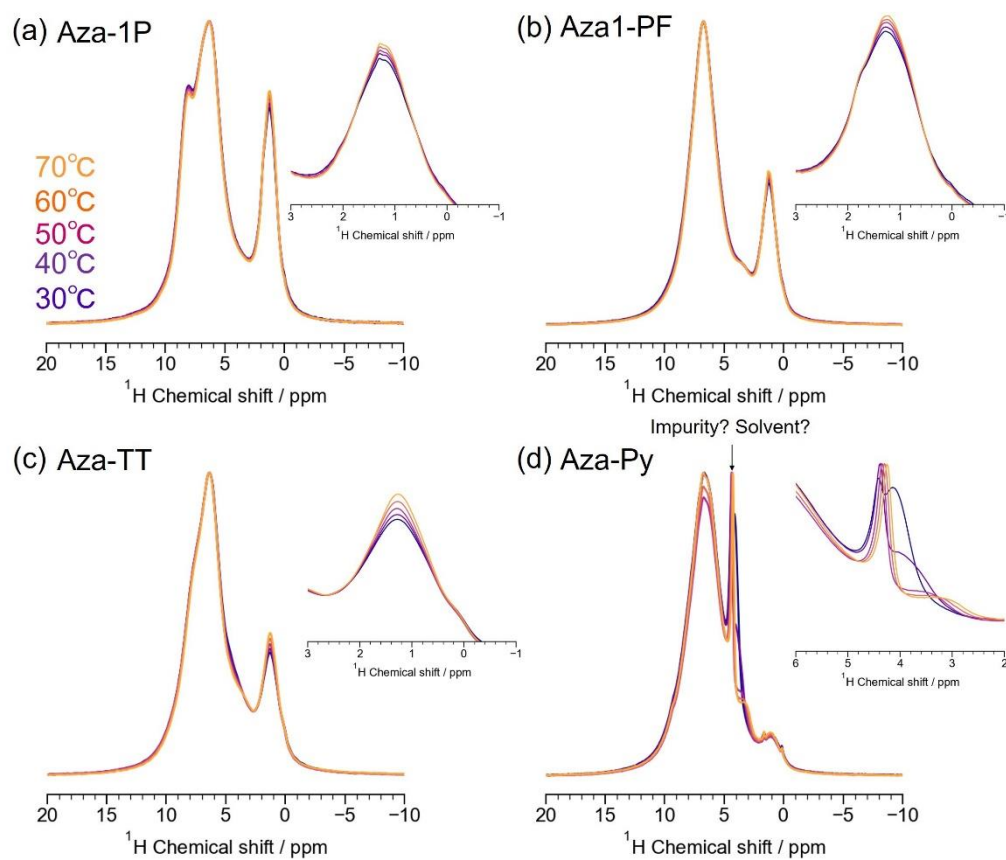


Figure S7. ^1H variable-temperature MAS NMR spectra of (a) **Aza-1P**, (b) **Aza-1PF**, (c) **Aza-TT**, and (d) **Aza-Py**.

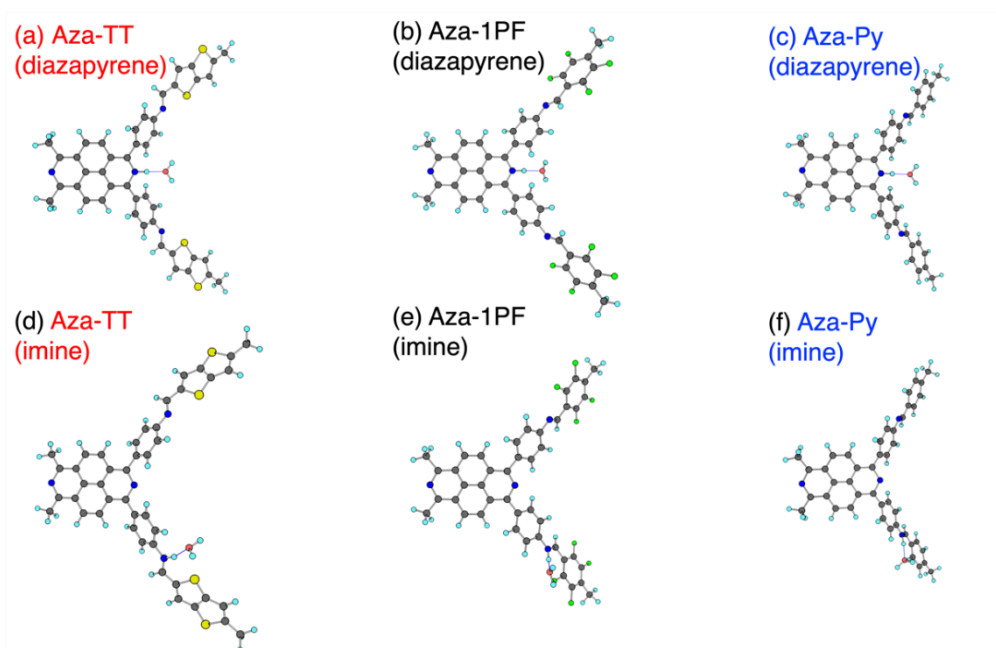


Figure S8. Theoretical model of protonated COFs with only one water molecule. The proton is located at the N site in diazapyrene of (a) **Aza-TT**, (b) **Aza-1PF**, and (c) **Aza-Py**. The proton at the N site in imine of (d) **Aza-TT**, (e) **Aza-1PF**, and (f) **Aza-Py**.

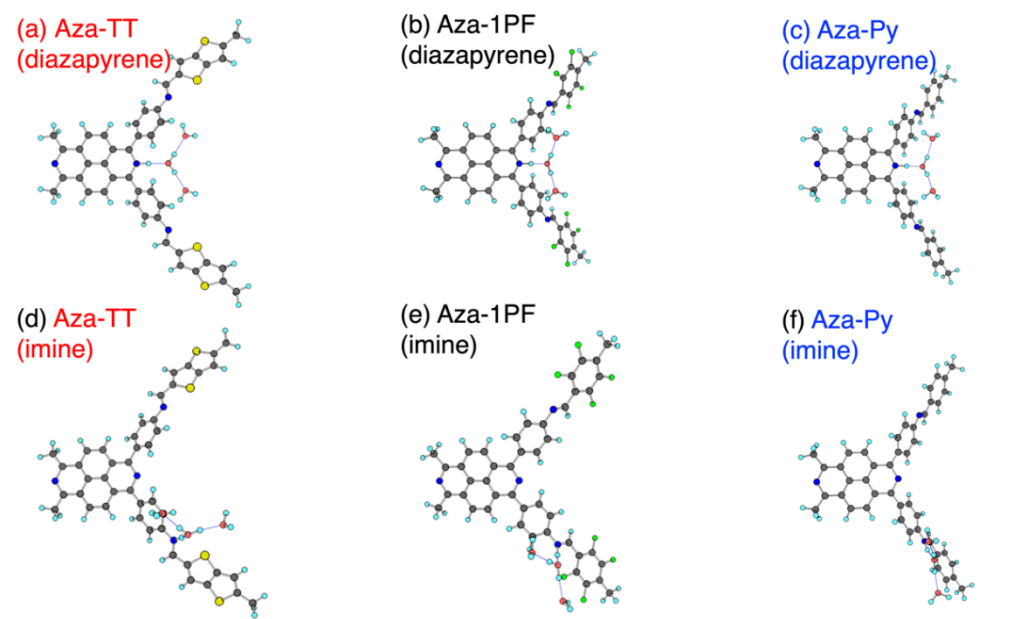


Figure S9. Theoretical model of protonated COFs with the developed hydrogen bonding network (modeled by $(\text{H}_2\text{O})_3$ cluster). The proton is located at the N site in diazapyrene of (a) **Aza-TT**, (b) **Aza-1PF**, and (c) **Aza-Py**. The proton at the N site in imine of (d) **Aza-TT**, (e) **Aza-1PF**, and (f) **Aza-Py**.

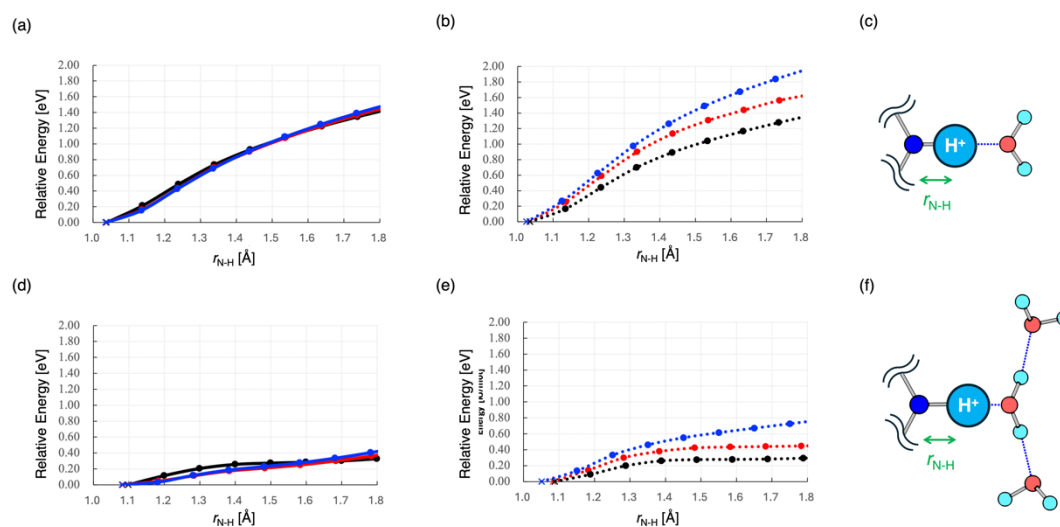


Figure S10. Relative energy changes according to the N-H bond distance ($r_{\text{N-H}}$) of protonated COFs, obtained from the DFT method. Here, the red, black, and blue colors represent **Aza-TT**, **Aza-1PF**, and **Aza-Py**, respectively. **Figures (a)** and **(b)** show calculation results with only one water molecule (see also schematic illustration of **(c)** and **Figure S8**) on the N sites of diazapyrene and imine linkage, respectively. **Figures (d)** and **(e)** are for results with developed hydrogen bonding network (see also schematic illustration of **(f)** and **Figure S9**) on the N sites of diazapyrene and imine linkage, respectively. These DFT calculations were performed at the level of B3LYP/6-31G**[2][3] with the Grimme's dispersion correction (D3) [4], using the Gaussian 16 program package [5]. When the $r_{\text{N-H}}$ extends to about 1.5 Å, the proton is transferred to the water molecule (cluster). In the only one water cases, the desorption energy of about 1.0 eV is evaluated among COFs, which is consistent with the experimental activation energy of **Aza-1PF**. In the developed hydrogen bonding network, about 0.3 eV is obtained for the proton desorption, which agrees with the experimental activation energy of **Aza-TT**. These DFT calculations suggest that low activation energy can be achieved when the hydrogen

bonding network is well-formed around the N site. However, experiments showed relatively high activation energy for **Aza-1PF**, which is probably due to fluorine atoms at the linkages in the **Aza-1PF** hampering the formation of the network.

Table S1. The adsorption/desorption (E_{ads}) energy of proton in the gas phase at the two active sites: N in the diazapyrenes and N in imine linkages. These DFT calculations were performed at the level of B3LYP/6-31G** [3][4] with the Grimme's dispersion correction (D3) [5], using the Gaussian 16 program package [6].

	Aza-TT/ eV	Aza-1PF/ eV	Aza-Py/ eV
E_{ads} of diazapyrenes	-3.84	-3.24	-3.91
E_{ads} of imine linkages	-2.97	-2.92	-3.32

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Chapter 3

Rolling Two-Dimensional Covalent Organic Framework (COF) Sheets into One-Dimensional Electronically Conductive Nanotubes

Abstract:

Mimicking the interconvertible carbon allotropes of 2-dimensional (2D) graphene and 1-dimensional (1D) carbon nanotubes, herein I report the in-situ transformation of 2D π -conjugated covalent organic frameworks (COFs) sheet into 1D nanotubular structures via self-assembly the sheets at solvent interfaces. The facile “roll-sheets” self-assembly resulted in coaxial nanotubes with uniform cross-sectional diameter, which was realized for diazapyrene-based COFs but not for the corresponding pyrene COF, although both possess similar chemical structures. Upon replacing the carbon atoms at 2,7-positions of pyrene with nitrogen, contrasting optical and electronic properties were realized, reflecting the rolled structure of the conjugated 2D sheets. The nanotubes exhibited a semiconducting nature with stable conducting pathways at ambient conditions. The nitrogen centers act as the site for charge carrier doping, as evidenced by the photoconductivity and electrical conductivity results.

Introduction

Low-dimensional materials are now at the center of future electronics, meeting the compelling demands for higher performance and lower power consumption. Graphene has been a benchmark material among various sp^2 hybridized 2-dimensional (2D) π -conjugated systems, which is known for its exceptionally wide dynamic range of electronic properties along with exotic electronic phases: from superconducting to highly localized phases of charges simply controlling their stacking geometries ^[64-66]. The important aspect of the graphene systems in their practical application in nanoelectronics is the existence of 1-dimensional (1D) analogs: carbon nanotubes, principally which can be achieved by rolling the 2D sheet of graphene. The transformation from 2D to 1D structures holding excellent electronic properties has been thus presumed to be a key to controlling the directional flow of electrons ^[36, 67]. Moreover, nano/micro-tubular structure is a highly important morphology in polymeric materials owing to their low density and several potential applications. However, their existence is extremely rare and often requires the usage of various templating agents ^[68], particularly in the case of covalent organic frameworks (COFs) material ^[69]. Moreover, template-free fabrication of nano- and micro-tubular structures from COFs is limited ^[70].

COFs are a rational choice as the alternative material for graphene. Basically, COFs are a class of reticulated crystalline porous polymers prepared by strong covalent linkages between organic building blocks in various geometries. Since the first COF was reported by Yaghi and his colleagues in 2005 ^[1], it has received tremendous attention due to its bottom-up tailor-made synthesis, crystalline porous network, low density, tunable pre- and post-functionalization ^[70-72], and for various applications such as gas storage ^[5, 73, 74], separation ^[75-77], catalysis ^[78-81], optoelectronics ^[59, 82, 83], and energy harvesting/storage

applications ^[13, 14, 84]. Recently, semiconducting COFs got special attention due to the intrinsic in-plane π conjugation as well as along the columnar π -stacking array, which strongly affects the optoelectronic, catalytic, and charge transport properties^[83]. An important design principle of electronic conductive pathways in COFs is to achieve the long-range ordered crystalline structure as it reduces the local potential for trapping at crystal boundaries and at structural defects via vibrational coupling ^[83, 85, 86].

In principle, 2D conjugated COFs can be designed as electronic conductors ^[87] and semiconductors by arranging π -conjugated building blocks in various topologies ^[88]. Theoretically, the topology of 2D COFs can be composed of trigonal^[89], tetragonal ^[90], kagome ^[91, 92], pentagonal ^[93], hexagonal ^[94], and dodecagonal using different building blocks ^[95, 96]. Among these, tetragonal and kagome lattices are potential platforms to realize extraordinary electronic ^[97], magnetic ^[36, 92, 98], and catalytic ^[7, 78, 79, 81] applications as per the theoretical and experimental modellings ^[99].

The topologies of COF layers lead, in contrast, to the significant reduction in electron density of states (DOS) via the reduction in the gravitational density of the materials and the larger inter-planar distances by the limited points of interactions relative to those in graphenes. Improved planarity of the layer is the principal strategy to give the tightly-bound layers in the well-ordered crystalline domains, which is also beneficial for the interplay of the higher structural stability and charge carrier density via chemical doping ^[78, 83].

In this context, tetraphenyl-substituted pyrene has been extensively used as the building block for the synthesis of the crystalline COF. Jiang *et al.* ^[36] reported a class of 2D COFs based on pyrene units as main functional groups and explored their photophysical properties ^[62, 100, 101]. The exceptionally stable framework formed a laminar

structure due to the lattice design of π -conjugation along the x and y directions ^[100], meanwhile, the π -stacked columns of 1D pyrene provided electron/hole conduction channels with an interlocking structure to prevent thermal perturbations. Due to the face-to-face π - π stacked columnar structure that maximizes the overlap of molecular π -orbitals, the COFs are in an ideal stacking mode for both 1- and 2-dimensional charge transport channels ^[90]. This allows electron transport to have orthogonal double complementary channels: both intra-layer and inter-layer transport ^[59, 82, 102].

The slipped stacked columns formed by the "armchair" configuration of pyrene have the "locked" structure, with sliding stacking columns and less offset leading to highly crystalline 2D COFs ^[59]. Moreover, it is expected that morphology, crystallinity, and stacking interactions of pyrene-based COFs can also be improved by lowering the torsional angle (53° to 39°). Hence, reducing the steric hindrance between the terminal 4-aminophenyl rings and the pyrene core by substituting the peripheral carbon atoms of pyrene with nitrogen atoms would also favor the interlayer charge transport owing to the wide range alignment of intermolecular interactions through shrinkage of longitudinal intermolecular distances, and may also lead to optimized opto-electronic and magneto-electronic properties ^[103]. For example, Banerjee *et al.* recently explored morphological diversity and the degree of crystallinity in porous polymers by simply altering the linker planarity ^[104]. By simply substituting the central benzene ring in 1,3,5-tris(4-aminophenyl)benzene (Tab) with triazine moiety, ribbon-shaped crystallites are obtained from spherical crystallites with a significant improvement in their crystallinity. Moreover, the transition from 2D to 1D enables the material to increase flexibility, which is helpful for the development of electric conductive inks and thin-film transistors in the flexible electronics industry ^[105, 106]. If I envisage to synthesize 1D structure on the basis of 2D

COF, the unique properties of COF could be reserved, which makes directional high electron migration possible over the layer. Moreover, substituting nitrogen atoms can act as the points of charge carrier doping, and thus the electrical conductivity of these resulting COFs can be tuned upon doping via protonation^[107] associated with their fine-tuning of electronic band gaps^[98].

Herein, I have prepared two isorecticular COFs using pyrene and diazapyrene as the respective binding blocks. The rationale behind choosing diazapyrene is to enhance the planarity by replacing the 2,7-carbon with nitrogen, leading to shorter stacking distances and high crystallinity via reduced steric repulsion between the C-H carbons and interlayer distances^[108]. Unlikely the expected highly ordered stacking mode of the planar COFs, I observed fairly uniformed 1D nanotubes resulting from the rolling up of the planar 2D COFs.

Results and Discussion

I designed and synthesized new COFs using tetra(4-aminophenyl)diazapyrene (Aza(NH₂)₄) as the building block, and condensed with tetrafluoroterephthaldehyde (1PF(CHO)₂) or thieno-[3,2-b]thiophene-2,5-dicarboxaldehyde (TT(CHO)₂) as a linker molecule to obtain **Aza-1PF** and **Aza-TT** COFs, respectively. Aza(NH₂)₄ was prepared according to the literature procedure^[108]. Pyrene-based COF (**Py-1PF**) as a reference was prepared through the common solvothermal synthesis method using Schiff base condensation reaction of amino-functionalized pyrene Py(NH₂)₄ with 1PF(CHO)₂ (Figure 1a). Free-standing films of these COFs were developed *in situ* during the condensation reaction. The uniform nature was confirmed in films of all the COFs under an optical microscope (Figure S1).

Although the crystallinity of the developed films is relatively lower than its powder forms ^[103]. However, compared to other tubular COF structures ^[70, 71] without sharp peaks as the signature of crystallinity in powder X-ray diffraction (PXRD) analysis, **Aza-1PF** and **Aza-TT** COFs showed distinct sharp peaks which verified their excellent crystallinity (Figure 1b, d). The comparison of crystallinity between COF films and corresponding monomers of **Py-1PF** COFs is shown in the Figure S2. The peaks of **Aza-1PF** at $2\theta = 3.88^\circ$, 5.59° , 7.82° , and 24.86° , which are attributed to the (100), (110), (200), and (001). The spacing between the planes is calculated to be 0.354 nm (Figure 1b). On the other hand, the peak of **Aza-TT** at 12.3° corresponds to (001), and the spacing between the planes is calculated to be 0.364 nm. Furthermore, several diffraction peaks were observed at $2\theta = 2.50^\circ$, 3.54° , 5.36° , and 7.27° , which are attributed to the (100), (110), (200), and (210), respectively (Figure 1d). In addition, the simulated PXRD patterns of both **Aza-1PF** and **Aza-TT** are in good agreement with the experimental results, confirming the crystalline slipped AA stacking structure with C_2/m symmetry models (Figure 1c, e). The PXRD profile was refined with the Pawley method in the Reflex module of BIOVIA Material Studio. (**Aza-TT** residuals were $R_p = 1.52\%$ and $R_{wp} = 2.31\%$, respectively (Figure S2)). **Py-1PF** is poor crystalline in nature containing relatively large portion of impurities (Figure S2).

The unusual nano-tubular structures with crystalline nature were traced directly by a series of microscopy techniques: Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Cryogenic Transmission Electron Microscopy (Cryo-TEM). SEM images (Figure 2a-d) revealed that a tubular morphology is observed clearly in the COF composed of diazapyrene building blocks with a uniform cross-sectional diameter of 20-40 nm, which is in sharp contrast to the detailed granular structure of **Py-1PF** COF

with large crystalline domains. The thin films of **Aza-1PF** and **Aza-TT** are given by the tubular structure interweaving. Generally, the formation of nanotube structures with very smooth surfaces is unusual in COFs.

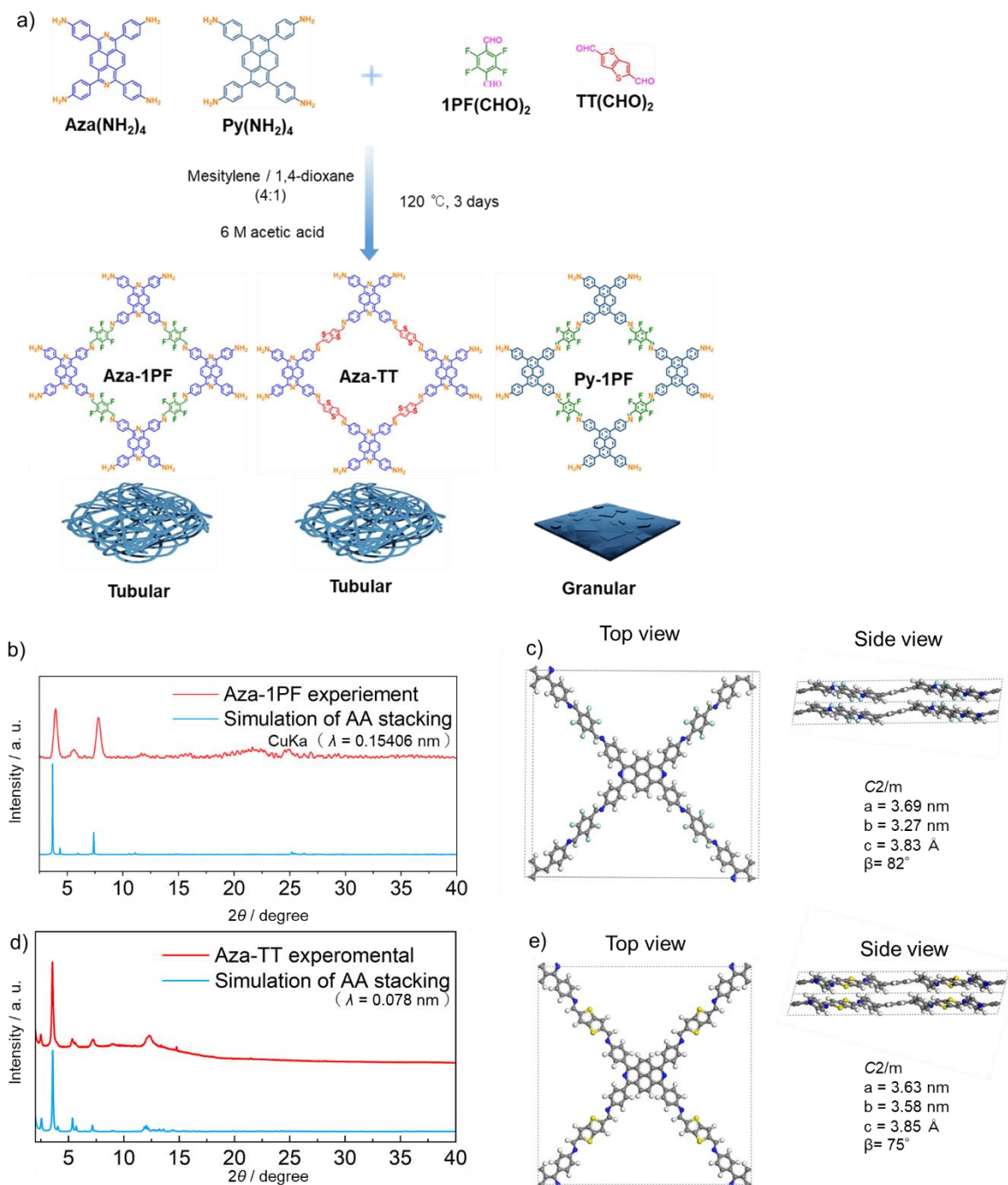


Figure 1. (a) Synthetic procedure and chemical structures of **Aza-1PF**, **Aza-TT**, and **Py-1PF** COFs. (b) XRD profile of **Aza-1PF** COF (red curve) and the Pawley-refined

pattern (blue curve). XRD patterns were simulated with the slipped AA-stacking mode (blue curve). (c) Structure models of the **Aza-1PF** COFs from the top and side views. (d) XRD profile of **Aza-TT** COF (red curve) and the Pawley-refined pattern (blue curve). XRD patterns were simulated with the slipped AA-stacking mode (blue curve). (e) Structure models of the **Aza-TT** COFs from the top and side views. (Gray: pyrene or phenyl carbon, Blue: nitrogen, Light blue: fluorine).

To get more details about the morphology of the synthesized COFs, AFM images (Figure 2e-h) were taken after transferring the COF films onto SiO₂ substrates. The rough surface of **Py-1PF** films was observed, consisting of granular-shaped crystals with an average size of ~250 nm. On the other hand, 1D nanotubular structures were clearly visualized with smooth surfaces for both **Aza-1PF** and **Aza-TT** films with their cross-sectional diameters of ~40 nm and ~20 nm, respectively (Figure 2i). This is consistent perfectly with the structures obtained by SEM. The average diameter obtained from the AFM histogram profile (Figure 2j) is estimated as ~40 nm with a multi-walled structure as evidenced by an XRD characteristic peak at 12.3° attributed to the inter-layer distances. The hollow structures of nanotubes of **Aza-1PF** and **Aza-TT** were clearly visible in the TEM images (Figure 2k-i). The diameters of nanotubes are thus all consistent in the series of AFM, SEM, and TEM imaging techniques.

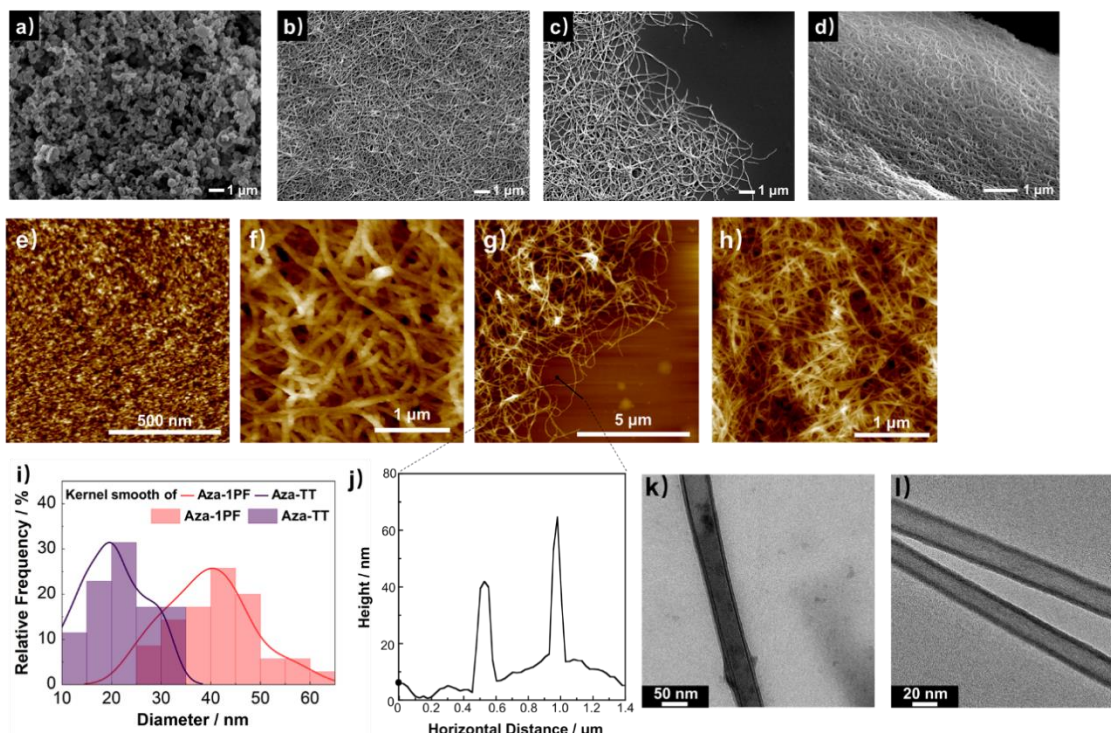


Figure 2. SEM images of (a) **Py-1PF** COF thin film, (b, c) **Aza-1PF** COF thin film. AFM images of (d) **Py-1PF** COF thin film, (e, f) **Aza-1PF** COF thin film. (g) Diameter distribution of **Aza-1PF** COF nanotube. (h) AMF profile of **Aza-1PF** COF thin film. TEM images of (k) **Aza-1PF** COF and (l) **Aza-TT** COF.

To examine the dynamic and reversible changes between 1-D nanotubular and 2-D sheet-like structures, TEM images were taken by dispersing the nanotube structures into ethanol through sonication. The TEM micrographs revealed that the **Aza-1PF** COF nanotube showed significant expansion in their diameter after sonication, due to the loosening of inter-layer stacking in their multilayered walls, going into over 100 nm (Figure 3a). The same structure was observed in SEM images as well (Figure 3c). Besides, the semi-rolled structure of an isolated sheet of **Aza-TT** COF was observed clearly (Figure 3d), suggesting the reversible nature of rolling and unrolling of COF 2D sheets.

Since the COF films grow at the junction at the liquid-liquid interface, growing COF

layers may have different affinities against diverse solutions. It is expected that the initially grown crystalline film will tend to minimize the contact area with the lower affinity solvent (mesitylene) and simultaneously increase the contact area with the higher affinity solvent (1,4-dioxane). The difference in the affinities between the COF film and the respective can be presumed as the major driving forces to roll it up into nanotubular structures. The diameter of the nanotubes can be determined by the unbalanced affinity of respective solvents against each **Aza-1PF** or **Aza-TT**. To examine this hypothesis, I have conducted a wetting contact angle measurement of diazapyrene-based COFs with mesitylene or 1,4-dioxane, which were used as solvents for the preparation of COFs.

It was observed that **Aza-1PF** COF had unbalanced affinity against the solvents represented by the respective contact angles of 3.6° and 11.1° for mesitylene and 1,4-dioxane (Figure S3); both were employed for the condensation reaction. On the other hand, the small change in the contact angles was observed as 13.3° and 15.9° for **Aza-TT** COF; this is the case impacting the diameter of the nanotubes from **Aza-1PF** and **Aza-TT**. The different diameters of nanotubes are a consequence of their different affinities with the liquid-liquid interface. A larger wetting contact angle tends to produce nanotubes with smaller diameters, whereas a smaller wetting contact angle leads to bigger diameters.

On the other hand, ultrasonication favors the opposite phenomena, which ultimately transformed into a semi-rolled structure from the tubular one (Figure 3a, d, c, and Figure S4). It should be noted that the electron beam diffraction pattern from the nanotubes gave an estimate of the inter-layer stacking of COFs at the side walls, showing the identical lattice spacing of $3.60 \text{ \AA}$ (**Aza-1PF**) and $3.45 \text{ \AA}$ (**Aza-TT**) to those in the PXRD measurement.

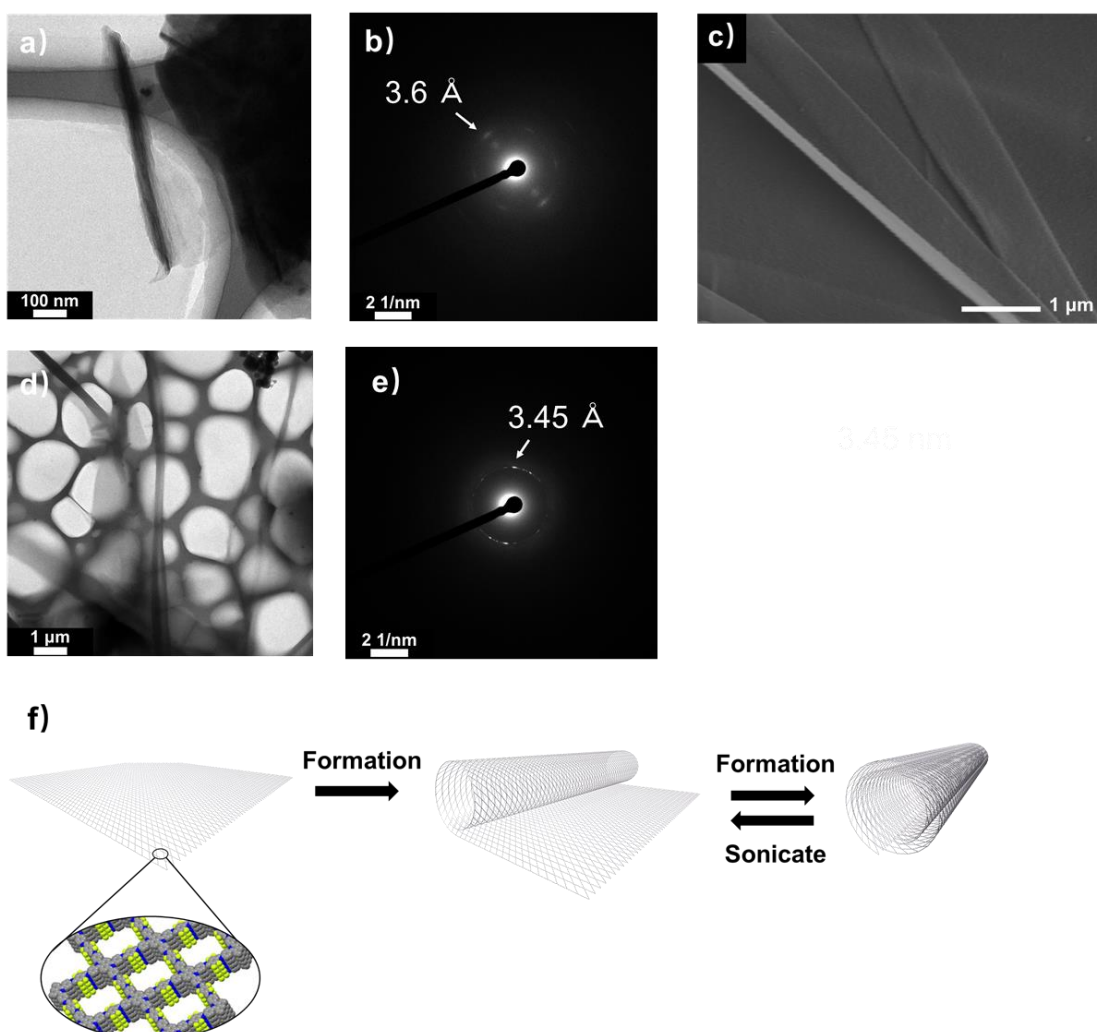


Figure 3. TEM images of (a) **Aza-1PF** and (b) **Aza-1PF** COFs. (c) SEM images of **Aza-1PF** COF. Selected area electron diffraction (SAED) pattern of (d)**Aza-1PF** and (e)**Aza-TT** COFs. (f) Schematic images of the formation of nanotube structure from sheet.

The formation of COFs was confirmed by Fourier-Transform Infrared (FT-IR) spectra (Figure 4a and S5). For **Aza-1PF** COF, the disappearance of the -CHO and -NH₂ as well as the appearance of the C=N band at 1608 cm⁻¹ indicated the formation of desired material composed of two building blocks. Moreover, structural characterizations of **Aza-1PF**, **Aza-TT**, and **Py-1PF** COFs were performed using Raman spectroscopy focusing on C=N and NH₂ functionalities (Figure 4b and S6), corroborated with the IR spectra.

Reflecting the 1D tubular nature of **Aza-1PF**, its peak intensity reduces significantly relative to that of **Py-1PF**. The characteristic signatures of the C=N formation were confirmed clearly for all the COFs.

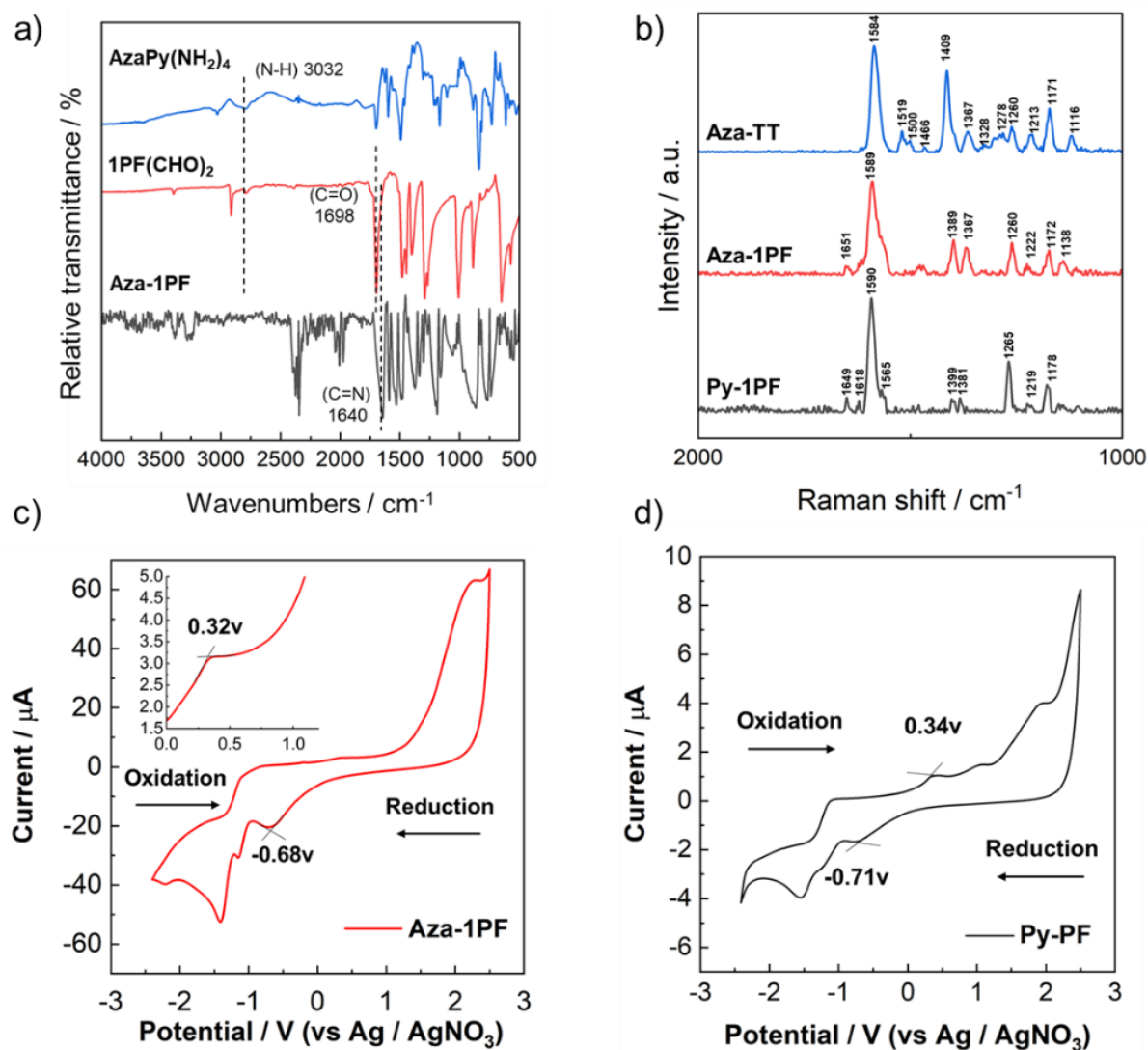


Figure 4. (a) FT-IR spectra of the **Aza-1PF** COF films and the precursors. (b) Raman spectra of **Aza-TT**, **Aza-1PF**, and **Py-1PF** COFs. Cyclic voltammograms of (c) **Aza-1PF** and (d) **Py-1PF** COFs with Pt counter and Ag/ AgNO_3 reference electrode, in a 0.1 M TBAP/acetonitrile electrolyte solution with the scan rate of 100 mV/s and potentials from -2.5 V to 2.5 V, respectively.

From UV-Vis electronic absorption spectra, diazapyrene-based COFs exhibited a broad optical transition band compared to the **Py-1PF** COF film, which impeded to deduce optical band gap energy directly. (Figure S7) Therefore, the cyclic voltammetry (CV) was conducted to measure the band gap energy. The CV curve of **Py-1PF** (Figure 4d), **Aza-1PF** (Figure 4), and **Aza-TT** COFs (Figure S8a) showed a quasi-reversible oxidation and an irreversible reduction peak due to the ligand moiety. The energy level of ferrocene/ferrocenium is 4.8 eV lower than the vacuum energy level ^[109], which allows us to calculate the HOMO and LUMO of COFs through the onset of first oxidation and reduction potentials. The calculated HOMO and LUMO energy of **Py-1PF** ≈ -5.04 and ≈ -3.99 eV; **Aza-1PF** ≈ -5.02 and ≈ -4.02 eV; **Aza-TT** ≈ -4.90 and ≈ -4.35 eV, respectively. Owing to the lower π -stacking interactions, **Py-1PF** COF exhibited ~ 100 meV downshift of HOMO and 100–400 meV upshift of LUMO levels compared to the diazapyrene-based COFs ^[100]. The HOMO-LUMO energy gap of diazapyrene-based COFs (**Aza-1PF**: 1.00 eV, **Aza-TT**: 0.55 eV) becomes narrower than pyrene-based COF (**Py-1PF**: 1.05 eV), which is well supported by the theoretical calculation ^[73], as shown in Figure S9. Moreover, the Fermi levels (E_F) of the COF films were measured using ultraviolet photoelectron spectroscopy (UPS). The values of E_F were determined as 5.46, 5.26, and 5.47 eV for **Aza-1PF**, **Aza-TT**, and **Py-1PF**, respectively. The E_F of diazapyrene-based COF films is slightly shallower than **Py-1PF** COF films. (Figure 5c and Figure S10)

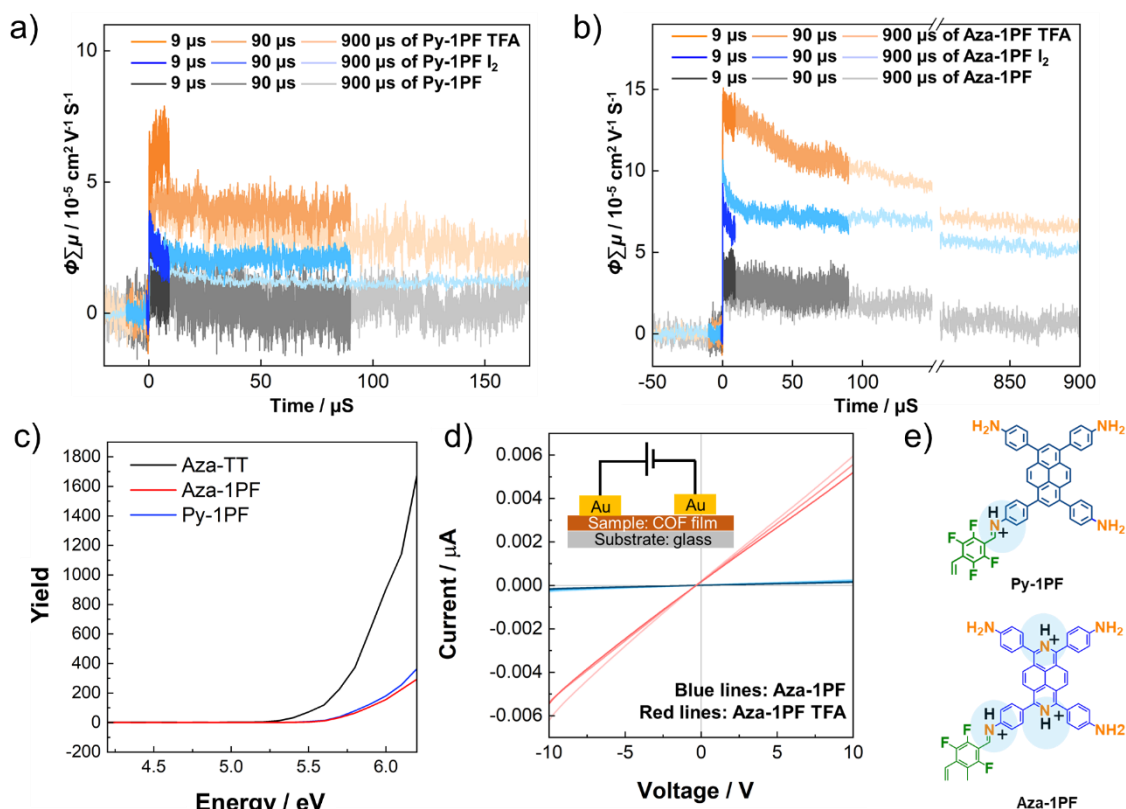


Figure 5. FP-TRMC transient decay profile of (a) **Aza-1PF** films and (b) **Py-1PF** films. (c) Ultraviolet photoelectron spectroscopy (UPS) of **Aza-TT**, **Aza-1PF**, and **Py-1PF** COF films. (d) I - V characteristics of **Aza-1PF** film and **Aza-1PF TFA** film under atmospheric pressure, room temperature, and room light. Schematic diagram of electronic devices (inside image). (e) Protonation of **Py-1PF** and **Aza-1PF** COFs.

In addition, all these developed COFs showed negligible photoluminescence via efficient vibrational relaxation, which is similar to the other reported imine-linked 2D COFs such as ILCOF-1^[110] and Py-DHPh^[111]. This could be due to strong π - π stacking interactions between the layers, providing non-radiative relaxation pathways (Figure S11).

The face-to-face stacked 2D conjugated COF layers have been demonstrated to lead to 1D columnar structure of conjugated chromophores leading to one-dimensional charge

transport pathways: the conventional strategy to design semiconducting COFs. In contrast, nanotubular structures of **Aza-1PF** COF are beneficial to promote efficient charge transport along the 1D tubular axes in parallel with the smooth surfaces of the walls, allowing us to fabricate nano-electronic devices via the interconnections.

The interconnections of 1D nanotubular structures, however, act as deep traps for the charge carriers; The injection through the limited contact area between nanotubes and electrodes is also critical, often leading to the localization of the carriers. To assess the inter-tubular electric conductivity of the nanotubes free from the above issues, I have used alternating-current (AC) mode Flash-Photolysis Time-Resolved Conductivity (FP-TRMC) measurements. Upon photo-carrier injection with an excitation at 355 nm (3.5 eV), a steep increase in the transient photoconductivity ($\Phi\Sigma\mu$) was observed in **Aza-1PF** COF, which is 3-fold higher than that of **Py-1PF** COF. This is probably due to the lower band gap energy of the former which favors the efficient charge carrier generation. (Figure 5e). Theoretical calculations suggested that the reduced band gaps in diazapyrene-based COFs are associated with the reduction (Figure S9). Unlike the case of Py-1PF, the 1D tubular Aza-1PF is composed of a few nm-thick stacking of the COF planes, confining the local motion of holes in the stacking direction. The higher electronic conductivity than Py-1PF is thus suggestive of the surpassing in-plane conductivity in the 1D tubular Aza-1PF contrasting to the developed conductive pathways along the stacking direction in Py-1PF.

It is noteworthy that the lifetime of the photo-generated charge carriers injected in **Aza-1PF** COF is estimated as $\tau \sim 500 \mu\text{s}$, far beyond $\tau \sim 20 \mu\text{s}$ in **Py-1PF** COF. The 1D nanotubular structures of **Aza-1PF** COF are expected to have a wider surface area allowing the access of impurities/counter charges for free charge carriers. However, the

significantly longer lifetime in **Aza-1PF** COF is suggestive of the conductive pathways confined into 1D structures providing less probability to recombine with the counter charges via low-dimensional diffusive motion of the carriers.

Inspired by the coexistence of wide surface area and conducting pathways, charge carrier doping against the tubular structures was conducted by vapor diffusion of iodine and protonation of diazapyrene units using trifluoroacetic acid (TFA) as a proton source. From the figure (Figure 5a-b) it is observed that both iodine doping and protonation led to significant enhancement of electrical conductivity. The $\Phi\Sigma\mu$ value of **Aza-1PF** COF increases to $1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from 3.9×10^{-5} (undoped) upon iodine doping. While, **Py-1PF** COF shows negligible enhancement of electrical conductivity (from $1.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $2.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), suggesting the advantage of 1D nanotubular structures in chemical doping without disruption of the conductive pathways. Pursuing efficient doping against the nanotubes via the strong interaction with diazapyrene units, next I tried to protonate the units by TFA. After doping of **Aza-1PF** COF with TFA, the photoconductivity value increased abruptly, and the doped COF showed two orders of magnitude higher photoconductivity than the undoped one at the end of transient ($\sim 1 \text{ ms}$). This validated the successful doping with the present TFA-based protocols. Surprisingly, the protonation causes no disruption of electronic conductive pathways by steric hindrance after the polymerization and rolling-up into nanotubular structures. Despite a decrease in the crystallinity of the doped COF, which necessitates stronger X-ray examination, the **Aza-1PF** COF maintains its crystallinity after doping (Figure S12): anticipating the **Aza-1PF** tubular COFs as an ideal platform for proton conducting materials. To investigate the possible protonation of nitrogen in diazapyrene, I performed doping **Aza-1PF** using phosphoric acid via the impregnation method. The protonation

impacted significantly on the electronic conductivity of Aza-1PF from $\sigma = 2.2 \times 10^3$ to $3.2 \times 10^2 \text{ S cm}^{-1}$ (Figure S16), however the enhancement is rather smaller than doping with TFA.

The 1D photo-/static conducting nature in pristine/against stable doping was verified also by direct-current (DC) mode conductivity measurements (Figure S13-15). I - V traces of random network structures of the nanotubes show a significant reduction of resistivity upon illumination with ambient light for all devices fabricated, confirming photoconductivity in the condensed (inter-linked) phase of conductive nanotubes. The effect of protonation was remarkable, as shown in Figure 5d, showing more than one order of magnitude increase in the conductivity up to $\sigma = 4.8 \times 10^{-3} \text{ S cm}^{-1}$ from $\sigma = 1.7 \times 10^{-4} \text{ S cm}^{-1}$. This is consistent with TRMC measurements, revealing the potential of **Aza-1PF** COF nanotubes as platforms for the modulation of electron transport along with the coaxial structures.

On the other hand, compared to fluorinated polymer electrolytes and various aromatic polymers, COFs demonstrated superior durability under harsh conditions. Additionally, the microporous structure of COFs offers advantages over polymer membranes by effectively confining proton carriers within the pores, minimizing leakage. Our previous work^[48] investigated the proton conductivity of powdered diazapyrene-based COFs. The structure of diazapyrene-based COFs incorporates two pyridine centers per unit, with multiple nitrogen sites serving as hydrogen bond acceptors and N-H sites acting as hydrogen bond donors. This configuration facilitates the introduction of external proton sources. The densely packed one-dimensional channels within the COF structure provide stable pathways for proton transport while offering abundant loading sites for proton sources. This precise atomic arrangement promotes rapid and seamless proton

transfer, thereby significantly enhancing proton conductivity. As a result, the proton conductivity of **Aza-1PF** increased by four orders of magnitude as the temperature rose from 25°C (298 K) to 95°C (368 K) within their continuous nanoporous network.

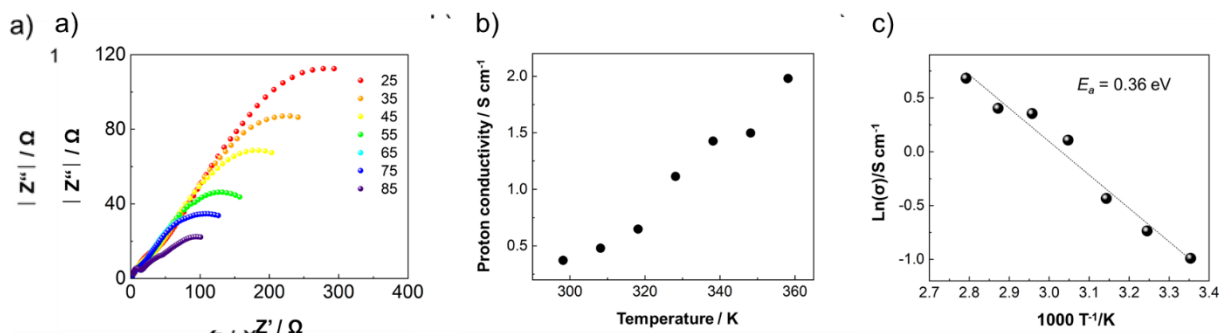


Figure 6. (a) Impedance spectra of **Aza-1PF** obtained at different temperatures with 98% relative humidity. (b) Proton conductivities of **Aza-1PF** were determined at different temperatures with 98% relative humidity. (c) Arrhenius plots constructed for **Aza-1PF**.

Moreover, we have further investigated the proton conductivity of **Aza-1PF** film samples owing to its higher crystallinity (Figure S17). As shown in Figure 6, the **Aza-1PF** thin film displayed remarkable proton conductivity of $0.37\ S\ cm^{-1}$ at 25°C (298 K) and 98% relative humidity. The proton conductivity of the **Aza-1PF** film samples gradually increased with temperature and achieved a value of $1.98\ S\ cm^{-1}$ at 85°C (358 K) under the similar humid conditions. The maximum value of proton conductivity of the film samples is significantly higher than most of the reported COFs reported under similar conditions (without using any external dopants) and even higher than powder samples of the same COFs^[48]. Theoretical calculations indicated that a well-developed hydrogen bonding network is crucial for proton conductivity in diazapyrene-based COFs, however in powder samples, the fluorine atoms at the linkage sites of **Aza-1PF** hindered the

formation of hydrogen bonding networks, resulting in the elevated activation energy and the relatively lower proton conductivity^[48]. The activation energy of proton conductivity in the **Aza-1PF** film was found to be 0.36 eV which is 1/3 of that in the power samples (1.01 eV), but slightly higher than the one recorded in **Aza-TT** where the hydrogen bonding network was presumed to be developed in the pores. This is consistent with the role of hydrogen bonding networks in proton conduction and highlights the advantages of the present 1D nanotubular structure to facilitate the proton conducting pathways.

Conclusion

1D nanotubular structure based on the planar conjugated COF (**Aza-1PF**) was successfully obtained by a facile protocol: rolling-up of COF sheets during in-situ solvothermal condensation reaction. The obtained nanotubes were multi-walled with inter-layer distances of 0.38 nm, which is competitive to the crystalline structure of stacked planar sp²-type 2D conjugated COFs. Unlike the multi-walled nature of **Aza-1PF** COF nanotubes, the cross-sectional diameter showed almost perfect uniformity at ~40 nm, and the coaxial tubular structure was also visualized with a series of microscopy techniques. The electronic structure of the multi-walled nanotubes is well represented by the stacking of the electronic conjugated layers of COFs, as reflected by frontier orbital levels, electronic transitions, and optical/electronic band gaps. Electronic conductivity measurements both in AC and DC modes verified the semiconducting nature along with 1D tubular structures, exhibiting clear photoconductivity upon excitation of optical band gaps and static electronic conductivity increase upon doping. The doping via vapor diffusion of iodine and protonation of the key building blocks: diazapyrenes was, in particular, effective for enhancement and immobilization of electrical conductivity not

only within the tubular structure but also the inter-linked state of nanotube networks. The present diazapyrene-based nanotubes will be powerful candidates in future nano-electronic materials.

Materials and Methods

Synthesis of the COF films (Aza-1PF COF) without substrates. Tetra(4-aminophenyl)diazapyrene (14.0 mg, 25 μmol , 1 eq.) and tetrafluoroterephthalaldehyde (10.2 mg, 49 μmol , 2 eq.) were placed in a 20 mL reaction tube, followed by the addition of mesitylene (8 mL), 1,4-dioxane (2 mL) and 6M acetic acid (1 mL). The tube was sealed with purging nitrogen and the reaction mixture was heated at 120 °C for 3 days. After cooling to room temperature, the precipitate was collected by filtration and washed with acetone and THF several times until no fluorescence of the filtrate was observed. The precipitate was then dried at 90 °C.

Flash-Photolysis Time-Resolved Microwave Conductivity (FP-TRMC) measurement. The intrinsic charge conductivity of COF films was evaluated by FP-TRMC measurement at ambient temperature and pressure. COF films were fixed with quartz substrate overcoated by CYTOP[®]. The transient charge carriers in the sample are optically excited by the third harmonic generation ($\lambda = 355 \text{ nm}$) laser pulse of the Spectra-Physics INDI-HG Nd:YAG laser (Size of sample: 1 cm^{-2} , Pulse duration time: 5–8 ns, Photon density: $9.1 \times 10^{15} \text{ photon cm}^{-2}$). The frequency and power of the probing microwaves are 9.1 GHz and 3 mW, and the measurements were performed in a microwave cavity with the Q value at 2000.

Electrical Conductivity Measurements. Static electrical conductivity measurement was performed by two-probe alignment with a Keithley 4200A-SCS parameter analyzer on

SiO₂ substrate for the device of COF films at 0.1 μm thick with 0.5 mm gap of Au electrodes. Iodine and TFA doping were carried out by vapor of the respective dopants at room temperature kept inside 50-mL glass bottles for 15 min and the electrical conductivity of resulting devices was measured in air.

Proton Conductivity Measurements. Proton conductivity was measured using ALS760E with a two-probe AC impedance technique. The films were placed between two electrodes in a custom humidity chamber, with relative humidity controlled by saturated salt solutions at a constant temperature. Samples were equilibrated at the set temperature for at least one hour before measurement.

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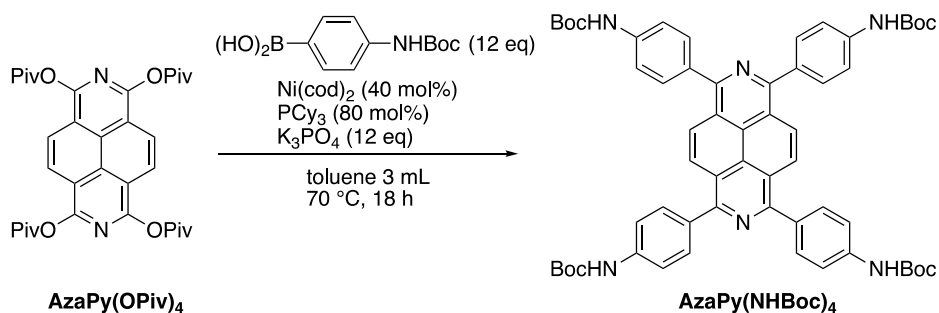
Chapter 3 Appendix

1. Synthesis of the building blocks

^1H NMR (400 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. Chemical shifts were reported as the delta scale in ppm relative to CDCl_3 ($\delta = 7.260$ ppm) and $\text{DMSO}-d_6$ ($\delta = 2.50$ ppm) for ^1H NMR. High-resolution (HR) atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectrum and high-resolution electrospray ionization time-of-flight (ESI-TOF) mass spectra were taken on a Bruker microTOF instrument using a positive ionization mode.

All reagents are purchased (Tokyo Chemical Industry (TCI) and FUJIFILM Wako Chemicals) were purchased from FUJIFILM Wako Chemicals and Tokyo Chemical Industry Co., Ltd. **AzaPy(OPiv) $_4$** was prepared according to the literature⁰ Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

1.1 Synthesis of Boc-protected aminophenyl-2,7-diazapyrene, AzaPy(NHBoc) $_4$

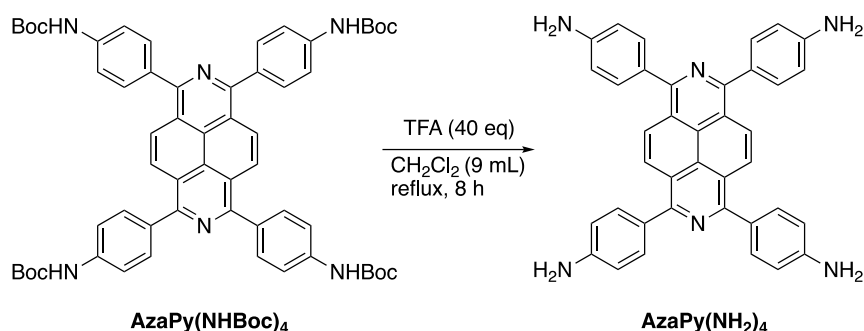


In a 50 mL J-Young tube was placed K_3PO_4 (509 mg, 2.44 mmol) and was heated under the reduced pressure (120°C , 1.0 Torr) for 1 h. After drying of K_3PO_4 , **AzaPy(OPiv) $_4$** (121 mg, 0.20 mmol) and 4-[(*tert*-butoxycarbonyl)-amino]phenylboronic acid (570 mg, 2.4 mmol) were added to the tube, and then $\text{Ni}(\text{cod})_2$ (22.2 mg, 0.080 mmol),

tricyclohexylphosphine (45.0 mg, 0.16 mmol), and toluene (6 mL) were taken in the reaction container in the globe box. The reaction mixture was stirred for 18 h at 70 °C. 10% Aqueous solution of ethylene diamine (6 mL) was added to the reaction mixture and the resulting solution was extracted with CHCl₃ (50 mL × 3). The combined organic layer was dried over Na₂SO₄ and concentrated in *vacuo*. The residue was purified by column chromatography (SiO₂) with CH₂Cl₂/EtOAc (30/1) and reprecipitation from CH₂Cl₂/hexane to give **AzaPy(NHBoc)₄** (57.9 mg, 0.060 mmol, 30% yield).

¹H NMR (400 MHz, CDCl₃): 8.29 (s, 4H), 7.89 (d, *J* = 11 Hz, 8H), 7.58 (d, *J* = 11 Hz, 8H), 6.64 (br s, 4H), 1.57 (s, 36H). HRMS (APCI) Calcd. For C₅₈H₆₀N₆O₈[M]⁺: 969.4545. Found: 969.4589.

1.2 Synthesis of 1,3,6,8-tetrakis(4-aminophenyl)2,7-diazapyrene, AzaPy(NH₂)₄



In a 50 mL Schlenk was placed **AzaPy(NHBoc)₄** (116 mg, 0.12 mmol) and CH₂Cl₂ (9 mL). Then, trifluoroacetic acid (TFA) (0.37 mL, 4.8 mmol) was added at 0 °C. The reaction mixture was refluxed for 8 h. The reaction was quenched with saturated aq. NaHCO₃ and extracted with CH₂Cl₂ (50 mL × 1) and EtOAc (50 mL × 3). The combined organic layer was dried over Na₂SO₄ and concentrated in *vacuo*. The residue was purified by column chromatography (amino-coating SiO₂) with CH₂Cl₂/EtOAc (2/1) and wash with CH₂Cl₂ to give **AzaPy(NH₂)₄** (43.8 mg, 0.077 mmol, 65% yield).

¹H NMR (400 MHz, DMSO-*d*₆): 8.21 (s, 4H), 7.62 (d, *J* = 11 Hz, 8H), 6.78 (d, *J* = 11 Hz, 8H), 5.49 (br s, 8H). HRMS (APCI) Calcd. For C₃₈H₂₈N₆ [M]⁺: 568.2370. Found: 568.2347.

2. Synthesis of COF

2.1 Synthesis of the Aza-1PF COF films.

AzaPy(NH₂)₄ (14.0 mg, 25 μmol, 1 eq.) and tetrafluoroterephthalaldehyde, 1PF(CHO)₂ (10.2 mg, 49 μmol, 2 eq.) were filled into a 20 mL reaction tube, followed by the addition of mesitylene (8 mL), 1,4-dioxane (2 mL) and 6M acetic acid (1 mL). The tube was sealed with purging nitrogen and the reaction mixture was heated at 120°C for 3 days. The separation of stratified immiscible liquid-liquid was observed and the film grows at the

liquid-liquid interface. After cooling to room temperature, the precipitate was collected by filtration, washed with acetone and THF several times until no fluorescence, and then dried at 90°C.

2.2 Synthesis of the Aza-TT COF films.

AzaPy(NH₂)₄ (14.0 mg, 25 μmol, 1 eq.) and thieno-[3,2-b]thiophene-2,5-dicarboxaldehyde, TT(CHO)₂ (9.66 mg, 49 μmol, 2 eq.) were filled into a 20 mL reaction tube, followed by the addition of mesitylene (5 mL), 1,4-dioxane (2 mL) and 6 M acetic acid (1 mL). The tube was sealed with purging nitrogen and the reaction mixture was heated at 120°C for 3 days. The separation of stratified immiscible liquid-liquid was observed and the film grows at the liquid-liquid interface. After cooling to room temperature, the precipitate was collected by filtration, washed with acetone and THF several times until no fluorescence, and then dried at 90°C.

2.3 Synthesis of the Py-1PF COF films.

Py(NH₂)₄ (14.0 mg, 20 μmol, 1 eq.) and tetrafluoroterephthalaldehyde, 1PF(CHO)₂ (5.6 mg, 49 μmol, 2 eq.) were filled into a 20 mL reaction tube, followed by the addition of mesitylene (8 mL), 1,4-dioxane (2 mL) and 6 M acetic acid (1 mL). The tube was sealed with purging nitrogen and the reaction mixture was heated at 120°C for 3 days. After cooling to room temperature, the precipitate was collected by filtration, washed with acetone and THF several times until no fluorescence, and then dried at 90°C.

3. Structure characterization

Powder X-ray diffraction (PXRD) measurements were carried out using CuKα (λ =

0.15406 nm) and Spring-8 (BL02B2 for powder diffraction, $\lambda = 0.5 \text{ \AA}$) instrument.

Transmission electron microscopy (TEM) was performed on JEM-2200FS equipped with a field emission gun operated at 200 kV.

Atomic Force Microscope (AFM) was measured with Bruker Multimode. The images were analyzed by Tapping mode.

Fourier-Transform Infrared (FT-IR) spectra were recorded on a JASCO FT-IR 4700 instrument. Solid samples were directly placed and analyzed for 64 scans.

Diffuse reflectance spectra were measured on the JASCO V-650 UV-Vis spectrophotometer referenced to barium sulfate powder as white standard.

***Scanning Electron Microscope (SEM)** was carried out with JEOL JSM-7001F.*

Raman spectra were recorded on a JASCO NRS-4100, Confocal Raman Microscope.

Fluorescence Spectroscopy were photoexcited using third harmonics of nanosecond Nd:YAG pulsed laser (355 nm, 0.12 mJ with the beam diameter of 5 mm, LS-2131M LOTIS-TII). Combination of a convex lens, an excitation rejection filter, and a bundled optical fiber was used to guide the light, which was then dispersed by the imaging spectrograph and detected by CCD array (Kymera 328i, Newton DU970P-BVF, Andor).

Cyclic voltammetry experiments were carried out using a JASCO J-1500 spectrometer with COFs films, with Pt counter and Ag/AgNO₃ reference electrode, in 0.1 M TBAP/acetonitrile electrolyte solution with the scan rate of 100mV/s and potentials from -2.5V to 2.5V, respectively.

Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted by RIKEN-Keiki's Nakashima PYSA

Two-probe conductivity was measured in an environmental chamber equipped with microprobes under ambient temperature in vacuo.

Flash-Photolysis Time-Resolved Microwave Conductivity (FP-TRMC) measurements were performed for COF films over a quartz substrate. The COFs were dried and evacuated in vacuo for 30 min prior to the measurement at 40°C. COFs on quartz plates were inserted into a TE-102 mode microwave cavity, and fixed at the position of electric field maximum in the cavity. The excitation light intensity through the crystal and quartz was monitored by an Ophir VEGA power meter with a PE-25 head. Transient microwave reflection from the cavity ($\Delta P_R(t)$) were evolved through a Schottky diode, amplified, and monitored by a Tektronics TDS3054 digital oscilloscope. Inside of the cavity was filled with dry nitrogen. The monitored $\Delta P_R(t)$ is converted immediately into transient photoconductivity $\phi \sum \mu(t)$ by,

$$\phi \sum \mu(t) = A \frac{\Delta P_R(t)}{e I_0 F_L P_R},$$

where, A , e , I_0 , F_L , and P_R are sensitivity factors, elementary charge, incident photon density of the excitation laser, correction factor for overlapping between special distribution of photo-generated charge carriers and electromagnetic field strength of probing microwave in the cavity, and static microwave reflection from the cavity, respectively.

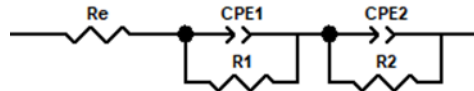
Proton Conductivity Measurement

Proton conductivity was measured using ALS760E with a two-probe AC impedance technique. The film samples were placed between two electrodes inside a custom-built humidity chamber, where the relative humidity (RH) was controlled using saturated salt aqueous solutions at a constant temperature. To ensure equilibrium, the samples were maintained at the set temperature for at least one hour before measurements.

The proton conductivity (σ) was calculated using the equation:

$$\sigma = \frac{t}{R \times A}$$

where σ is the proton conductivity (S/cm), t is the thickness of the sample (cm), R is the resistance (Ω), and A is the pellet's cross-sectional area (cm²).



Scheme S1 illustrates the equivalent circuit model used to represent proton conduction in COFs, including components such as electrode resistance R_e , charge transfer resistance R_1 and R_2 , and a constant phase element $CPE1$ and $CPE2$.

The activation energy E_a for proton conduction was determined using the Arrhenius equation:

$$\sigma = \sigma_0 \times \exp\left(-\frac{E_a}{k_B \times T}\right)$$

where σ_0 is the pre-exponential factor, k_B is the Boltzmann constant, and T is the temperature (K). This approach provided insights into the relationship between proton conductivity and temperature.

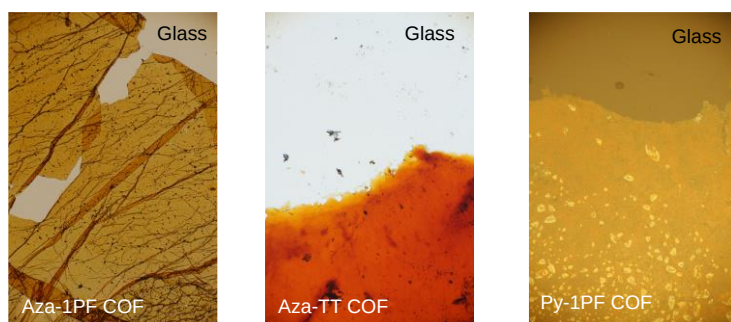


Figure S1. Optical microscope picture of Aza-1PF, Aza-TT, and Py-1PF COF thin film over glass.

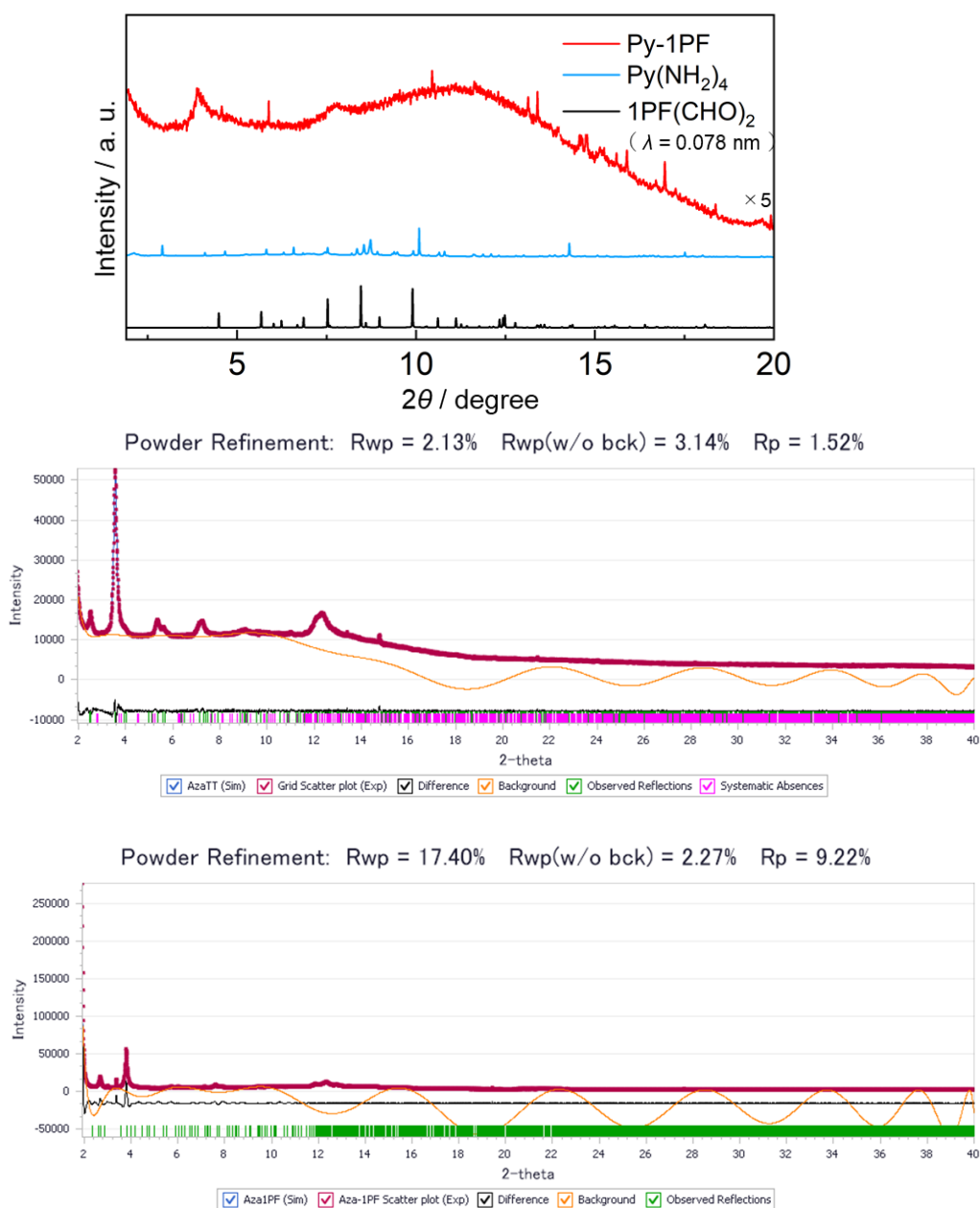


Figure S2. PXRD profile of Py-1PF COFs films (red curve) and monomers (blue and black curve), and refinement with the Pawley method of Aza-1PF and Aza-TT COFs.

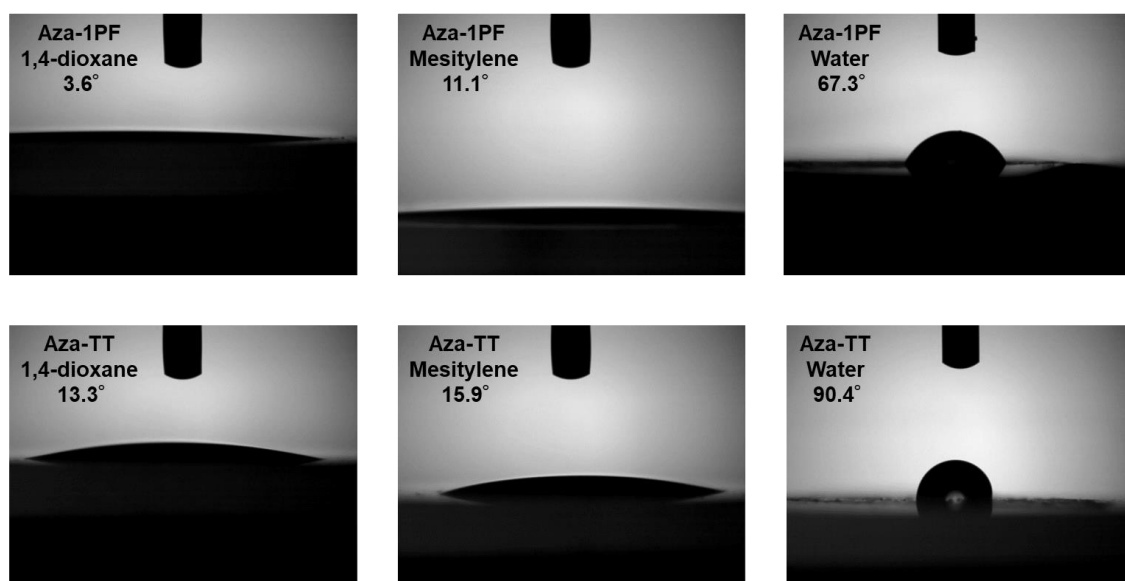


Figure S3. Contact angle measurements of Aza-1PF and Aza-TT COF films against 1,4-dioxane, mesitylene, and water respectively.

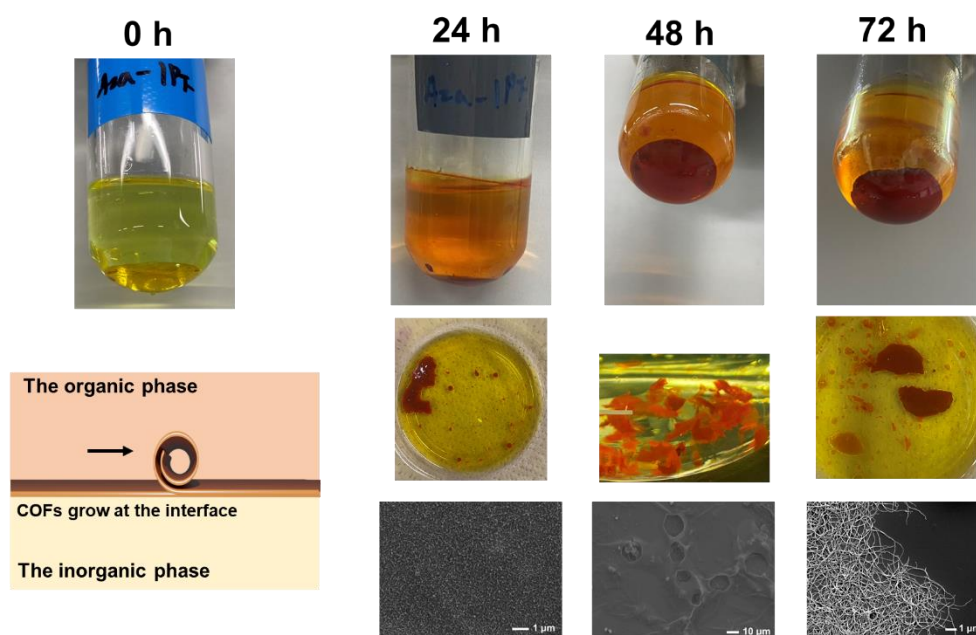


Figure S4. Photo and SEM image of Aza-1PF COF films time dependence structure.

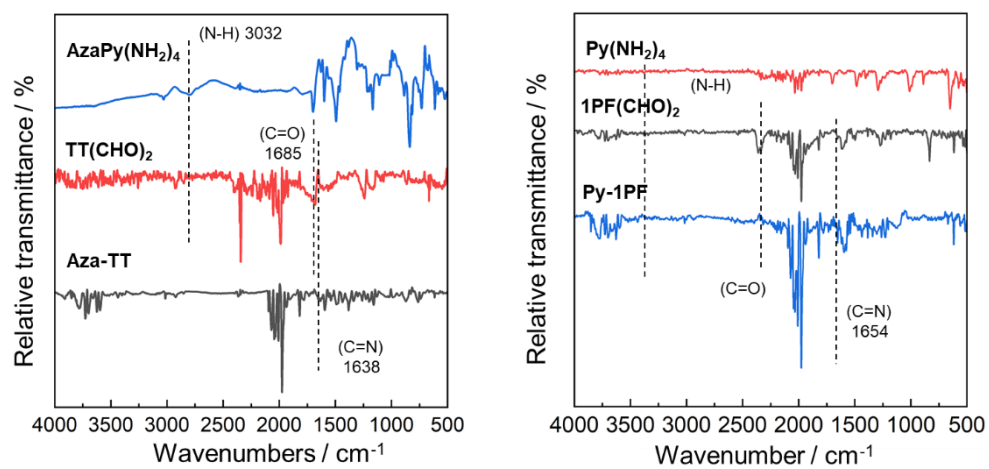


Figure S5. FT-IR spectrum of the Aza-TT and Py-1PF COFs films. The peak at 1638 cm^{-1} and 1654 cm^{-1} indicating C=N of Aza-TT and Py-1PF were observed.

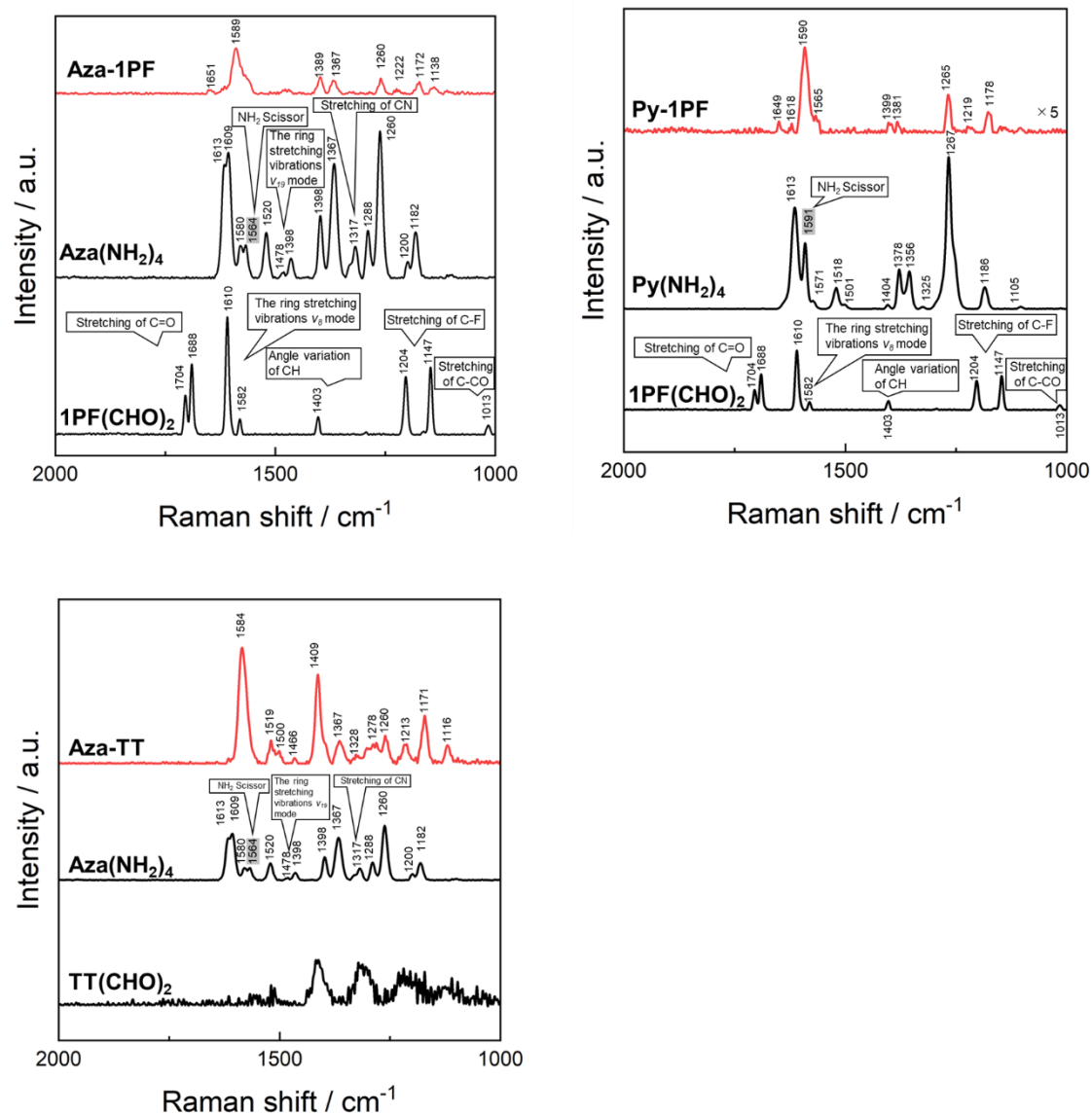


Figure S6. Raman Spectra of Aza-1PF COF, Py-1PF COF, and Aza-TT COF and their reagents.

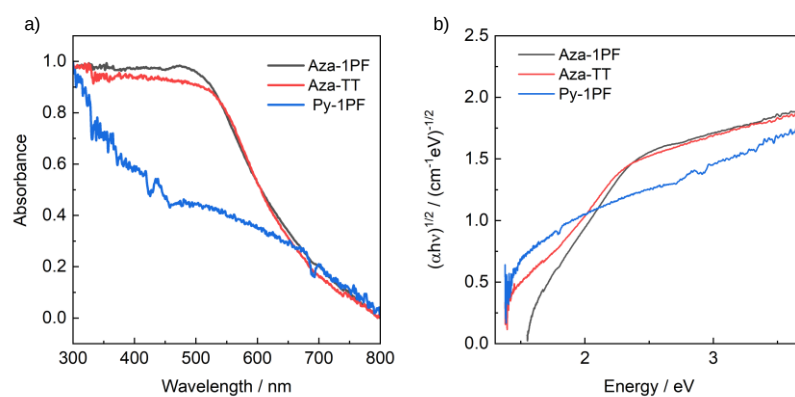


Figure S7. (a) UV-vis diffuse reflectance spectra of the COFs films. (b) Tauc plots

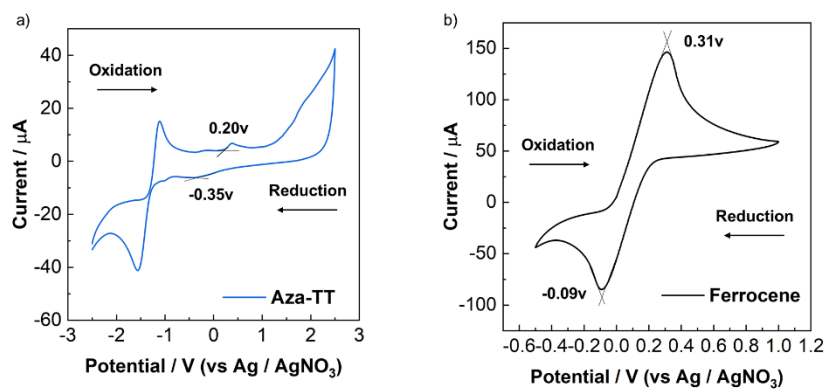


Figure S8. (a) Aza-TT with Pt counter and Ag/AgNO₃ reference electrode, in 0.1 M TBAP/acetonitrile electrolyte solution with the scan rate of 100mV/s and potentials from -2.5 V to 2.5 V, and (b) ferrocene with Pt counter and Ag/AgNO₃ reference electrode, in 0.1 M TBAP/acetonitrile electrolyte solution with the scan rate of 100mV/s and potentials from -0.5 V to 1.0 V respectively.

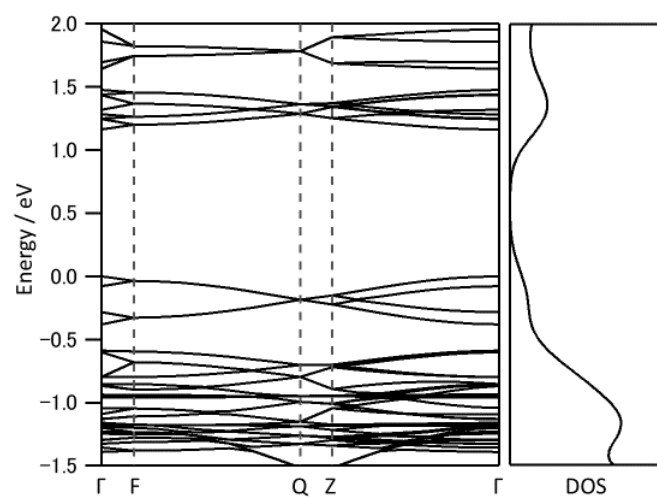


Figure S9. Theoretical calculation of Aza-based COFs.

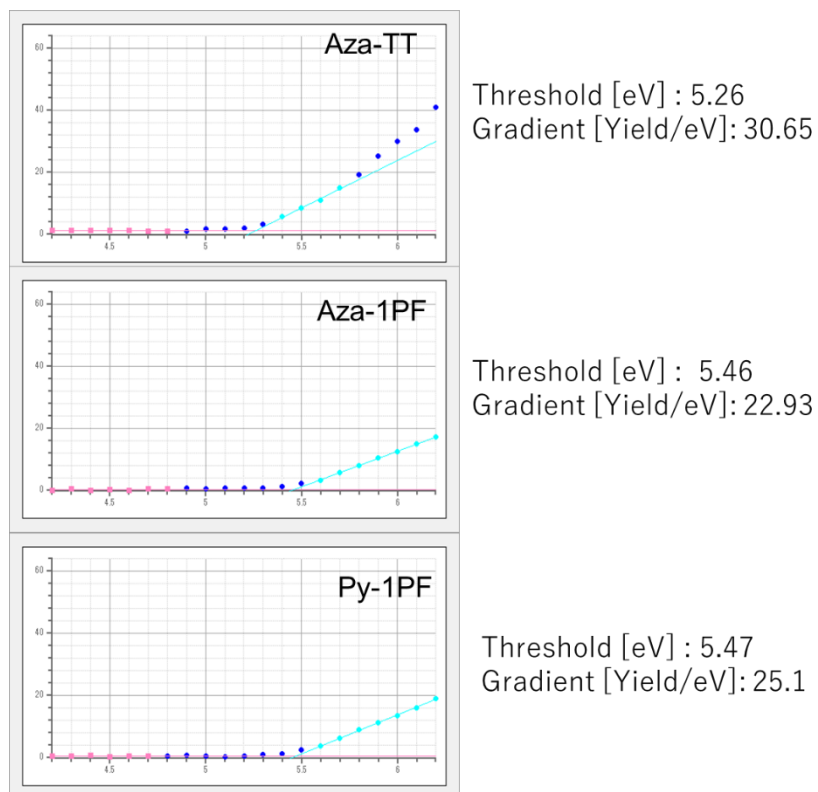


Figure S10. Ultraviolet photoelectron spectroscopy (UPS) of Aza-TT, Aza-1PF and Py-1PF COF films.

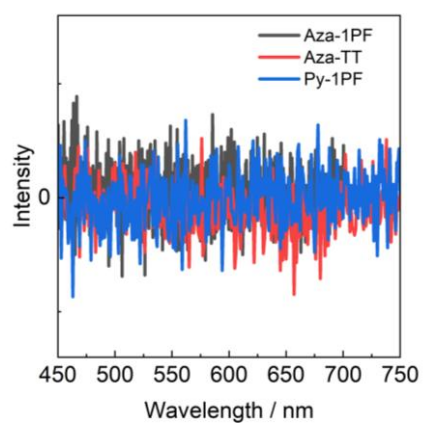


Figure S11. Fluorescence spectra of COFs films over glass substrate upon excitation at 355 nm.

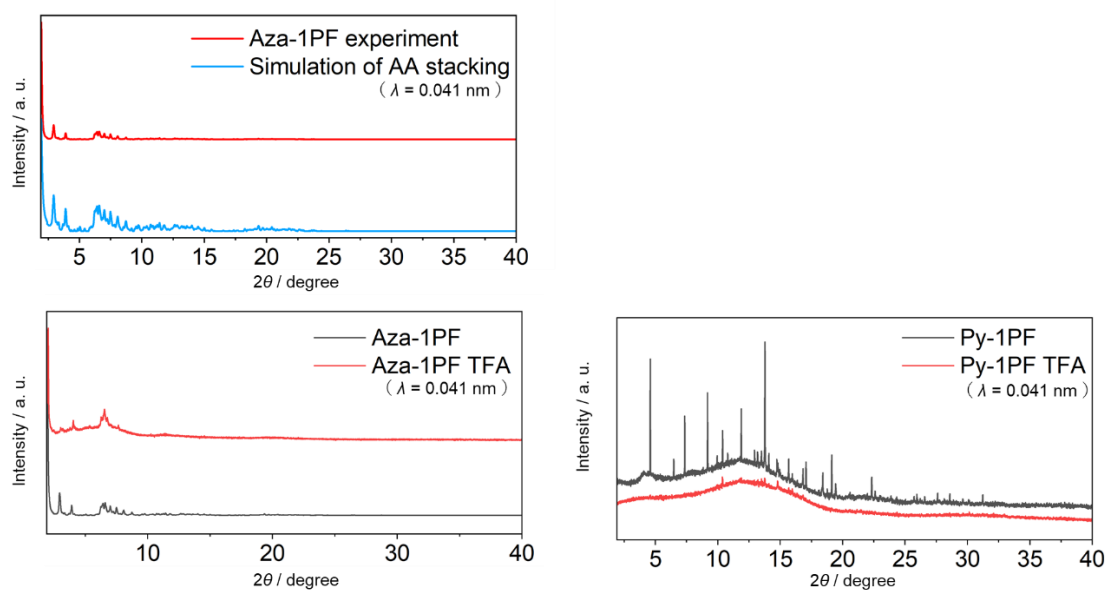


Figure S12. XRD profile of COFs films after doping with TFA.

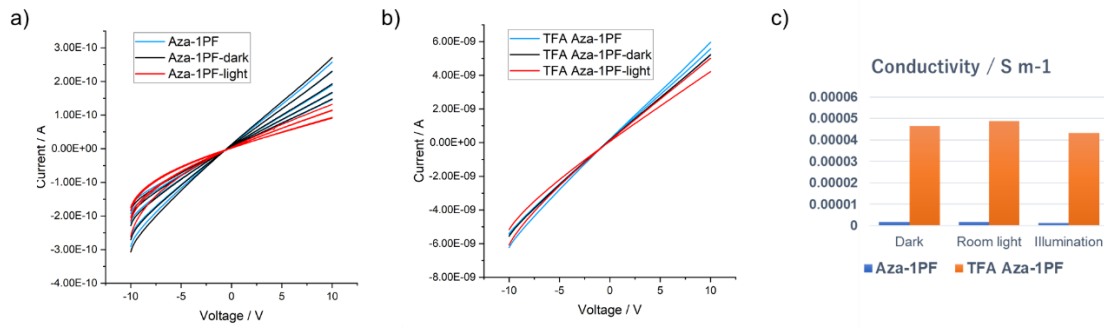


Figure S13. *I-V* characteristics of (a) Aza-1PF film and (b) Aza-1PF TFA film under atmospheric pressure, room temperature with different lighting environments (dark, room light, and the illumination of 2250 mW cm⁻²) (d) The conductivity of Aza-1PF film and Aza-1PF TFA film under room temperature, atmospheric pressure with different lighting environment (dark, room light and illumination of 2250 mW cm⁻²)

The conductivity produced as follows equation:

$$\sigma = \frac{1}{\rho} = \frac{L}{RS}$$

where, L is the length as 1 mm, and S is produced from thickness (2500 nm) multiply by electrode length (3.0 mm).

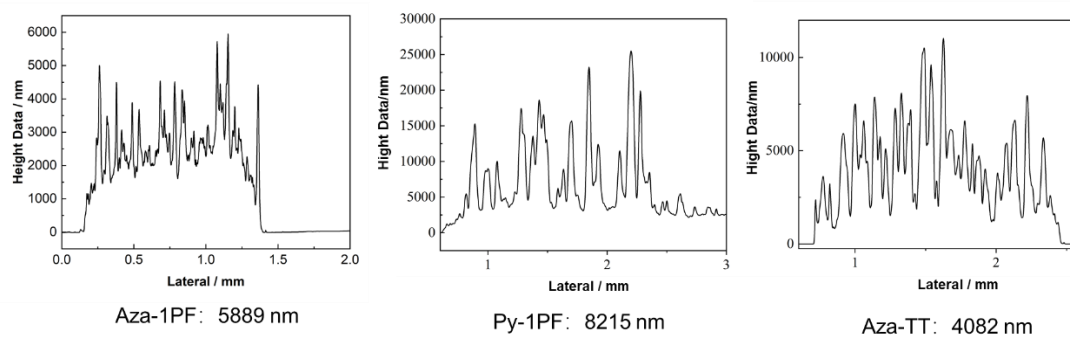


Figure S14. The thickness of the film was measured by DektakXT.

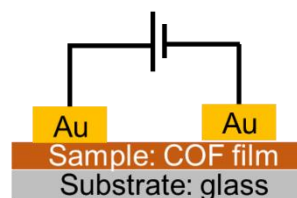
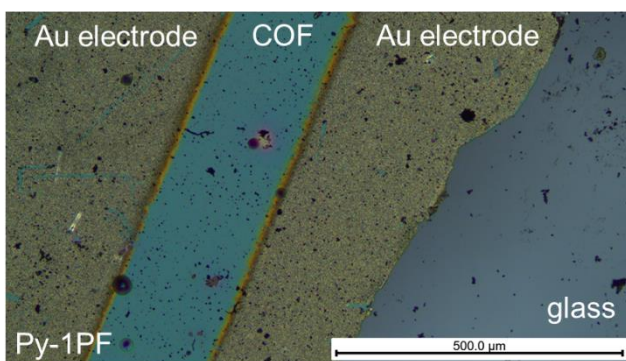
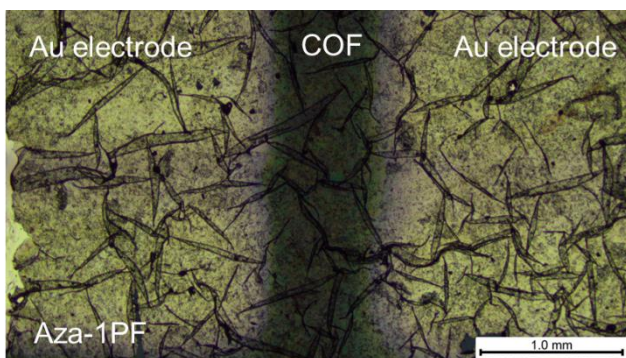


Figure S15. Optical microscope picture of Aza-1PF and Py-1PF device.

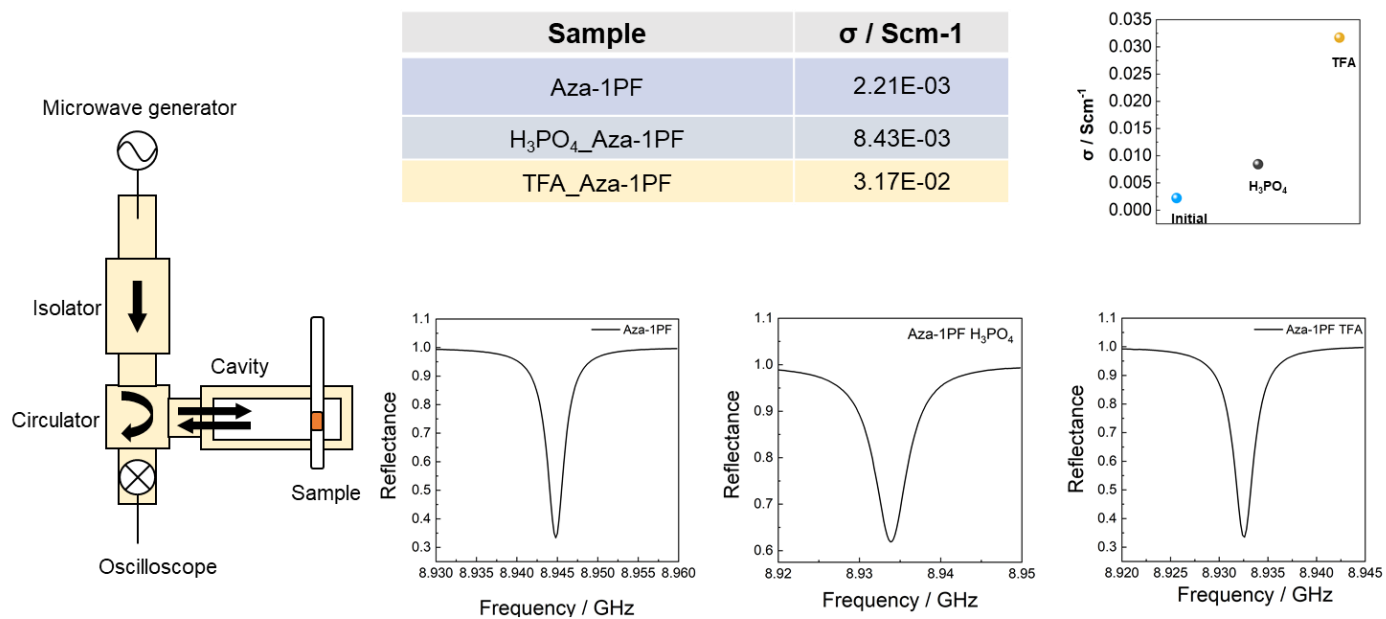


Figure S16. Block diagram of the microwave circuit and microwave reflectance spectra of Aza-1PF COF films.

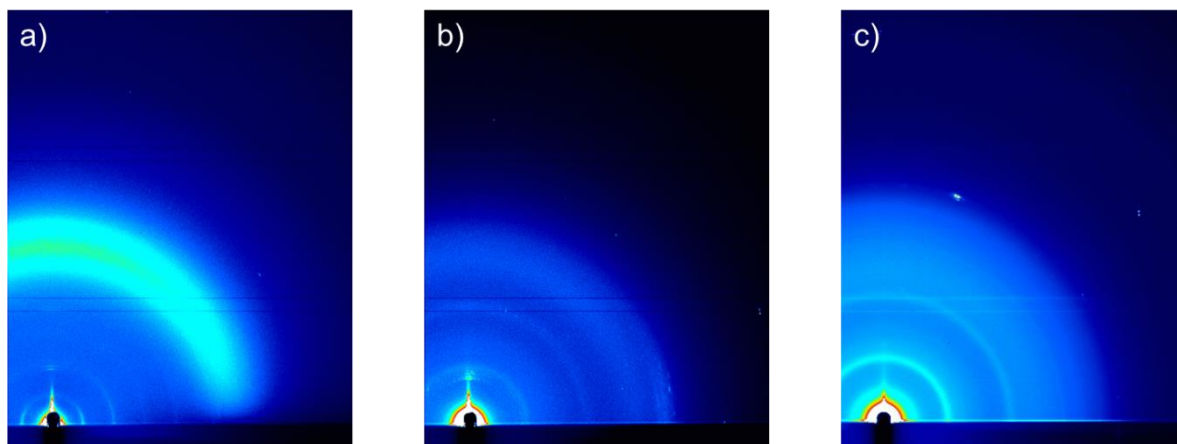


Figure S17. The GIWAXS pattern of (a) **Aza-1PF**, (b)**Aza-TT**, and (c)**Py-1PF** COF thin films on Si substrate.

Reference

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General Conclusion

In this thesis, I achieve a shrinkage of longitudinal intermolecular space as well as wide range alignment of intermolecular interactions by limiting the rotational angle of terminal 4-aminophenyl groups. Unlike conventional π -conjugation, a novel concept of intermolecular electronic conjugation can be achieved in this azapyrene configuration. This enhanced intermolecular electronic conjugation is expected to increase further the crystallinity as well as density-of-states (DOS), leading to extraordinary opto-electronic and proton conductivity.

In chapter 1, highly crystalline COFs were synthesized using a bottom-up approach. By substituting pyrene with 2,7-diazapyrene, nearly "flat" 2D COF layers were formed by controlling the torsion angles of the linker molecules. This structure exhibited limited pore sizes and excellent thermodynamic stability ($\sim 500^\circ\text{C}$), with an ordered face-to-face (slipped AA-type) stacking arrangement. The 2D framework, with a moderate optical bandgap (E_g of ~ 2.1 eV), revealed the planar nature of diazapyrene-based COFs.

In chapter 2, highly ordered and crystalline COFs based on the tetragonal structure of 2,7-diazapyrene were obtained. Microwave conductivity measurements confirmed that the stacking of 2D conjugated frameworks with small E_g values facilitated the formation of highly stable conductive channels in the crystalline state. Additionally, the nitrogen centers in the diazapyrene units played a key role as active sites for proton conduction, with a maximum proton conductivity of $\sigma = 10^{-2} \text{ S cm}^{-1}$ achieved along the continuous nanopore structure surrounded by the active sites. The study indicated that tetragonal COFs based on diazapyrene serve as highly crystalline 2D materials with unique electrical and proton-conducting properties.

In chapter 3, by mimicking the interchangeable carbon allotropes of 2D graphene and 1D carbon nanotubes, the process of transforming 2D COF sheets into 1D nanotubular structures through self-assembly at the solvent interface was explored. This simple "rolling the sheets" self-assembly resulted in coaxial nanotubes with uniform cross-sectional diameters, a process realized with diazapyrene-based COFs rather than pyrene COFs, despite their similar chemical structures. Replacing the 2,7-position carbon atoms of pyrene with nitrogen highlighted contrasting optical and electronic properties due to the rolled structure of the 2D conjugated sheets. The nanotubes exhibited semiconductor properties under ambient conditions, with stable conductive channels. Photoconductivity and electrical conductivity results indicated that nitrogen centers acted as active sites for charge carrier doping.

At the end, through this thesis, four types of 2,7-diazapyrene-based COFs were successfully synthesized with high crystallinity and porosity. By reducing the rotation angle of phenyl groups, tighter interlayer packing was achieved, and the extended planar structure. Under high humidity conditions, these COFs exhibited significant temperature-dependent proton conductivity, highlighting their potential for application in low-temperature proton-conducting membranes and switches. Among them, Aza-1PF-based COF was obtained 1D multi-walled nanotubes with an interlayer spacing of 0.38 nm through the in-situ rolling of COF sheets during solvothermal condensation. Microscopy techniques revealed uniform cross-sectional diameters of approximately 40 nm and a well-defined coaxial tubular structure. Conductivity measurements confirmed the semiconducting nature of these nanotubes, with pronounced photoconductivity and enhanced static conductivity following optical excitation and doping (via iodine vapor diffusion and protonation). These findings underscore the promise of diazapyrene-based

nanotubes in future nano-electronic materials.

List of Publication

Chapter 1 and Chapter 2

1. "Ultrafine Spatial Modulation of Diazapyrene-Based Two-Dimensional Conjugated Covalent Organic Frameworks"

Li Zhuowei, Takahiro Tsuneyuki, Takahiro Tsuneyuki, Rajendra Prasad Paitandi, Takumi NakazatoMasahiro, OdawaraYusuke, TsutsuiTakayuki, TanakaYoshihiro, MiyakeHiroshi, ShinokuboMakito, TakagiTomomi, ShimazakiMasanori, TachikawaKatsuaki, SuzukiHironori, KajiSamrat, Ghosh, Shu Seki. *J. Am. Chem. Soc.*, 2024, 146.33: 23497-23507.

Chapter 3

2. "Rolling Two-Dimensional Covalent Organic Framework Sheets into One-Dimensional Electronically Conductive Nanotubes"

Zhuowei Li, Rajendra Prasad Paitandi, Yusuke Tsutsui, Wakana Matsuda, Masaki Nobuoka, Bin Chen, Samrat Ghosh, Takayuki Tanaka, Masayuki Suda, Tong Zhu, Hiroshi Kageyama, Yoshihiro Miyake, Hiroshi Shinokubo, and Shu Seki. -- Submitted

Supplementary Publication

3. "Electrons lighter than ever."

Seki, Shu, and **Zhuowei Li**. *Nat. Mater.* 2023, 22.7: 807-808.

4. "An n-type semiconducting diazaporphyrin-based hydrogen-bonded organic framework."

Takahiro Sakurai, Tappei Tanabe, Hiroaki Iguchi, **Zhuowei Li**, Wakana Matsuda, Yusuke Tsutsui, Shu Seki, Ryotaro Matsuda and Hiroshi Shinokubo. *Chem. Sci.*, 2024, 15.32: 12922-12927.

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