New Idea for Narrowing an Energy Gap by Selective Perturbation for One of the Frontier Molecular Orbitals

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Abstract

In this manuscript, we will illustrate the new idea for narrowing energy gaps between frontier molecular orbitals (FMOs) by selectively perturbing the levels of highest occupied molecular orbitals (HOMOs) and/or lowest unoccupied molecular orbitals (LUMOs). Initially, the basic concept on the isolated FMOs is explained by employing pentaazaphenalene (5AP) derivatives. It was found that electronic structures of the isolated LUMO of 5AP can be preserved even when incorporated into polymer chains if the connecting points are separated from the isolated LUMO. The mechanism and their unique electronic properties are summarized. Next, conversely, isolated HOMO and LUMO are able to be perturbed by the conjugation effects independently. On the basis of this fact, the near infrared (NIR)-absorbing molecules can be obtained by selectively elevating HOMO and lowering LUMO energy levels. We also mention the strategies for enhancing luminescent properties to 5AP derivatives. Finally, we demonstrate that the isolated LUMO can be found in commodity luminescent dyes, such as boron dipyrromethene (BODIPY). By selectively lowering the LUMO energy level through the aza-substitution at the skeletal carbon where the isolated LUMO is distributed, NIR-emissive polymers can be obtained. Versatility of the isolated FMOs for obtaining optoelectronic organic materials is explained in this review.

Introduction

Conjugated materials having a narrow energy gap between frontier molecular orbitals (FMOs) are recognized as a platform for developing optoelectronic organic devices because of various advantageous electronic properties. For example, a narrow-energy gap material is applicable for constructing efficient organic photovoltaic cells. Because of light-absorption ability in the longer-wavelength regions, narrow-energy gap materials have been utilized as an efficient light antenna. In particular, commodity compounds are not able to capture near-infrared (NIR) light (700 nm–2 μm), narrow-energy gap materials are of importance for improving device efficiencies by capturing the lower-energy light. As another instance, because of intrinsic physical characters of NIR light, such as high transparency through vital bodies, water and quartz, NIR-emissive dyes have been utilized for developing optical sensors as well as bioprobes. Thus, development of NIR-emissive dyes is an area of particular interest with high relevance.

To obtain a narrow energy gap, mainly there are four strategies. The first choice and the robust strategy for decreasing degree of energy gaps is the extension of π-conjugated systems. A narrow energy gap can be realized by simultaneously elevating HOMO and lowering LUMO levels by enlarging π-conjugated rings such as polycyclic aromatics and/or elongating one-dimensional π-conjugated systems such as conjugated polymers. Rigid and planar structures are favorable for receiving the effect by the π-conjugation extension. Secondly, a narrow energy gap can be obtained by the combination of electron-donating (D) and accepting (A) units connected with π-conjugated bridges. Since the HOMO and LUMO belong to the D and A units, respectively, the width of

energy gaps can be tuned by the combination of each unit according to the preprogrammed design. Furthermore, by introducing the π-conjugated bridge, far more red shifts of emission bands are expected. Thus, D–A type polymers have been utilized as an NIR-luminescent layer in OLEDs.[1] Thirdly, by employing heteroatom complexation, a narrower energy gap is able to be obtained. For instance, the LUMO energy level is lowered through the electronic interaction with silicon.[2] Consequently, a narrow energy gap can be obtained. From this view point, we regarded minimum functional units as an "element-block", and deep-red and NIR-emissive materials have been developed based on the narrow-energy gap "element-block".[3] The forth strategy is to employ heavy atom effect for obtaining phosphorescence. By heavy metal complexation, large spin-orbit coupling facilitate intersystem crossing and phosphorescence processes are often facilitated. By preventing oxygen access and thermal motions, highly-efficient luminescence can be obtained. There are a wide variety of NIR-emissive rare metal complexes with π-conjugated ligands, such as porphyrin and phthalocyanine derivatives.

To a certain extent, desired molecules with a narrow energy gap, followed by optical bands in longer wavelength region, can be obtained by selecting the appropriate molecular designs as mentioned above. However, there are still limitations especially for obtaining deep red and NIR-emissive dyes and polymers. One of critical problems is caused by relatively-larger molecular weights of the luminescent dyes with optical bands in the longer wavelength region. In order to obtain a narrow energy gap, the molecules usually have expanded π-system. Therefore, emission dyes often show poor solubility in water as well as organic solvents. This tendency is also applicable in the

design for D–A type conjugated materials and other heteroatom and metal-coordinating molecules. This issue is critical for the preparation of homogeneous films, which is necessary for obtaining organic devices through wet processes. Furthermore, these extended π-systems are unfavorable for obtaining solid-state luminescent properties. Due to non-specific intermolecular interactions such as π-stacking, concentration quenching readily occurs, resulting in emission annihilation. Moreover, in the bioimaging, the NIR-emissive dyes with smaller molecular weights are required. Especially, to deliver the imaging probes into the brain through the brain blood barrier, it is known that the molecular weight should be below 400 Da.[4] Thus, the development of dyes with a small size and molecular weight is strongly required to create next generation of optoelectronic materials in material science and biotechnology.

Herein, we illustrate the new design concept for realizing a narrow energy gap between FMOs not through π-conjugation expansion but through the selective modulation of each HOMO and/or LUMO. We recently discovered that some molecules have spatially-isolated HOMO and/or LUMO from another FMO. By introducing substituents and replacing the skeletal carbon to nitrogen, the energy level of the isolated HOMO or LUMO can be selectively perturbed. In this review, we illustrate the idea of the isolated FMO by employing 5AP derivatives (Figure 1) and demonstrate selective perturbation to one of FMOs by the substituent effect. As an example, we explain the transformation of the red-emissive BODIPY derivative to NIR-emissive dyes based on the idea of the selective perturbation to the isolated FMO.

Discovery of Spatially-Separated FMOs

Initially, we explain the term "isolated FMOs" (Figure 1). When the lobe in HOMO and the node in LUMO are observed at the skeletal carbon, we define this lobe of FMOs as an isolated FMO. It should be noted that this electronic structure is different from those in conventional D–A systems, where the HOMO and LUMO are localized in different units and groups. The isolated FMOs should be located in the same molecular skeleton, while each lobe exists on the spatially-separated skeletal atoms from each other. This unique electronic structure was firstly recognized in the 5AP derivatives and its-containing polymers.

Azaphenalenes are a class of fused three-ring compounds in which the carbon at the center in phenalene is replaced to nitrogen (Figure 1).[5] In comparison to phenalene, which readily forms anion and radical, azaphenalene shows higher stability even in the neutral state since the unpaired electrons of the center nitrogen participated in conjugation systems to external 14π electronic systems. By increasing the number of nitrogen substitution, stability can be enhanced by lowering HOMO levels. Indeed, from the first synthesis of 9b-azaphenalene in 1976,[5b] various azaphenalene derivatives have been obtained as a neutral form, and their electronic properties have been investigated.[5a–5l] To understand their fundamental electronic structures, influence of the substituent effects on optical properties was evaluated, while there were very few examples to offer electronic conjugation including azaphenalenes and other π-conjugated molecules. Furthermore, electron donating and accepting ability in π-conjugated systems was also veiled. We firstly focused on their roles in electronic conjugation systems. Because of stability and applicability for chemical modification, we used penta-substituted azaphenalenes (5AP).

The series of alternating copolymers composed of 5AP and various kinds of comonomers were prepared, and their electronic properties were examined (Scheme 1).[6,7] From the UV–vis absorption measurements, it was found that two absorption bands in the near-UV and visible regions were hypsochromically shifted by introducing electron-accepting comonomers (Figure 2, Table 1). According to the theoretical calculations, the former and the latter are attributable to the electronic transitions mainly between HOMO–LUMO+1 and HOMO–LUMO, respectively. Notably, as shown in Figure 3, HOMO and LUMO+1 of the polymers are perturbed by changing the comonomer units through the conjugation effect except for the benzothiaziazole (BThz)-containing polymer. The degree of peak shifts was in order of the strength of electron-donating and -accepting abilities. It is reasonable because these molecular orbitals (MOs) are originated from the comonomer units. Similarly to conventional conjugated polymers, energy levels were elevated and lowered by introducing electron-donating and accepting units, respectively. It should be emphasized that the LUMO level originated from the LUMO of 5AP was hardly influenced even in the polymers. In the BThz polymer, multiple bands were observed in the absorption spectrum (Figure 2). From the theoretical calculation, it was shown that the insensitive LUMO of 5AP should be located as a LUMO+2 in the polymer, and degenerated LUMO and LUMO+1 originating from LUMO of the BThz unit are obtained (Figure 3). Corresponding to the peak shifts of the absorption bands in the visible region, the solution colors were drastically varied (Figure 4). We mention again that the MO originating from the LUMO of 5AP is insensitive toward the comonomer units.

To survey the electronic structures at the 5AP unit in the polymer, lobes of MOs in the model compounds were calculated (Figure 5). The HOMO and LUMO+1 are delocalized in all the polymer model compounds through 5AP, meanwhile the LUMO is completely localized at the 5AP moiety. In the BThz model, LUMO+2 is found only in the 5AP unit. This means that the LUMO of 5AP is isolated even in the conjugation system. In all cases, significant lobes are hardly observed at the connecting points to the adjacent comonomers. Therefore, the MO should be separated from electronic interactions. From these results, we realized the existence of "the isolated LUMO".

Development of NIR-Absorbing Molecules through Selective Perturbation of FMOs

To comprehend the origin of the isolation effect from electronic interaction only observed in the LUMO of 5AP, we focused on the lobes of 5AP (Figure 6).[8] Three types of 5AP derivatives having *tert*-butyl, phenyl and both groups at 2, 5, 7 and 9 positions in the 5AP ring. In the series of LUMOs, the substituent effect at 7,9-positions were hardly observed, whereas electronic conjugation seemed to be extended especially by the phenyl groups at the 2,5-positions. Conversely, the opposite tendencies were obtained from the HOMOs, where π-conjugation can be extended only through the 7,9-positions. Basically, the 5AP ring has the lobs of LUMO at 2,5-positions and the nodes at 7,9-positions. Therefore, electronic interaction with LUMO not only from EDG/EWG but also from π-conjugation units should be ignored when bonded at the 7,9-positions. In the above polymers, the connecting points were at the 7,9-positions. Therefore, the intrinsic property of LUMO was preserved even in the polymer main-chains from the substituent effects. In summary, the spatially-separated distributions of lobes of HOMO

and LUMO in the single skeleton are the origin of the isolated FMOs.

In Figure 6, next we paid attention to the delocalization of MOs by introducing the phenyl groups into the 2,5-positions in LUMO and the 7,9-positions in HOMO. We presumed that the selective perturbation to one of FMOs might be applicable by selecting the substituent positions and types of EDG and EWG for realizing a narrow energy gap. To evaluate the validity of this idea on selective perturbation of HOMO and LUMO, the series of 5AP derivatives were designed (Scheme 2). By introducing the aromatic substituents at 2,5- and 7,9-positions, influence on energy levels of each FMO were monitored.

Initially, from the UV–vis absorption measurements, the energy gaps of FMOs were estimated (Figure 7). The bathochromic shifts, indicating narrower energy gaps, were detected from the 2,5- and 7,9-substituted 5APs with EWGs and EDGs, respectively. These opposite tendencies can be explained by the energy levels of FMOs estimated from cyclic voltammetry measurements (Figure 8). The introduction of strong EDGs, such as the diphenylaminophenyl groups, into the 7,9-positions in 5AP plays a significant role in elevating HOMO energy levels by +0.60 eV comparing to the pristine 5AP, meanwhile the LUMO of the 2,5-substituted 5AP was lowered by the introduction of strong EWGs, such as cyano groups, by –0.63 eV. These data clearly indicate that energy levels of each FMO can be tuned by selecting the electron affinity and the positions of the substituents.

By applying the selective perturbation, the narrow energy gap molecules were

obtained.[9] The 5AP derivatives having EDGs at the 7,9-positions and EWGs at the 2,5-positions were designed for independently lifting HOMO energy levels and lowering LUMO ones, respectively (Figure 9). As shown in Figure 10, the absorption band attributable to the HOMO–LUMO transition was observed from the tetra-substituted 5AP with bistrifluorophenyl and dimethylaminophenyl groups in the NIR region ($\lambda_{abs,max} = 728$ nm). Moreover, the onset value of the absorption band, which represents the energy gap between FMOs, was obtained at 875 nm, meaning that the extremely-narrow gap is able to be obtained. The energy levels determined from electrochemical measurements clearly indicate that selective perturbations to FMOs were induced by the substituent effects. According to the theoretical calculations, electronic delocalization including the substituents was proposed when the aryl groups are bonded at the 7,9-positions in HOMOs and the 2,5-positions in LUMOs. These data clearly indicate that the selective perturbation should be a powerful strategy for realizing a narrow energy gap between FMOs in the absence of expansion of π-conjugated systems.

Transformation of Molecular Orbital Symmetry for Inducing Emission Property

Wide applicability of the molecular structures having the isolated FMOs are shown here. We explain the design strategy for inducing luminescence from 5AP. Halpern *et al.* reported 1,3,4,6,7,9,9b-heptaazaphenalene is emissive.[10] However, the detail mechanism is still veiled because these emission bands are from the symmetry-forbidden transition. On the basis of this fact, we presumed that the emission property should be induced if the symmetry of FMOs can be transformed. To realize this idea, we designed the amine-substituted 5AP (A5AP).[11]

MO patterns of HOMO and LUMO of 5AP are assigned as pseudo-D_{3h} symmetry (Figure 11). Therefore, the HOMO–LUMO transition of 5AP should be symmetry-forbidden, followed by slight luminescence.[5e,9] Indeed, only the faint $S_2 \rightarrow S_0$ emission of 5AP was previously reported.[5e] By introducing the dialkylamine substituent into the 2-position, the π-conjugated system of A5AP has pseudo-C_{2v} symmetry. Consequently, significant emission should be obtained from the allowed HOMO–LUMO transition. Theoretical calculations can support this speculation. A5AP should have much larger oscillator strengths in the S_0–S_1 transition ($f = 0.0241$ and 0.0184 in absorption and emission transitions, respectively) than those of 5AP ($f = 0.0066$ and 0.0040 in absorption and emission transitions, respectively). These data mean that A5AP can work as a luminophores with the isolated FMOs.

We synthesized the series of A5AP derivatives with various substituents at the 7,9-positions where only lobes of HOMOs exist. The tendency of peak shifts in UV−vis absorption spectra was almost same with those of 5AP (Figure 12). By introducing strong EDGs, red-shifted emission bands were observed by elevating only HOMOs. Emission spectra were monitored with the same solutions (Figure 13). It should be noted that all A5AP derivatives showed emission in the visible region, whereas the 5AP derivative hardly showed emission. Furthermore, depending on the type of the aryl unit, emission color can be tuned. Similarly to absorption spectra, emission bands tended to be observed in the longer wavelength region by introducing EDGs. These data indicate that transformation of the MO symmetry is capable while maintaining the isolated FMOs.

Enhance of Luminescent Property Using Boron-Complexation

To extend the idea on the transformation of molecular symmetry for facilitating electronic transition between FMOs, we next aimed to realize the perturbation of one of FMOs by boron complexation, followed by enhancement to light-absorption and subsequent luminescent properties.[11] The boron complexes were constructed with the 5AP ligand and their optical properties were compared to those of the model without boron (Figure 14). Accordingly, small absorption and almost no emission were obtained in the visible region from the model compounds. In contrast, obvious enhancement of magnitude of light absorption ability and clear red emission were exhibited from the boron complex although the emission quantum yield was still below the detectable level.

From the theoretical calculations, it was revealed that the forbidden HOMO–LUMO transition was greatly shuffled by the boron complexation (Figure 15). The HOMO of 5AP is downshifted by the formation of the B–N dative bond. Further, the new electronic orbital is generated and located as the HOMO, while the isolated LUMO of 5AP can be preserved. As a result, light-absorption ability and emission property were enhanced compared to those of the pristine 5AP derivative. By the boron complexation, drastic shuffling of one of FMOs, followed by breaking through symmetry forbidden, can be realized.

Isolated FMOs in Commodity Dyes and Application for NIR Emission

Finally, we illustrate the application of the idea of isolated FMOs for modulating commodity luminescent dyes. The formation of spatially-separated FMOs was reported in other π-conjugated molecules such as azulenes[12], porphyrins[13] and

dimesitylboryl-substituted pyrenes.[14] From the commodity luminophores, we have paid attention to boron dipyrromethene (BODIPY) which has large magnitude of light-absorption ability and intense luminescence.[15] By chemical modification based on the expansion of π-conjugated systems, NIR emission can be also accomplished.[16] In particular, BODIPYs are also feasible as a monomer for constructing luminescent polymers. In this part, we demonstrate the transformation of the BODIPY-containing polymer to the NIR-emissive material without losses of advantageous properties, such as a sharp spectrum shape and an electron-carrier ability.[16]

According to the theoretical calculation with the BODIPY skeleton, the significant lobe was observed at the *meso*-position in the LUMO, meanwhile any lobe was hardly detected at the same skeletal carbon in the HOMO, meaning that BODIPY has the typical isolated LUMO (Figure 16). On the basis of these results, we prepared the alternating polymers containing tetraphenyl BODIPY. From the optical measurements, it was shown that the BODIPY-containing polymers can show large magnitude of absorption and intense emission in the deep-red region ($\lambda_{abs,max}$ = 603 nm, $\lambda_{em,max}$ = 648 nm).

Next, in order to realize NIR emission by the selective reduction to the isolated LUMO, we replaced the skeletal carbon to nitrogen. In the case of phenalene, the increase in the number of the aza-substitution at the outside ring contributes to the enhancement of stability toward oxidized decomposition by lowering HOMO levels. We expected the similar lowering effect only for the LUMO energy level of BODIPY by substituting the skeletal carbon at the *meso*-position, where the isolated LUMO exists,

to nitrogen. To evaluate influence of the aza-substitution on electronic properties of BODIPY, we performed theoretical calculations and confirmed that its LUMO level should be selectively lowered (Figure 17). The HOMO level was lowered by 0.05 eV by the aza-substitution, whereas the LUMO level was drastically reduced by 0.43 eV. As a result, the narrower energy gap ($\Delta\Delta E_{gap} = -0.38$ eV) was proposed.

The polymers were synthesized, and their optical properties were investigated (Figure 18). As proposed from the theoretical calculations, significant red-shifts were observed in absorption and emission spectra. It should be mentioned that the sharp shapes of optical bands can be maintained after the aza-substitution. Because areas of π-conjugated systems were same through the aza-substitution, peak broadening is able to be suppressed, and only red-shifts in optical spectra are received. Moreover, we also evaluated the electron carrier ability of the polymer films in electron-only devices prepared by the wet process. Almost high values were obtained from the both devices, meaning that optical properties can be selectively tuned by the aza-substitution without losses of electric functions.

Conclusion

We briefly reviewed the idea of selective perturbation of one of FMOs by targeting the isolated FMOs. By focusing on distribution of lobes of each MO, we are capable of finding the isolated HOMO and/or LUMO. By selecting the substituent position where the isolated FMO exists, efficient perturbation of energy levels can be induced. Consequently, a narrow energy gap between FMOs can be achieved without π-conjugation expansion. In this manuscript, we illustrated the idea mainly by

employing 5AP derivatives. The energy level in commodity luminescent dye, BODIPY, can be also tuned based on this strategy. In addition, it can be proposed further applications especially for obtaining advanced luminescent materials as well as overcoming problems by selective perturbation to the isolated FMOs. For example, by the combination with the isolated HOMO and the aza-substituent, blue-luminescent materials might be obtained by enlarging an energy gap between FMOs. As another instance, small sized NIR dyes might be expected from the molecular design based on selective perturbation of one of FMOs. Moreover, by selecting the type of element, further modulation of electronic structures could be expected. Thus, we can say that this concept has wide versatility and still huge potential for developing new generation of optoelectronic materials.

References

1.   A. Zampetti, A. Minotto, F. Cacialli, *Adv. Funct. Mater*. **2019**, *29*, 1807623.

2.   a) Y. Tokoro, K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1350. b) Y. Tokoro, K. Tanaka, Y. Chujo, *RSC Adv*. **2015**, *5*, 23331. c) Y. Tokoro, K. Tanaka, Y. Chujo, *Org. Lett*. **2013**, *15*, 2366. d) Y. Tokoro, H. Yeo, K. Tanaka, Y. Chujo, *Polym. Chem*. **2013**, *4*, 5237. e) Y. Tokoro, H. Yeo, K. Tanaka, Y. Chujo, *Chem. Commun*. **2012**, *48*, 8541.

3.   a) K. Tanaka, Y. Chujo, *Polym. J*. **2020**, *52*, 555. b) M. Gon, K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn*. **2019**, *92*, 7. c) M. Gon, K. Tanaka, Y. Chujo, *Polym. J*. **2018**, *50*, 109. d) Y. Chujo, K. Tanaka, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 633.

4.   W. M Pardridge, *J. Cereb. Blood Flow Metab*. **2012**, *32*, 1959.

4.   a) G. R. Underwood, *J. Org. Chem.* **1968**, *33*, 1313. b) F. David, T. T. Gough, D. Leaver, *J. Chem. Soc., Perkin Trans.* **1976**, *1*, 341. c) J. T. Shaw, C. M. Balik, J. L. Holodnak, S. Prem, *J. Heterocyclic Chem*. **1976**, *30*, 127. d) A. T. Balaban, M. Banciu, V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-Derivatives and Their Valence Isomers*, Vol. 3, CRC Press: Boca Raton, FL, **1987**. e) W. Leupin, J. Wirz, *J. Am. Chem. Soc.* **1980**, *102*, 6068. f) J. P. Boutique, J. J. Verbist, J. G. Fripiat, J. Delhalle, G. Pfister-Guillouzo, G. J. Ashwell, *J. Am. Chem. Soc.* **1984**, *106*, 4374. g) M. A. Rossman, N. J. Leonard, S. Urano, P. R. LeBreton, *J. Am. Chem. Soc.* **1985**, *107*, 3884. h) H. Gotou, K. Kurata, Y.

Tominaga, Y. Matsuda, *J. Org. Chem.* **1985**, *50*, 4028. i) W. Leupin, D. Magde, G. Persy, J. Wirz, *J. Am. Chem. Soc.* **1986**, *108*, 17. j) M. Shahbaz, S. Urano, P. R. LeBreton, M. A. Rossman, R. S. Hosmane, N. J. Leonard, *J. Am. Chem. Soc.* **1984**, *106*, 2805. k) R. S. Hosmane, M. A. Rossman, N. J. Leonard, *J. Am. Chem. Soc.* **1982**, *104*, 5497. l) U. T. Shaw, C. E. Brotherton, R. W. Moon, T. W. Coffindaffer, D. A. Miller, *J. Heterocyclic Chem.* **1981**, *18*, 75. m) Y. Morita, S. Suzuki, K. Sato, T. Takui, *Nat. Chem.* **2011**, *3*, 197. n) S. Zheng, J. Lan, S. I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **2003**, *125*, 5786. o) Y. Morita, T. Aoki, K. Fukui, S. Nakazama, K. Tamaki, S. Suzuki, A. Fuyuhiro, K. Yamamoto, K. Sato, D. Shiomi, A. Naito, T. Takui, K. Nakasuji, *Angew. Chem. Int. Ed.* **2002**, *41*, 1793. p) Y. Morita, K. Fukui, S. Suzuki, T. Aoki, S. Nakazawa, K. Tamaki, A. Fuyuhiro, K. Yamamoto, K. Sato, D. Shiomi, A. Naito, T. Takui, K. Nakasuji, *Polyhedron* **2003**, *22*, 2199. q) Y. Morita, S. Suzuki, K. Fukui, S. Nakazawa, H. Kitagawa, H. Kishida, H. Okamoto, A. Naito, A. Sekine, Y. Ohashi, M. Shiro, K. Sasaki, D. Shiomi, K. Sato, T. Takui, K. Nakasuji, *Nat. Mater.* **2008**, *7*, 48. r) Y. Morita, S. Suzuki, K. Fukui, S. Nakazawa, K. Sato, D. Shiomi, T. Takui, K. Nakasuji, *Polyhedron* **2003**, *22*, 2215.

6.   a) H. Yeo, K. Tanaka, M. Hirose, Y. Chujo, *Polym. J.* **2014**, *46*, 688. b) H. Watanabe, M. Hirose, K. Tanaka, K. Tanaka, Y. Chujo, *Polym. Chem.* **2016**, *7*, 3674.

7.   H. Watanabe, K. Tanaka, Y. Chujo, *J. Org. Chem.* **2019**, *84*, 2768.

8.   H. Watanabe, J. Ochi, K. Tanaka, Y. Chujo, *Eur. J. Org. Chem.* **2020**, *2020*, 777.

9.   M. A. Rossman, R. S. Hosmane, N. J. Leonard, *J. Phys. Chem.* **1984**, *88*, 4324.

10.   H. Watanabe, M. Hirose, K. Tanaka, Y. Chujo, *Chem. Commun.* **2017**, *53*, 5036.

11.   H. Watanabe, Y. Kawano, K. Tanaka, Y. Chujo, *Asian J. Org. Chem.* **2020**, *9*, 259.

12.   a) P. A. Plattner, *Helv. Chim. Acta* **1941**, *24*, 283E. b) R. S. H. Liu, *J. Chem. Educ.* **2002**, *79*, 183. c) K. Tsurui, M. Murai, S.-Y. Ku, C. J. Hawker, M. J. Robb, *Adv. Funct. Mater.* **2014**, *24*, 7338. d) Y. Yamaguchi, K. Ogawa, K. Nakayama, Y. Ohba, H. Katagiri, *J. Am. Chem. Soc.* **2013**, *135*, 19095. e) Y. Yamaguchi, M. Takubo, K. Ogawa, K. Nakayama, T. Koganezawa, H. Katagiri, *J. Am. Chem. Soc.* **2016**, *138*, 11335.

13.   a) M. Gouterman, *J. Chem. Phys.* **1959**, *30*, 1139. b) H. Fujii, *J. Am. Chem. Soc.* **1993**, *115*, 4641.

14.   a) A. G. Crawford, A. D. Dwyer, Z. Liu, A. Steffen, A. Beeby, L.-O. Pålsson, D. J. Tozer, T. B. Marder, *J. Am. Chem. Soc.* **2011**, *133*, 13349. b) J. Merz, J. Fink, A. Friedrich, I. Krummenacher, H. H. Al Mamari, S. Lorenzen, M. Haehnel, A. Eichhorn, M. Moos, M. Holzapfel, et al., *Chem. - A Eur. J.* **2017**, *23*, 13164. c) L. Ji, R. M. Edkins, A. Lorbach, I. Krummenacher, C. Brückner,

A. Eichhorn, H. Braunschweig, B. Engels, P. J. Low, T. B. Marder, *J. Am. Chem. Soc.* **2015**, *137*, 6750.

15. a) H. Yamane, K. Tanaka, Chujo, Y. *Polym. J*. **2018**, *50*, 271. b) H. Yamane, S. Ohtani, K. Tanaka, Y. Chujo, *Tetrahedron Lett*. **2017**, *58*, 2989. c) K. Tanaka, T. Yanagida, H. Yamane, A. Hirose, R. Yoshii, Y. Chujo, *Bioorg. Med. Chem. Lett*. **2015**, *25*, 5331. d) R. Yoshii, H. Yamane, K. Tanaka, Y. Chujo, *Macromolecules* **2014**, *47*, 3755. e) K. Tanaka, H. Yamane, R. Yoshii, Y. Chujo, *Bioorg. Med. Chem.* **2013**, *21*, 2715. f) R. Yoshii, A. Nagai, K. Tanaka, Y. Chujo, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1726.

16. R. Yoshii, H. Yamane, A. Nagai, K. Tanaka, H. Taka, H. Kita, Y. Chujo, *Macromolecules* **2014**, *47*, 2316.

Figures and Tables
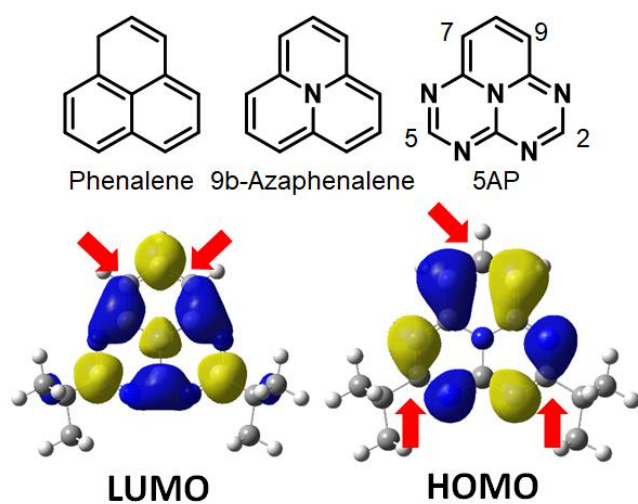
Figure 1. Chemical structures of 5AP and its FMOs (red arrows: node). Reproduced from Ref. 6b with permission from The Royal Society of Chemistry.
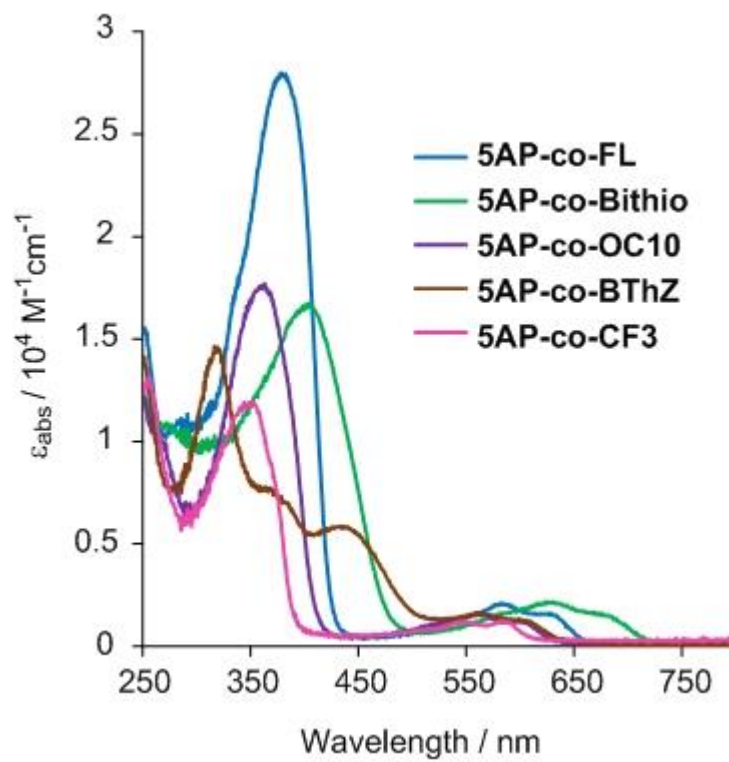
Figure 2. UV−vis absorption spectra of the polymers in the chloroform solutions $(1.0 \times 10^{-5}$ M). Reproduced from Ref. 6b with permission from The Royal Society of Chemistry.
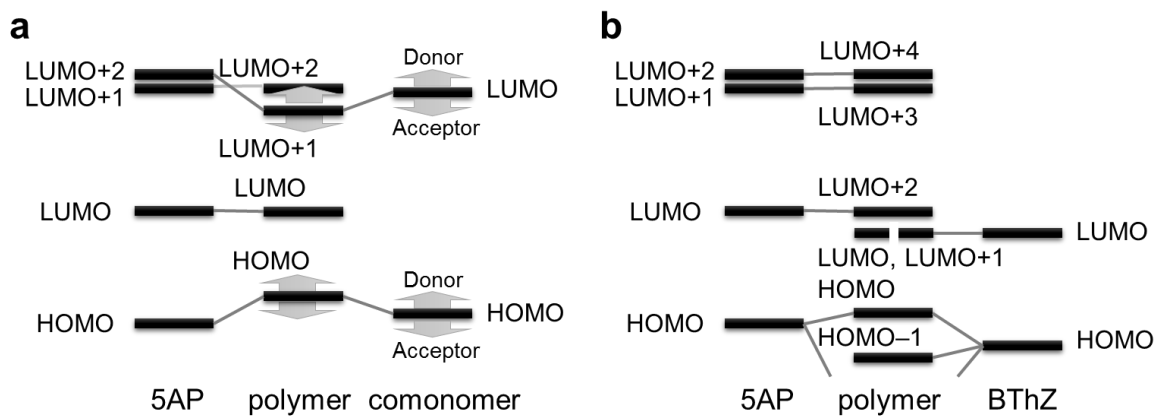
Figure 3. Schematic diagrams of the energy levels of the polymers derived from mixing of the MOs of **5AP** and (a) various comonomers and (b) **BThZ**. Reproduced from Ref. 6b with permission from The Royal Society of Chemistry.

Figure 4. Appearance of the polymer solutions in chloroform under ambient condition.

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HOMO (−5.45 eV)   LUMO (−2.45 eV)

FL   LUMO+1 (−1.77 eV)   LUMO+2 (−1.50 eV)

HOMO (−5.34 eV)   LUMO (−2.58 eV)

Bithio   LUMO+1 (−1.94 eV)   LUMO+2 (−1.69 eV)

HOMO (−5.33 eV)   LUMO (−2.12 eV)

OC10   LUMO+1 (−1.24 eV)   LUMO+2 (−1.16 eV)

HOMO−1 (−6.79 eV)   HOMO (−5.76 eV)   LUMO (−2.80 eV)

BThZ

LUMO+1 (−2.71 eV)   LUMO+2 (−2.51 eV)   LUMO+3 (−1.60 eV)   LUMO+4 (−1.56 eV)

HOMO (−6.22 eV)   LUMO (−2.85 eV)

CF3

LUMO+1 (−2.18 eV)   LUMO+2 (−2.02 eV)   LUMO+3 (−1.88 eV)
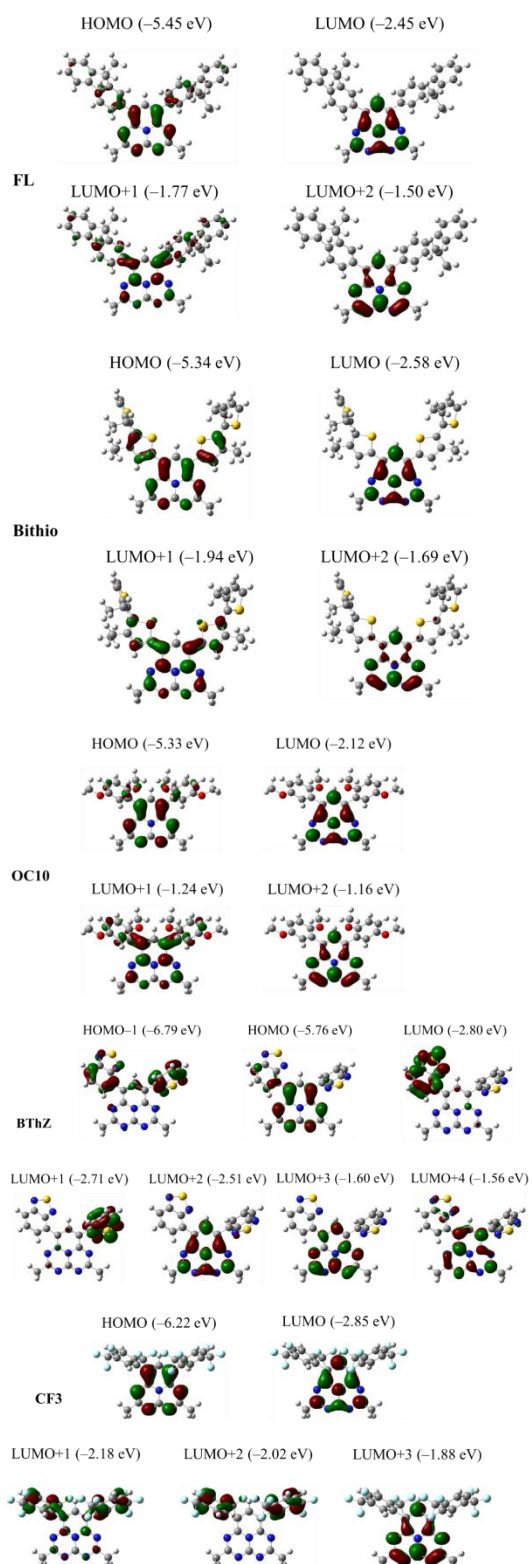
Figure 5. Selected MO patterns and the energy levels of model compounds
(B3LYP/6-31G+(d,p) level). Reproduced from Ref. 6b with permission from The Royal

Society of Chemistry.

Scheme 1. Alternating copolymers containing 5AP

Ar =

5AP-co-FL

5AP-co-Bithio

5AP-co-BThZ

5AP-co-CF$_3$

5AP-co-OC$_{10}$
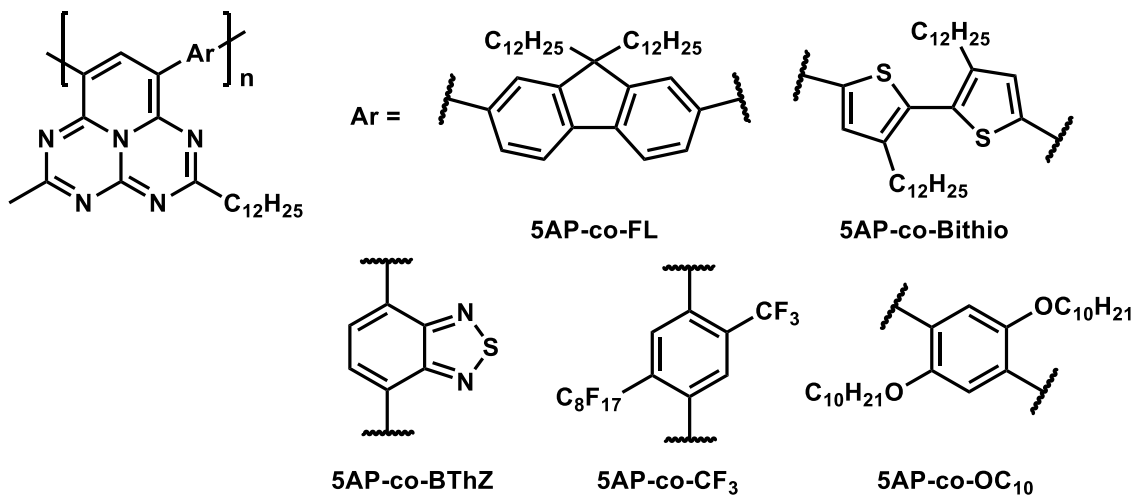
Table 1. Absorption properties of the polymers[a]

Polymer	λ_{max} (nm)	$\varepsilon_{\lambda max}$ (M^{-1}cm^{-1})	$\lambda_{long,vis}$ (nm)	$\varepsilon_{\lambda long,vis}$ (M^{-1}cm^{-1})
5AP-co-FL	379	28,000	627	1,500
5AP-co-Bithio	404	17,000	689	1,300
5AP-co-OC10	363	18,000	615	1,000
5AP-co-BThZ	317	15,000	615	1,000
5AP-co-CF3	255	13,000	593	1,100

[a]Measured in chloroform (1.0×10^{-5} M per 5AP unit).

Scheme 2. Chemical structures of 2,5- or 7,9-substituted 5APs
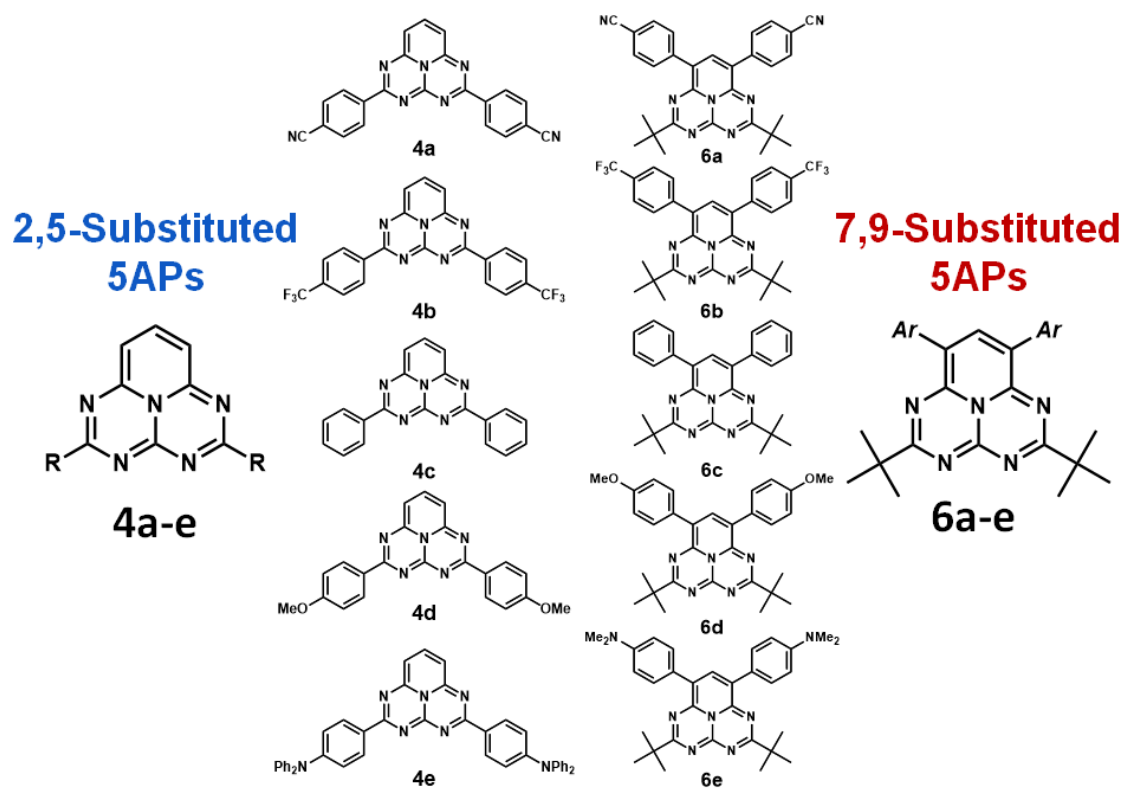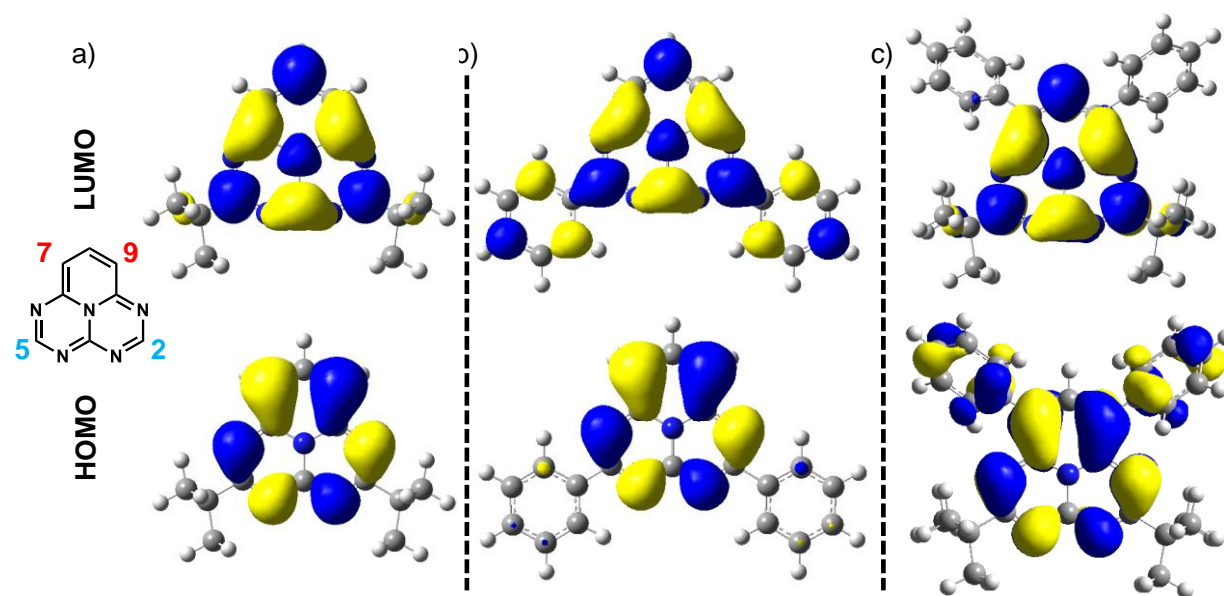
Figure 6. Frontier orbitals of (a) **2**, (b) **4c** and (c) **6c** at B3LYP/6-31+G(d,p) level of theory. Adapted with permission from ref. 7. Copyright 2019 American Chemical Society.
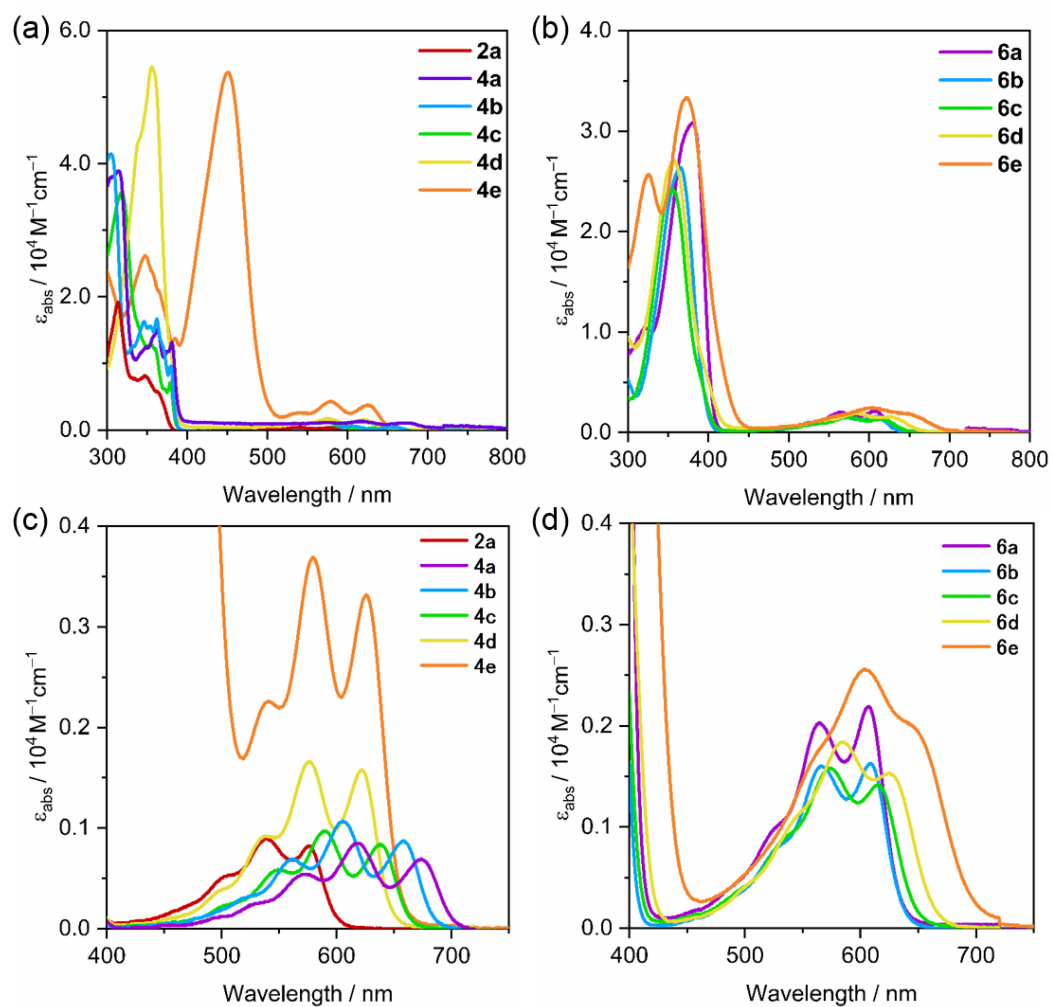
Figure 7. UV–vis absorption spectra of (a) **2a**, **4a-e** and (b) **6a-e** (1.0×10^{-5} M in chloroform). Enlarged spectra in the visible region of (c) **2a**, **4a-e** and (d) **6a-e** (1.0×10^{-4} M in chloroform). Adapted with permission from ref. 7. Copyright 2019 American Chemical Society.
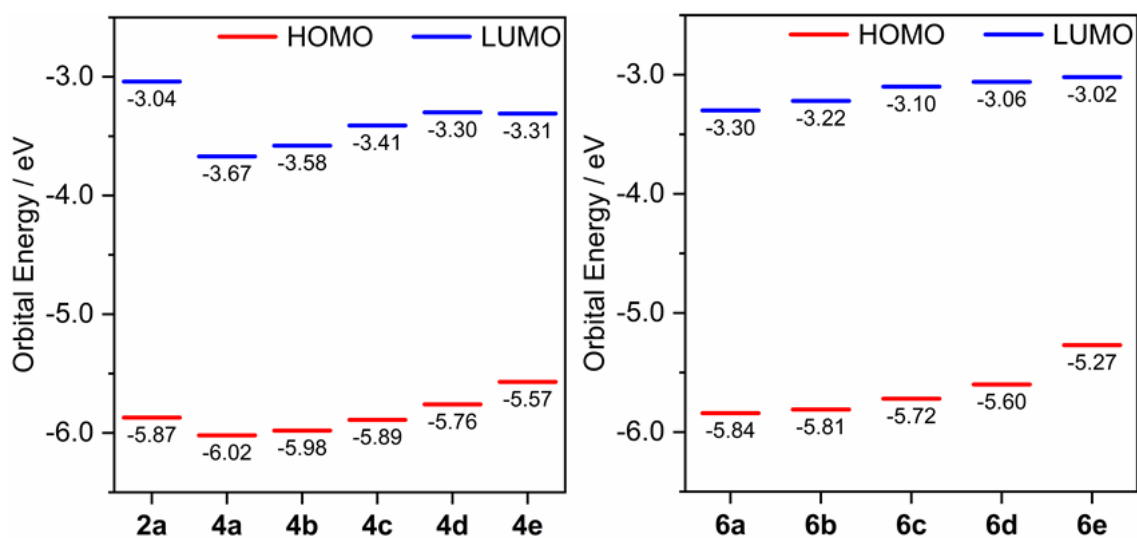
Figure 8. Energy levels of HOMOs and LUMOs estimated from cyclic voltammetry measurements. Adapted with permission from ref. 7. Copyright 2019 American Chemical Society.
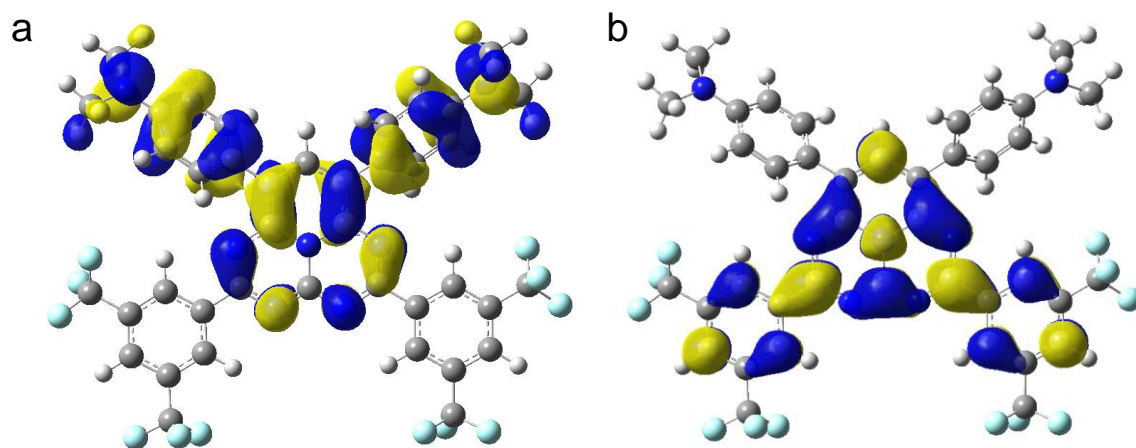
Figure 9. (a) HOMO and (b) LUMO of **4bd** calculated at B3LYP/6-31+G(d,p) level of theory. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA.
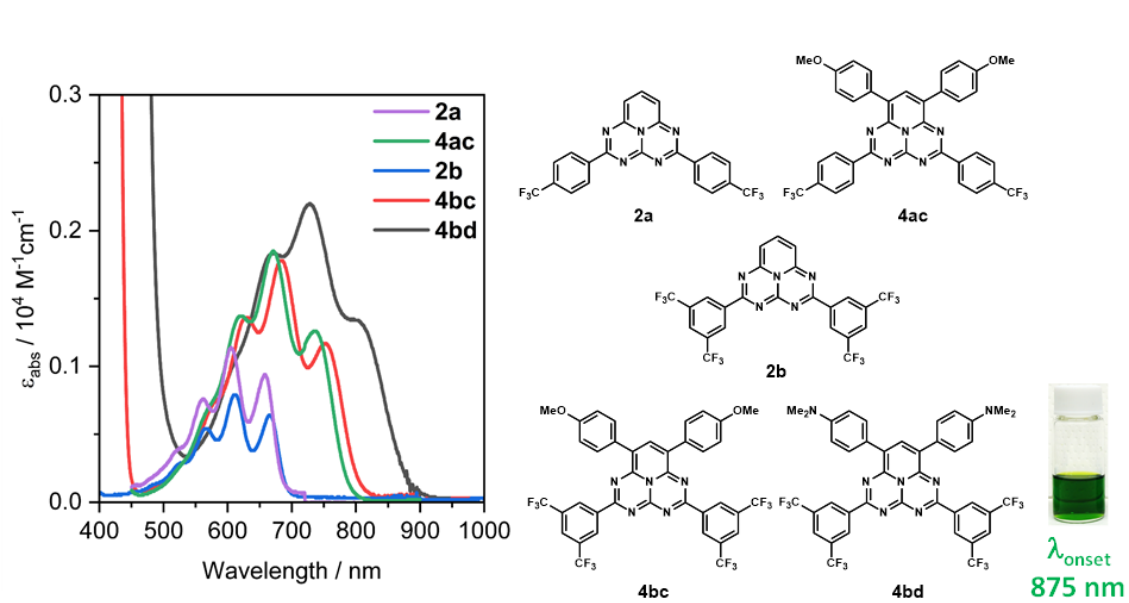
Figure 10. UV−vis absorption spectra of tetra-substituted 5APs. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA.
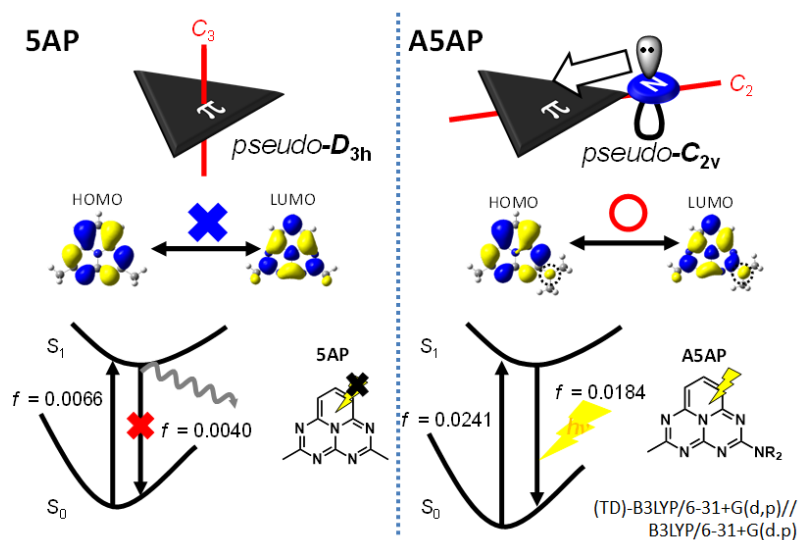
Figure 11. Schematic illustration on the transformation of orbital symmetry by introducing the amine group. Reproduced from Ref. 10 with permission from The Royal Society of Chemistry.
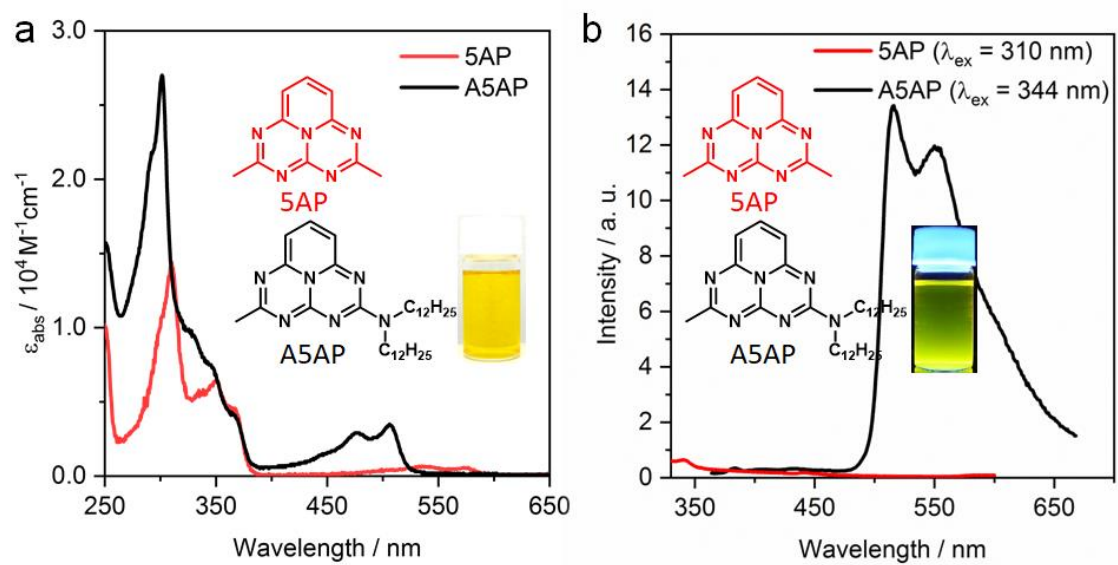
Figure 12. (a) UV−vis absorption and (b) emission spectra of 5AP and A5AP. Reproduced from Ref. 10 with permission from The Royal Society of Chemistry.
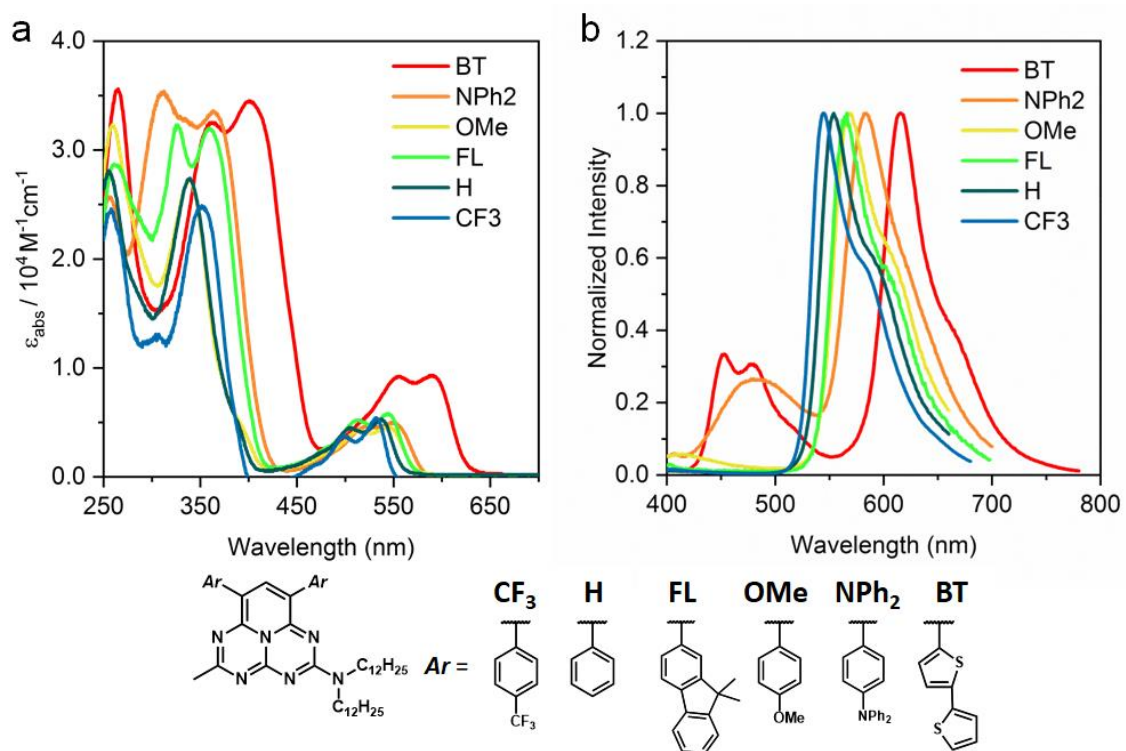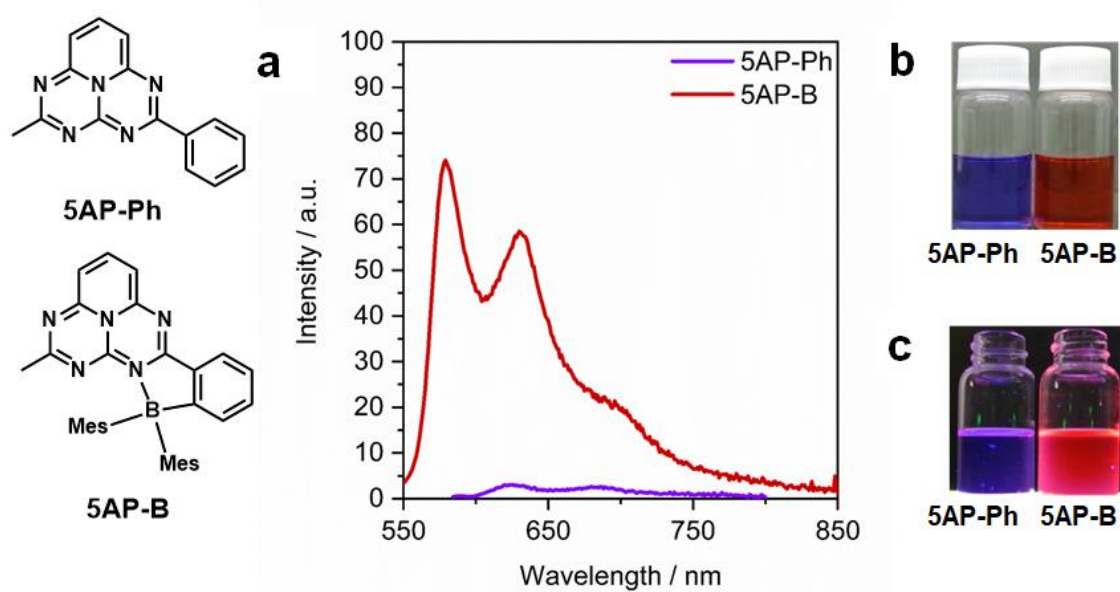
Figure 13. (a) UV−vis absorption and (b) emission spectra of A5AP derivatives. Reproduced from Ref. 10 with permission from The Royal Society of Chemistry.

Figure 14. (a) Emission spectra of 5AP-Ph and 5AP-B in chloroform (1.0×10^{-4} M). Pictures of the chloroform solutions of 5AP-Ph and 5AP-B (b) without and (c) with UV irradiation (365 nm). Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA.
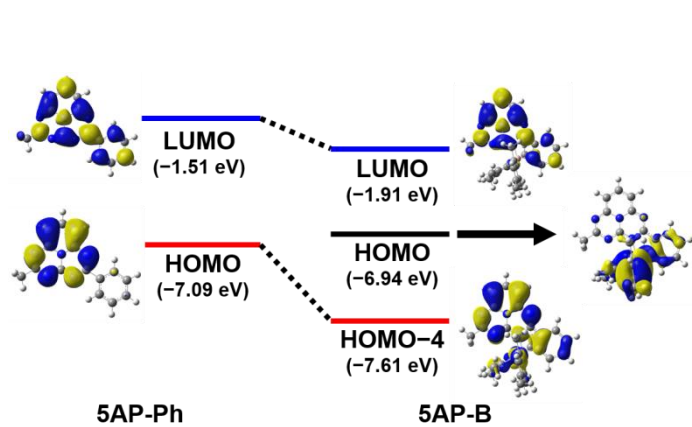
Figure 15. Schematic diagram representing the effect by the complexation of boron atom to 3-nitrogen atom. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA.
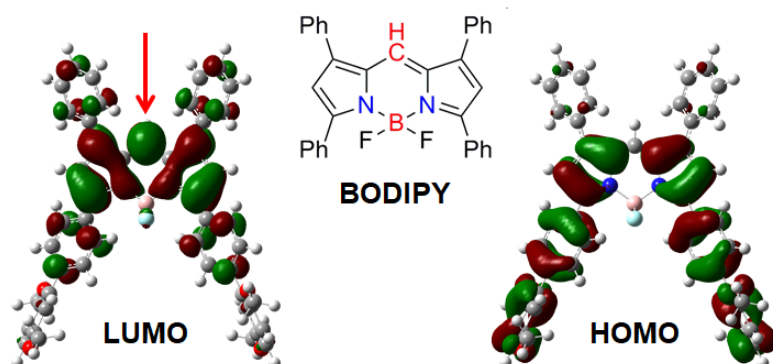
Figure 16. Lobes of FMOs of tetraphenyl BODIPY (red arrow: *meso* position). Adapted with permission from ref. 16. Copyright 2014 American Chemical Society.
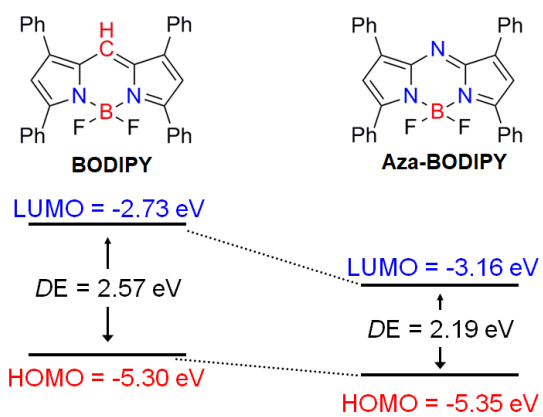
Figure 17. Estimated energy levels of BODIPYs before and after the aza-substitution.
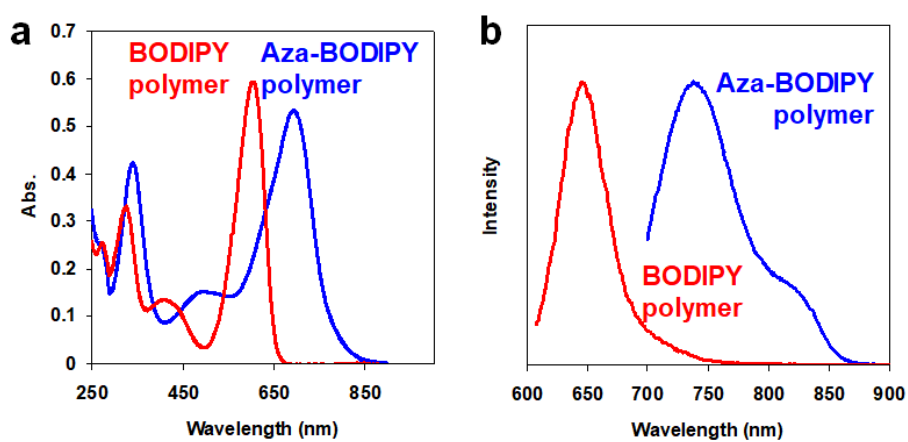
Figure 18. (a) UV–vis absorption and (b) emission spectra of BODIPY (red) and aza-BODIPY-containing polymers (blue). Adapted with permission from ref. 16. Copyright 2014 American Chemical Society.

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