

Internal and external pockets in pillar[*n*]arene sheets and their host-guest binding beyond cavity volume limitations

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ABSTRACT: Constructing binding pockets by hierarchically assembling tailored building blocks and understanding the structure–property relationships are challenging goals. Herein, amphiphilic pillar[5]arene and pillar[6]arene were prepared and used to construct 2D sheets, which consisted of well-defined hydrophobic and hydrophilic interlayers. In the hydrophobic interlayers, internal hydrophobic pockets were created by packing pairs of pillar[*n*]arenes, and external hydrophobic pockets were simultaneously generated from gaps between pillar[*n*]arenes due to electrostatic attractions. Aromatic hydrocarbons were accommodated in these hydrophobic pockets by ball-milling. Due to the external pockets, bulky guests larger than the pillar[*n*]arene cavity sizes were also captured in the sheets.

Introduction

Binding pockets are generated by the hierarchical assembly of primary building blocks in nature.^{1,2} For example, the primary structure of a polypeptide organizes into a helical secondary structure, which then assembles into a three-dimensional tertiary superstructure with binding pockets. These pockets contribute to the specific binding properties of the superstructure.³ In artificial systems, macrocycle is a promising primary structure for creating functional superstructures using their pre-organized intrinsic pockets (Figure 1A).^{4–7} Functions of both the intrinsic pockets (macrocyclic cavities) in the primary structures and internal pockets formed by discrete secondary structures have been studied extensively.⁸ However, the use of integrated external pockets, created by external surfaces of the molecules in tertiary superstructures is still in its early stages.^{9,10}

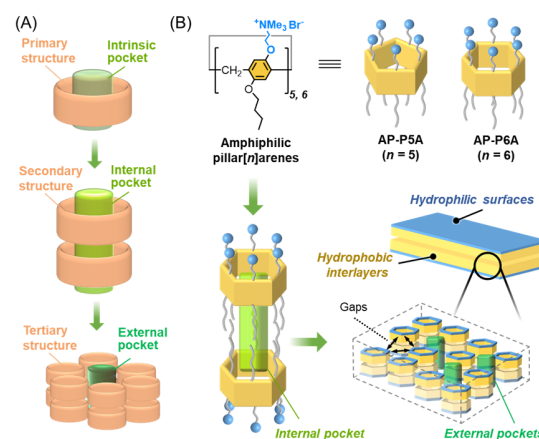


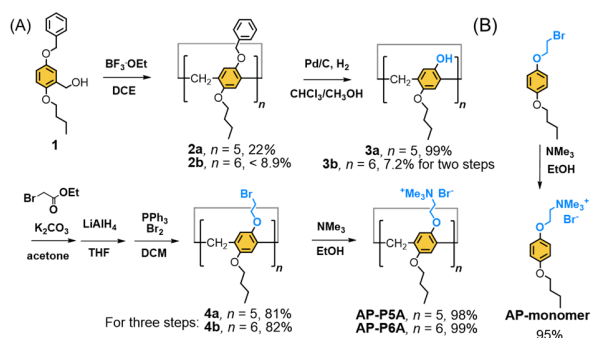
Figure 1. Schematics of macrocycles for functional superstructures. (A) Macrocycles and their hierarchical assemblies with internal and external pockets. (B) Structures of amphiphilic pillar[*n*]arenes and their arrangement into sheets with hydrophobic pockets.

Pillar[*n*]arenes (Figure 1B), which were first reported by our group in 2008, possess intrinsic electron-rich cavities with unique binding properties.¹¹ The symmetrical

polygonal shapes of pillar[*n*]arenes enable well-defined packing, providing internal pockets in the solid-state¹² that contribute to the wide use of these materials in storage,¹³ separation,¹⁴ and sensing.¹⁵ However, most studies have focused on the internal pockets formed by primary cavities or secondary capsular structures. The function in external pockets has rarely been investigated due to the challenges in their design.¹⁶ Rational design of external binding pockets can exploit the collective properties of the whole to surpass the sum of parts. For example, through collaborative packing of secondary structures, external pockets larger than the intrinsic cavity sizes can be formed to overcome the cavity volume limitations (Figure 1A, bottom). To achieve this goal, customizable superstructures could be constructed using functional pillar[*n*]arenes as building blocks, though this remains challenging.

In this study, amphiphilic pillar[5]arene (**AP-P5A**) and pillar[6]arene (**AP-P6A**) were used as building blocks (Figure 1B). Pairs of pillar[*n*]arenes formed supramolecular capsules, creating secondary structures with internal pockets.¹⁷ Through packing of the capsules,¹⁸ tertiary 2D sheets were then constructed. The sheets comprised hydrophilic surfaces and hydrophobic interlayers, resembling the elementary structures of cell membranes.¹⁹ Interestingly, due to the electrostatic attractions between capsules, pillar[*n*]arenes packed loosely and yielded voids as external pockets²⁰ in the hydrophobic interlayers. Hydrocarbon guests were accommodated in these internal and external pockets by ball-milling. The sizes of capturing guests have been previously limited by the intrinsic cavity volumes of the host molecules, because guests have to fit the cavities of the primary hosts in complexation.²¹ In this work, bulky guests that exceeded the intrinsic cavity sizes were captured in the external pockets. This process overcame the cavity volume limitation in host–guest binding via collective interactions within the tertiary structures.

Result and discussion



Scheme 1. Synthetic Routes for Amphiphilic Pillar[*n*]arenes and the Amphiphilic Monomer. (A) AP-P5A and AP-P6A. (B) AP-monomer.

Synthesis. To prepare supramolecular capsules from amphiphilic pillar[*n*]arenes, hydrophilic and hydrophobic groups must be installed separately on the upper and lower rims of the macrocycles. The synthesis of them is challenging because constitutional isomers are always generated during the cyclization, requiring arduous purification process.^{22a} Therefore, only few such pillar[5]arenes have been reported,²² and the corresponding pillar[6]arenes remain elusive. Through a

pre-orientation strategy,²³ both rim-differentiated pillar[5]arene **2a** and pillar[6]arene **2b** were obtained by using 2,5-dialkoxybenzyl alcohol **1** as a precursor (Scheme 1A). After careful column chromatography, **2a** was purified in 22% yield and was conveniently converted to **3a** by hydrogenating the benzyl groups. However, because **2b** and by-products, which contains the constitutional isomers, showed similar R_f values on TLC and the same chemical composition, **2b** could not be fully purified after chromatography and recrystallization, and product was isolated in 8.9% yield as an inseparable isomeric mixture (Scheme S3). The mixture containing **2b** was then hydrogenated to yield **3b**, which was purified easily by chromatography, in 7.2% yield over two steps. Compared with the isomers with benzyl groups, the constitutional isomers with hydroxyl groups exhibited larger differences in R_f values, making purification easier. This hydroxyl effect also contributed to the easy purification of rim-differentiated pillar[*n*]arenes with hydroxyl and decyl groups, where their cyclic pentamer and hexamer precursors could only be partly purified by preparative GPC (Figure S1). This hydrogenation pathway may be a convenient method to obtain rim-differentiated pillar[6]arenes with greater structural diversity because of the easy purification and versatile hydroxyl groups. Compounds **3a** and **3b** were then esterified with ethyl 2-bromoacetate, reduced by LiAlH_4 , and brominated with PPh_3/Br_2 to yield **4a** and **4b**, respectively, in high yields. Each step was highly efficient; therefore, chromatography was only performed once at the last step. Nucleophilic substitution of the bromide group on **4a** and **4b** with trimethyl amine converted the bromide groups to ammonium cations, furnishing amphiphilic pillar[*n*]arenes **AP-P5A** and **AP-P6A**, respectively, in quantitative yields. An amphiphilic monomer, **AP-monomer** was also prepared as a control experiment (Scheme 1B).

Crystalline assemblies and binding pockets. Single crystals of amphiphilic pillar[*n*]arenes were prepared and the sheet arrangements were observed clearly on the molecular level. Single crystals of **AP-P5A** were obtained by slow evaporation of methanol/acetonitrile solutions and single crystals of **AP-P6A** were obtained by slow evaporation of acetone into a methanol/water solution. The single crystals were colorless thin blocks (Figures S2, S7). In the crystal structure of **AP-P5A**, the rim-differentiated pillar[5]arene with a pentagonal cavity was clearly visible as the primary structure, and five bromide anions were located on the cationic side (Figure 2A). The secondary structures were molecular capsules formed by pairs of pillar[5]arenes, providing deep hydrophobic cavities as internal pockets (yellow green regions).²³ Similar structures were observed for **AP-P6A** (Figure 2B). Because of the labile conformation of the pillar[6]arene, the molecule adopted a torsional conformation rather than forming a symmetrical hexagonal cavity. As tertiary structures, sheets were assembled from the capsular secondary structures, and hydrophilic and hydrophobic interlayers were observed (Figures 2C, 2D). As indicated by the crystal structure of **AP-P5A**, the hydrophilic interlayers were supported by electrostatic attractions between bromides and ammoniums²⁵, and the hydrophobic

interlayers were supported by CH- π interactions between alkyl chains and benzenes (SI, Section 3.2).

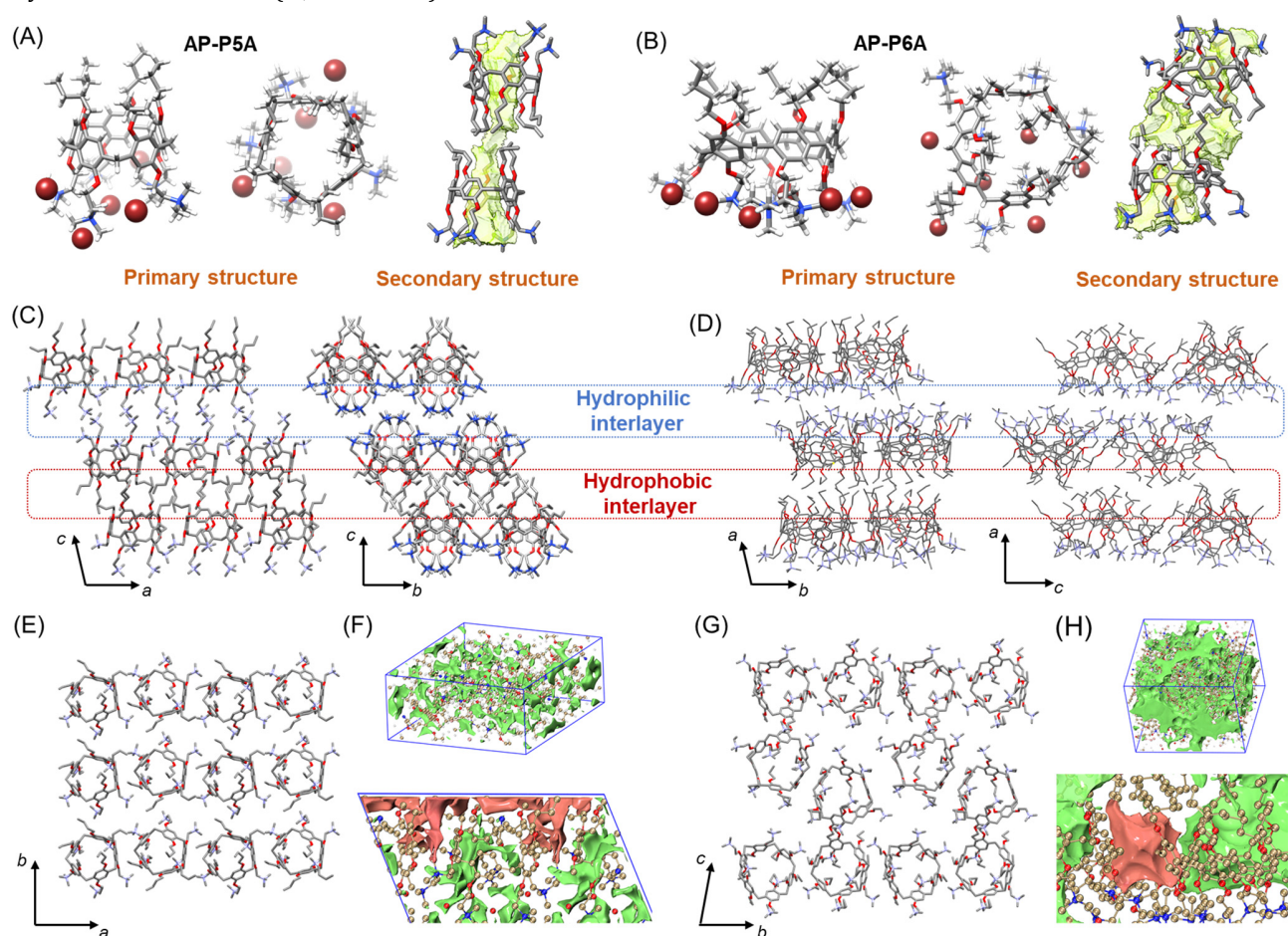


Figure 2. Crystal structures of the pillar[n]arenes. Primary structures of the macrocycles and secondary structures with internal hydrophobic pockets (yellow green regions) formed by pairs of pillar[n]arenes in (A) **AP-P5A** and (B) **AP-P6A**. Assembly within the hydrophobic and hydrophilic interlayers in (C) **AP-P5A** and (D) **AP-P6A**. (E) Top view of pentagonal packing of **AP-P5A** on a 2D plane. (F) External pockets of **AP-P5A** in a single cell visualized from calculated voids (green clouds, isovalue = 0.85) (top). And selected hydrophobic pockets (red clouds) that are surrounded by external walls and alkyl chains of **AP-P5A** (bottom). Solvent molecules were not squeezed. (G) Top view of hexagonal packing of **AP-P6A** on a 2D plane. (H) External pockets of **AP-P6A** in a single cell visualized from calculated voids (green clouds, isovalue = 0.85) (top). And selected hydrophobic pockets (red clouds) that are surrounded by external walls and alkyl chains of **AP-P6A** (bottom). Solvent molecules were not squeezed.

On 2D planes, there was no dense polygonal packing but there were unexpected loose packing patterns with voids (Figures 2E, 2G). Electrostatic attractions between the ammonium cations and bromides on one side of pillar[n]arenes rotated the repeating units with increasing torsion angles (SI, section 3.3). Therefore, the symmetrical pillar-shaped conformation was broken, resulting in loose packing. **AP-P6A** exhibited looser packing than **AP-P5A** because of the more labile conformation of **AP-P6A**. The voids in the macrocyclic packing regulated the external pockets in the tertiary structures, which were surrounded by the exo-walls and substituents of the pillar[n]arenes. To visualize the external pockets, the void spaces in single cells were simulated.²⁶ For **AP-P5A**, 34% of the volume was unoccupied and 814 Å³ was averaged for each macrocycle (Figure 2F), whereas for **AP-P6A**, 45% of the volume was unoccupied and 1536 Å³ was averaged for each macrocycle (Figure 2H).

Sheets in powder and aqueous states. Scanning electron microscopy (SEM) confirmed that the sheet structures remained in powder form, and lamellae were observed in the micrographs (Figures 3A, S17, S18). Furthermore, the experimental powder X-ray diffraction (PXRD) patterns of the powder samples closely matched the simulated patterns from the single crystals, indicating a similar microscopic arrangement (Figures S11). Peaks from the (001), (002) layers, and (100), (200) layers were observed for **AP-P5A** and **AP-P6A**, respectively (Figure 3B).²⁷ The interlayer spacing (12.8 Å for **AP-P5A** and 14.5 Å for **AP-P6A**) matched that observed in molecular modeling for one repeating unit (14.8 Å), implying that the (001) and (100) layers were supported by capsular secondary structures. The spacing in **AP-P5A** was shorter than that in **AP-P6A** because of the interweaving of alkyl chains observed in the **AP-P5A** crystal structures (Figure 2C). Increasing the length of the alkyl chains from butyl to decyl

resulted in longer interlayer spacing, corroborating the layered assembly in the solid state (See section 8 in SI for details about decyl pillar[*n*]arenes). In contrast, the experimental PXRD pattern of the **AP-monomer** did not match the simulation for the single crystal (Figure S13), highlighting the importance of polygonal shapes in retaining the sheet assemblies.

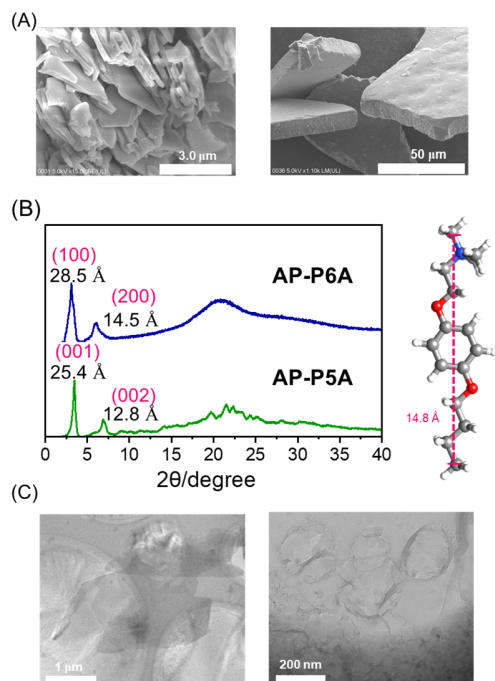


Figure 3. Observations of pillar[*n*]arene sheets. (A) SEM images of **AP-P5A** (left) and **AP-P6A** (right) powder samples. (B) PXRD patterns of **AP-P5A** and **AP-P6A**, and length of the monomer in pillar[*n*]arenes. (C) Cryogenic TEM images of **AP-P5A** (left) and **AP-P6A** (right) in water (10 mM).

After dispersing the solids in water, homogeneous dispersions were obtained and showed Tyndall effect, indicating the assembly in water (Figure S19). To figure out the assembly morphologies, cryogenic transmission electron microscopy (TEM) (Figure 3C) and negatively stained TEM (Figures S14, S15) were measured, which revealed that pillar[*n*]arenes retained their 2D sheet superstructures in water. **AP-P6A** showed blurrier sheet edges than **AP-P5A** (Figure 3C), probably due to the looser packing of **AP-P6A** observed in the crystal structure in Figure 2G. Atomic force microscopy (AFM) images showed sheets with thickness around 3 nm, consistent with the heights of capsular secondary structures (Figure S16). These results indicated that after dispersing in water, the lamella sheets were exfoliated with water via hydration in the hydrophilic interlayers. The aqueous assemblies were also characterized by UV/vis, ¹H NMR, and dynamic light scattering analysis, implying dynamic sheet assemblies with low critical aggregation concentrations (SI, Section 5).

Host-guest properties of the binding pockets. The internal and external pockets in the tertiary structures, which were confirmed by the crystal structures (Figure 2), were expected to accommodate guest molecules with suitable sizes. Therefore, the binding properties of **AP-P5A**

and **AP-P6A** sheets were investigated by using aromatic hydrocarbons, which exhibit unique chemical and physical properties due to their delocalized π -electrons.²⁸ Linear guests, such as 1,4-bis(phenylethynyl)benzene (BPEB), *p*-terphenyl (TP), and anthracene, as well as bulky guests, such as perylene, pyrene, and coronene, which are hardly dissolved in water, were investigated (Figure S31). The hydrophobicity and conjugated π -electrons of the guests can facilitate encapsulation in the hydrophobic pockets through multiple CH- π and π - π interactions. Solubilization is often achieved by heating or sonicating a mixture of an insoluble hydrocarbon and an aqueous surfactant dispersion.²⁹ However, these methods did not work with an aqueous dispersion of **AP-P5A** or **AP-P6A** sheets. The UV/vis spectra (Figure S32) showed that only BPEB was slightly dissolved and the other guests remained insoluble. From a previous report,³⁰ although interaction between BPEB and pillar[5]arene was inhibited by solvation (Figure S33), BPEB can be captured by the pillar[5]arene cavity in neat systems due to the matching sizes (BPEB: 4.2 Å; pillar[5]arene: 4.7 Å) (Figure 4A, top). The inefficiency in solubilization may arise from the rigid macrocyclic packing and hydrophilic surfaces of sheets in water, which prevent the guests from entering the hydrophobic pockets.

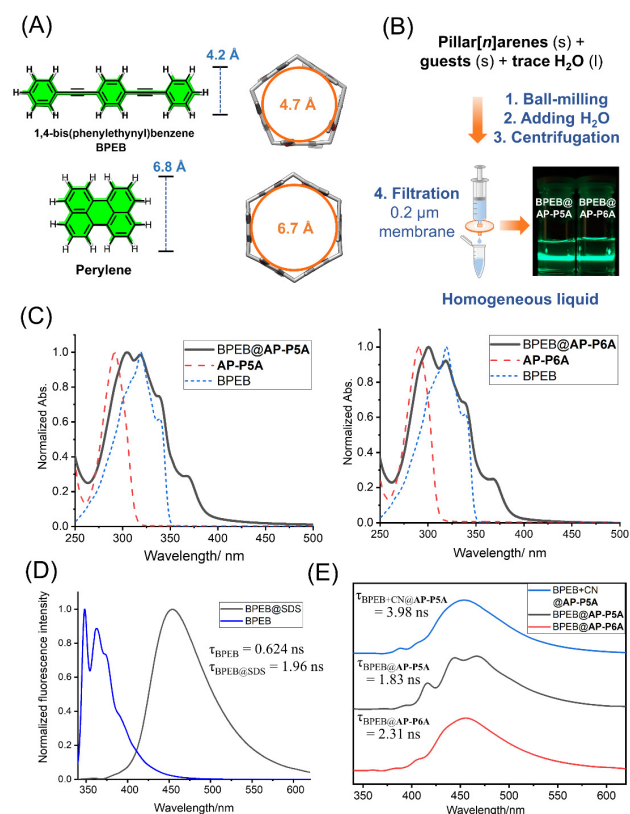


Figure 4. Binding properties of the pillar[*n*]arene sheets through ball-milling. (A) Left: widths of representative guests, linear BPEB and bulky perylene; right: sizes of pillar[*n*]arene cavities. (B) Schematic of the water-solubilization of aromatic hydrocarbons by ball-milling and Tyndall effect of the obtained dispersion. (C) Left: normalized UV/vis spectra of BPEB@**AP-P5A** (H₂O), **AP-P5A** (H₂O), and BPEB (CHCl₃); right: normalized UV/vis spectra of BPEB@**AP-P6A** (H₂O), **AP-P6A** (H₂O), and BPEB (CHCl₃). (D) Normalized fluorescence spectra

($\lambda_{\text{ex}} = 319$ nm) of BPEB (CHCl_3) and BPEB@SDS (H_2O). Fluorescence lifetimes of BPEB and BPEB@SDS were monitored at 340 nm and 450 nm, respectively. (E) Fluorescence spectra ($\lambda_{\text{ex}} = 319$ nm) of BPEB@**AP-P5A**, BPEB@**AP-P6A**, and (BPEB+CN)@**AP-P5A** in water. Fluorescence lifetimes were monitored at 450 nm.

To overcome these barriers and accommodate the guest species in the hydrophobic pockets, the sheets were mechanically crushed by ball-milling.³¹ Amphiphilic pillar[*n*]arene sheets and equal mass amount (around 7 eq.) of BPEB were mixed, and a trace amount of water was added for liquid-assisted grinding (Figure S51).³² After ball-milling, water was added to dissolve the products and the insoluble part (excess guest) was filtered off after centrifugation (Figure 4B). **AP-P5A** and **AP-P6A** both gave homogeneous aqueous dispersions that showed Tyndall effect, indicating the retaining the sheet assemblies. Combined UV/vis spectra of the pillar[*n*]arenes and BPEB were observed (Figure 4C, black lines), implying the efficient encapsulation of BPEB in the hydrophobic pockets by ball-milling. Using the same protocol, BPEB was treated with monomer **AP-monomer** of the macrocycle or commercial surfactants (such as sodium dodecyl sulfate, SDS), but the treatments resulted in either no solubilization or poorer solubilization, respectively (Figure S52). This highlights the importance of using macrocycles to dissolve BPEB with their pre-organized hydrophobic pockets. New peaks around 370 nm in UV/vis spectra came from the co-facial aggregation of BPEB,³³ indicating the stacking of BPEB in pockets. The cavity size of pillar[*n*]arenes is not sufficient for BPEB stacking; therefore, the binding of stacked BPEB in external pockets could occur.

Fluorophores can be used as probe to detect the stacking mode and chemical environments of themselves; therefore, fluorescence spectra were then measured to depict the binding mode. BPEB in chloroform showed a monomer emission at 350–370 nm (Figure 4D, blue line). When SDS was used as surfactant to dissolve BPEB in water, BPEB was sealed and stacked in the formed micelles, exhibiting broad and structureless excimer emission with longer lifetime (Figure 4D, black line). After the accommodation of BPEB in pillar[*n*]arene sheets, red-shifted and broadened bands at 400–600 nm were observed in fluorescence spectra, which can be assigned to excimer emissions due to the stacking guests (Figure 4E, red and gray lines). Moreover, fine structures from 350 nm to 475 nm were detected, probably due to the monomer emission from the individual guests in the internal pockets.³⁴ Compared with **AP-P6A**, more distinct fine peaks were detected with **AP-P5A**. This is attributed to the better size-matching between BPEB and **AP-P5A** cavity, leading to more BPEB guests being accommodated in the internal pockets of the **AP-P5A** sheets. Succinonitrile (CN), which binds strongly to pillar[5]arenes ($>10^4 \text{ M}^{-1}$)^{35a} was then used as a competitive guest during ball-milling to occupy the internal pockets. As a result, guests in the internal pockets were displaced, leading to a significant decrease in the fine peaks, while the broad excimer emission from guests in the external pockets remained (Figure 4E, blue line). From these results, the proposed binding mode with linear guests was illustrated in Figure 5A. Linear guests can go into both the internal and

external pockets in the sheets, and stack in the external pockets.

Stoichiometry during binding was then investigated by using ^1H NMR spectra. The host–guest complexes in D_2O showed no ^1H NMR signals from guests because their molecular motion in the pockets was restricted, resulting in greatly broadened signals (Figure S34).^{21b} After evaporating water, the obtained solid composites were dissolved in $\text{DMSO-}d_6$ to disassemble the sheet complexes, and signals from the hosts and guests were both detected in ^1H NMR spectra. Based on their integral values (SI, Section 6.1, Figures S35, S36), the stoichiometric ratios of BPEB to host were calculated as 1.0:1.0 for **AP-P5A**, and 0.94:1.0 for **AP-P6A** (Figure 5B). Competitive guest CN binds strongly to pillar[5]arenes in their intrinsic cavities but negligibly to pillar[6]arenes ($<2.0 \text{ M}^{-1}$).^{35b} Thus, they can occupy the internal pockets in the sheets. Because of the different binding affinity, the guest-to-host (G/H) ratio for **AP-P5A** decreased to 0.65, whereas the ratio only decreased to 0.80 for **AP-P6A** after adding CN during ball-milling.

Other linear guests, such as 1,2-bis(4-(phenylethynyl)phenyl)ethyne (BPEPE) and TP, also showed excimer emission in water after ball-milling (Figures S56, S57), confirming the binding in both internal and external pockets. The matching sizes of the **AP-P5A** internal pockets and the linear guests resulted in higher G/H ratios than for **AP-P6A** (Figures 5B, S50). However, the strategy did not work with 1,2-diphenylethyne (DPE). No obvious changes in UV/vis spectra were detected and the fluorescence came solely from the pillar[*n*]arenes (Figure S58). The guest was too short to make sufficient contact with CH- π binding sites in the capsular secondary structures, leading to inefficient binding and G/H ratio of zero. Similar length-sorting was also observed when using acenes as guests (Figures S59–S61).

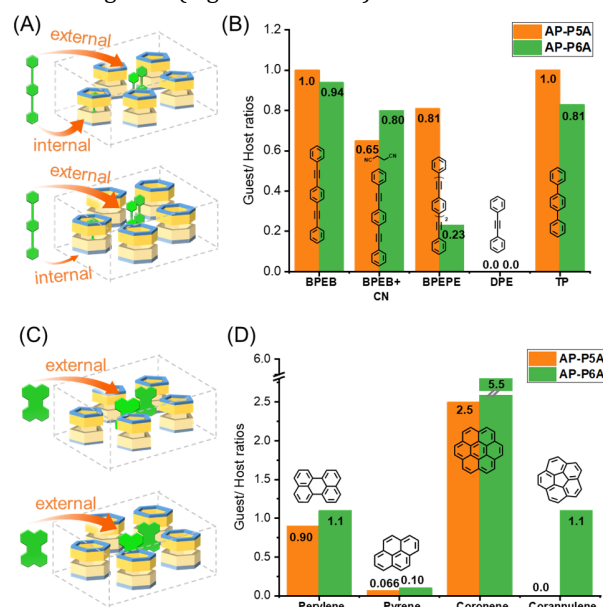


Figure 5. Interaction modes and stoichiometry in binding between pillar[*n*]arenes and guests. (A) Schematic of the capture of linear guests by both internal and external pockets. (B) Histogram of G/H ratios of different linear guests. (C)

Schematic of the capture of bulky guests by external pockets. (D) Histogram of G/H ratios of different bulky guests.

Bulky guest molecule perylene was then tested with the ball-milling method. The molecule was too large (6.8 Å wide) even for the pillar[6]arene cavity (6.7 Å); consequently, perylene could not enter the internal pockets (Figure 4A, bottom). Nevertheless, perylene became solubilized in water after ball-milling, as its characteristic absorption were clearly observed in the UV/vis spectra (Figure S62). Despite the size mismatch with internal pockets, perylene was accommodated in the external pockets. Meanwhile, excimer emission was observed in the fluorescent spectra,³⁶ indicating that perylene stacked in the pockets. The proposed binding mode was illustrated in Figure 5C. The G/H ratio of perylene was calculated as 0.90 for **AP-P5A** and 1.0 for **AP-P6A** (Figure 5D, S43, S44). Other bulky guests, such as pyrene and coronene, were also accommodated in external pockets and showed excimer emission (Figures S63, S64). The curved aromatic hydrocarbons, corannulene, was captured in **AP-P6A** but produced an insoluble solid with **AP-P5A** (Figure S65). In contrast to the accommodation of linear guests involving both internal and external pockets, looser packing and larger external pockets in **AP-P6A** allowed more efficient accommodation of bulky guests, resulting in higher G/H ratios.

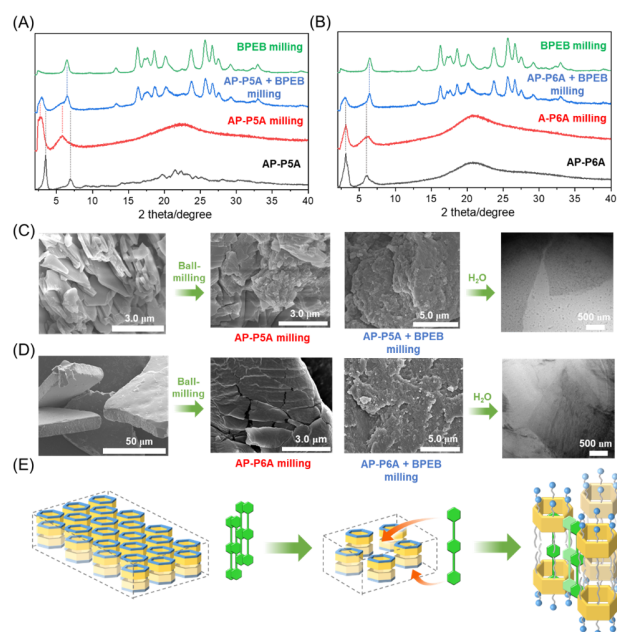


Figure 6. Analysis of the interaction pathway during ball-milling. (A) PXRD patterns of pristine **AP-P5A** and of **AP-P5A**, **AP-P5A** + BPEB, and BPEB after ball-milling. (B) PXRD patterns of pristine **AP-P6A** and of **AP-P6A**, **AP-P6A** + BPEB, and BPEB after ball-milling. (C) SEM images of pristine **AP-P5A** (left), and **AP-P5A** and **AP-P5A** + BPEB after ball-milling (middle), and cryogenic TEM images of **AP-P5A** + BPEB after dispersing in water and filtration (right). (D) SEM images of pristine **AP-P6A** (left), **AP-P6A** and **AP-P6A** + BPEB after ball-milling (middle), and cryogenic TEM images of **AP-P6A** + BPEB after dispersing in water and filtration (right). (E) Proposed accommodation process during ball-milling.

To clarify the interaction pathway during ball-milling, DLS, PXRD analysis, SEM and cryogenic TEM were conducted (Figures S66–S76). After ball-milling pillar[*n*]arenes, their PXRD patterns were broader, indicating a decrease in crystallinity caused by ball-milling breaking crystals (Figures 6A, 6B).³¹ Characteristic diffractions from the (001) and (002) planes in **AP-P5A** shifted to lower angles, implying an increase in interlayer spacing. The spacing for the new (002) plane was calculated as 15.3 Å, matching the length in the repeating unit (Figure 3B). Therefore, the interwoven alkyl chains in **AP-P5A** were parted by mechanical forces. In contrast, the layers in **AP-P6A** were already well-separated; thus, there was no obvious peak shift. Crushed sheets by ball-milling were implied by the decreased sizes in DLS (Figure S66) and clearly observed in SEM images (Figures 6C, 6D, middle). The crushed sheet species and well-separated alkyl chains enabled easy accommodation of guest molecules. After milling pillar[*n*]arenes with BPEB, the PXRD patterns contained both pillar[*n*]arene and BPEB peaks (Figures 6A, 6B). The spacing of (001) and (002) in **AP-P5A** decreased, most likely to fit the length of BPEB in the internal pockets. SEM images showed the mixed morphology of pillar[*n*]arene sheets and BPEB granules (Figures 6C, 6D, middle), demonstrating the proximity of the host and guest. After dispersing the milled mixtures in H₂O, sheets were still observed in the aqueous dispersion of the complex according to SEM (Figures S71, S72). To avoid possible rearrangement during the SEM sample preparation, cryogenic TEM was then measured, which enabled the study of assemblies in their near-native states.³⁷ After scrutinizing the cryogenic TEM images (Figures 6C, 6D (right), S75 and S76), only sheet assemblies were observed, indicating that the sheets retained their morphologies when forming the complexes with guest molecules in aqueous dispersion.³⁸ A proposed pathway is shown in Figure 6E. The mechanical force crushed the dense assemblies of the materials, producing an intimate mixture that allowed the guest molecules to enter the internal and external pockets in the sheets.

Conclusion

Amphiphilic pillar[*n*]arenes were prepared by installing separate hydrophilic ammonium cations and hydrophobic alkyl chains on two rims in pillar[5]arene and pillar[6]arene. Pairs of these primary building blocks formed capsular secondary structures, which stacked into tertiary sheet structures. The hydrophobic chains resulted in microphase separation, producing sheets with hydrophilic and hydrophobic interlayers. Internal and external hydrophobic pockets were observed in the hydrophobic interlayers. The internal pockets were generated inside the capsules from secondary structures. The external pockets were constructed as the voids between the exo-walls of the capsules, resulting from the conformation change of pillar[*n*]arenes via electrostatic attractions. The larger cavity size and more labile conformation of the pillar[6]arene resulted in larger pocket volumes than the pillar[5]arene.

The hydrophobic pockets accommodated aromatic hydrocarbons and facilitated their aqueous solubility. The binding limitations resulting from the pillar[*n*]arene cavity

sizes were overcome because bulky guests larger than the cavity sizes were accommodated in the external pockets. Higher guest uptake ratios for linear guests were obtained with the pillar[5]arene because its internal pocket size matched the size of the guests, whereas higher guest uptake ratios for bulky guests were obtained with the pillar[6]arene because of its larger external pockets. Previous studies on macrocycles have primarily focused on the host–guest behaviors in their intrinsic cavities.¹⁰ This work expands the functional volumes of macrocycles by binding within external pockets in the tertiary structures, furthering our understanding of the structure–property relationship. The competitive or synergistic effects between the internal and external pockets in binding fluorophores will be investigated in future to mediate luminescence by environment change. In addition, electrostatic interaction between macrocycles is a practical way to construct external pockets. And by further molecular structure design to control the interaction, external pockets with tailored binding abilities are expected to be achieved.

ASSOCIATED CONTENT

Instrumentation, experimental procedures, additional data, and further discussions (PDF).

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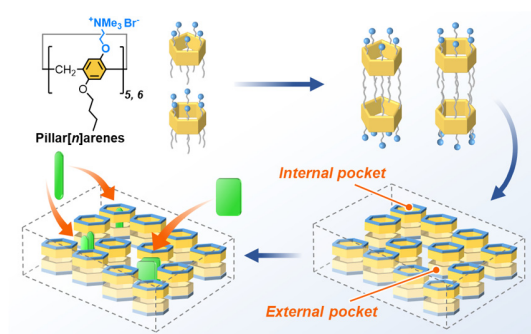
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[38] The dispersions of complexes were concentrated for cryo-TEM measurements. This concentration process can lead to aggregation and be the main reason of the largely increased sizes in cryo-TEM, compared with the sizes of sheets without guests in Figure 3C.

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Internal and external pockets in pillar[*n*]arene sheets and their host–guest binding beyond cavity volume limitations

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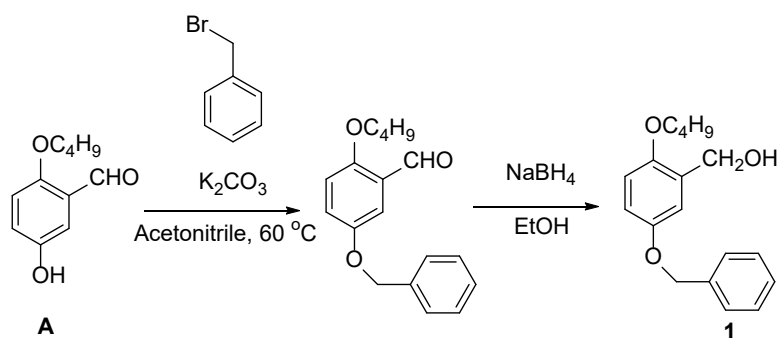
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1. General Information

All commercially available reagents and solvents were used as received. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JNM-ECS400, JNM-ECZ500R and JNM-ECA600P spectrometers at room temperature. Chemical shifts were reported in ppm versus tetramethylsilane or deuterium solvents. UV-vis absorption spectra were recorded on JASCO V-750 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-8550 fluorescence spectrometer. 10 mm quartz cuvettes were used for both UV-vis and fluorescence measurements. Fluorescence lifetime decay profiles were recorded with Hamamatsu Photonics QuantaTaurus-Tau C16361. High resolution ESI-MS was recorded on Exactive Plus (Thermo Fisher Scientific). Recycling GPC were conducted on JAI LaboACE LC-5060 with and JAIGEL-2HR. Dynamic light scattering (DLS) measurement was performed at 30 °C using 633 nm laser on a ZetaSizer device, model Nano-ZS (Malvern. Panalytical Ltd.). Backward scattering (scattering angle: 173 °) was adopted for all samples to prevent multiple light scattering in highly turbid samples. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku Smart Lab high-resolution diffractometer. Scanning electron microscope (SEM) images were acquired with HITACHI SU8220 FE-SEM at accelerating voltages of 5.0 kV. TEM images were acquired with JEOL JEM-2200FS. A laboratory-built AFM with commercially-available controllers (ARC2, Asylum Research, Oxford Instruments, and Nanonis OC4.5, SPECS GmbH) was used for the AFM analyses.

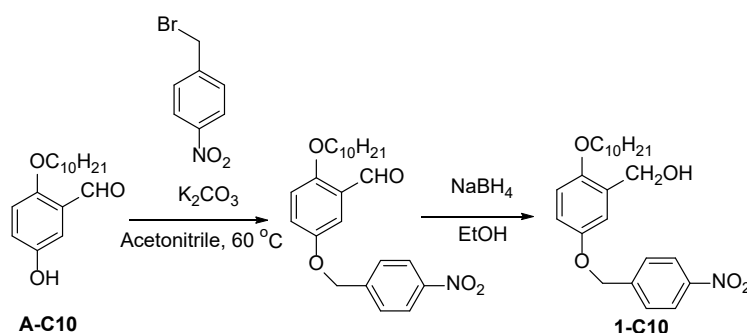
2. Synthetic procedures and characterization data



Scheme S1. Preparation of precursor 1

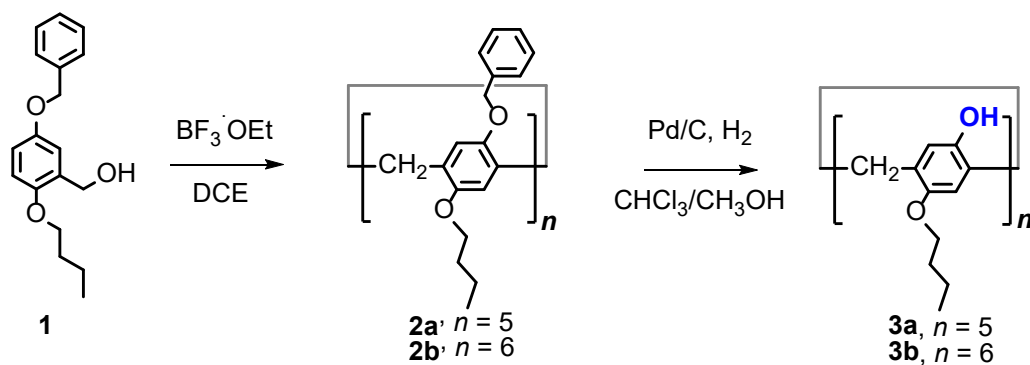
To a solution of A^[S1] (1.9 g, 10 mmol) and potassium carbonate (1.7 g, 12 mmol) in acetonitrile (50 mL) was added benzyl bromide (1.4 mL, 12 mmol). The reaction mixture was stirred at 60 °C for 12 h. The solid was filtered off, and the filtrate was concentrated under reduce pressure. The residue was suspended in ethanol (20 mL), and sodium borohydride (0.57 g, 15 mmol) was then added carefully. The mixture was stirred at room temperature for 1 h. Saturated NH_4Cl aqueous solution (50 mL) was added slowly to quench the reaction. The resulting mixture was extracted with

dichloromethane (3 × 50 mL). The organic phase was combined and washed with brine (50 mL), dried over anhydrous sodium sulfate. After filtration and removal of the solvent under vacuum, the residue was chromatographed with a silica gel column using dichloromethane as an eluent to give **1** (2.9 g, 99%) as colorless oil: ¹H-NMR (500 MHz, CDCl₃) δ 7.30-7.43 (m, 5H), 6.95 (d, *J* = 2.9 Hz, 1H), 6.84 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 5.02 (s, 2H), 4.66 (d, *J* = 6.5 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 1H), 1.75-1.80 (m, 2H), 1.46-1.53 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ¹³C-NMR (126 MHz, CDCl₃) δ 152.69, 151.28, 137.24, 130.26, 128.56, 127.89, 127.46, 115.84, 114.19, 112.06, 70.68, 68.25, 62.41, 31.45, 19.39, 13.86. HRMS (ESI) calcd. for [C₁₈H₂₂O₃+Na]⁺ [*M*+Na]⁺ *m/z* 309.1461; found *m/z* 309.1458.



Scheme S2. Preparation of precursor **1-C10**

To a solution of **A-C10**^[S2] (5.6 g, 20 mmol) and potassium carbonate (3.3 g, 24 mmol) in acetonitrile (100 mL) was added 1-(bromomethyl)-4-nitrobenzene (5.2 g, 24 mmol). The reaction mixture was stirred at 60 °C for 12 h. The solid was filtered off, and the filtrate was concentrated under reduce pressure. The residue was suspended in ethanol (50 mL), and sodium borohydride (1.1 g, 30 mmol) was then added carefully. The mixture was stirred at room temperature for 1 h. Saturated NH₄Cl aqueous solution (50 mL) was added slowly to quench the reaction. The resulting mixture was extracted with dichloromethane (3 × 50 mL). The organic phase was combined and washed with brine (50 mL), dried over anhydrous sodium sulfate. After filtration and removal of the solvent under vacuum, the residue was chromatographed with a silica gel column using dichloromethane as an eluent to give **1-C10** (7.9 g, 95%) as yellow solid: ¹H-NMR (500 MHz, CDCl₃) δ 8.24 (dt, *J* = 9.0, 2.1 Hz, 2H), 7.58-7.61 (m, 2H), 6.96 (dd, *J* = 2.7, 0.4 Hz, 1H), 6.78-6.83 (m, 2H), 5.13 (s, 2H), 4.67 (d, *J* = 6.5 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 2.37 (t, *J* = 6.6 Hz, 1H), 1.76-1.81 (m, 2H), 1.42-1.46 (m, 2H), 1.24-1.36 (m, 12H), 0.87-0.90 (m, 3H); ¹³C-NMR (126 MHz, CDCl₃) δ 151.97, 151.62, 144.82, 130.52, 127.56, 123.81, 115.69, 114.14, 112.06, 69.37, 68.57, 62.19, 31.89, 29.57, 29.55, 29.38, 29.35, 29.31, 26.16, 22.68, 14.12; HRMS (ESI) calcd. for [C₂₄H₃₃O₅N₁+Na]⁺ [*M*+Na]⁺ *m/z* 438.2251; found 438.2250.



Scheme S3. Preparation of rim-differentiated pillar[*n*]arenes with butyl groups

Macrocyclization:

To a stirred solution of **1** (1.1 g, 4.0 mmol) in 1,2-dichloroethane (500 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.10 mL, 0.80 mmol). The mixture was stirred at room temperature for 3 h. The solution was then washed by water (100 mL) and brine (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was chromatographed with a silica gel column using a mixture of *n*-hexane and dichloromethane (from *v*: *v* = 2 : 1 to *v*: *v* = 1 : 1) as an eluent (R_f values on silica gel with *n*-hexane/dichloromethane = 3/2: **2a**, 0.45; **2b**, 0.15.).

2a was obtained in 0.24 g (22%) as white solid: $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.17-7.24 (m, 25H), 6.86 (s, 5H), 6.85 (s, 5H), 4.44 (s, 10H), 3.90 (t, J = 5.8 Hz, 10H), 3.83 (s, 10H), 1.78-1.84 (m, 10H), 1.55-1.59 (m, 10H), 1.00 (t, J = 7.4 Hz, 15H); $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ 150.14, 149.45, 138.20, 128.34, 128.28, 128.21, 127.48, 127.16, 114.81, 69.44, 68.02, 32.22, 29.55, 19.72, 14.21. HRMS (ESI) calcd. for $[\text{C}_{90}\text{H}_{100}\text{O}_{10}+\text{Na}]^+$ $[\text{M}+\text{Na}]^+$ m/z 1363.7209; found 1363.7214.

2b (crude) was obtained in 0.095 g (< 8.9 %) as pale-yellow solid: crude $^1\text{H-NMR}$ (Figure S76). HRMS (ESI) calcd. for $[\text{C}_{108}\text{H}_{120}\text{O}_{12}+\text{Na}]^+$ $[\text{M}+\text{Na}]^+$ m/z 1631.8672; found 1631.8663.

Hydrogenation:

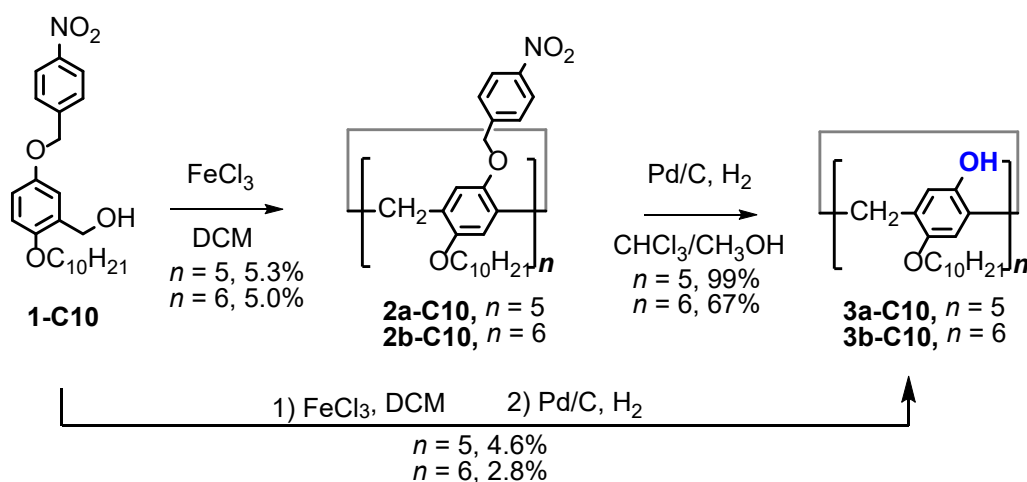
2a (0.15 g) was dissolved in chloroform/methanol (*v*: *v* = 1/1) and Pd/C (10% wt, 0.15 g) was added. The resulting mixture was stirred under H_2 atmosphere at 60 °C overnight. After filtering over Celite, the solvent was removed under vacuum. The residue was flash chromatographed with a silica gel column using a mixture of dichloromethane and methanol (*v*: *v* = 125 : 1) as an eluent to give **3a** (0.10g, 99%) as white solid.

3a: $^1\text{H-NMR}$ (600 MHz, $\text{DMSO-}d_6$) δ 8.49 (s, 5H), 6.79 (s, 5H), 6.65 (s, 5H), 3.81 (brs, 10H), 3.53 (s, 10H), 1.71-1.75 (m, 10H), 1.48-1.54 (m, 10H), 0.95 (t, J = 7.4 Hz, 15H); $^{13}\text{C-NMR}$ (151 MHz, $\text{DMSO-}d_6$) δ 148.01, 147.17, 127.75, 125.84, 117.52, 113.56, 67.19, 31.44, 28.61, 18.90, 13.76. HRMS (ESI) calcd. for $[\text{C}_{55}\text{H}_{70}\text{O}_{10}+\text{Na}]^+$ $[\text{M}+\text{Na}]^+$ m/z 913.4861; found 913.4857.

2b (crude, 0.10 g) was dissolved in chloroform/methanol (*v*: *v* = 1/1) and Pd/C (10% wt, 0.10 g) was added. The resulting mixture was stirred under H_2 atmosphere at 60 °C

overnight. After filtering over Celite, the solvent was removed under vacuum. The residue was chromatographed with a silica gel column using a mixture of dichloromethane and methanol (from v: v = 150: 1 to v: v = 100: 1) as an eluent to give **3b** 0.054 g as white solid. The yield for **3b** for two steps was 7.2%.

3b: $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.42 (s, 6H), 6.69 (s, 6H), 6.67 (s, 6H), 4.03 (t, J = 6.8 Hz, 12H), 3.65 (s, 12H), 1.84-1.90 (m, 12H), 1.51-1.58 (m, 12H), 1.03 (t, J = 7.4 Hz, 18H); $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ 148.78, 147.68, 127.47, 125.76, 118.04, 113.81, 69.51, 31.10, 30.98, 19.23, 13.92. HRMS (ESI) calcd. for $\text{C}_{66}\text{H}_{84}\text{O}_{12}\text{Cl}^-$ $[\text{M}+\text{Cl}]^-$ m/z 1103.5657; found 1103.5669.



Scheme S4. Preparation of rim-differentiated pillar[n]arenes with decyl groups.

Macrocyclization:

To a stirred solution of **1-C10** (0.33 g, 0.80 mmol) in dichloromethane (80 mL) was added FeCl_3 (0.013 g, 0.080 mmol). The mixture was stirred at room temperature for 3 h. The solution was then washed by water (50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was chromatographed with a silica gel column using a mixture of *n*-hexane and dichloromethane (v: v = 1 : 4) as an eluent to get a mixture of **2a-C10**, **2b-C10** and other constitutional isomers. (R_f values on silica gel with *n*-hexane/dichloromethane = 1/5: **2a-C10**, 0.23; **2b-C10**, 0.26.) The mixture was then purified by preparative GPC (Figure S1) to give **2a-C10** (0.017 g, 5.3%) and **2b-C10** (0.016 g, 5.0%) as yellow solid.

2a-C10: $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 8.14 (dt, J = 9.0, 2.0 Hz, 10H), 7.37 (d, J = 8.9 Hz, 10H), 6.88 (s, 5H), 6.76 (s, 5H), 4.62 (s, 10H), 3.88 (brs, 10H), 3.82 (s, 10H), 1.82 (brs, 10H), 1.50-1.55 (m, 10H), 1.34-1.40 (m, 10H), 1.26-1.31 (m, 10H), 1.11-1.22 (m, 40H), 0.83 (t, J = 7.2 Hz, 15H); $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ 150.78, 148.83, 147.42, 145.10, 128.81, 128.24, 127.31, 123.69, 115.23, 114.96, 69.38, 68.34, 31.88, 29.75, 29.57, 29.53, 29.31, 26.26, 22.65, 14.15. HRMS (ESI) calcd. for $[\text{C}_{144}\text{H}_{186}\text{N}_6\text{O}_{24}\text{Na}]^+$ $[\text{M}+\text{Na}]^+$ m/z 2406.341; found 2406.342.

2b-C10: $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.76 (brs, 12H), 6.97 (brs, 12H), 6.82 (s, 6H), 6.43 (brs, 6H), 4.42 (s, 12H), 3.84 (brs, 24H), 1.77 (t, J = 7.2 Hz, 12H), 1.44 (t, J = 7.4

Hz, 12H), 1.27-1.34 (m, 72H), 0.88 (t, $J = 7.0$ Hz, 18H); ^{13}C -NMR (126 MHz, CDCl_3) δ 151.08, 149.12, 147.10, 144.45, 128.06, 127.61, 127.51, 123.45, 115.56, 68.80, 31.93, 29.77, 29.73, 29.68, 29.63, 29.39, 26.34, 22.70, 14.12. HRMS (ESI) calcd. for $[\text{C}_{120}\text{H}_{155}\text{N}_5\text{O}_{20}\text{Na}]^+ [\text{M}+\text{Na}]^+ m/z$ 2009.116; found: 2009.113.

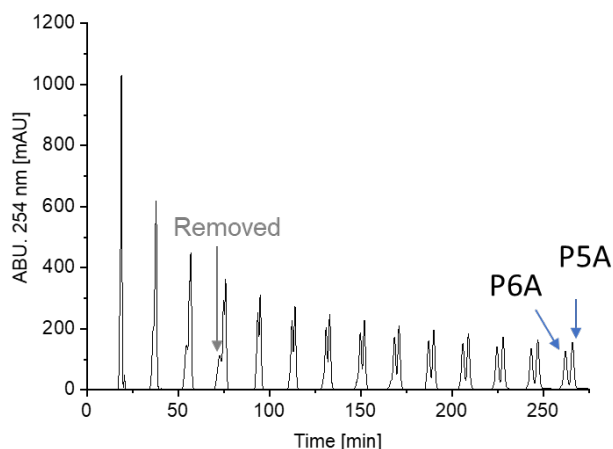


Figure S1. Purification of **2a-C10** and **2b-C10** via recycling GPC (solvent: chloroform; flow rate: 10 mL/min).

Hydrogenation:

2a-C10 (0.070 g) was dissolved in chloroform/methanol (v: v = 1/1) and Pd/C (10% wt, 0.070 g) was added. The resulting mixture was stirred under H_2 atmosphere at 60 °C overnight. After filtering over Celite, the solvent was removed under vacuum. The residue was chromatographed with a silica gel column using a mixture of dichloromethane and methanol (v: v = 400: 1) as an eluent to give **3a-C10** (0.045 g, 99%) as white solid.

3a-C10: ^1H -NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.36 (s, 5H), 6.70 (s, 5H), 6.54 (s, 5H), 3.82 (brs, 5H), 3.51 (brs, 5H), 3.44 (brs, 10H), 1.64 (brs, 10H), 1.37 (brs, 10H), 1.19 (brs, 60H), 0.77 (t, $J = 6.6$ Hz, 15H); ^{13}C -NMR (151 MHz, $\text{DMSO}-d_6$) δ 148.66, 147.64, 128.29, 126.40, 117.91, 113.77, 67.92, 32.05, 30.13, 29.91, 29.56, 26.44, 22.76, 14.18. HRMS (ESI) calcd. for $[\text{C}_{85}\text{H}_{130}\text{O}_{10}+\text{Na}]^+ [\text{M}+\text{Na}]^+ m/z$ 1333.9556; found 1333.9556.

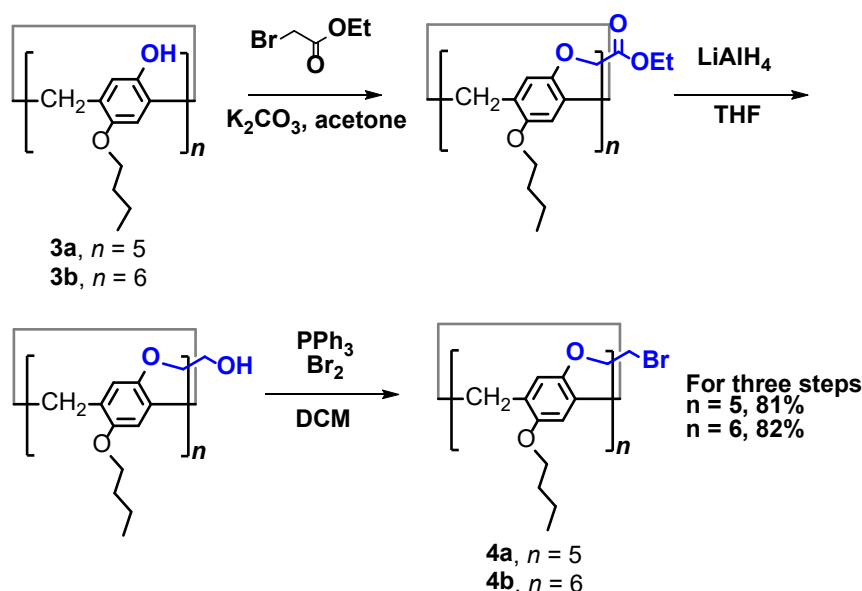
2b-C10 (0.050 g) was dissolved in chloroform/methanol (v: v = 1: 1) and Pd/C (10% wt, 0.050 g) was added. The resulting mixture was stirred under H_2 atmosphere at 60 °C overnight. After filtering over Celite, the solvent was removed under vacuum. The residue was chromatographed with a silica gel column using a mixture of dichloromethane and methanol (v: v = 200: 1) as an eluent to give **3b-C10** (0.022 g, 67%) as white solid.

3b-C10: ^1H -NMR (500 MHz, CDCl_3) δ 7.44 (s, 6H), 6.68 (s, 6H), 6.67 (s, 6H), 4.01 (t, $J = 6.9$ Hz, 12H), 3.64 (s, 12H), 1.85-1.91 (m, 12H), 1.47-1.52 (m, 12H), 1.29-1.41 (m, 72H), 0.89 (t, $J = 7.0$ Hz, 18H); ^{13}C -NMR (126 MHz, CDCl_3) δ 148.82, 147.64, 127.45, 125.74, 118.03, 113.82, 69.79, 31.93, 30.98, 29.56, 29.39, 29.33, 29.05, 25.96, 22.70, 14.15. HRMS (ESI) calcd. for $[\text{C}_{102}\text{H}_{156}\text{O}_{12}+\text{Na}]^+ m/z$ 1596.1489; found 1596.1480.

A combined process for two steps:

To a stirred solution of **1-C10** (0.33 g, 0.80 mmol) in dichloromethane (80 mL) was added FeCl_3 (0.013 g, 0.080 mmol). The mixture was stirred at room temperature for 3 h. The solution was then washed by water (50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was chromatographed with a silica gel column using a mixture of *n*-hexane and dichloromethane (v: v = 1: 4) as an eluent to get a mixture of **2a-C10**, **2b-C10** and other constitutional isomers in 0.072 g.

The mixture (0.15 g) was dissolved in chloroform/methanol (v: v = 1: 1) and Pd/C (10% wt, 0.15 g) was added. The resulting mixture was stirred under H_2 atmosphere at 60 °C overnight. After filtering over Celite, the solvent was removed under vacuum. The residue was chromatographed with a silica gel column using a mixture of dichloromethane and methanol (v: v = 500: 1 to v: v = 200: 1) as an eluent to give **3a-C10** (0.020 g, 4.6%) and **3b-C10** (0.012 g, 2.8%) as white solid. (R_f values on silica gel with dichloromethane/methanol = 100/1: **3a-C10**, 0.33; **3b-C10**, 0.17.)



Scheme S5. Preparation of pillar[*n*]arenes 4

Esterification:

For $n = 5$: to a solution of **3a** (0.071 g, 0.080 mmol) and potassium carbonate (0.17 g, 1.2 mmol) in acetone (3 mL) was added ethyl 2-bromoacetate (0.13 mL, 1.2 mmol). The reaction mixture was stirred at 60 °C for 12 h. Water (20 mL) was added to quench the reaction. The resulting mixture was extracted with dichloromethane (3×20 mL). The organic phase was combined and washed with brine (20 mL), dried over anhydrous sodium sulfate. The mixture was then filtered and dried under vacuum.

For $n = 6$: **3b** (0.086 g, 0.080 mmol), potassium carbonate (0.20 g, 1.44 mmol), ethyl 2-bromoacetate (0.16 mL, 1.44 mmol), and acetone (3 mL) were used. Other procedures were the same.

Reduction:

The residue was dissolved in 5 mL dry tetrahydrofuran, and LiAlH₄ (0.030 g, 0.80 mmol) was added in portion at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 4 h before quenched by 3M HCl aqueous solution (10 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The organic phase was combined and washed with brine (20 mL), dried over anhydrous sodium sulfate. The mixture was then filtered and dried under vacuum.

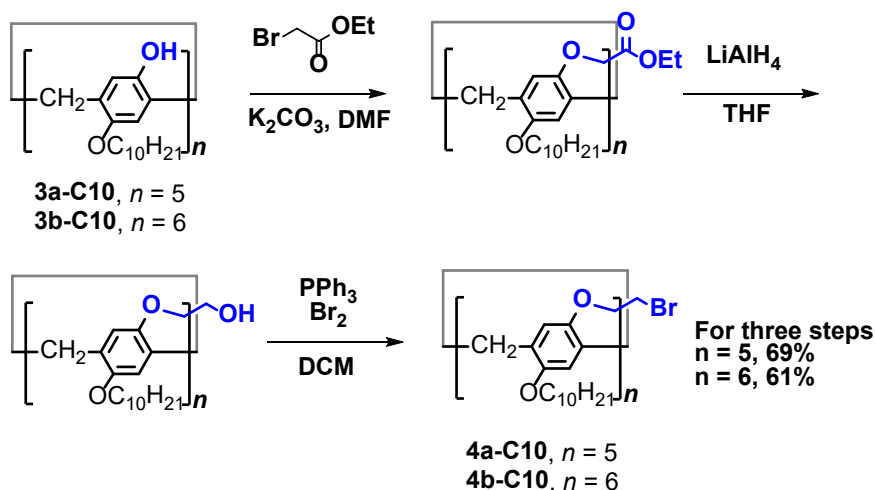
Bromination:

For *n* = 5: the residue and PPh₃ (0.26 g, 1.0 mmol) were dissolved in 10 mL dry dichloromethane, and Br₂ (0.052 mL, 1.0 mmol) was added slowly. The reaction mixture was stirred at room temperature overnight before quenched by saturated NaHCO₃ aqueous solution (10 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The organic phase was combined and washed with brine (20 mL), dried over anhydrous sodium sulfate. After filtration and removal of the solvent under vacuum, the residue was chromatographed with a silica gel column using a mixture of *n*-hexane and dichloromethane (v: v = 3: 1 to v: v = 2: 1) as an eluent to give **4a** (0.092 g, 81%) as white solid.

For *n* = 6, PPh₃ (0.31 g, 1.2 mmol) and Br₂ (0.062 mL, 1.2 mmol) were used. Other procedures were the same. The chromatographed with a silica gel column using a mixture of *n*-hexane and dichloromethane (v: v = 2: 1) as an eluent gave **4b** (0.11 g, 82%) as white solid.

4a: ¹H-NMR (500 MHz, CDCl₃) δ 6.90 (s, 5H), 6.80 (s, 5H), 4.17 (t, *J* = 5.8 Hz, 10H), 3.87 (t, *J* = 6.5 Hz, 10H), 3.80 (s, 10H), 3.58 (t, *J* = 5.8 Hz, 10H), 1.75-1.80 (m, 10H), 1.51-1.56 (m, 10H), 0.98 (t, *J* = 7.4 Hz, 15H); ¹³C-NMR (126 MHz, CDCl₃) δ 150.62, 148.94, 128.93, 128.41, 116.30, 114.74, 69.07, 68.01, 31.96, 30.76, 29.46, 19.52, 14.02. HRMS (ESI) calcd. for [C₆₅H₈₅O₁₀Br₅+Na]⁺ [M+Na]⁺ *m/z* 1443.1908; found *m/z* 1443.1952.

4b: ¹H-NMR (500 MHz, CDCl₃) δ 6.76 (s, 6H), 6.74 (s, 6H), 4.08 (t, *J* = 6.0 Hz, 12H), 3.82 (t, *J* = 6.6 Hz, 12H), 3.82 (s, 12H), 3.47 (t, *J* = 6.0 Hz, 12H), 1.71-1.77 (m, 12H), 1.46-1.52 (m, 12H), 0.95 (t, *J* = 7.4 Hz, 18H); ¹³C-NMR (126 MHz, CDCl₃) δ 151.13, 149.49, 128.29, 128.09, 115.86, 114.92, 69.06, 68.19, 31.87, 30.68, 30.29, 19.45, 13.97. HRMS (ESI) calcd. for C₇₈H₁₀₂O₁₂Br₆Na⁺ [M+Na]⁺ *m/z* 1727.2364; found 1727.2360.



Scheme S6. Preparation of pillar[n]arenes **4-C10**

Esterification:

For $n = 5$: to a solution of **3a-C10** (0.079 g, 0.060 mmol) and potassium carbonate (0.12 g, 0.90 mmol) in *N,N*-dimethylformamide (5 mL) was added ethyl 2-bromoacetate (0.10 mL, 0.90 mmol). The reaction mixture was stirred at 60 °C for 12 h. Water (20 mL) was added to quench the reaction. The resulting mixture was extracted with dichloromethane (3×20 mL). The organic phase was combined and washed with brine (20 mL), dried over anhydrous sodium sulfate. The mixture was then filtered and dried under vacuum.

For $n = 6$: **3b** (0.047 g, 0.030 mmol), potassium carbonate (0.075 g, 0.54 mmol), ethyl 2-bromoacetate (0.060 mL, 0.54 mmol), and *N,N*-dimethylformamide (3 mL) were used. Other procedures were the same.

Reduction:

For $n = 5$: the residue was dissolved in 5 mL dry tetrahydrofuran, and LiAlH_4 (0.023 g, 0.60 mmol) was added in portion at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 4 h before quenched by 3M HCl aqueous solution (5 mL). The resulting mixture was extracted with dichloromethane (3×20 mL). The organic phase was combined and washed with brine (20 mL), dried over anhydrous sodium sulfate. The mixture was then filtered and dried under vacuum.

For $n = 6$: LiAlH_4 (0.011 g, 0.30 mmol) was used, and the mixture of 2 mL dry tetrahydrofuran and 2 mL dry dichloromethane was used as solvent. Other procedures were the same.

Bromination:

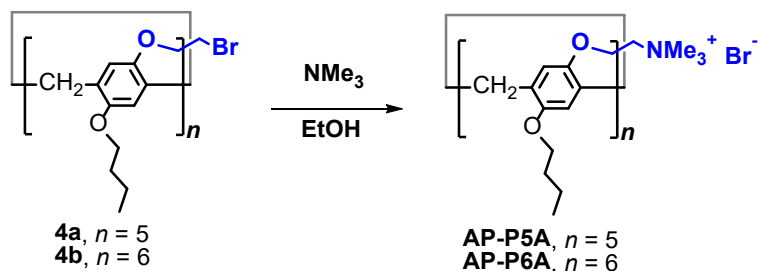
For $n = 5$: the residue and PPh_3 (0.24 g, 0.90 mmol) were dissolved in 10 mL dry dichloromethane, and Br_2 (0.046 mL, 0.90 mmol) was added slowly. The reaction mixture was stirred at room temperature overnight before quenched by saturated NaHCO_3 aqueous solution (10 mL). The resulting mixture was extracted with dichloromethane (3×20 mL). The organic phase was combined and washed with brine (20 mL), dried over anhydrous sodium sulfate. After filtration and removal of the

solvent under vacuum, the residue was chromatographed with a silica gel column using a mixture of *n*-hexane and dichloromethane (v: v = 2: 1) as an eluent to give **4a-C10** (0.076 g, 69%) as white solid.

For *n* = 6, PPh₃ (0.12 g, 0.45 mmol), Br₂ (0.023 mL, 0.45 mmol) were used. Other procedures are the same. The chromatographed with a silica gel column using a mixture of *n*-hexane and dichloromethane (v: v = 2: 3) as an eluent gave **4b-C10** (0.039 g, 61%) as white solid.

4a-C10: ¹H-NMR (400 MHz, CDCl₃) δ 6.92 (s, 5H), 6.81 (s, 5H), 4.18 (t, *J* = 5.8 Hz, 10H), 3.87 (t, *J* = 6.4 Hz, 10H), 3.79 (s, 10H), 3.60 (t, *J* = 5.8 Hz, 10H), 1.77-1.84 (m, 10H), 1.49-1.56 (m, 10H), 1.17-1.40 (m, 60H), 0.85 (t, *J* = 7.0 Hz, 15H); ¹³C-NMR (101 MHz, CDCl₃) δ 150.69, 149.04, 129.03, 128.49, 116.33, 114.73, 69.18, 68.40, 32.05, 30.93, 29.96, 29.77, 29.74, 29.50, 26.47, 22.82, 14.28. HRMS (ESI) calcd. for [C₉₅H₁₄₅O₁₀Br₅+Na]⁺ [M+Na]⁺ *m/z* 1863.6647; found 1863.6708.

4b-C10: ¹H-NMR (600 MHz, CDCl₃) δ 6.77 (s, 6H), 6.71 (s, 6H), 4.06 (t, *J* = 5.9 Hz, 12H), 3.83 (t, *J* = 7.0 Hz, 12H), 3.82 (s, 12H), 3.45 (t, *J* = 6.0 Hz, 12H), 1.75-1.80 (m, 12H), 1.45-1.50 (m, 12H), 1.28-1.37 (m, 72H), 0.89 (t, *J* = 7.0 Hz, 18H); ¹³C-NMR (151 MHz, CDCl₃) δ 151.09, 149.50, 128.13, 115.73, 114.95, 69.01, 68.57, 31.96, 30.72, 30.29, 29.88, 29.77, 29.73, 29.70, 29.42, 26.39, 22.71, 14.13. HRMS (ESI) calcd. for [C₁₁₄H₁₇₄O₁₂Br₆+Na]⁺ *m/z* 2231.7998; found 2231.7985.



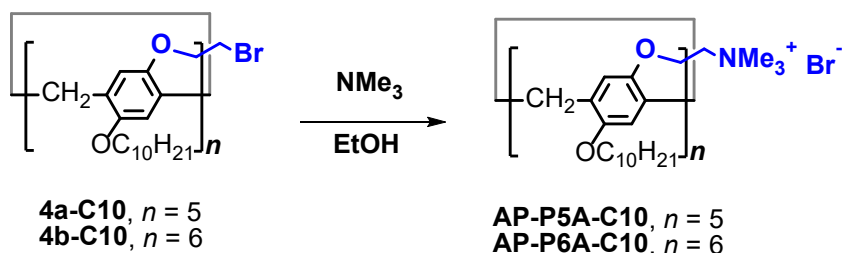
Scheme S7. Preparation of amphilic pillar[*n*]arenes **AP-P5A** and **AP-P6A**.

To a suspension of **4a** (0.071 g, 0.050 mmol) or **4b** (0.086 g, 0.050 mmol) in ethanol (12 mL) was added 3 mL trimethylamine (3 M in ethanol). The resulting mixture was refluxed to give a homogeneous solution. After 2 days, the solvent was removed under vacuum. The residue was washed with 2 mL ethyl acetate and dried to give **AP-P5A** (0.084 g, 98%) or **AP-P6A** (0.10 g, 99%) as white solid.

AP-P5A: ¹H-NMR (600 MHz, D₂O) δ 6.98 (s, 5H), 6.63 (s, 5H), 4.49 (brs, 10H), 3.90 (brs, 10H), 3.82 (brs, 10H), 3.50 (brs, 10H), 3.28 (brs, 45H), 1.30 (brs, 10H), 1.03 (brs, 10H), 0.61 (t, *J* = 6.8 Hz, 15H); ¹³C-NMR (151 MHz, D₂O) δ 151.93, 149.31, 130.16, 129.92, 117.00, 116.77, 69.64, 66.34, 64.19, 54.94, 31.62, 29.71, 19.32, 13.63; HRMS (ESI) calcd. for [C₈₀H₁₃₀O₁₀N₅Br₃]²⁺ [M-2Br]²⁺ *m/z* 778.8678; found 778.8685.

AP-P6A: ¹H-NMR (600 MHz, D₂O) δ 7.12 (s, 6H), 6.35 (s, 6H), 4.54 (s, 12H), 3.92 (brt, *J* = 4.5 Hz, 12H), 3.89 (brs, 12H), 3.40 (brt, *J* = 5.3 Hz, 12H), 3.32 (s, 54H), 1.20-1.23 (m, 12H), 0.96-0.91 (m, 12H), 0.56 (t, *J* = 7.3 Hz, 18H); ¹³C-NMR (126 MHz,

D₂O) δ 150.72, 148.64, 129.26, 127.70, 116.04, 114.23, 68.42, 65.63, 62.98, 54.12, 31.16, 28.84, 18.96, 13.42; HRMS (ESI) calcd. for $[\text{C}_{96}\text{H}_{156}\text{O}_{12}\text{N}_6\text{Br}_4]^{2+}$ $[\text{M}-2\text{Br}]^{2+}$ m/z 950.4252; found 950.4243.

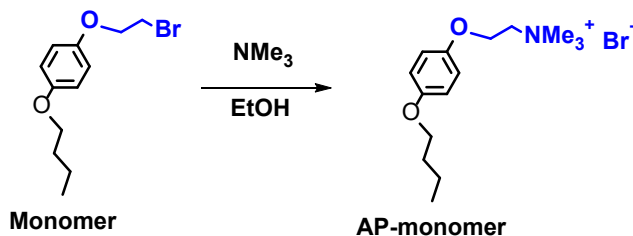


Scheme S8. Preparation of amphiphilic pillar[*n*]arenes **AP-P5A-C10** and **AP-P6A-C10**.

To a suspension of **4a-C10** (0.050 g, 0.027 mmol) or **4b-C10** (0.037 g, 0.017 mmol) in ethanol (5 mL) and tetrahydrofuran (5 mL) was added 2 mL trimethylamine (3 M in ethanol). The resulting mixture was refluxed to give a homogeneous solution. After 2 days, the solvent was removed under vacuum. The residue was washed with 2 mL ethyl acetate and dried to give **AP-P5A-C10** (0.074 g, 99%) or **AP-P6A-C10** (0.044 g, 99%) as white solid.

AP-P5A-C10: ¹H-NMR (600 MHz, CD₃OD) δ 6.90 (s, 5H), 6.80 (s, 5H), 4.46 (brs, 10H), 4.00 (brs, 10H), 3.84 (s, 10H), 3.69 (brs, 10H), 3.33 (s, 45H), 1.74 (brs, 10H), 1.51 (brs, 10H), 1.28-1.42 (m, 60H), 0.89 (t, $J = 7.0$ Hz, 15H); ¹³C-NMR (126 MHz, CD₃OD) δ 152.69, 150.04, 130.72, 130.21, 117.07, 116.92, 70.20, 67.11, 64.83, 55.22, 33.06, 31.12, 30.95, 30.86, 30.82, 30.50, 27.70, 23.67, 14.37. HRMS (ESI) calcd. for $[\text{C}_{110}\text{H}_{190}\text{O}_{10}\text{N}_5\text{Br}_3]^{2+}$ $[\text{M}-2\text{Br}]^{2+}$ m/z 989.1026; found 989.1041.

AP-P6A-C10: ¹H-NMR (600 MHz, CD₃OD) δ 7.11 (s, 6H), 7.08 (s, 6H), 4.62 (brs, 12H), 4.10 (s, 12H), 4.04 (t, $J = 6.6$ Hz, 12H), 4.01 (t, $J = 5.0$ Hz, 11H), 3.50-3.52 (m, 24H), 1.89-1.94 (m, 12H), 1.61-1.66 (m, 11H), 1.52-1.56 (m, 72H), 1.10 (t, $J = 6.8$ Hz, 18H); ¹³C-NMR (151 MHz, CD₃OD) δ 153.26, 150.75, 130.19, 129.95, 117.30, 117.24, 70.58, 66.76, 64.76, 55.07, 33.08, 32.47, 31.00, 30.84, 30.80, 30.74, 30.49, 27.53, 23.69, 14.36. HRMS (ESI) calcd. for $[\text{C}_{132}\text{H}_{228}\text{N}_6\text{O}_{12}\text{Br}_3]^{3+}$ $[\text{M}-3\text{Br}]^{3+}$ m/z 775.4983; found 775.4976.



Scheme S9. Preparation of amphiphilic monomer.

To a solution of **Monomer**^[S3] (0.20 g, 0.73 mmol) in ethanol (20 mL) was added 10

mL trimethylamine (3 M in ethanol). After 2 days, the solvent was removed under vacuum. The residue was washed with 5 mL ethyl acetate and dried to give **AP-Monomer** (0.23 g, 95%) as white solid.

AP-Monomer: $^1\text{H-NMR}$ (400 MHz, D_2O) δ 6.94-7.00 (m, 4H), 4.44 (brs, 2H), 3.97-4.03 (m, 2H), 3.76-3.78 (m, 2H), 3.23 (s, 9H), 1.64-1.73 (m, 2H), 1.36-1.46 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C-NMR}$ (101 MHz, D_2O) δ 153.08, 151.57, 116.25, 116.03, 69.29, 65.15, 62.53, 54.01, 30.57, 18.60, 13.09. HRMS (ESI) calcd. for $[\text{C}_{15}\text{H}_{26}\text{O}_2\text{N}_1]^+ [\text{M}]^+ m/z$ 252.1958; found 252.1967.

3. X-ray diffraction data

3.1 Single crystal results

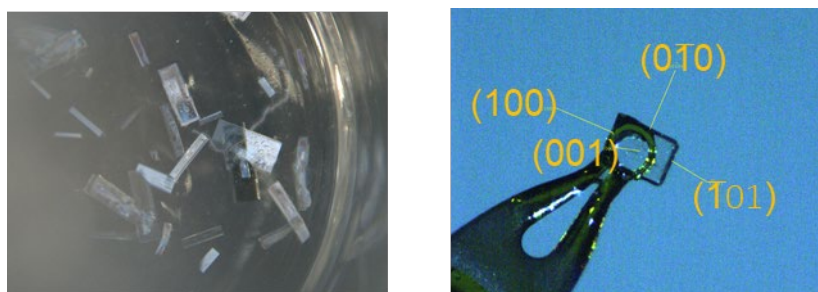


Figure S2. Morphology of single crystals of **AP-P5A** obtained by slowly evaporating its methanol/acetonitrile solution.

Table S1. Crystal data and structure refinement for **AP-P5A**.

Empirical formula	$\text{C}_{85}\text{H}_{145.5}\text{N}_{7.5}\text{O}_{14}\text{Br}_5$
Formula weight	1896.13
Temperature/K	153
Crystal system	monoclinic
Space group	$\text{P2}_1/\text{a}$
$a/\text{\AA}$	25.3755(9)
$b/\text{\AA}$	14.5802(5)
$c/\text{\AA}$	28.4082(8)
$\alpha/^\circ$	90
$\beta/^\circ$	112.4716(9)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	9712.4(6)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.297
μ/mm^{-1}	2.977

F(000)	3980.0
Crystal size/mm ³	0.34 × 0.24 × 0.04
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	6.734 to 133.068
Index ranges	-30 ≤ h ≤ 30, -17 ≤ k ≤ 16, -33 ≤ l ≤ 33
Reflections collected	135639
Independent reflections	17104 [R _{int} = 0.0349, R _{sigma} = 0.0248]
Data/restraints/parameters	17104/3002/1774
Goodness-of-fit on F ²	1.061
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0386, wR ₂ = 0.1078
Final R indexes [all data]	R ₁ = 0.0421, wR ₂ = 0.1120
Largest diff. peak/hole / e Å ⁻³	0.69/-0.57
CCDC number	2403414

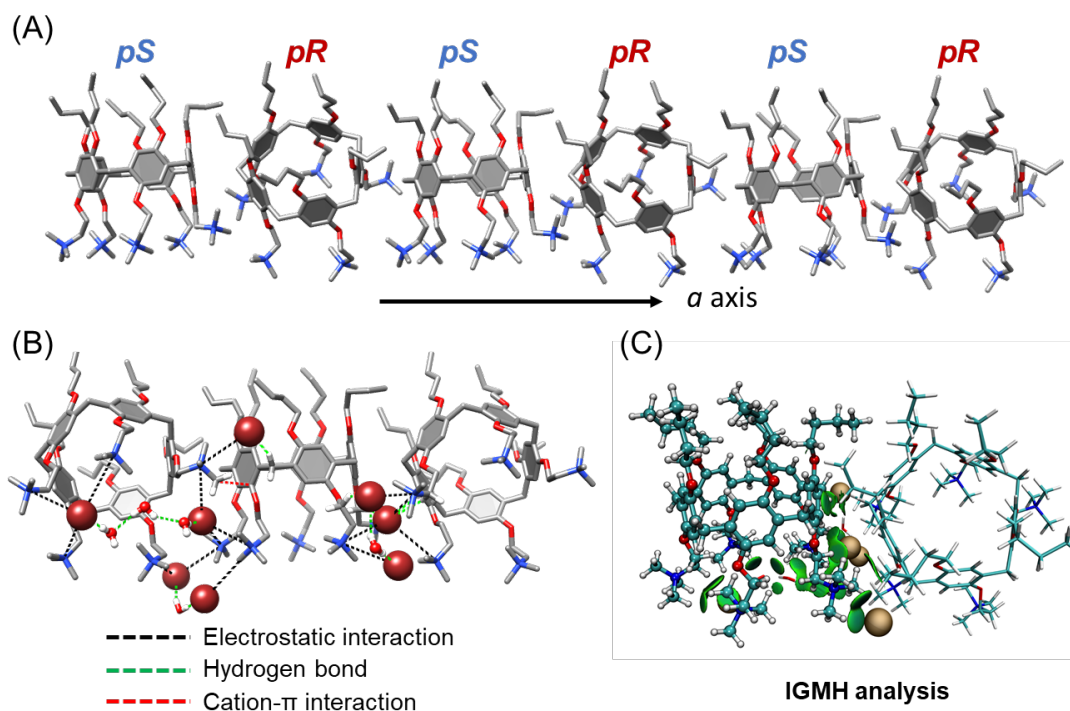


Figure S3. (A) Alternating chiral assembly of **AP-P5A** along *a* axis. (B) Supramolecular interactions along *a* axis. (C) IGMH analysis of pairs of **AP-P5A** along *a* axis based on the crystallographic structure. Green regions show the attractive noncovalent interactions.

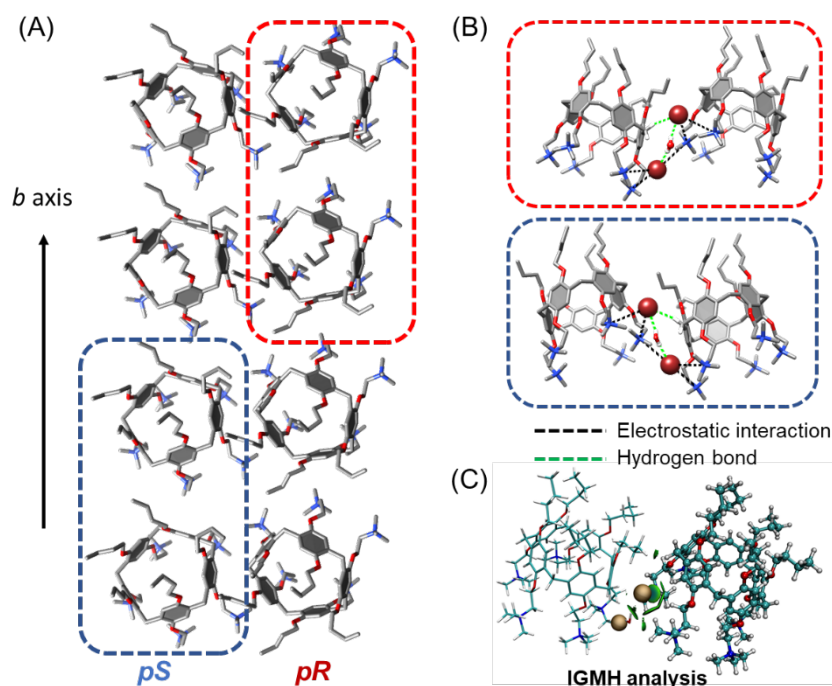


Figure S4. (A) Homochiral assembly of **AP-P5A** along *b* axis. (B) Supramolecular interactions along *b* axis. (C) IGMH analysis of pairs of **AP-P5A** along *b* axis based on the crystallographic structure. Green regions show the attractive noncovalent interactions.

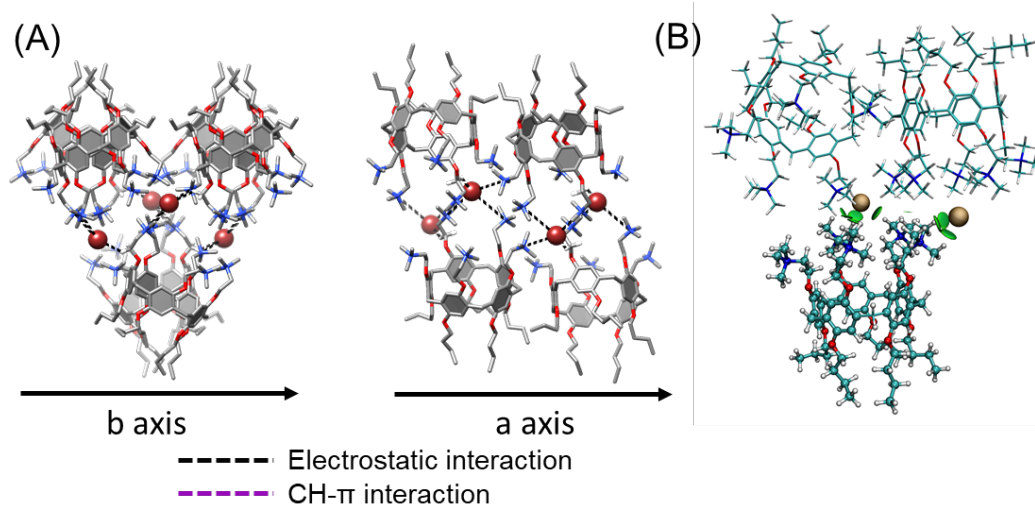


Figure S5. (A) Supramolecular interactions within the hydrophilic interlayer of **AP-P5A**. (B) IGMH analysis of between **AP-P5A** within the hydrophilic interlayer based on the crystallographic structure. Green regions show the attractive noncovalent interactions.

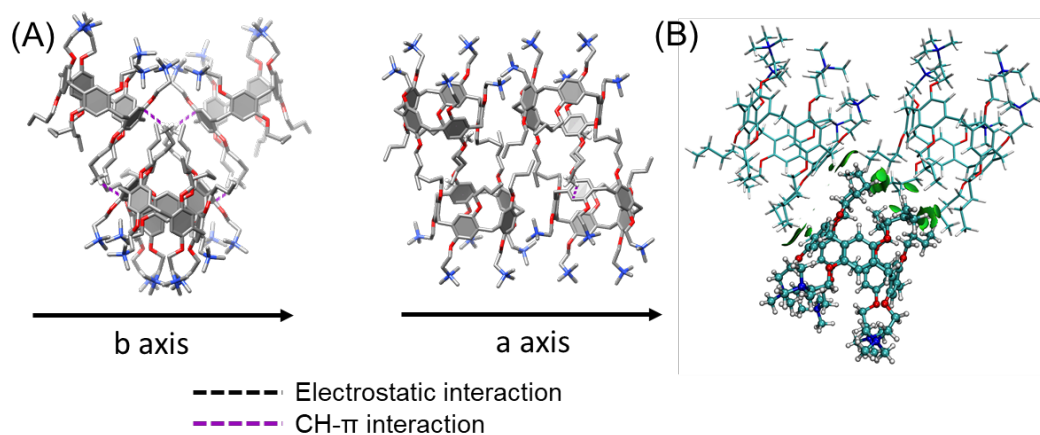


Figure S6. (A) Supramolecular interactions within the hydrophobic interlayer of **AP-P5A**. (B) IGMH analysis of between **AP-P5A** within the hydrophobic interlayer based on the crystallographic structure. Green regions show the attractive noncovalent interactions.

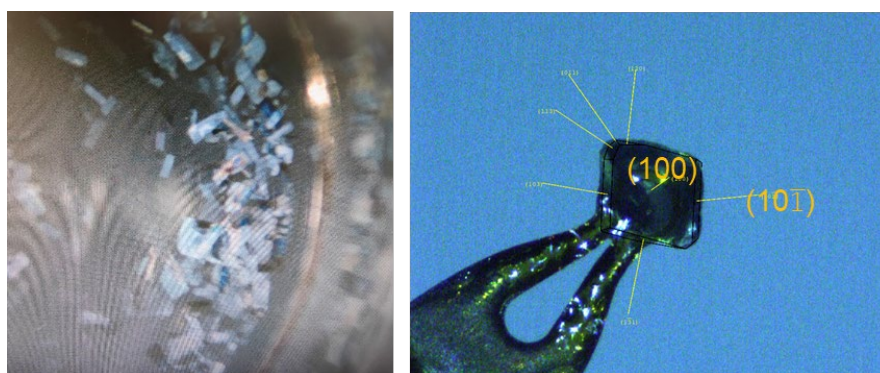


Figure S7. Morphology of single crystals of **AP-P6A** obtained by slowly evaporating acetone into its methanol/water (1:1) solution.

Table S2. Crystal data and structure refinement for **AP-P6A**. The quality of the single crystal was not good enough. Therefore, supramolecular interactions along each axis were not analyzed.

Empirical formula	$C_{112}H_{204.5}N_6O_{25.25}Br_6$
Formula weight	2518.76
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	26.839(3)
$b/\text{\AA}$	28.517(2)
$c/\text{\AA}$	35.995(3)
$\alpha/^\circ$	94.472(5)
$\beta/^\circ$	90.677(4)

$\gamma/^\circ$	100.256(4)
Volume/ $\text{\AA}^3$	27017(4)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.238
μ/mm^{-1}	2.657
F(000)	10644.0
Crystal size/ mm^3	$0.39 \times 0.37 \times 0.09$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54178$)
2 Θ range for data collection/ $^\circ$	4.104 to 90
Index ranges	$-24 \leq h \leq 24$, $-25 \leq k \leq 26$, $-33 \leq l \leq 33$
Reflections collected	240314
Independent reflections	43543 [$R_{\text{int}} = 0.3705$, $R_{\text{sigma}} = 0.2179$]
Data/restraints/parameters	43543/19112/5707
Goodness-of-fit on F^2	1.915
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.2674$, $wR_2 = 0.4979$
Final R indexes [all data]	$R_1 = 0.4323$, $wR_2 = 0.5915$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.02/-0.40
CCDC number	2403376



Figure S8. Morphology of single crystals of **AP-monomer** obtained by slowly evaporating ethyl acetate into its ethanol solution.

Table S3. Crystal data and structure refinement for **AP-monomer**.

Empirical formula	$\text{C}_{16}\text{H}_{30}\text{NO}_3\text{Br}$
Formula weight	364.32
Temperature/K	153
Crystal system	triclinic
Space group	P-1
a/ $\text{\AA}$	9.3021(4)
b/ $\text{\AA}$	9.3109(4)
c/ $\text{\AA}$	22.4483(9)
$\alpha/^\circ$	94.0012(15)

$\beta/^\circ$	96.7446(12)
$\gamma/^\circ$	106.1294(14)
Volume/ $\text{\AA}^3$	1844.09(13)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.312
μ/mm^{-1}	3.111
$F(000)$	768.0
Crystal size/ mm^3	$0.1 \times 0.05 \times 0.003$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54178$)
2Θ range for data collection/ $^\circ$	7.978 to 136.59
Index ranges	$-11 \leq h \leq 11, -11 \leq k \leq 11, -26 \leq l \leq 27$
Reflections collected	21308
Independent reflections	6466 [$R_{\text{int}} = 0.0463, R_{\text{sigma}} = 0.0693$]
Data/restraints/parameters	6466/53/415
Goodness-of-fit on F^2	1.091
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0363, wR_2 = 0.1015$
Final R indexes [all data]	$R_1 = 0.0374, wR_2 = 0.1025$
Largest diff. peak/hole / $\text{e \AA}^{-3}$	0.39/-0.62
CCDC number	2403371

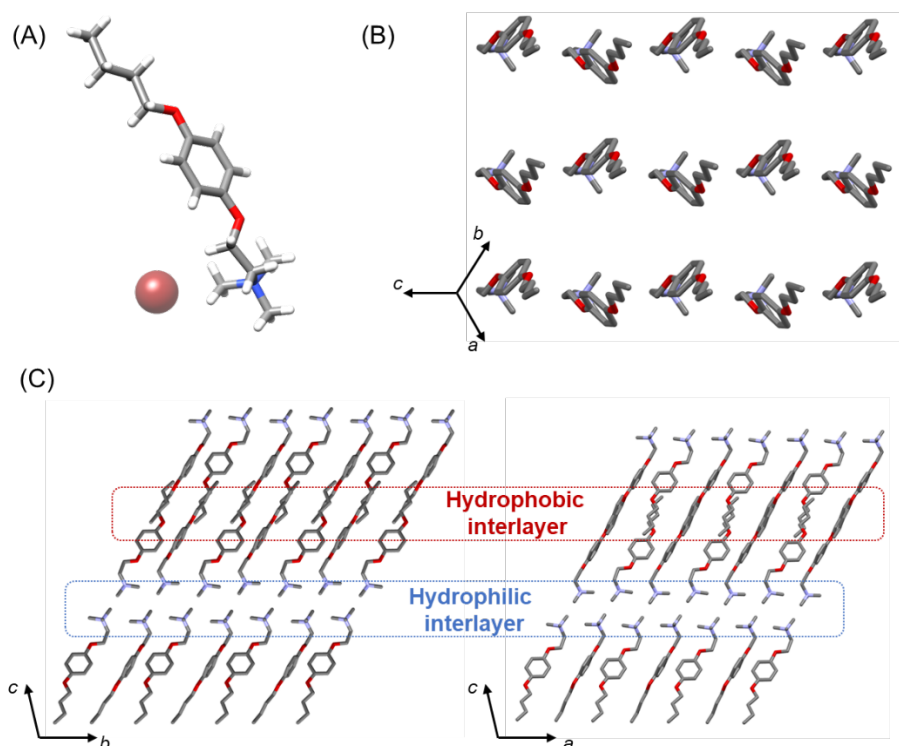


Figure S9. (A) Crystallographic structure of **AP-monomer**. (B) Top view of packing of **AP-monomer** on 2D plane. (C) Assembly within hydrophobic and hydrophilic

interlayers in **AP-monomer**.

3.2 Additional discussion of supramolecular interactions in single-crystals

The good quality of single crystal of **AP-P5A** enables the detailed analysis of supramolecular interactions. **AP-P6A** didn't yield single crystals in good quality. Although the microscopic packing can be seen, the analysis of supramolecular interactions is not responsible in **AP-P6A**.

In **AP-P5A**, the macrocycles adopted a 1D assembly along the *a* axis with alternating chirality, which was supported by electrostatic interactions, hydrogen bonds, and cation- π interactions (Figure S3). The bromides were also connected by water molecules through hydrogen bonds. Along the *b* axis, a 1D assemblies with homochirality were observed, which were supported by the electrostatic interactions and hydrogen bonds (Figure S4). Along the *c* axis, hydrophilic and hydrophobic interlayers were supported by electrostatic interactions between bromides and ammoniums (Figure S5), and by CH- π interactions between alkyl chains and benzenes, respectively (Figure S6).

3.3 Additional discussion of packing in single-crystals

Alkoxy-substituted pillar[*n*]arenes prefer to adopt pillar-shaped conformation in crystal state, in which torsion angles for each unit are around 90° with deviations of ~3° (Figure S10 and Table S4, column 2, 3). The symmetric shapes enable polygonal dense packing to minimize the energies of the system. As a result, tubular or herringbone assemblies are usually observed in crystalline alkoxy-substituted pillar[*n*]arenes. Because of the dense packing in these systems, gaps between pillar[*n*]arenes are small; therefore, guest molecules are generally captured by the internal cavities.

In this work, ammonium cations and butoxy groups were installed separately on the two rims in **AP-P5A** and **AP-P6A**. This unsymmetric decoration totally changed the packing way of pillar[*n*]arenes. Because of the strong electrostatic interactions, cations and bromides packed densely on the 2D hydrophilic interlayers. To ensure the dense packing of cations, the flexible repeating units rotate. Torsion angles of repeating units in **AP-P5A** deviated by 1–20° from 90°, whereas in **AP-P6A**, they deviated by 4–58° (Table S4, column 4, 5). The average deviations ($\Delta\phi$) are 8.12° for **AP-P5A** and 24.7° for **AP-P6A**. Larger cavity of **AP-P6A** led to a more labile conformation compared to **AP-P5A**, resulting in greater deviations. As a result, the symmetrical conformation of pillar[*n*]arenes were broken, leading to loose packing between the skeletons and generating large voids in crystal state. Greater deviations in **AP-P6A** made larger voids as larger external pockets.

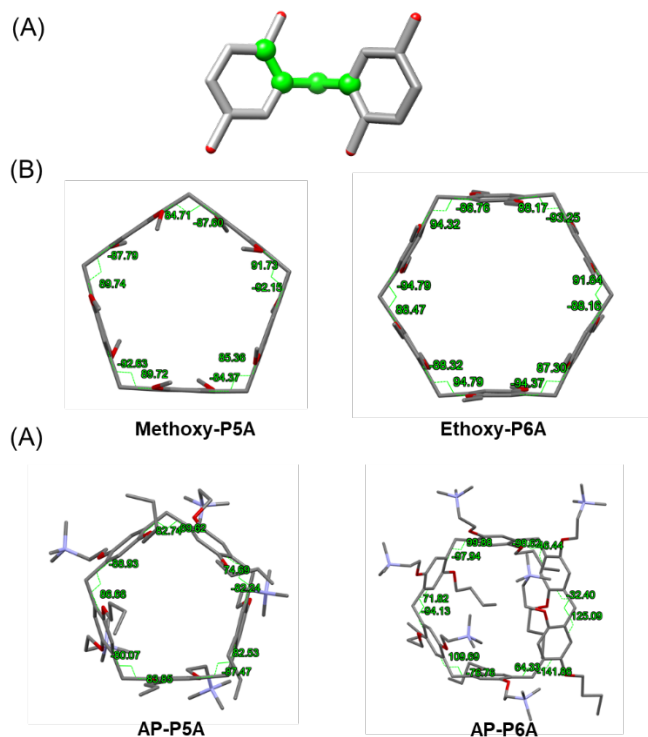


Figure S10. (A) Atoms used in defining the torsion angles of pillar[*n*]arenes. (B) Torsion angles of each repeating units in methoxy-substituted pillar[5]arene^{11a} and ethoxy-substituted pillar[6]arene^{14b}. (C) Torsion angles of each repeating units in **AP-P5A** and **AP-P6A**.

Table S4. Torsion angles in methoxy-P5A, ethoxy-P6A, **AP-P5A** and **AP-P6A**.

Entry	Methoxy-P5A		Ethoxy-P6A		AP-P5A		AP-P6A	
	φ	$\Delta\varphi$	φ	$\Delta\varphi$	φ	$\Delta\varphi$	φ	$\Delta\varphi$
1	84.71	5.29	86.76	3.24	69.62	20.38	99.88	9.88
2	87.6	2.4	88.17	1.83	74.69	15.31	99.62	9.62
3	91.73	1.73	93.25	3.25	82.24	7.76	46.44	43.56
4	92.15	2.15	91.84	1.84	82.53	7.47	32.4	57.6
5	85.36	4.64	88.16	1.84	87.47	2.53	125	35
6	84.37	5.63	87.3	2.7	83.85	6.15	141.86	51.86
7	89.72	0.28	94.37	4.37	80.07	9.93	64.33	25.67
8	92.63	2.63	94.79	4.79	86.68	3.32	76.76	13.24
9	89.74	0.26	88.32	1.68	88.93	1.07	109.69	19.69
10	87.79	2.21	88.47	1.53	82.74	7.26	94.13	4.13
11			94.79	4.79			71.82	18.18
12			94.32	4.32			97.94	7.94
Average		2.72		3.02		8.12		24.70

* $\Delta\varphi = |\varphi - 90^\circ|$

3.4 Powder results

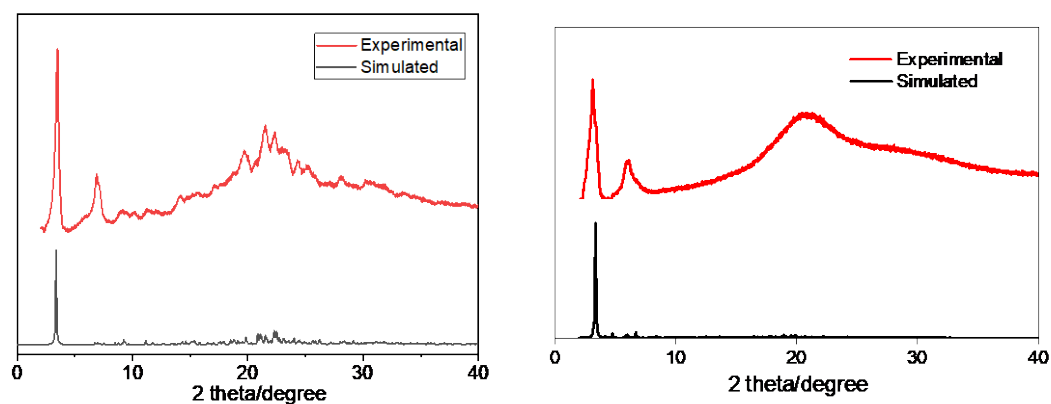


Figure S11. Experimental and simulated powder X-ray diffraction patterns of **AP-P5A** (left) and **AP-P6A** (right).

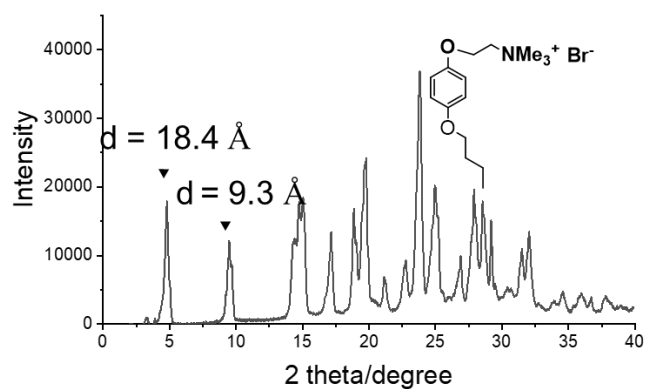


Figure S12. Powder X-ray diffraction patterns of **AP-monomer**.

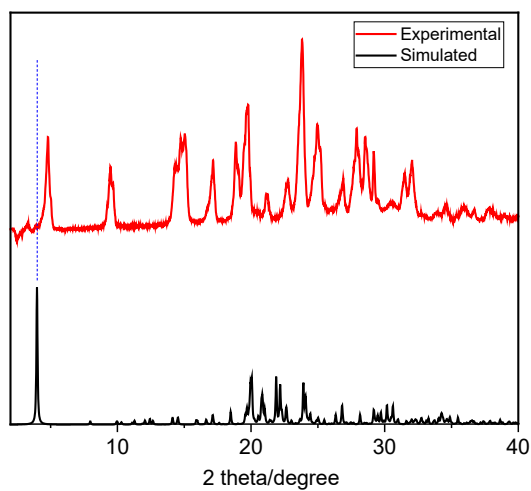


Figure S13. Experimental and simulated powder X-ray diffraction patterns of **AP-monomer**. Calculated (001) spacing from single crystal is 22.1 Å, which is smaller than the spacing in pillar[*n*]arenes. This can be rationalized by the interweaving of the alkyl chains, that can be seen from the crystallographic structure (Figure S9). The spacing from the first two peaks in experimental PXRD patterns were calculated as 18.4 Å and 9.3 Å, which can also be ascribed to interlayer spacing of (001) and (002). Smaller spacing comes from the deeper interweaving of monomers in powder samples.

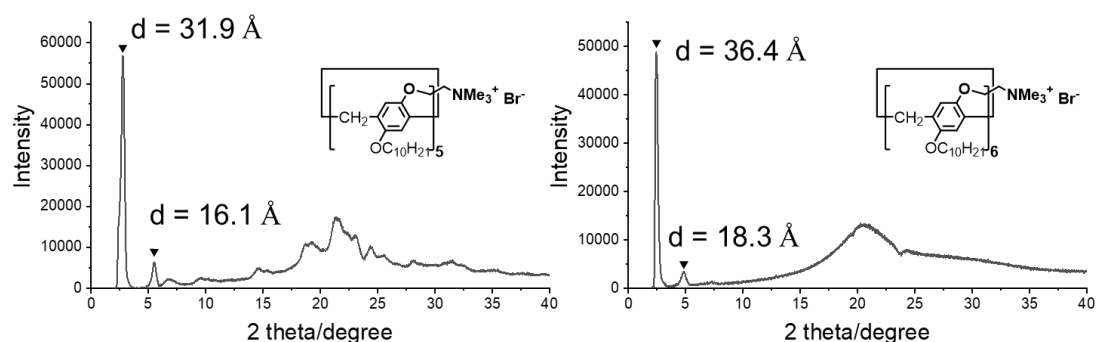


Figure S14. Powder X-ray diffraction patterns of **AP-P5A-C10** (left) and **AP-P6A-C10** (right).

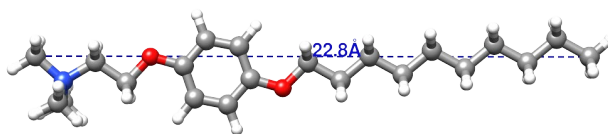


Figure S15. Length of the monomer in amphiphilic pillar[*n*]arenes with decyl chains.

4. Microscopic images of the sheets

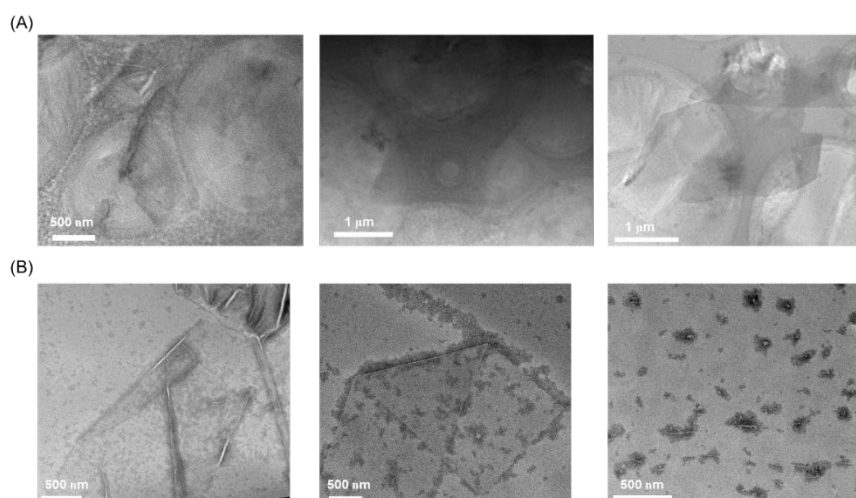


Figure S16. (A) Cryo-TEM images and (B) negatively-stained TEM images of **AP-P5A** in water (10 mM). Sheets were observed in both methods. In negatively-stained TEM, nanofibers can also be detected, which could come from the disassociation of the sheets.

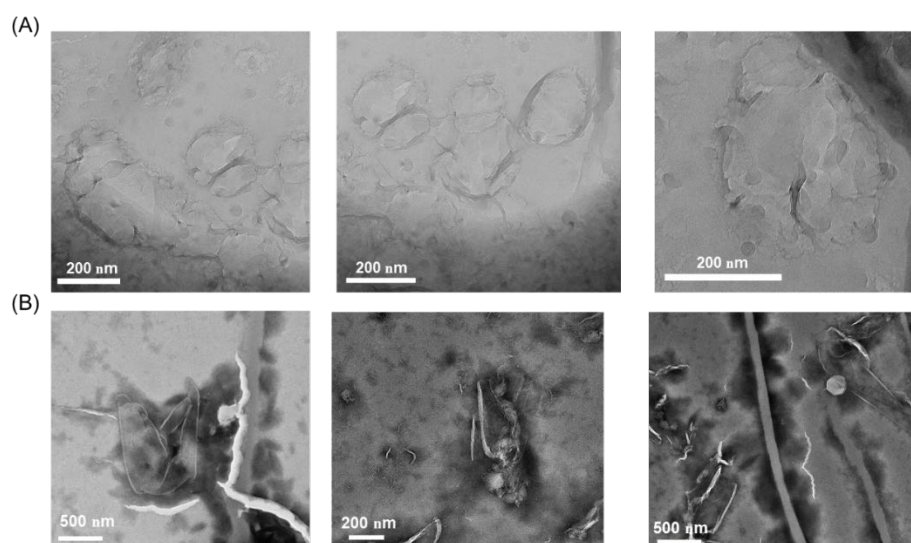


Figure S17. (A) Cryo-TEM images and (B) negatively-stained TEM images of **AP-P6A** in water (10 mM). Sheets were observed in both methods. In negatively-stained TEM, nanofibers can also be detected, which could come from the disassociation of the sheets.

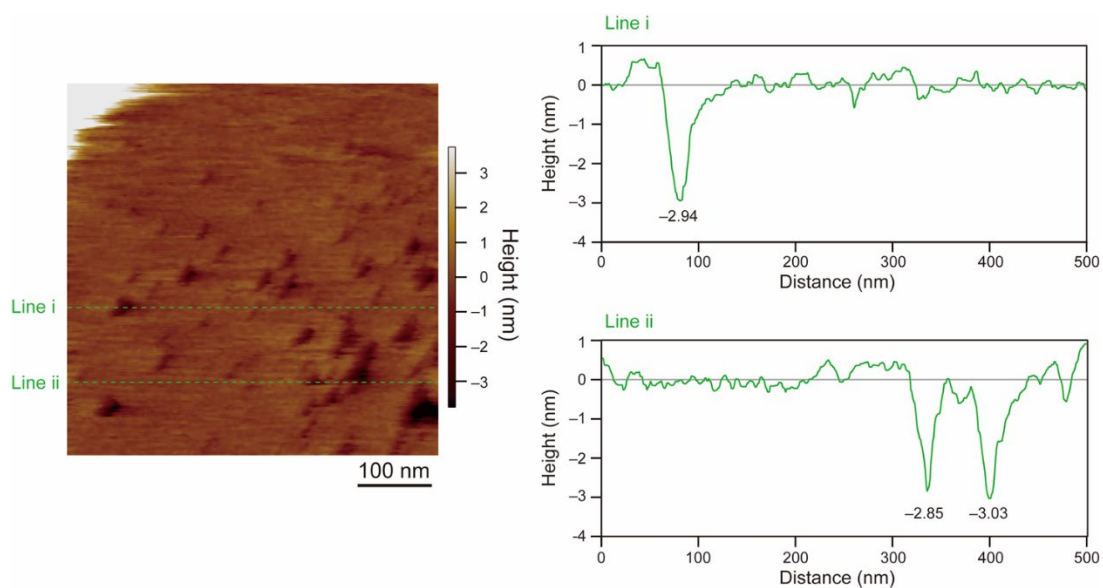


Figure S18. AFM images for **AP-P6A**.

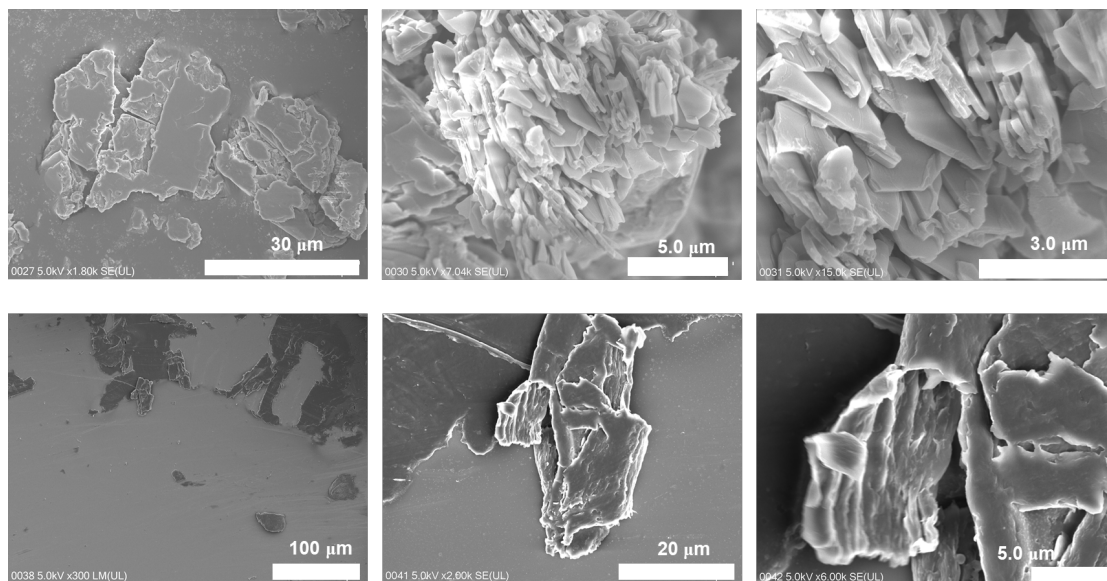


Figure S19. SEM images for **AP-P5A** from powder samples (top) and 0.2 mM in H₂O dispersion (bottom).

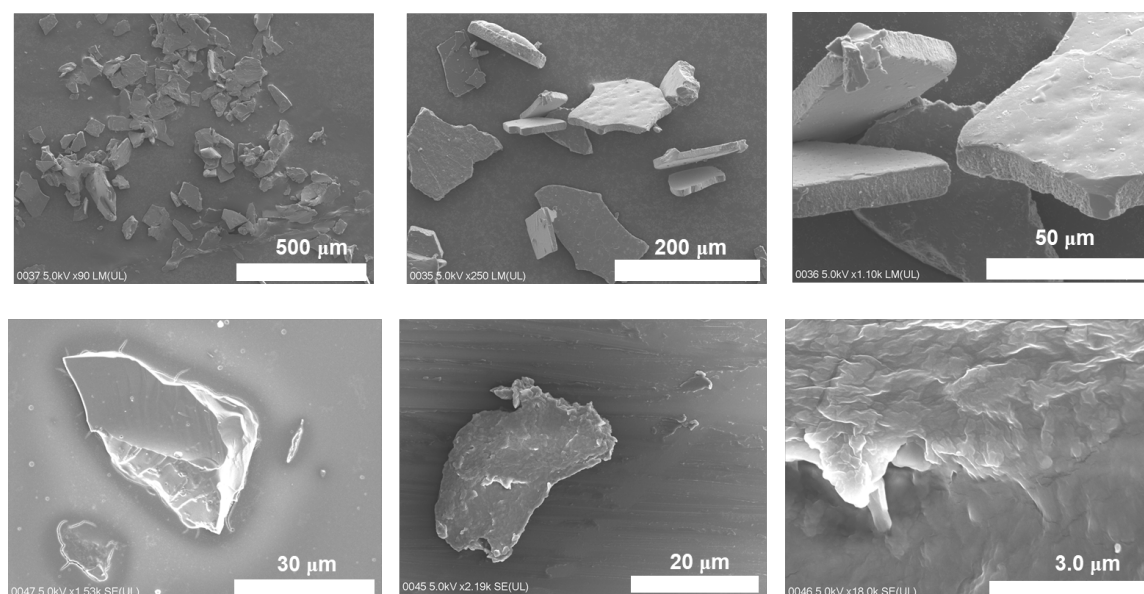


Figure S20. SEM images for **AP-P6A** from powder samples (top) and 0.2 mM in H₂O dispersion (bottom).

5. Assembly in water

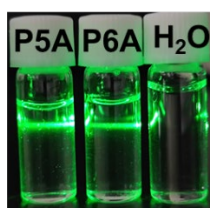


Figure S21. Tyndall effect of **AP-P5A** and **AP-P6A** in water.

5.1 UV/visible and fluorescence spectra

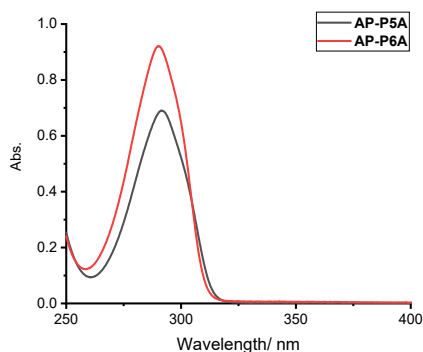


Figure S22. UV/visible spectra of **AP-P5A** and **AP-P6A** (50 μ M in H_2O).

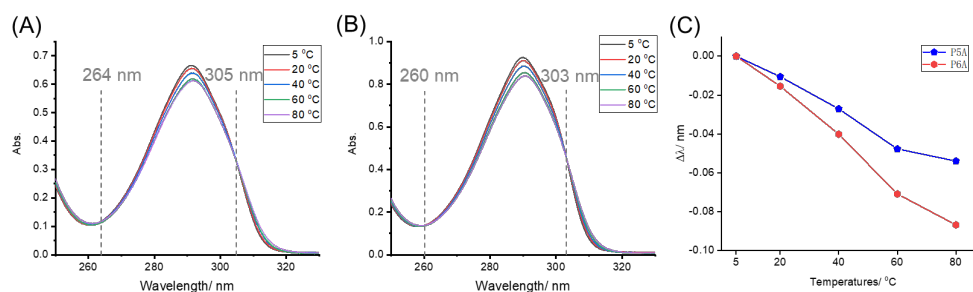


Figure S23. UV/visible spectra of (A) **AP-P5A** and (B) **AP-P6A** at different temperatures (50 μ M in H_2O). (C) Wavelength changes in maximum absorbance with increasing temperatures. Isosbestic points were observed for both **AP-P5A** and **AP-P6A**, indicating the equilibrium between different species. The changes in absorbance are small ($\Delta\lambda < 0.1$ nm from 5 $^{\circ}C$ to 80 $^{\circ}C$), suggesting relative stable assemblies with temperature. Probably because of the more labile conformation of **AP-P6A**, it showed a faster decreasing in absorbance than **AP-P5A**.

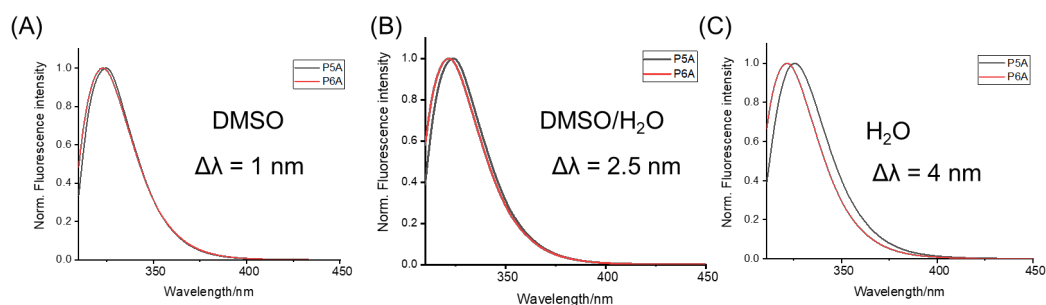


Figure S24. Normalized fluorescence spectra ($\lambda_{ex} = 290$ nm) of **AP-P5A** and **AP-P6A** and differences in their maximum emission wavelengths in (A) DMSO; (B) DMSO/ H_2O = 1/1; and (C) H_2O . The difference in maximum emission wavelengths was caused by the assembly, as $\Delta\lambda$ increased with water portion increasing. Fluorescence lifetimes in water were monitored at 330 nm with $\tau_{AP-P5A} = 1.73$ ns, $\tau_{AP-P6A} = 1.67$ ns.

5.2 ^1H NMR measurements

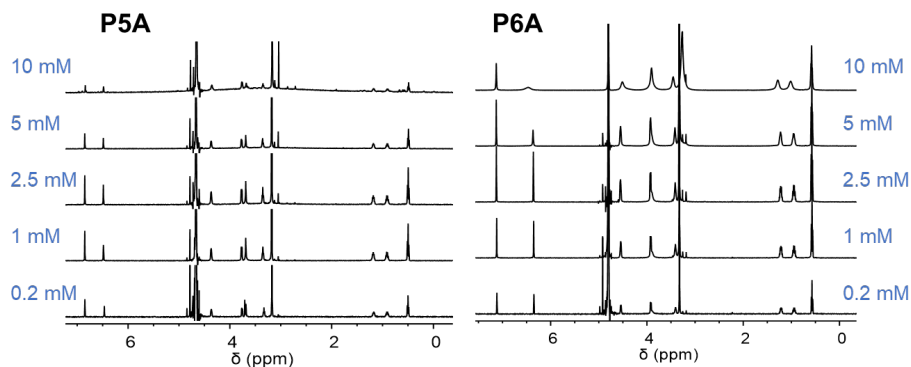


Figure S25. ^1H NMR spectra of **AP-P5A** and **AP-P6A** in D_2O at 25 °C in varying concentrations.

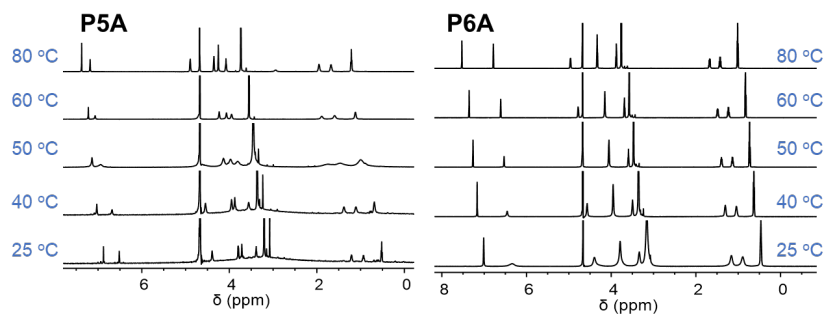


Figure S26. ^1H NMR spectra of **AP-P5A** and **AP-P6A** in D_2O in 10 mM at varying temperatures.

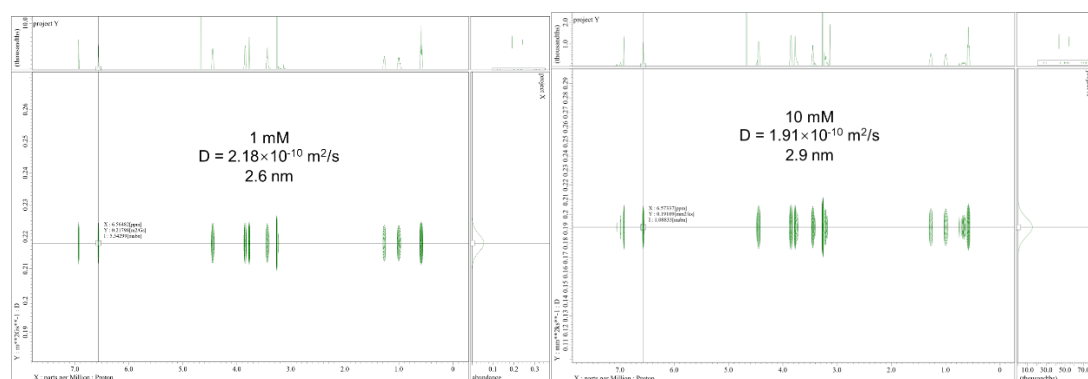


Figure S27. DOSY spectra of **AP-P5A** in D_2O in 1 mM and 10 mM at 30 °C.

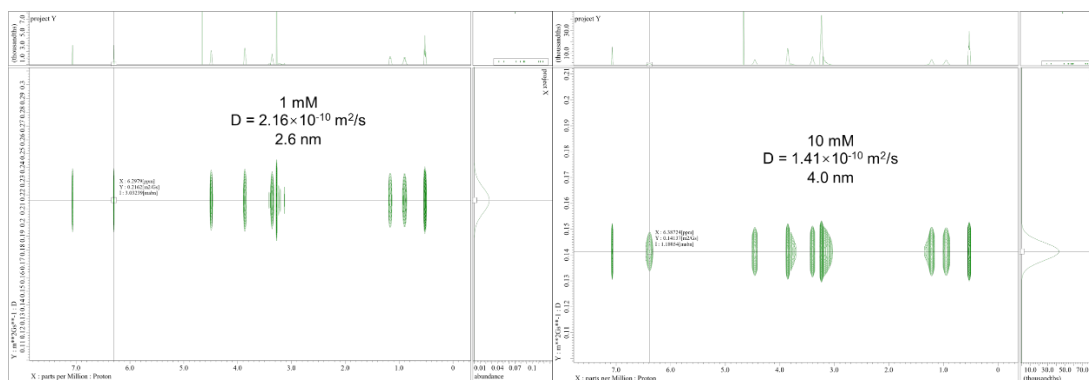


Figure S28. DOSY spectra of **AP-P6A** in D_2O in 1 mM and 10 mM at 30 °C.

5.3 Dynamic light scattering (DLS) measurements

For DLS measurements, we used water dispersion of **AP-P5A** and **AP-P6A** at 0.1 mM and 1 mM concentrations. At each concentration, the data were recorded at 20 °C, 40 °C, 60 °C, 80 °C, and cooling back to 20 °C. From the intensity correlation functions (ICFs), a combination of two kinds of diffusion motion, a faster a slower one, can be observed (Figure S29). The faster diffusion mode corresponds to the Brownian motion of the target assembly and the slower mode might be related to the deformation of the assembly. To calculate the assembly sizes, we attempted to extract the fast mode signal out of slow modes by performing fitting calculations with a custom-made formula. Three assumptions were made to construct the fitting formula:

- (1) Only the fast and slow diffusion modes exist in the system.
- (2) Fast mode has some "distribution" in its relaxation time (this corresponds to polydisperse particle size distribution).
- (3) Slow mode has a specific relaxation rate.

Under these assumptions, ICFs were successfully fitted with the formula:

$$g(\tau)^{(2)} - 1 = \underbrace{\sigma_f^2 \left\{ A \exp\left(-\left(\frac{\tau}{\tau_f}\right)^\beta\right) \right\}}_{\text{Fast mode}} + \underbrace{(1-A) \exp\left(-\frac{\tau}{\tau_s}\right)}_{\text{Slow mode}}$$

(fitting parameters)
 σ_f^2 : Y-intercept of ICF
 A : Fraction of fast mode
 τ_f : Relaxation time of fast mode
 β : Stretch exponent of fast mode
 τ_s : Relaxation time of slow mode

The corresponding diffusion coefficient (D) and hydrodynamic diameter (d_H) were then calculated from the fitting parameters (Tables S5 and S6).

Diffusion coefficient	$D = \frac{1}{q^2 \tau_f}$	(physical parameters)
Hydrodynamic diameter	$d_H = \frac{k_B T}{3\pi\eta D}$	q : Scattering vector k_B : Boltzmann constant T : Absolute temperature η : Dynamic viscosity of the media (water)

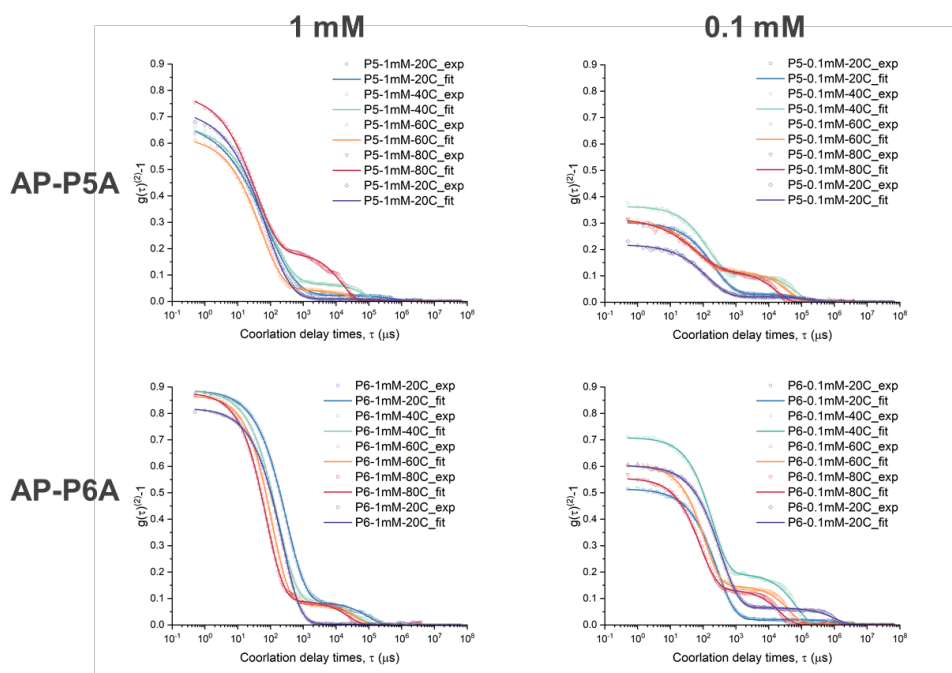


Figure S29. DLS intensity autocorrelation functions for **AP-P5A** and **AP-P6A** and the fitting results.

Table S5. Fitting parameters and calculated diffusion coefficient (D) and hydrodynamic diameter (d_H) of **AP-P5A**.

AP-P5A		σ_f^2 (-)	A (-)	τ_f (μs)	β (-)	τ_s (μs)	D ($m^2 s^{-1}$)	d_H (nm)
1 mM	20°C	0.6889	0.8172	222.23	0.5287	1453757.81	6.46×10^{-12}	66.39
	40°C	0.6749	0.6823	152.21	0.6111	169089.03	9.46×10^{-12}	74.27
	60°C	0.6264	0.7355	100.27	0.7045	63604.51	1.44×10^{-11}	72.54
	80°C	0.7905	0.5163	54.54	0.6830	30248.32	2.67×10^{-11}	54.71
	20°C (cooling)	0.7314	0.8888	194.05	0.6023	1606770.67	7.40×10^{-12}	57.97
0.1 mM	20°C	0.3032	0.6772	355.94	0.7904	253036.40	4.03×10^{-12}	106.33
	40°C	0.3635	0.4548	177.55	0.9000	137281.63	8.11×10^{-12}	86.63
	60°C	0.3084	0.3833	84.53	0.7956	77503.05	1.71×10^{-11}	61.15
	80°C	0.3192	0.3934	84.38	0.6209	34012.00	1.73×10^{-11}	84.65
	20°C (cooling)	0.2189	0.6931	229.93	0.7493	520904.08	6.24×10^{-12}	68.69

Table S6. Fitting parameters and calculated diffusion coefficient (D) and hydrodynamic diameter (d_H) of **AP-P6A**.

AP-P6A		σ_I^2 (-)	A (-)	τ_f (μ s)	β (-)	τ_s (μ s)	D (m^2s^{-1})	d_H (nm)
1 mM	20°C	0.8883	0.6887	515.52	0.8180	191612.35	2.78×10^{-12}	154.00
	40°C	0.8889	0.6896	283.89	0.8543	88288.68	5.07×10^{-12}	138.52
	60°C	0.8687	0.6911	172.64	0.9631	77478.01	8.39×10^{-12}	124.89
	80°C	0.8799	0.6758	119.12	0.9352	46201.25	1.22×10^{-11}	119.49
	20°C (cooling)	0.8325	0.8642	501.29	0.8263	3182419.98	2.86×10^{-12}	149.75
0.1 mM	20°C	0.5148	0.8058	489.17	0.8587	4904043.10	2.93×10^{-12}	146.13
	40°C	0.7089	0.4766	252.22	0.9683	136467.97	5.71×10^{-12}	123.07
	60°C	0.6043	0.5033	144.86	1.0000	85120.45	9.99×10^{-12}	104.79
	80°C	0.5559	0.5059	113.47	0.9478	43036.82	1.28×10^{-11}	113.83
	20°C (cooling)	0.6032	0.6717	546.77	0.8586	2150480.31	2.62×10^{-12}	163.34

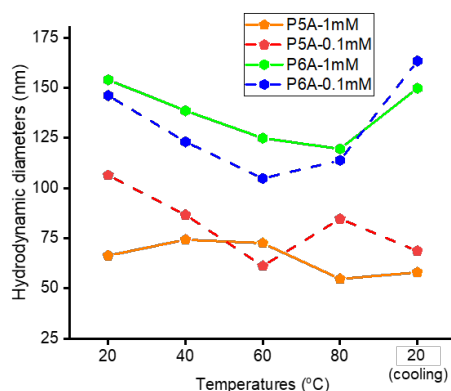


Figure S30. Summary of the hydrodynamic diameters at different conditions.

5.4 Additional discussion of DOSY and DLS experiments

In DOSY measurements, **AP-P5A** and **AP-P6A** showed similar hydrodynamic diameters, and 3-4 nm particles were dominant. In DLS measurements, the assembly system showed ~ 100 nm assemblies. And the hydrodynamic diameters were much larger than those obtained from DOSY. The reason may result from that DLS mainly detects larger assemblies due to much stronger light scattering, and DOSY mainly observes smaller assemblies with active molecular motion.

To figure out the assembly structures, cryo-TEM was measured (see section 4 in SI for detail). TEM observation in this resolution is only reliable for observing objects larger than ca. 10 nm. So, the small assemblies were not observed. Instead, sheets with a lateral size in hundreds of nanometers can be detected, matching the results from DLS. In summary, the main assemblies of pillar[n]arenes are sheets.

6. The binding between pillar[*n*]arene sheets and aromatic hydrocarbons

Ball-milling method: 0.3 mg pillar[*n*]arenes and 0.3 mg guests were added into a stainless-steel grinding vial (1.5 mL) with two stainless steel balls (5 mm). 2 μ L of water was dripped onto one steel ball. The vial was sealed and mixed in a Retsch MM400 mill at 30.0 Hz for 60 min. The crude mixture was transferred into a vial with water and centrifugated, and then filtered with 0.2 μ m membrane to yield a homogeneous aqueous dispersion. The dispersion was diluted to 3 mL for ensuing optical measurements.

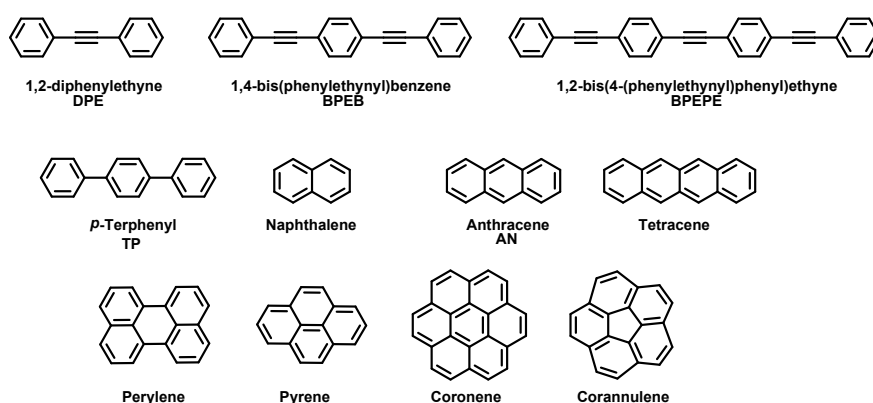


Figure S31. Structures of aromatic hydrocarbons used in this work.

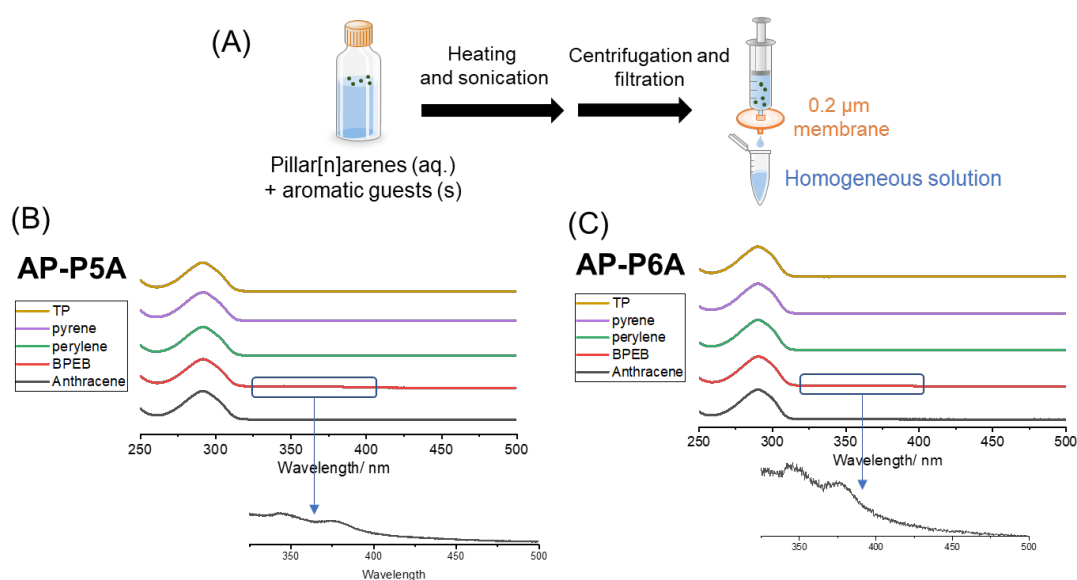


Figure S32. (A) Sonicating and heating method to interact with aromatic hydrocarbons in water. (B) UV/vis spectra using **AP-P5A** with different guests after the method. (C) UV/vis spectra using **AP-P6A** with different guests after the method.

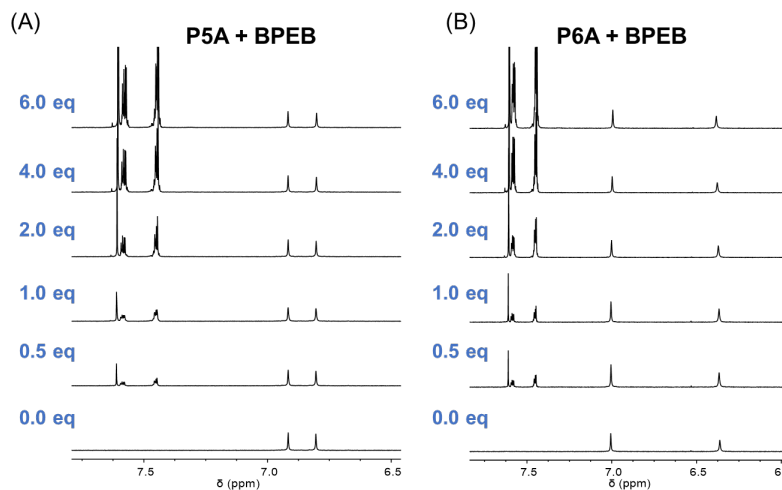


Figure S33. Part of ^1H NMR spectra after adding $\text{CDCl}_3/\text{DMSO-}d_6$ solution of BPEB into DMSO- d_6 solution of (A) **AP-P5A** and (B) **AP-P6A**. No obvious changes were detected in ^1H NMR by titrating BPEB into DMSO- d_6 solution of **AP-P5A** and **AP-P6A**. The results indicated their weak binding due to solvation.

6.1 Host/guest ratio from ^1H NMR

After dissolving the host–guest complexes in D_2O , guest molecules showed no ^1H NMR signals, because of restriction of molecular motion in the pockets (Figure S34). And the signals can be significantly broadened. After evaporating water, the resulting solid composites were all dissolved in DMSO- d_6 , and signals from host and guest can both be detected (Figures S34–S48).

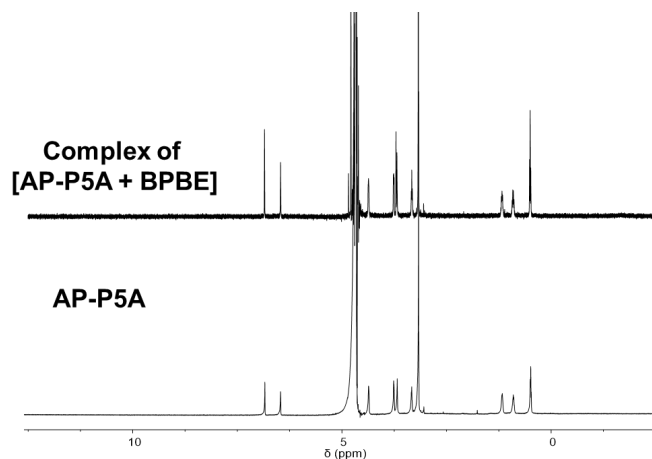


Figure S34. ^1H NMR spectra of **AP-P5A** and complex between **AP-P5A** and BPEB in D_2O .

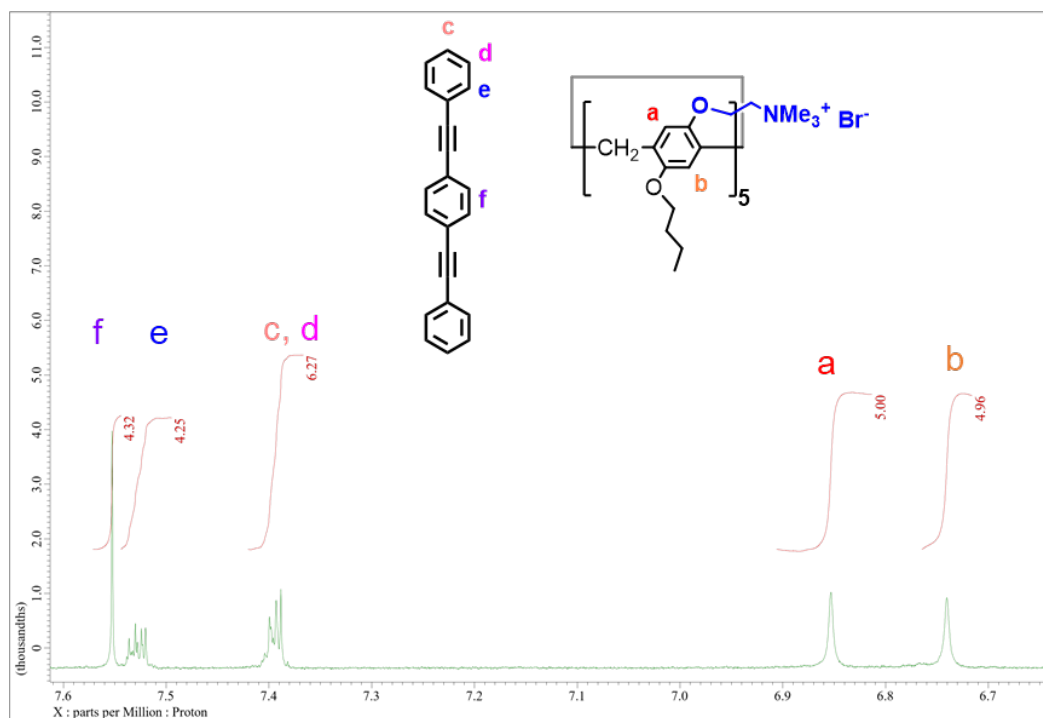


Figure S35. Partial ^1H NMR peaks and their integral values from ball-milling BPEB and AP-P5A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_f .

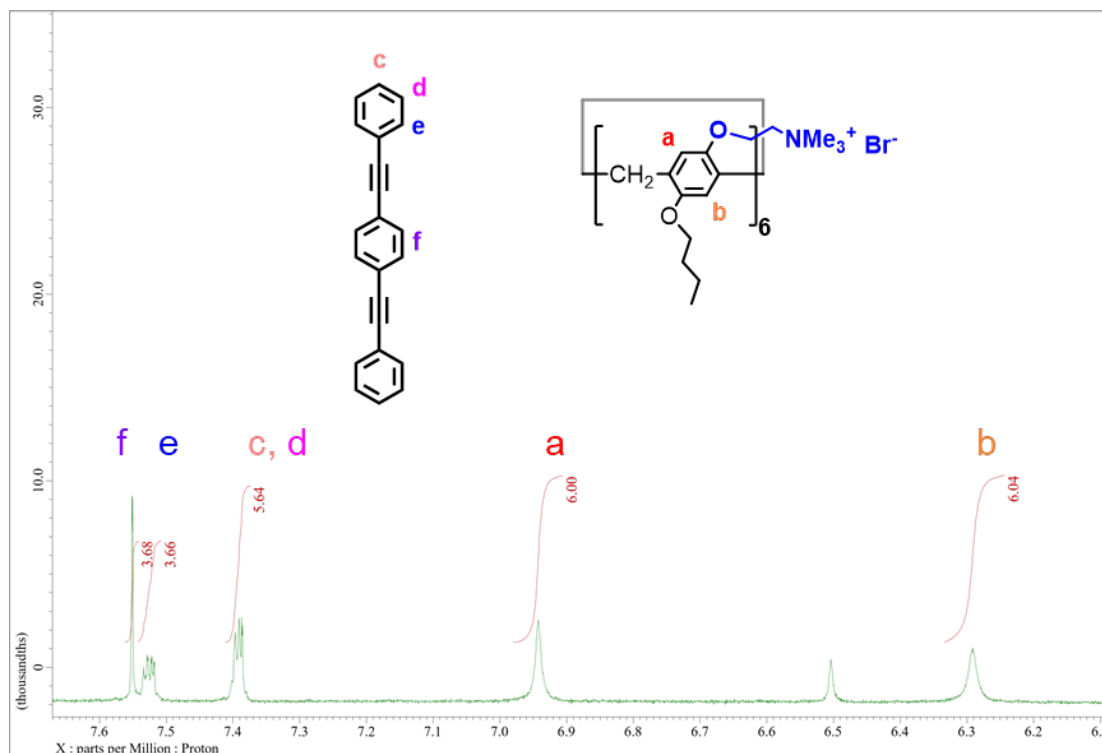


Figure S36. Partial ^1H NMR peaks and their integral values from ball-milling BPEB and AP-P6A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_f .

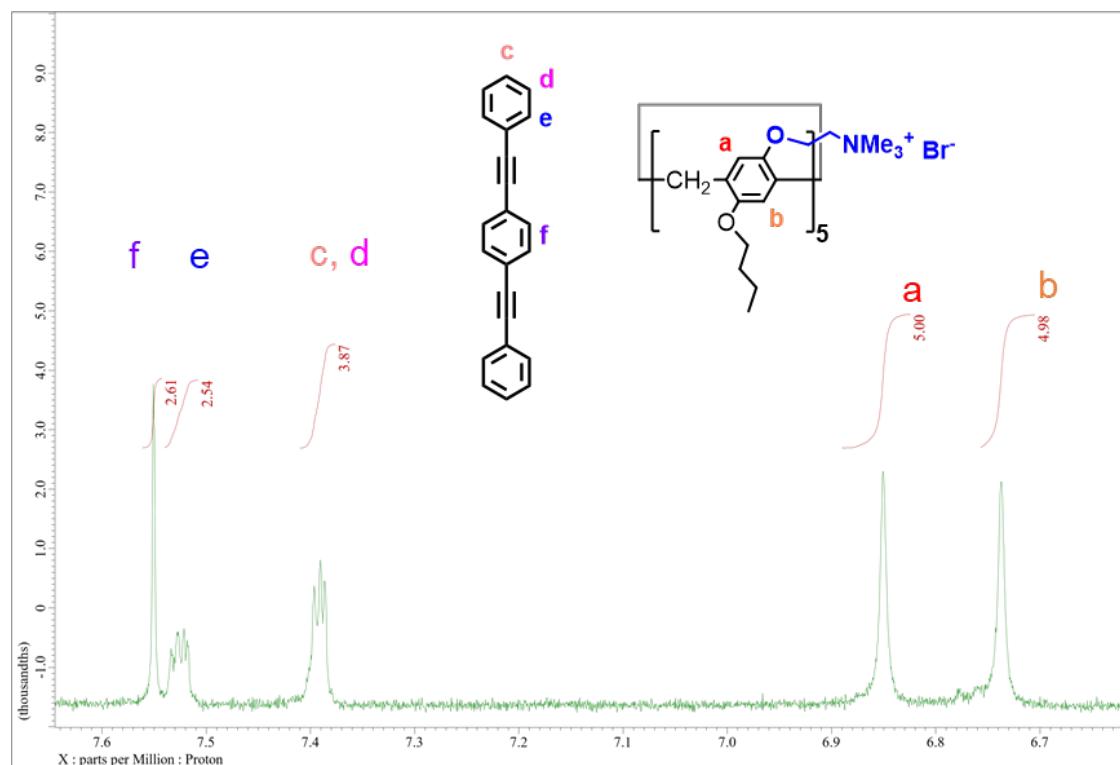


Figure S37. Partial ^1H NMR peaks and their integral values from ball-milling BPEB, succinonitrile, and AP-P5A in $\text{DMSO-}d_6$. The G/H ratio was calculated from the integral values from H_a and H_f .

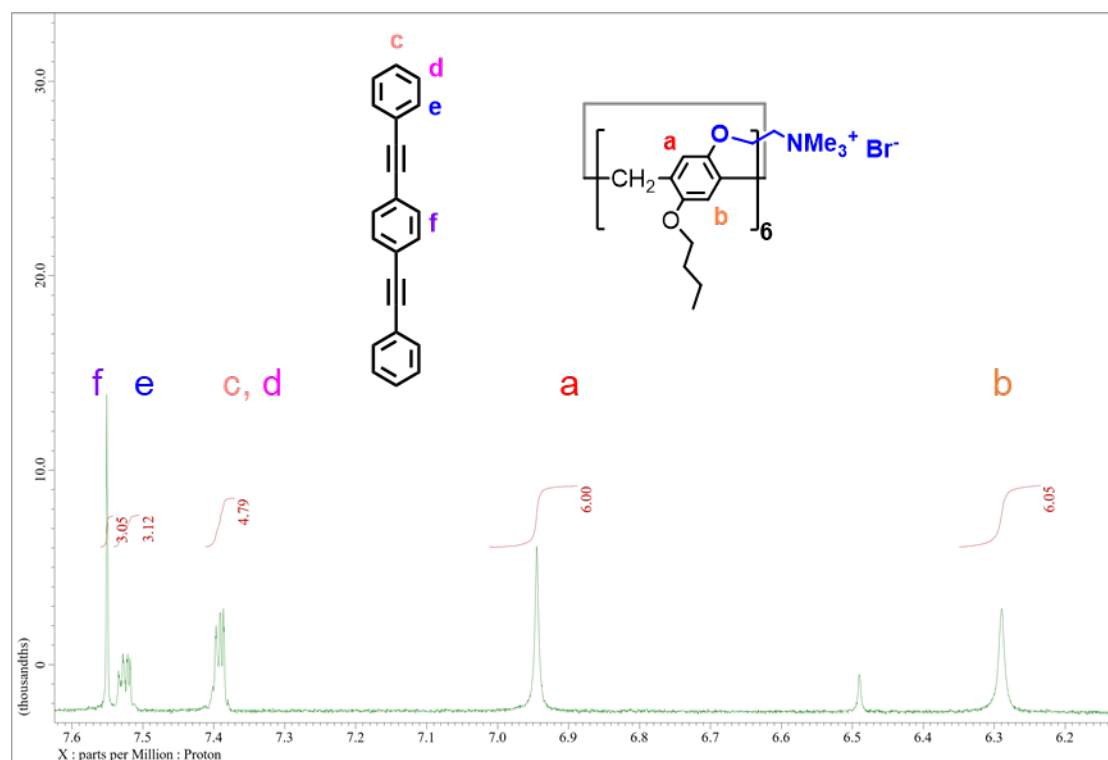


Figure S38. Partial ^1H NMR peaks and their integral values from ball-milling BPEB, succinonitrile, and AP-P6A in $\text{DMSO-}d_6$. The G/H ratio was calculated from the integral values from H_a and H_f .

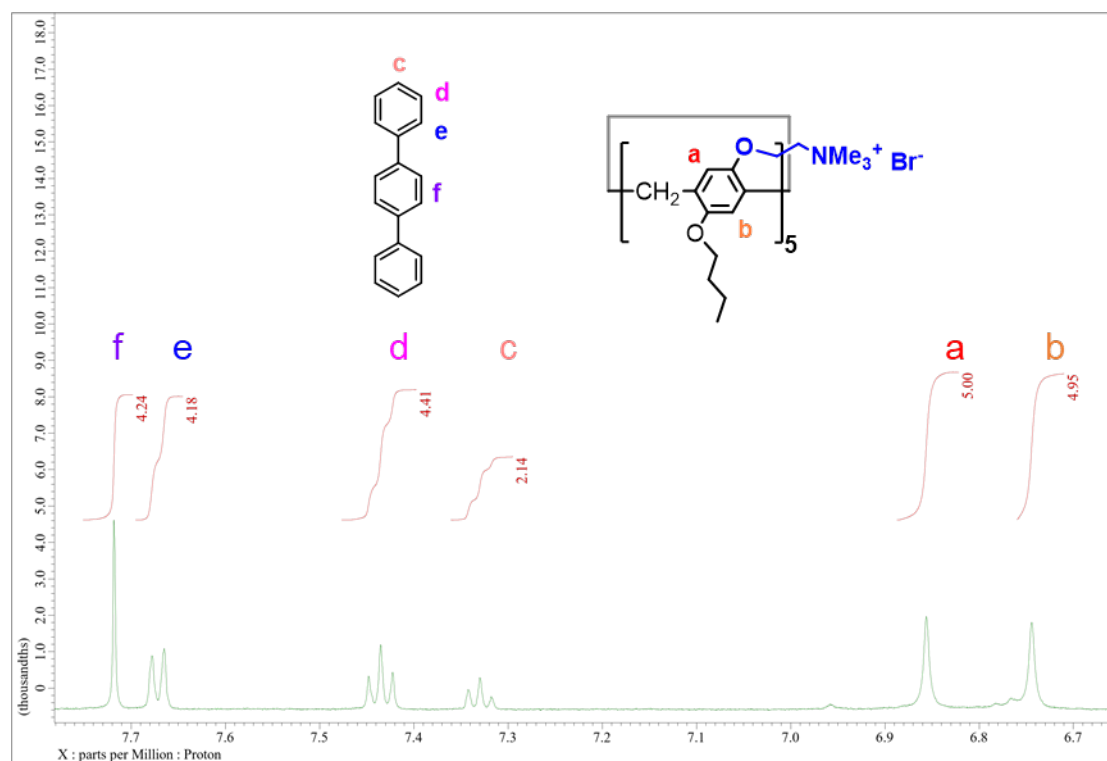


Figure S39. Partial ^1H NMR peaks and their integral values from ball-milling TP and AP-P5A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_f.

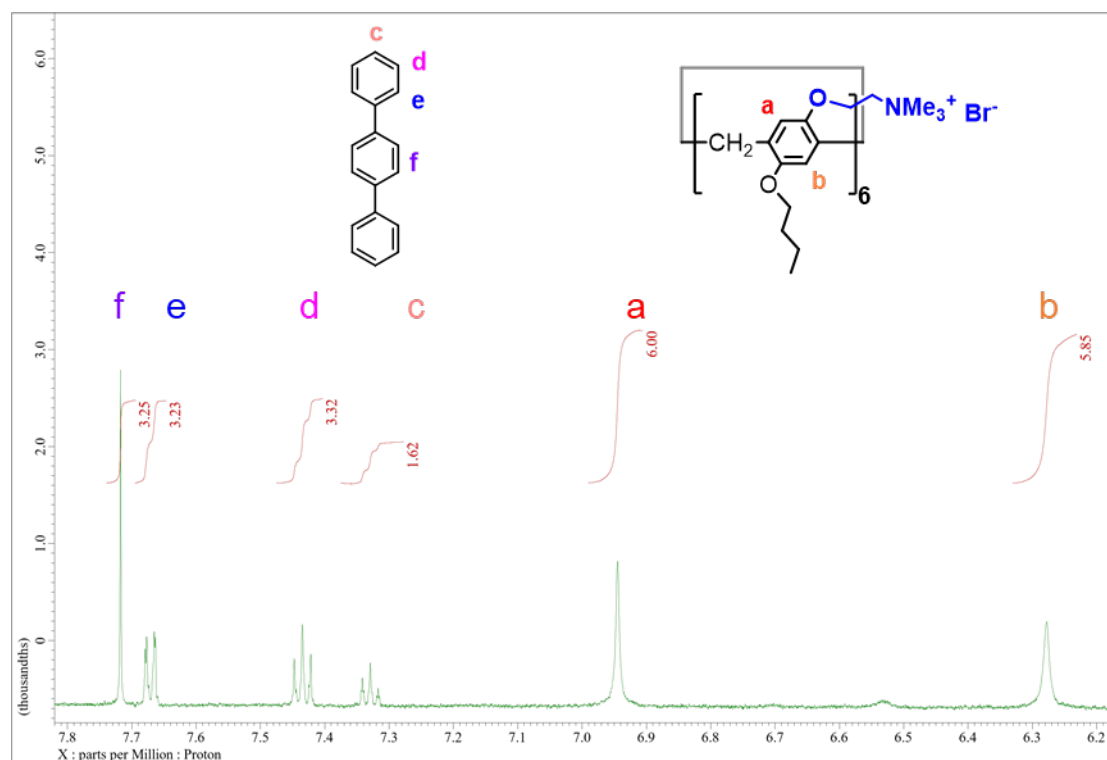


Figure S40. Partial ^1H NMR peaks and their integral values from ball-milling TP and AP-P6A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_f.

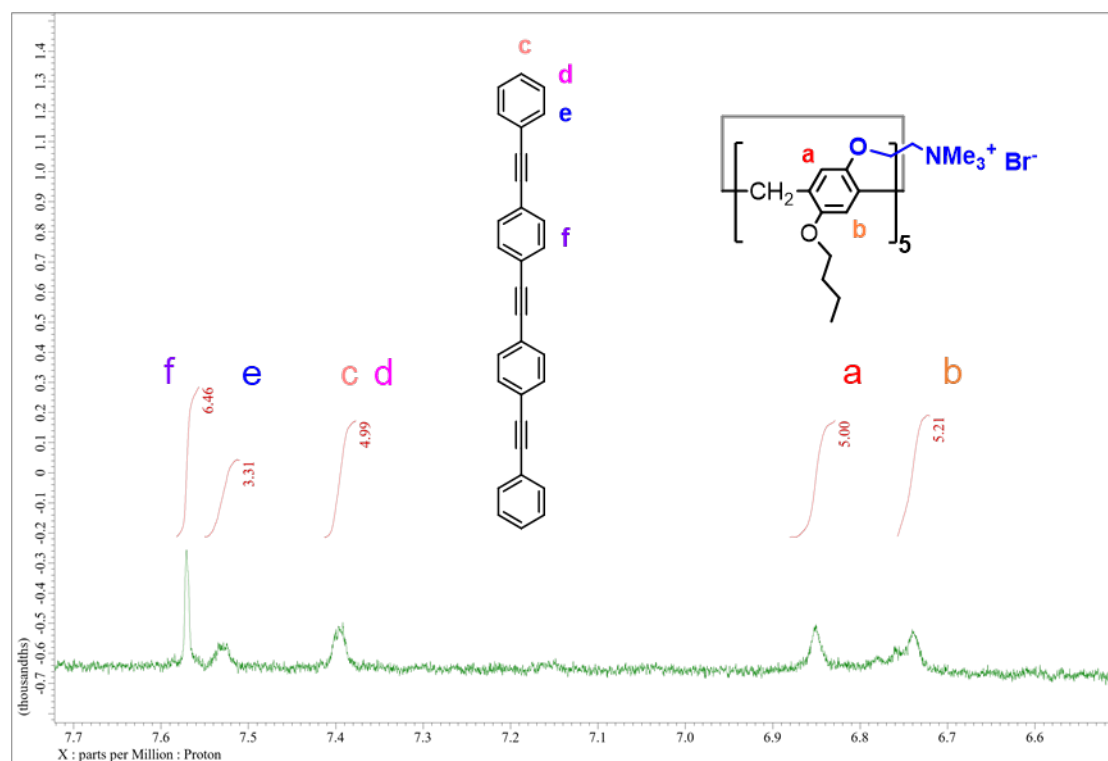


Figure S41. Partial ^1H NMR peaks and their integral values from ball-milling TPTE and AP-P5A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_f .

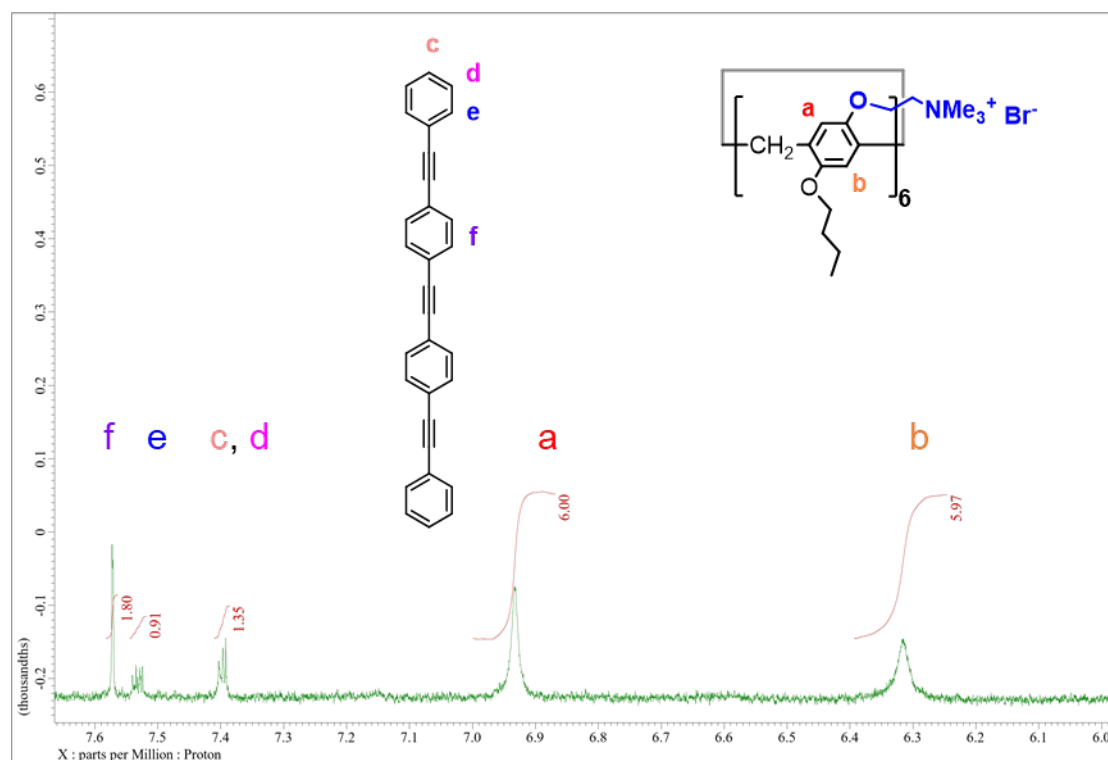


Figure S42. Partial ^1H NMR peaks and their integral values from ball-milling TPTE and AP-P6A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_f .

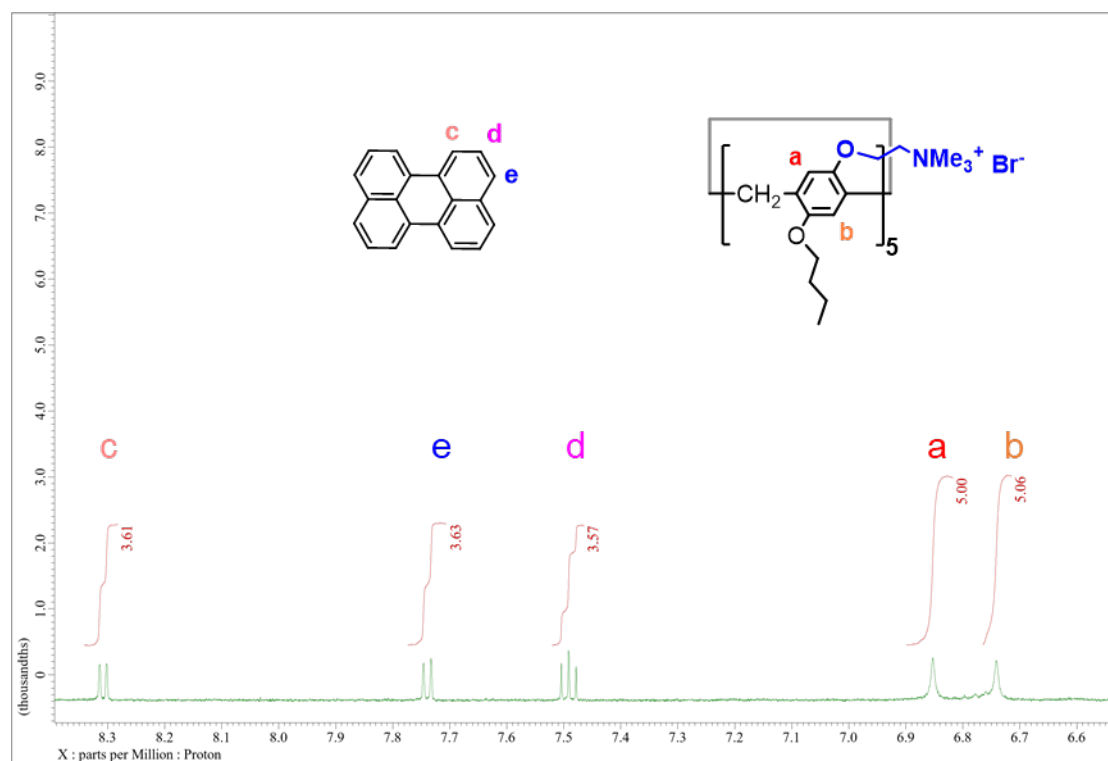


Figure S43. Partial ^1H NMR peaks and their integral values from ball-milling perylene and AP-P5A in $\text{DMSO-}d_6$. The G/H ratio was calculated from the integral values from H_a and H_c .

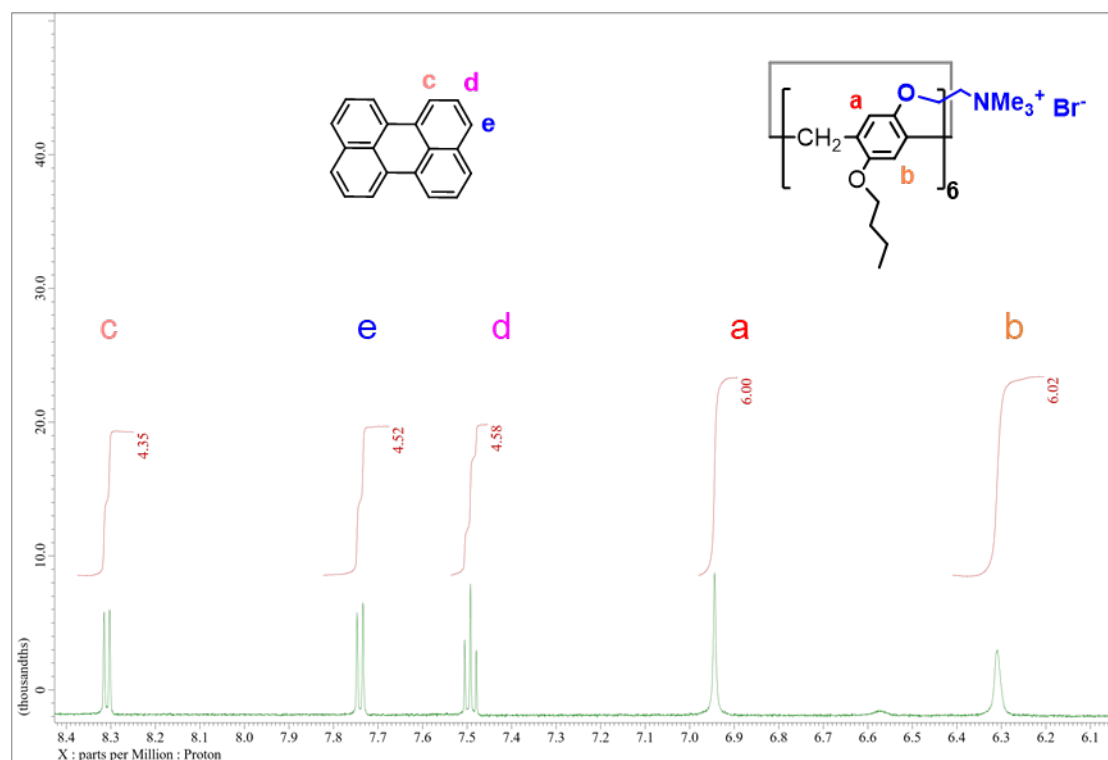


Figure S44. Partial ^1H NMR peaks and their integral values from ball-milling perylene and AP-P6A in $\text{DMSO-}d_6$. The G/H ratio was calculated from the integral values from H_a and H_c .

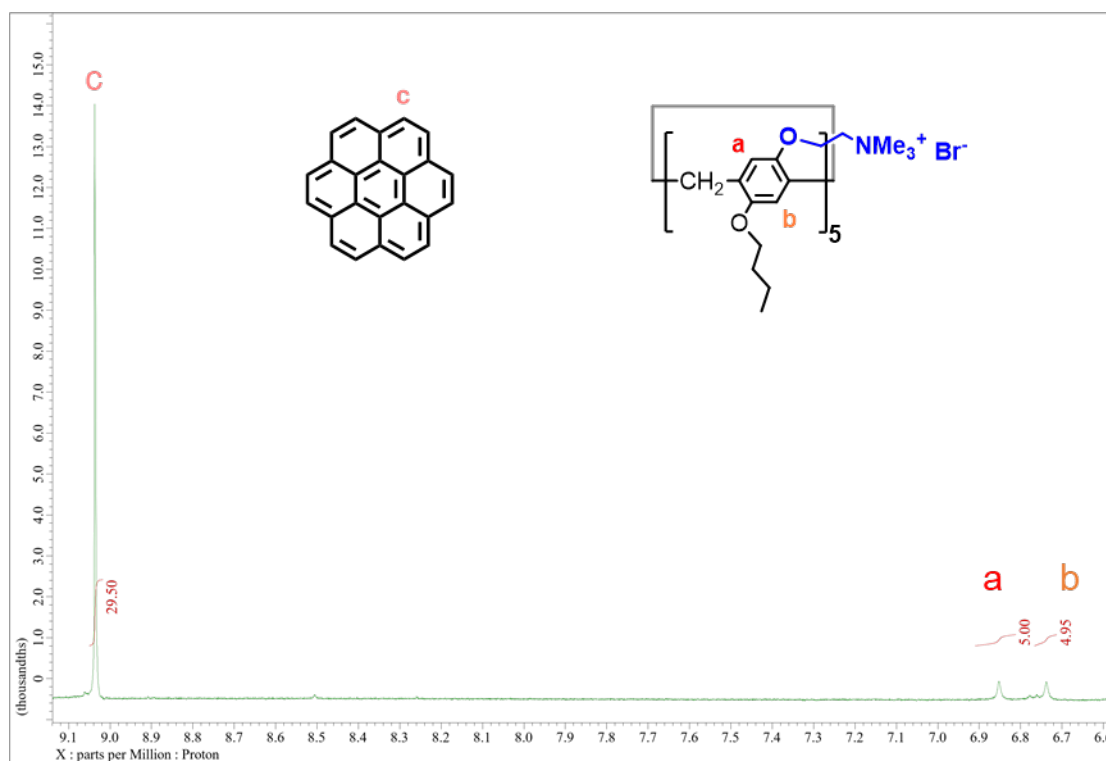


Figure S45. Partial ^1H NMR peaks and their integral values from ball-milling coronene and AP-P5A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_c .

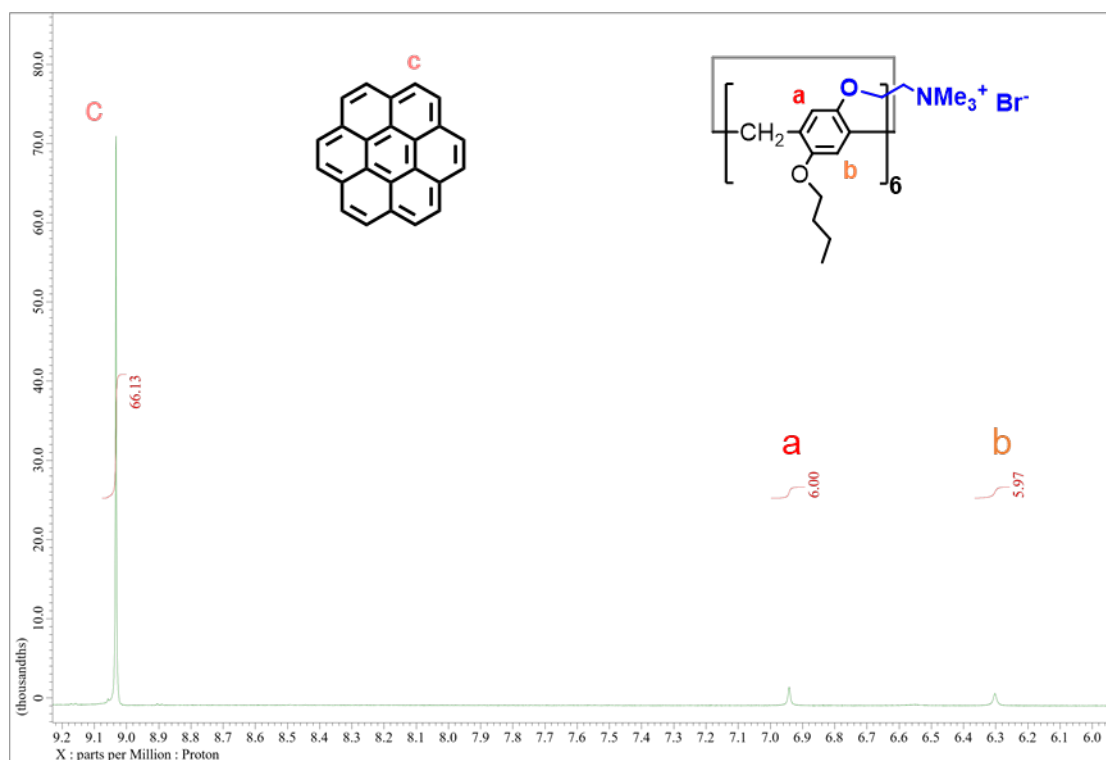


Figure S46. Partial ^1H NMR peaks and their integral values from ball-milling coronene and AP-P6A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_c .

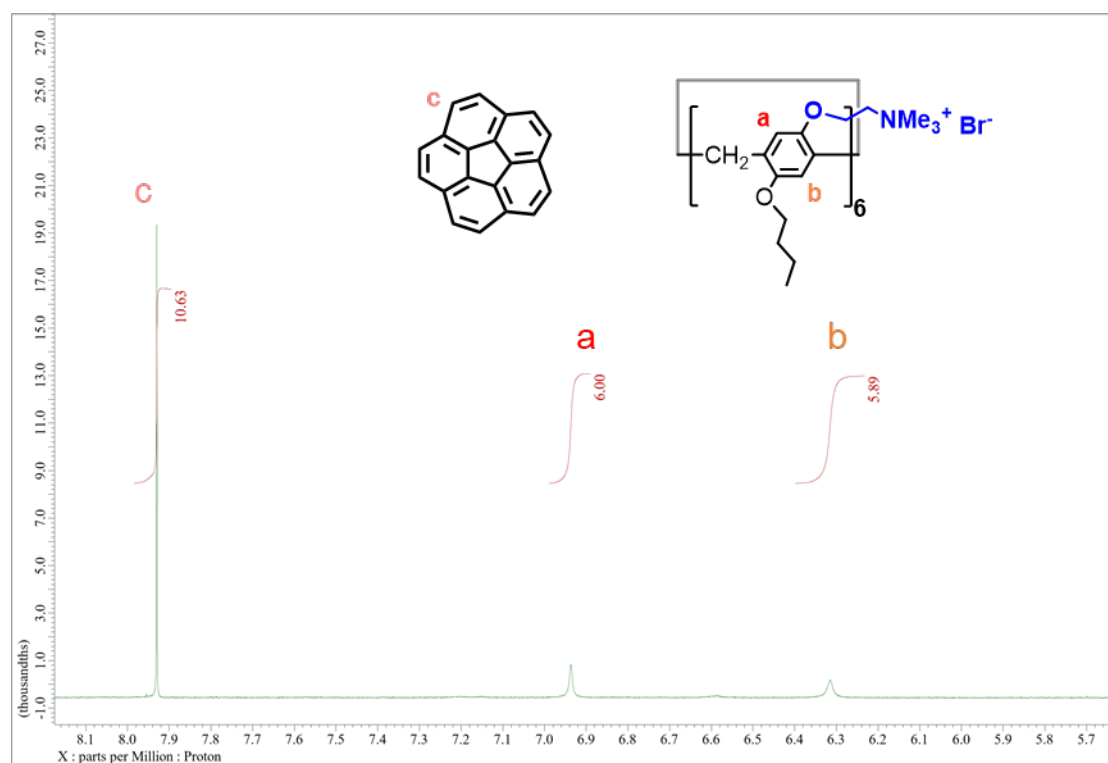


Figure S47. Partial ^1H NMR peaks and their integral values from ball-milling corannulene and AP-P6A in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_a and H_c .

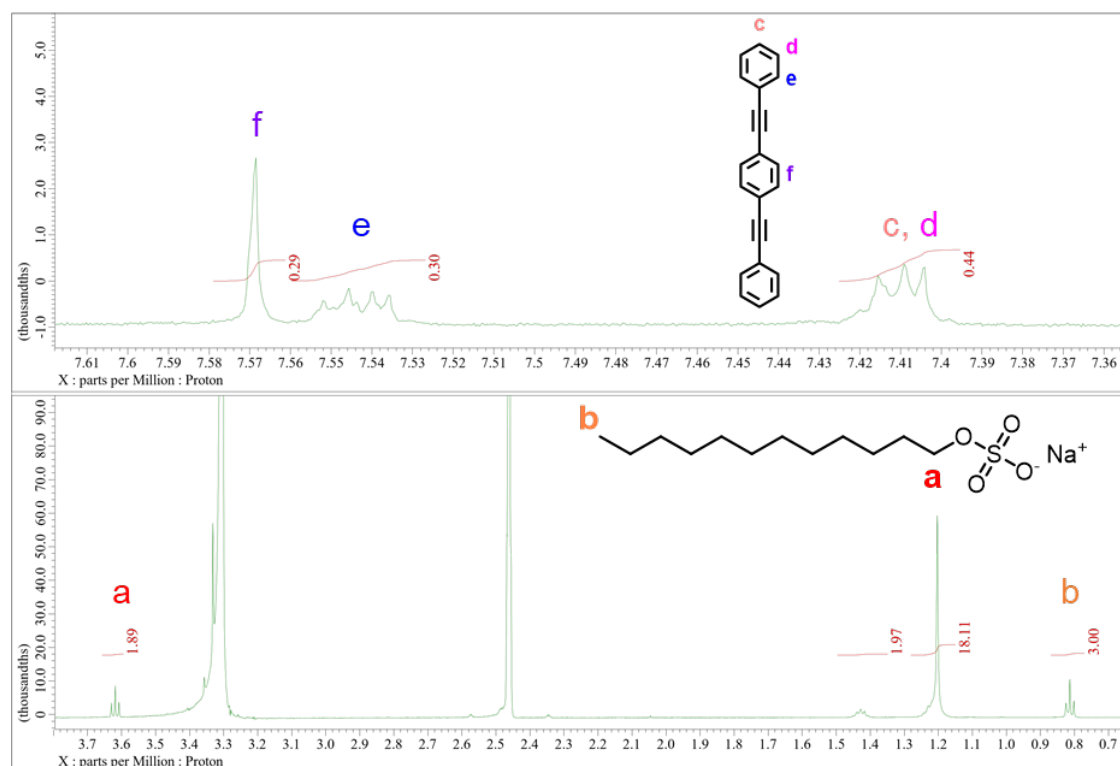


Figure S48. Partial ^1H NMR peaks and their integral values from ball-milling BPEB and SDS in $\text{DMSO}-d_6$. The G/H ratio was calculated from the integral values from H_b and H_f as 0.073/1.

Table S7. Host/guest ratios between pillar[*n*]arenes and different guests.

Guests	AP-P5A	AP-P6A
BPEB	1.0: 1.0	1.0: 0.94
BPEB + succinonitrile	1.0: 0.65	1.0: 0.80
BPEPE	1.0: 0.81	1.0: 0.23
TP	1.0: 1.0	1.0: 0.81
Perylene	1.0: 0.90	1.0: 1.1
Coronene	1.0: 2.5	1.0: 5.5
Corannulene	-	1.0: 1.1
Pyrene*	1.0: 0.066	1.0: 0.10

* Estimated from UV/vis spectrum.

6.2 Additional discussion about H/G ratios

Because ^1H NMR signals from pyrene were not observed, the host/guest ratios were estimated from the UV/vis spectrum by the absorbance at 290 nm for pillar[*n*]arenes and 335 nm. And the ratios were smaller than 10: 1. The peaks for other guests, anthracene and tetracene were also not observed in ^1H NMR, probably resulted from their low stoichiometric ratios. And the ratios were difficult to be calculated from UV/vis spectra due to the overlap in absorption peaks.

It is tricky to evaluate the binding strengths of pillar[*n*]arenes towards different guests from the H/G ratios, because the ratios were largely affected by the solid packing of guests themselves. However, the difference between **AP-P5A** and **AP-P6A** can be roughly evaluated within the same guest. Although **AP-P5A** and **AP-P6A** showed close ratios towards BPEB, the ratio for **AP-P5A** largely decreased with competitive guest, and the ratio for **AP-P6A** only slightly decreased. This was resulted from that **AP-P5A** bound more strongly with competitive guest than **AP-P6A** did due to the matching size of the internal cavity. The effect from internal cavity can also be observed with TP and BPEPE, while **AP-P5A** showed larger ratio than **AP-P6A** did. For bulky guest ratios for **AP-P6A** were larger than those from **AP-P5A**, resulting from the larger external pockets.

6.3 UV/visible and fluorescence spectra

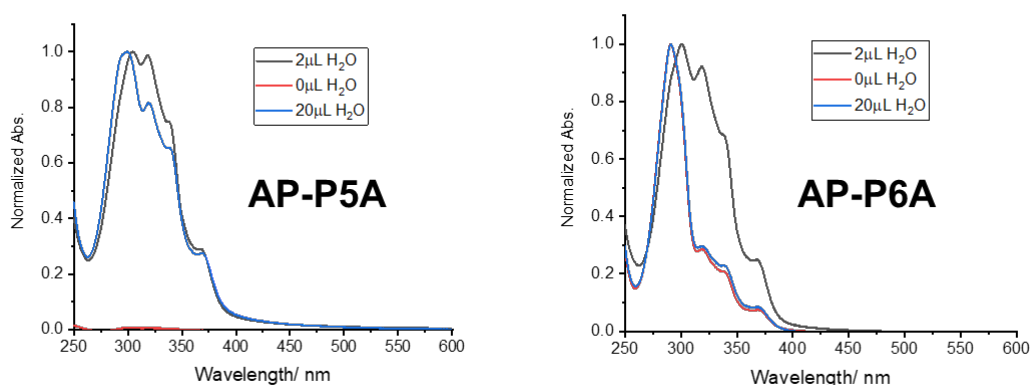


Figure S49. Normalized UV/visible spectra of after ball-milling protocol involving BPEB and pillar[*n*]arenes with different volumes of water as additives. Without water, the milling of **AP-P5A** and BPEB gave insoluble solid.

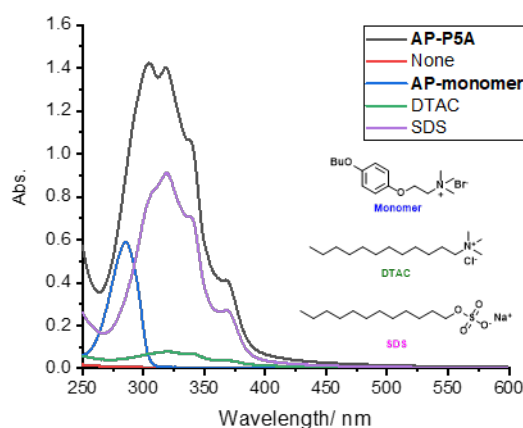


Figure S50. UV/visible spectra after ball-milling protocol involving BPEB and different surfactants. Higher UV absorbance of guest was observed with **AP-P5A** than other commercial surfactants. SDS showed the highest efficiency among the other non-macrocyclic surfactants; therefore, its guest/host ratio was calculated using ¹H NMR (Figure S48). The ratio (0.073) between SDS and BPEB was much smaller than that between **AP-P5A** and BPEB (1.0). These results implied the advantage from pre-organized hydrophobic pockets.

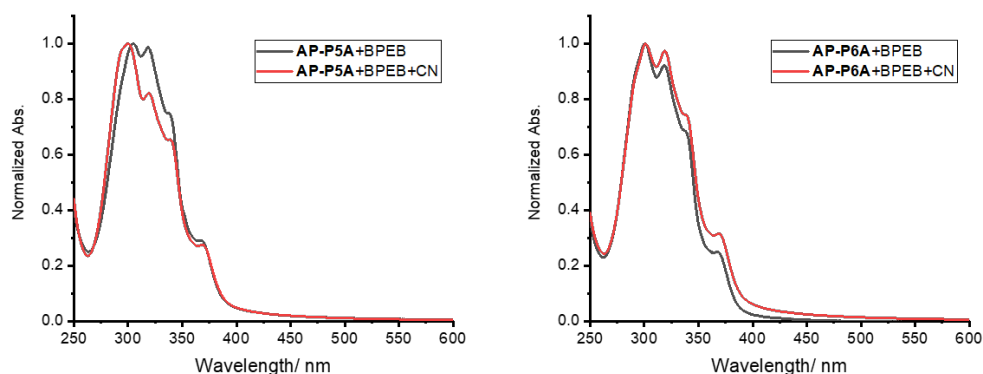


Figure S51. Normalized UV/visible spectra of after ball-milling protocol involving BPEB and pillar[n]arenes with or without succinonitrile (CN).

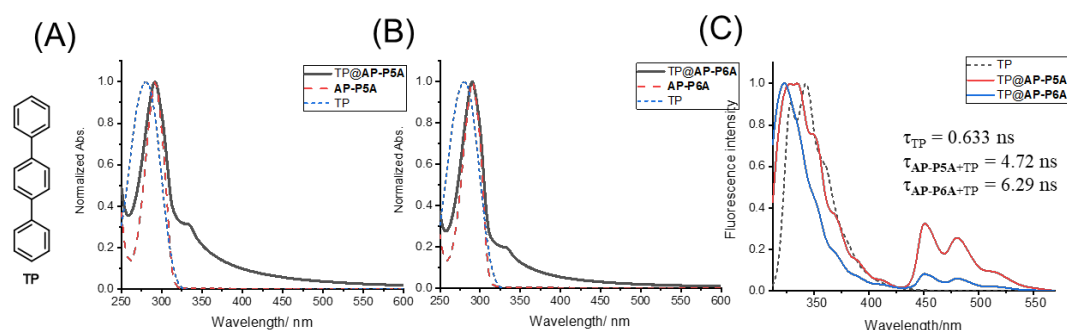


Figure S52. (A) Normalized UV/visible spectra of TP@AP-P5A (H₂O), AP-P5A (H₂O), and TP (CHCl₃). (B) Normalized UV/visible spectra of TP@AP-P6A (H₂O), AP-P6A (H₂O), and TP (CHCl₃). (C) Normalized fluorescence spectra ($\lambda_{ex} = 292$ nm) of TP (CHCl₃), TP@AP-P5A (H₂O), and TP@AP-P6A (H₂O). Fluorescence lifetime of TP was monitored at 350 nm; fluorescence lifetimes of TP@AP-P5A and TP@AP-P6A were monitored at 475 nm.

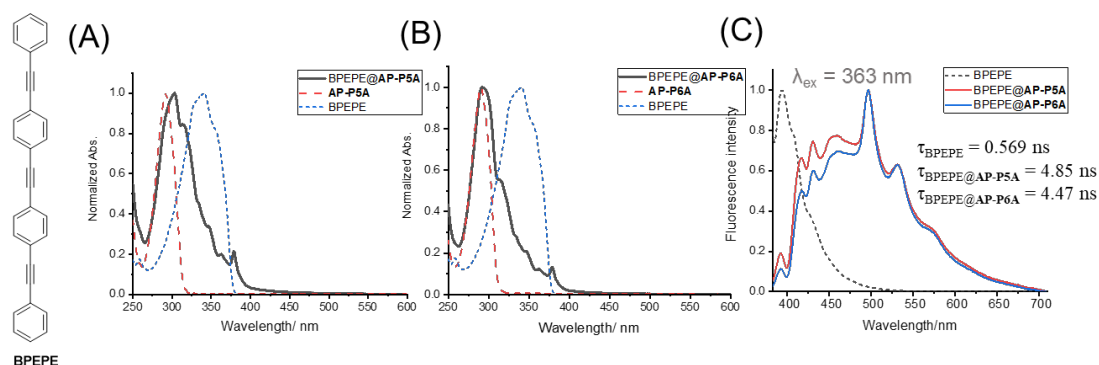


Figure S53. (A) Normalized UV/visible spectra of BPEPE@AP-P5A (H₂O), AP-P5A (H₂O), and BPEPE (CHCl₃). (B) Normalized UV/visible spectra of BPEPE@AP-P6A (H₂O), AP-P6A (H₂O), and BPEPE (CHCl₃). (C) Normalized fluorescence spectra ($\lambda_{ex} = 363$ nm) of BPEPE (CHCl₃), BPEPE@AP-P5A (H₂O), and BPEPE@AP-P6A (H₂O).

Fluorescence lifetime of BPEPE was monitored at 405 nm; fluorescence lifetimes of BPEPE@AP-P5A and BPEPE@AP-P6A were monitored at 500 nm.

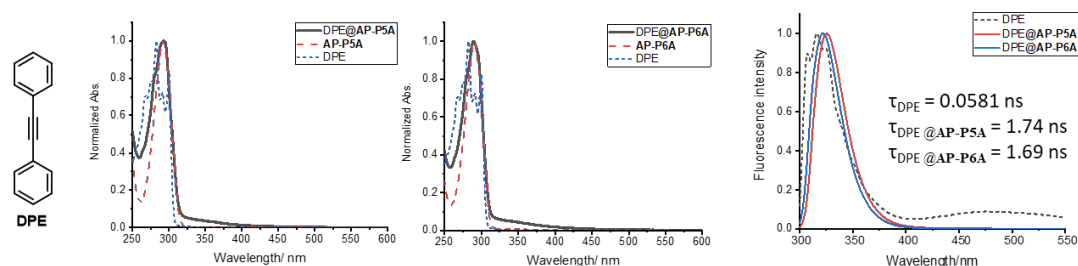


Figure S54. (A) Normalized UV/visible spectra of DPE@AP-P5A (H₂O), AP-P5A (H₂O), and DPE (CHCl₃). (B) Normalized UV/visible spectra of DPE@AP-P6A (H₂O), AP-P6A (H₂O), and DPE (CHCl₃). (C) Normalized fluorescence spectra (λ_{ex} = 280 nm) of DPE (CHCl₃), DPE@AP-P5A (H₂O), and DPE@AP-P6A (H₂O). Fluorescence lifetimes were monitored at 330 nm, the values were close to the results of AP-pillar[n]arenes (Figure S24).

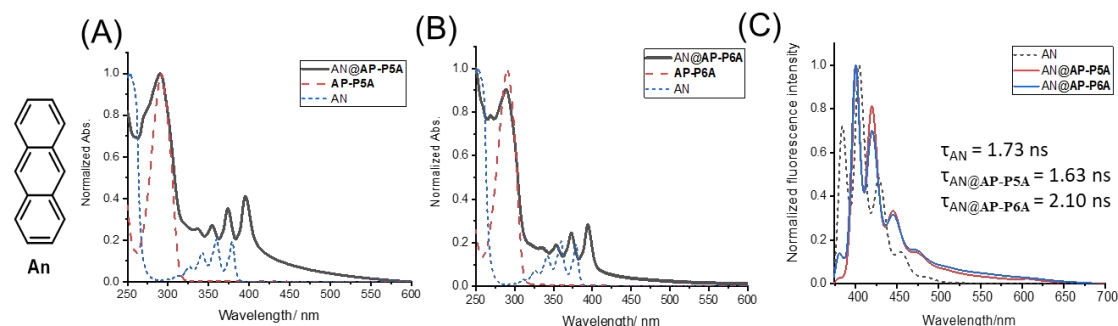


Figure S55. (A) Normalized UV/visible spectra of AN@AP-P5A (H₂O), AP-P5A (H₂O), and AN (CHCl₃). (B) Normalized UV/visible spectra of AN@AP-P6A (H₂O), AP-P6A (H₂O), and AN (CHCl₃). (C) Normalized fluorescence spectra (λ_{ex} = 354 nm) of AN (CHCl₃), AN@AP-P5A (H₂O), and AN@AP-P6A (H₂O). Fluorescence lifetime of AN was monitored at 400 nm; fluorescence lifetimes of AN@AP-P5A and AN@AP-P6A were monitored at 450 nm.

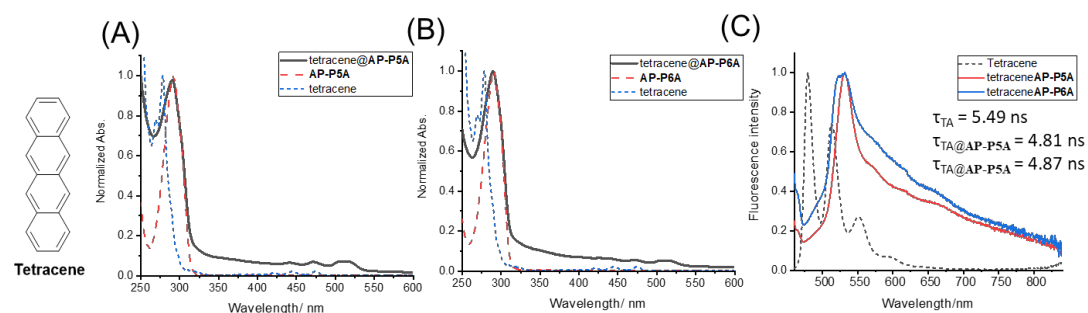


Figure S56. (A) Normalized UV/visible spectra of tetracene@AP-P5A (H₂O), AP-P5A (H₂O), and tetracene (CHCl₃). (B) Normalized UV/visible spectra of tetracene@AP-P6A (H₂O), AP-P6A (H₂O), and tetracene (CHCl₃). (C) Normalized fluorescence

spectra ($\lambda_{\text{ex}} = 440 \text{ nm}$) of tetracene (CHCl_3), tetracene@AP-P5A (H_2O), and tetracene@AP-P6A (H_2O). Fluorescence lifetime of tetracene was monitored at 480 nm; fluorescence lifetimes of tetracene@AP-P5A and tetracene@AP-P6A were monitored at 530 nm.

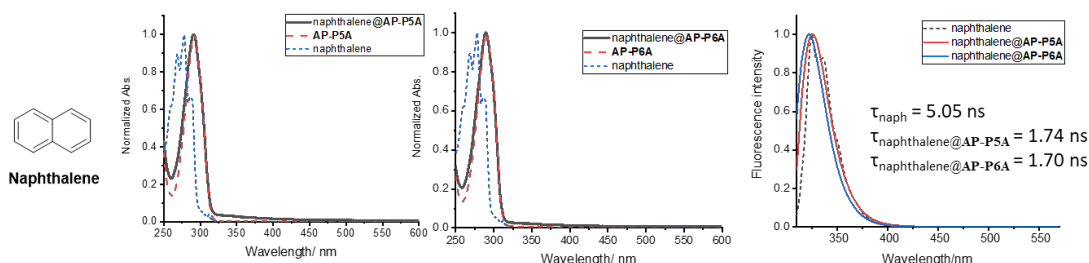


Figure S57. (A) Normalized UV/visible spectra of naphthalene@AP-P5A (H_2O), AP-P5A (H_2O), and naphthalene (CHCl_3). (B) Normalized UV/visible spectra of naphthalene@AP-P6A (H_2O), AP-P6A (H_2O), and naphthalene (CHCl_3). (C) Normalized fluorescence spectra ($\lambda_{\text{ex}} = 290 \text{ nm}$) of naphthalene (CHCl_3), naphthalene@AP-P5A (H_2O), and naphthalene@AP-P6A (H_2O). Fluorescence lifetimes were monitored at 330 nm, and the values were close to the results of AP-pillar[n]arenes (Figure S24).

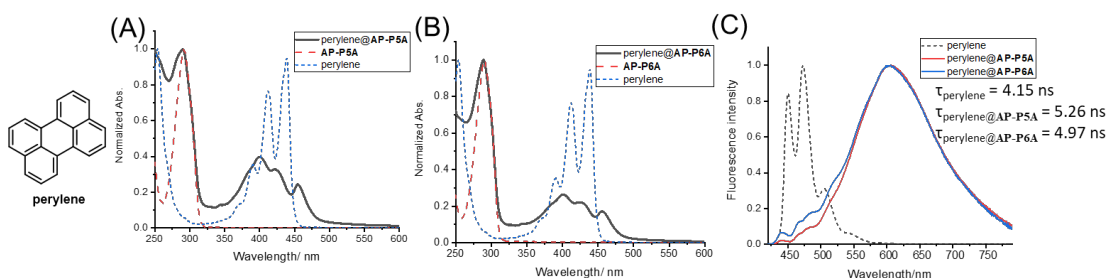


Figure S58. (A) Normalized UV/visible spectra of perylene@AP-P5A (H_2O), AP-P5A (H_2O), and perylene (CHCl_3). (B) Normalized UV/visible spectra of perylene@AP-P6A (H_2O), AP-P6A (H_2O), and perylene (CHCl_3). (C) Normalized fluorescence spectra ($\lambda_{\text{ex}} = 400 \text{ nm}$) of perylene (CHCl_3), perylene@AP-P5A (H_2O), and perylene@AP-P6A (H_2O). Fluorescence lifetime of perylene was monitored at 480 nm; fluorescence lifetimes of perylene@AP-P5A and perylene@AP-P6A were monitored at 600 nm.

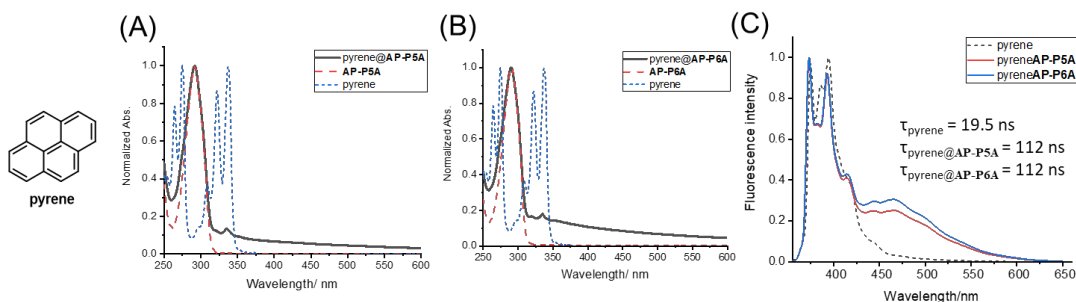


Figure S59. (A) Normalized UV/visible spectra of pyrene@AP-P5A (H₂O), AP-P5A (H₂O), and pyrene (CHCl₃). (B) Normalized UV/visible spectra of pyrene@AP-P6A (H₂O), AP-P6A (H₂O), and pyrene (CHCl₃). (C) Normalized fluorescence spectra (λ_{ex} = 335 nm) of pyrene (CHCl₃), pyrene@AP-P5A (H₂O), and pyrene@AP-P6A (H₂O). Fluorescence lifetimes were monitored at 400 nm.

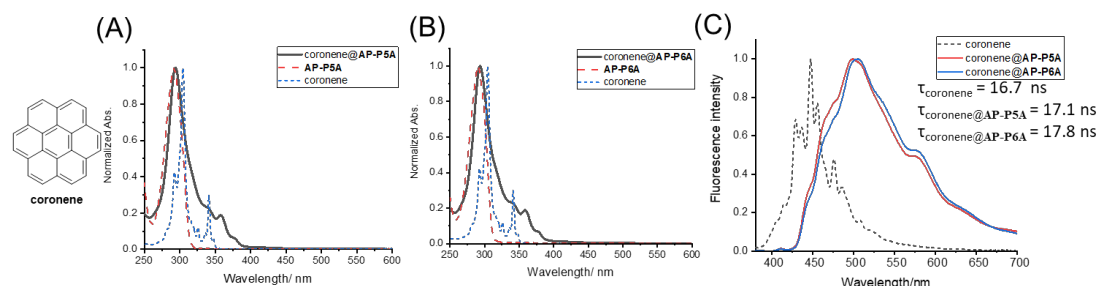


Figure S60. (A) Normalized UV/visible spectra of coronene@AP-P5A (H₂O), AP-P5A (H₂O), and coronene (CHCl₃). (B) Normalized UV/visible spectra of coronene@AP-P6A (H₂O), AP-P6A (H₂O), and coronene (CHCl₃). (C) Normalized fluorescence spectra (λ_{ex} = 360 nm) of coronene (CHCl₃), coronene@AP-P5A (H₂O), and coronene@AP-P6A (H₂O). Fluorescence lifetime of coronene was monitored at 450 nm; fluorescence lifetimes of coronene@AP-P5A and coronene@AP-P6A were monitored at 520 nm.

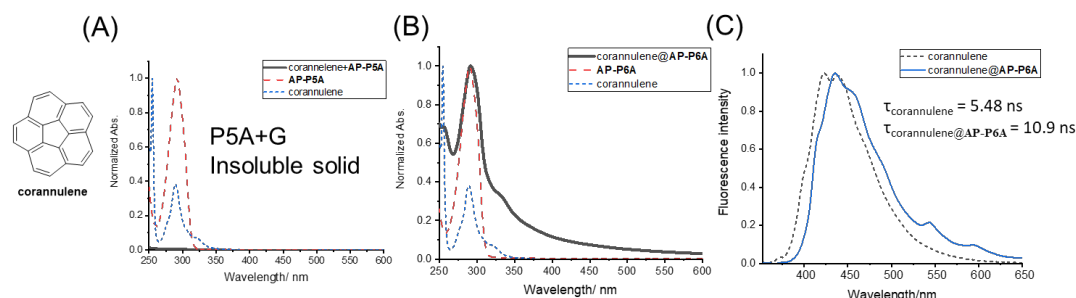


Figure S61. (A) Normalized UV/visible spectra of corannulene@AP-P5A (H₂O), AP-P5A (H₂O), and corannulene (CHCl₃). (B) Normalized UV/visible spectra of corannulene@AP-P6A (H₂O), AP-P6A (H₂O), and coronene (CHCl₃). (C) Normalized fluorescence spectra (λ_{ex} = 333 nm) of corannulene (CHCl₃), and corannulene@AP-P6A (H₂O). Fluorescence lifetimes were monitored at 440 nm.

7. Characterization of the assembly after ball-milling

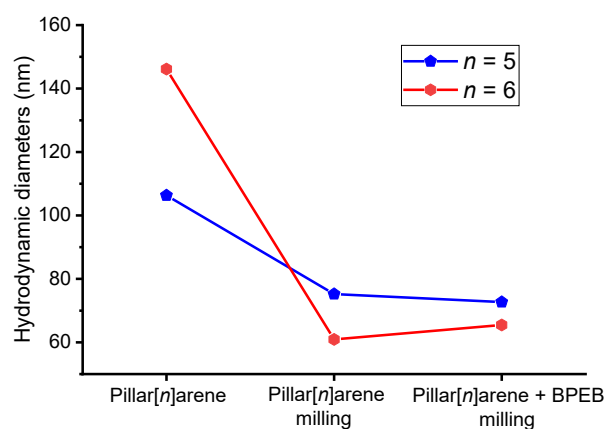


Figure S62. Summary of the hydrodynamic diameters before and after ball-milling from DLS measurements (approximately 0.1 mM based on pillar[n]arenes). After milling pillar[n]arenes, the diameters decreased, indicating that the sheets were crushed into smaller species. The sizes hardly changed when milling pillar[n]arenes with BPEB, suggesting the small change in assembly morphologies.

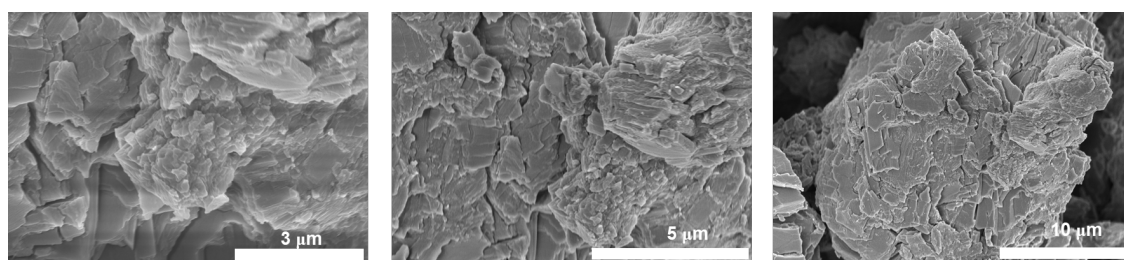


Figure S63. SEM images for AP-P5A after ball-milling.

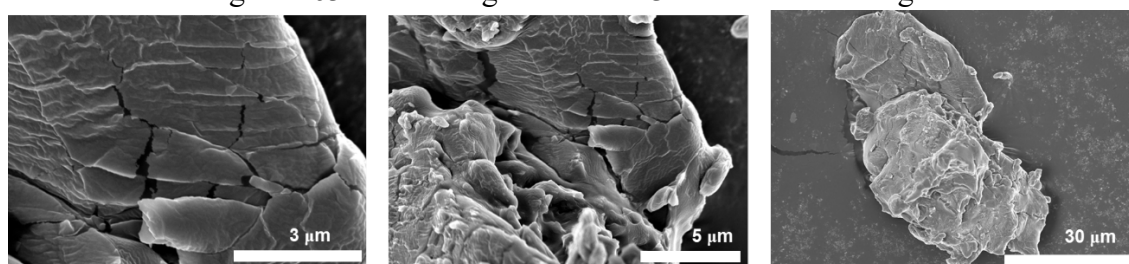


Figure S64. SEM images for AP-P6A after ball-milling.

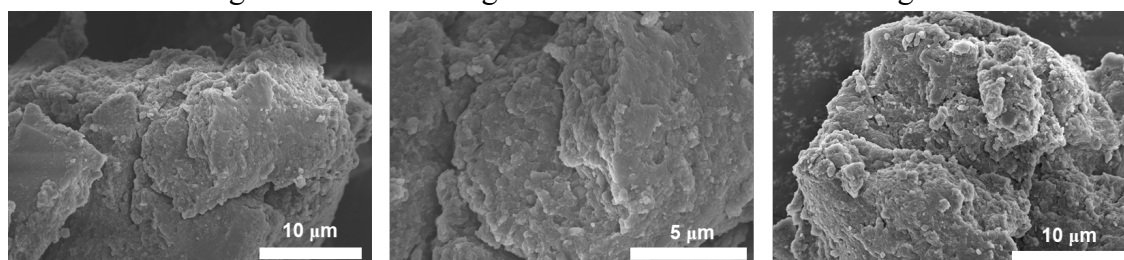


Figure S65. SEM images for solids obtained from the mixture of AP-P5A and BPEB after ball-milling.

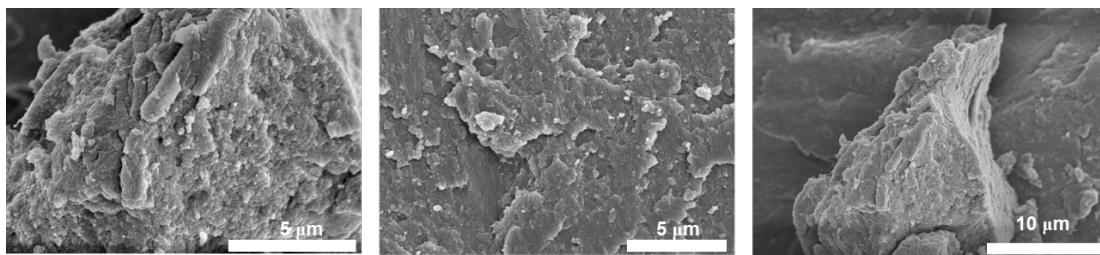


Figure S66. SEM images for solids obtained from the mixture of **AP-P6A** and BPEB after ball-milling.

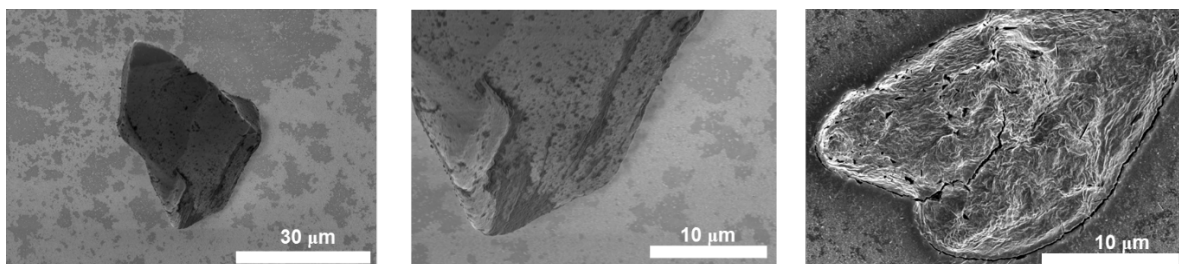


Figure S67. SEM images for aqueous dispersion (approximately 0.2 mM based on **AP-P5A**) from the mixture of **AP-P5A** and BPEB after ball-milling.

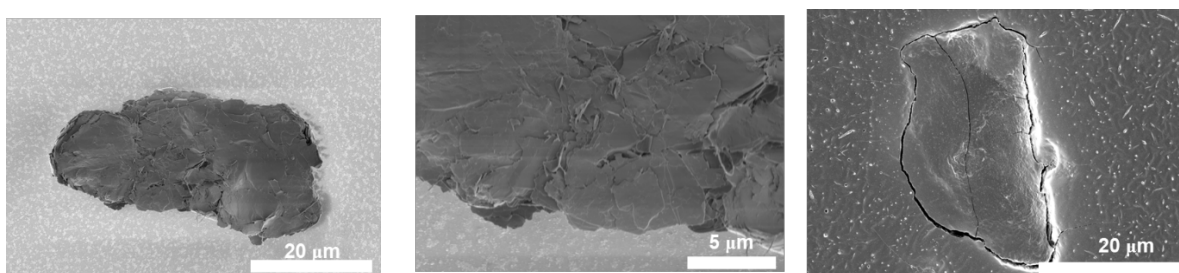


Figure S68. SEM images for aqueous dispersion (approximately 0.2 mM based on **AP-P6A**) from the mixture of **AP-P6A** and BPEB after ball-milling.

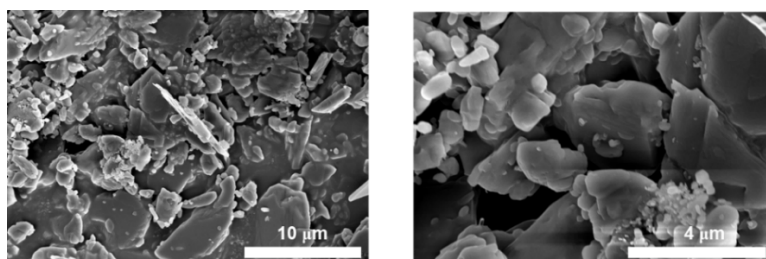


Figure S69. SEM images for commercial BPEB.

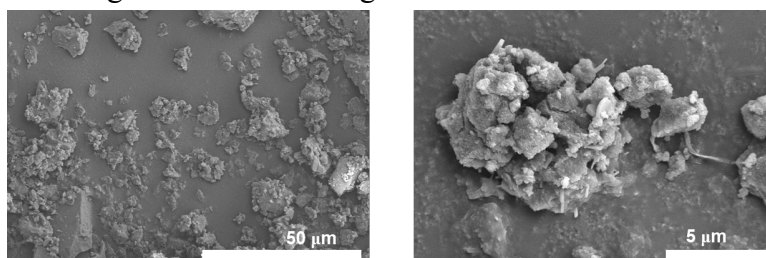


Figure S70. SEM images for BPEB after ball-milling.

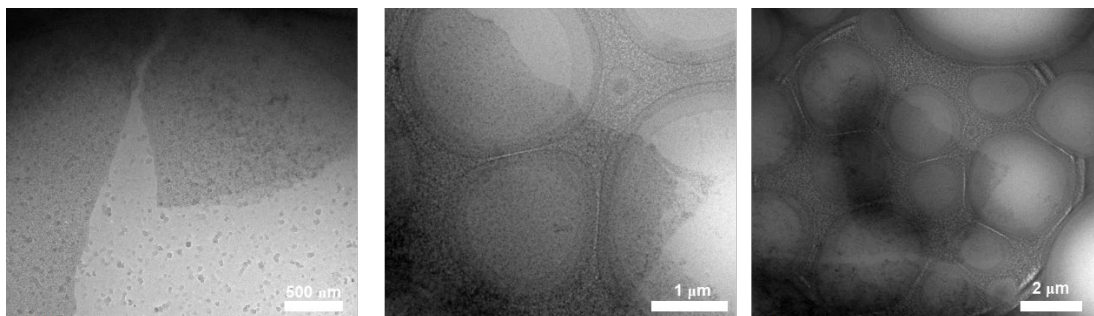


Figure S71. Cryo-TEM images for aqueous dispersion (approximately 10 mM based on **AP-P5A**) from the mixture of **AP-P5A** and BPEB after ball-milling.

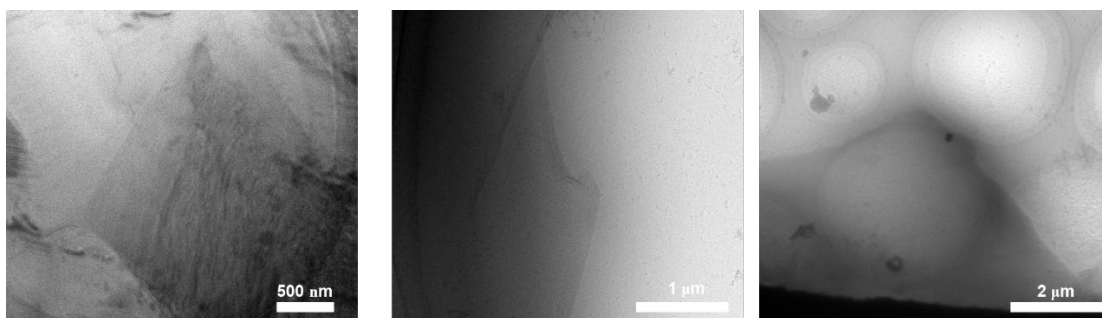


Figure S72. Cryo-TEM images for aqueous dispersion (approximately 10 mM based on **AP-P6A**) from the mixture of **AP-P6A** and BPEB after ball-milling.

8. NMR data

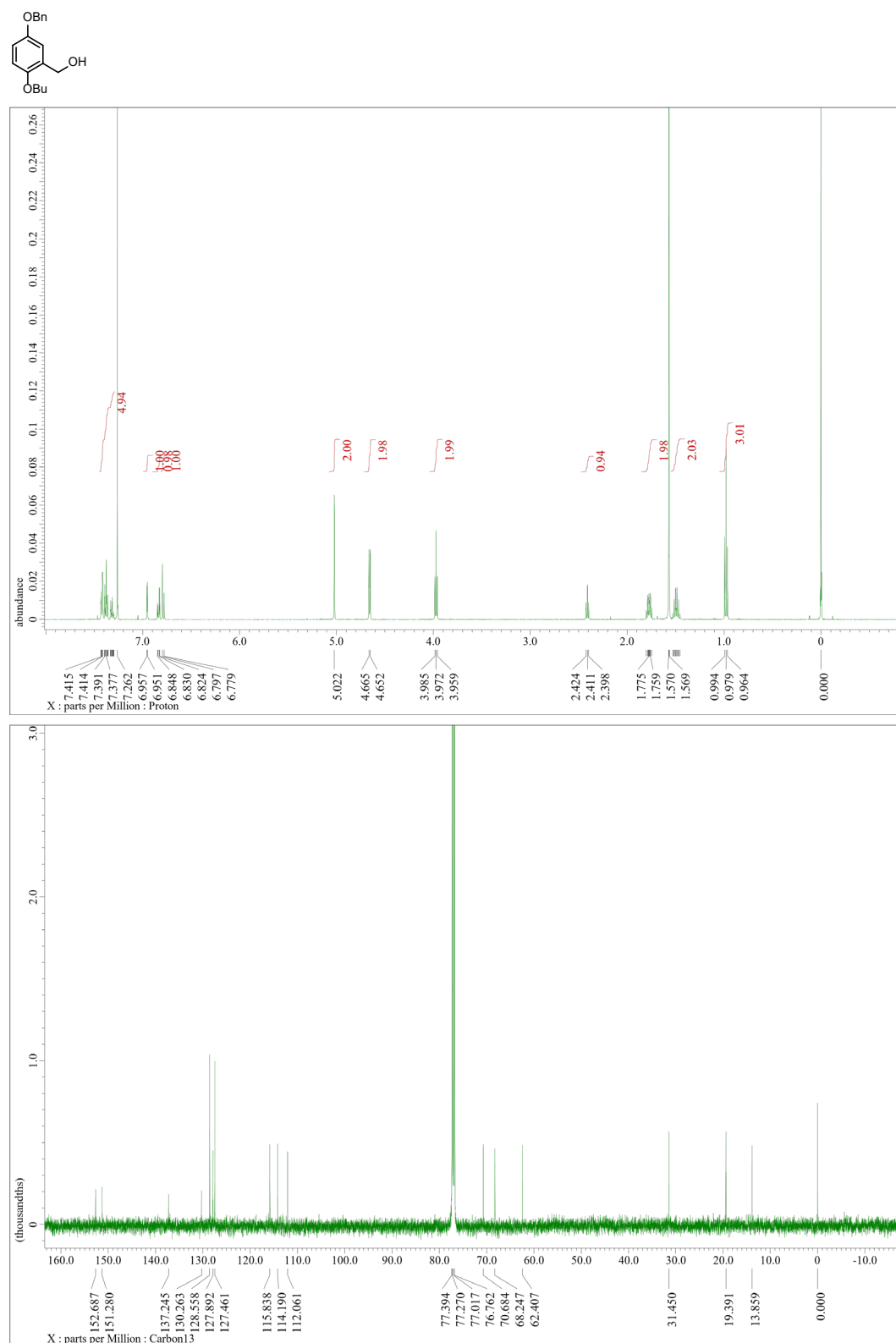


Figure S73. ¹H and ¹³C NMR spectra of **1** (500 MHz, CDCl₃, 298 K).

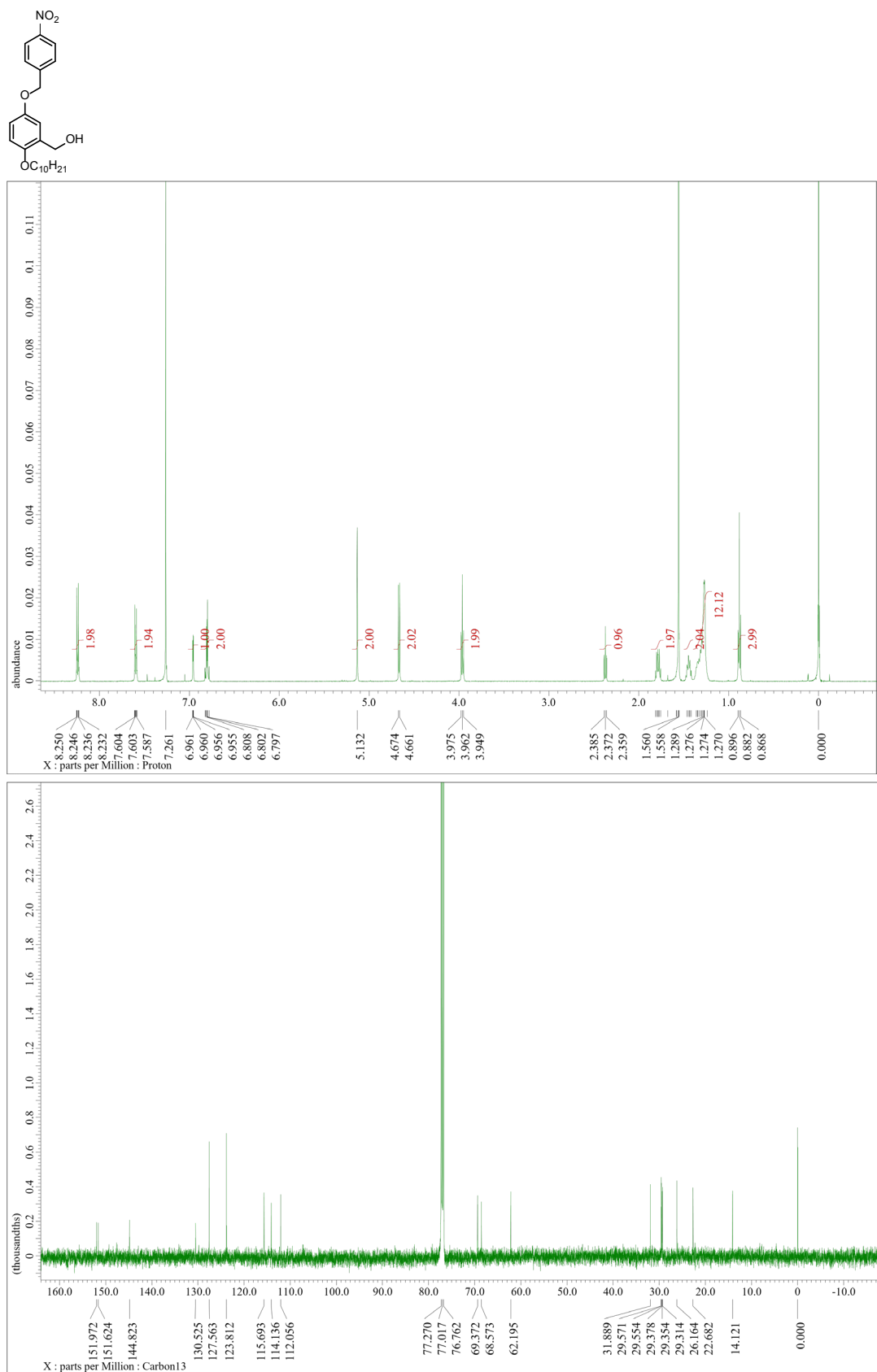


Figure S74. ¹H and ¹³C NMR spectra of **1-C10** (500 MHz, CDCl₃, 298 K).

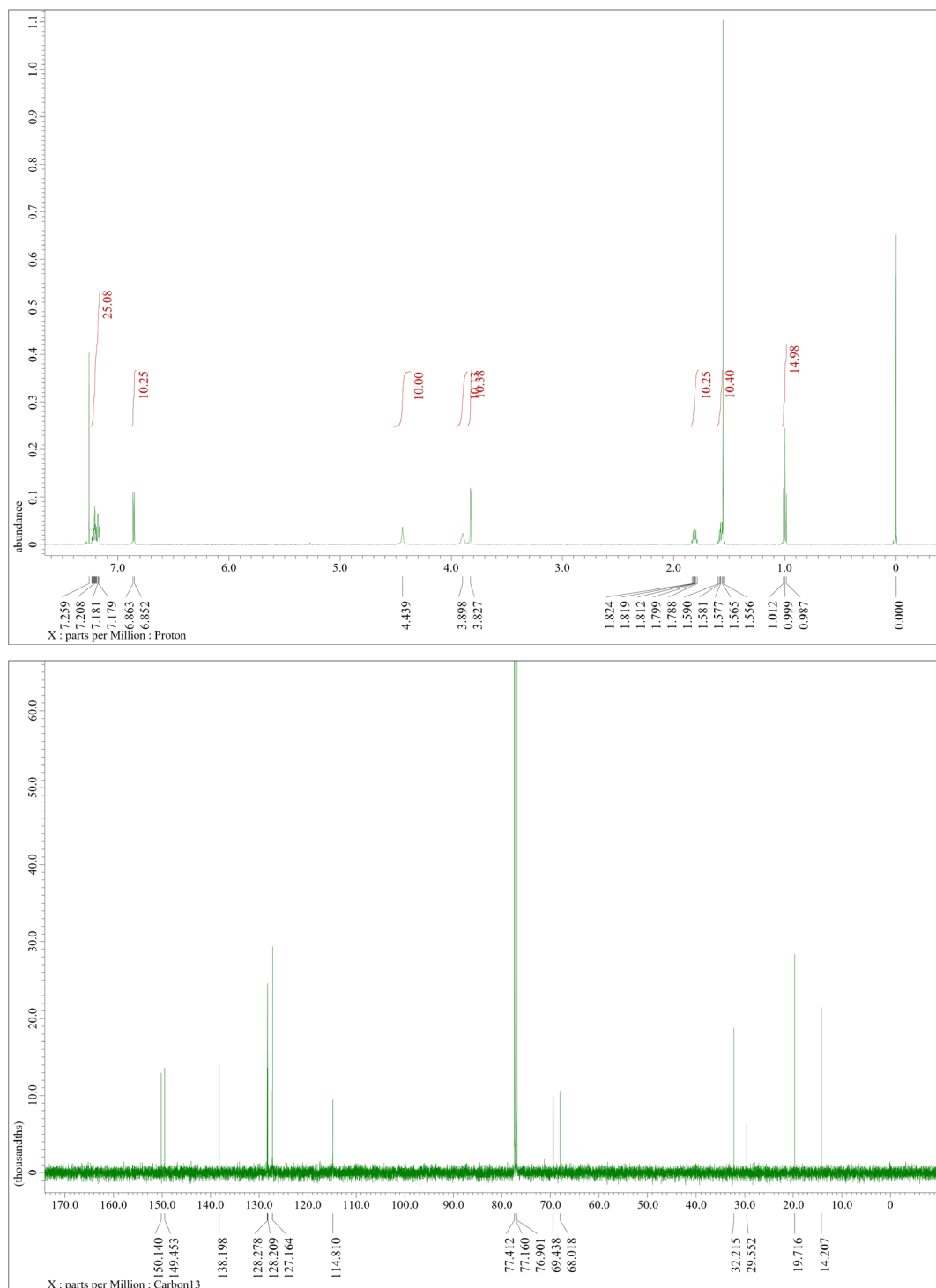


Figure S75. ^1H and ^{13}C NMR spectra of **2a** (500 MHz, CDCl_3 , 298 K).

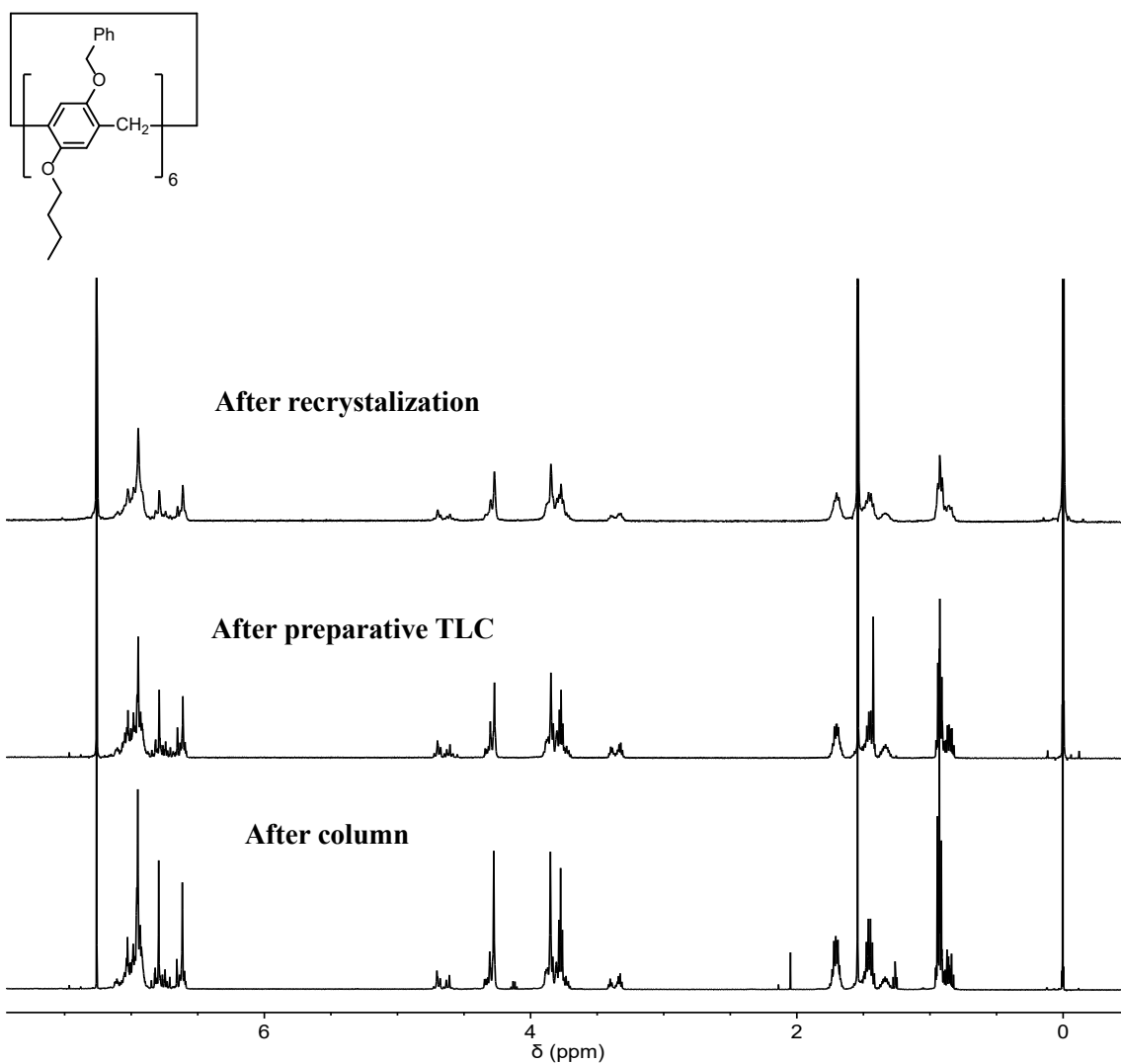


Figure S76. Crude ¹H NMR spectra of **2b** after different purification methods (500 MHz, CDCl₃, 298 K).

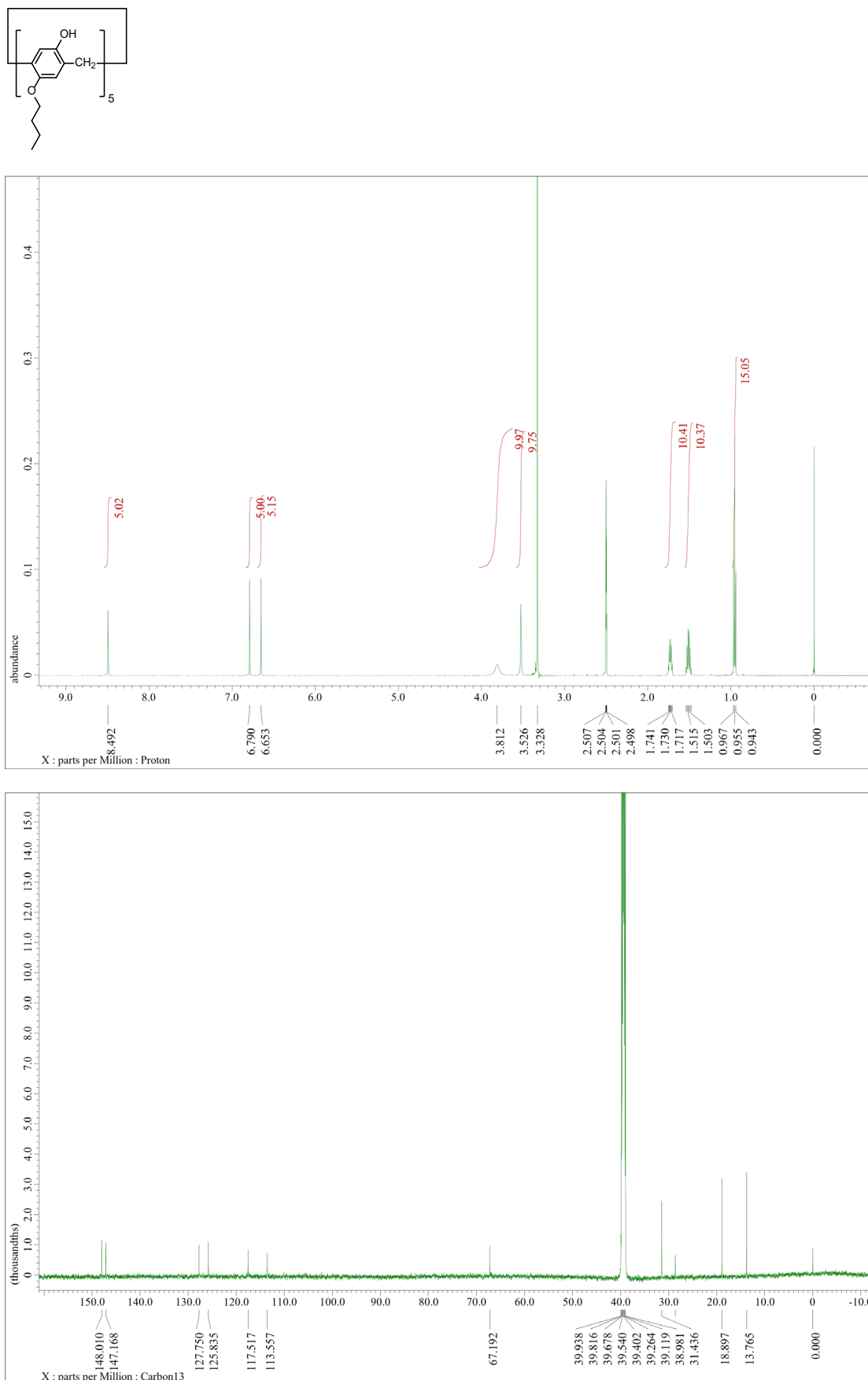


Figure S77. ¹H and ¹³C NMR spectra of **3a** (500 MHz, DMSO-*d*₆, 298 K).

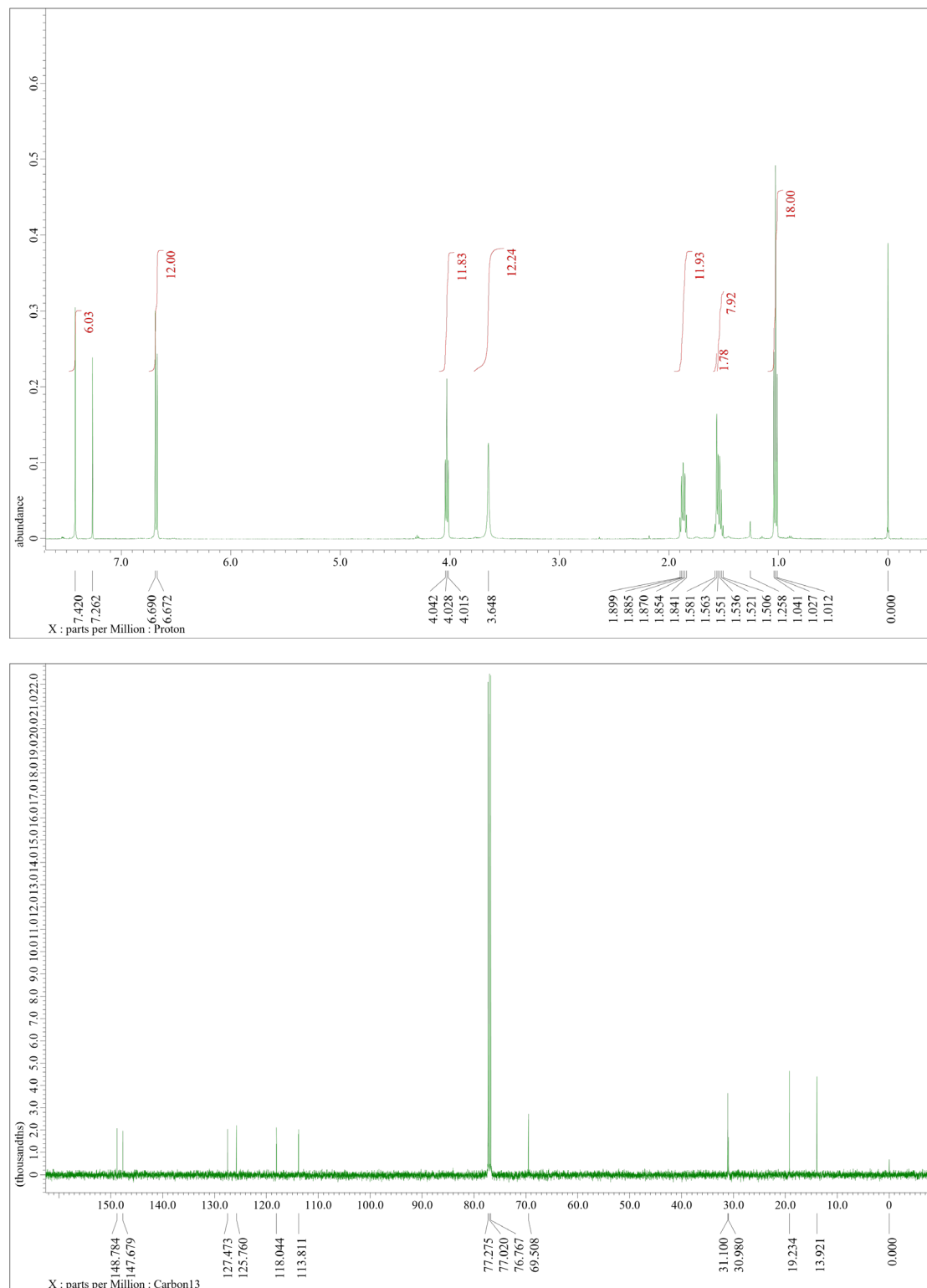
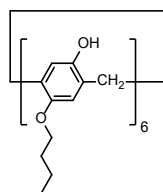


Figure S78. ¹H and ¹³C NMR spectra of **3b** (500 MHz, CDCl₃, 298 K).

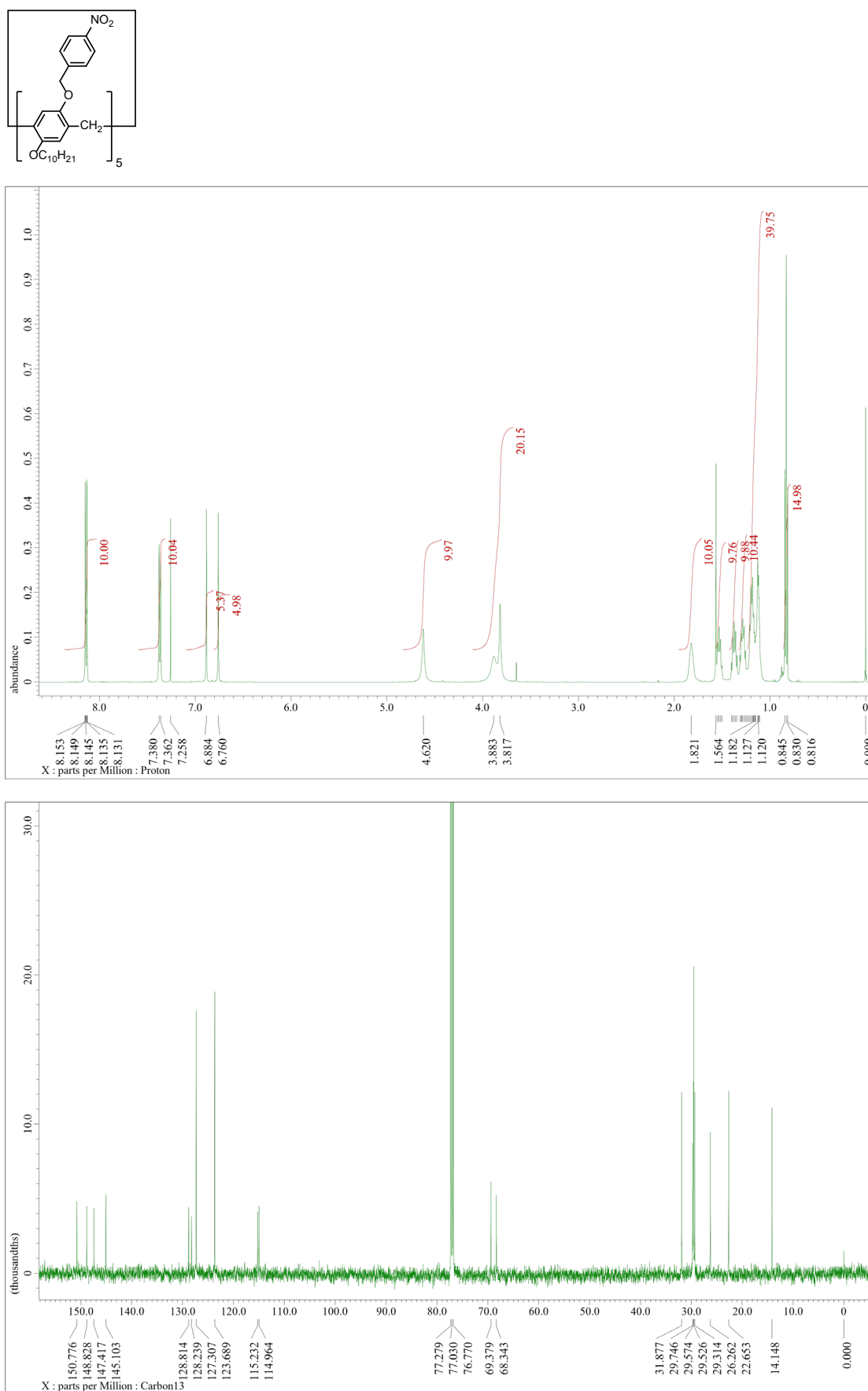


Figure S79. ¹H and ¹³C NMR spectra of **2a-C10** (500 MHz, CDCl₃, 298 K).

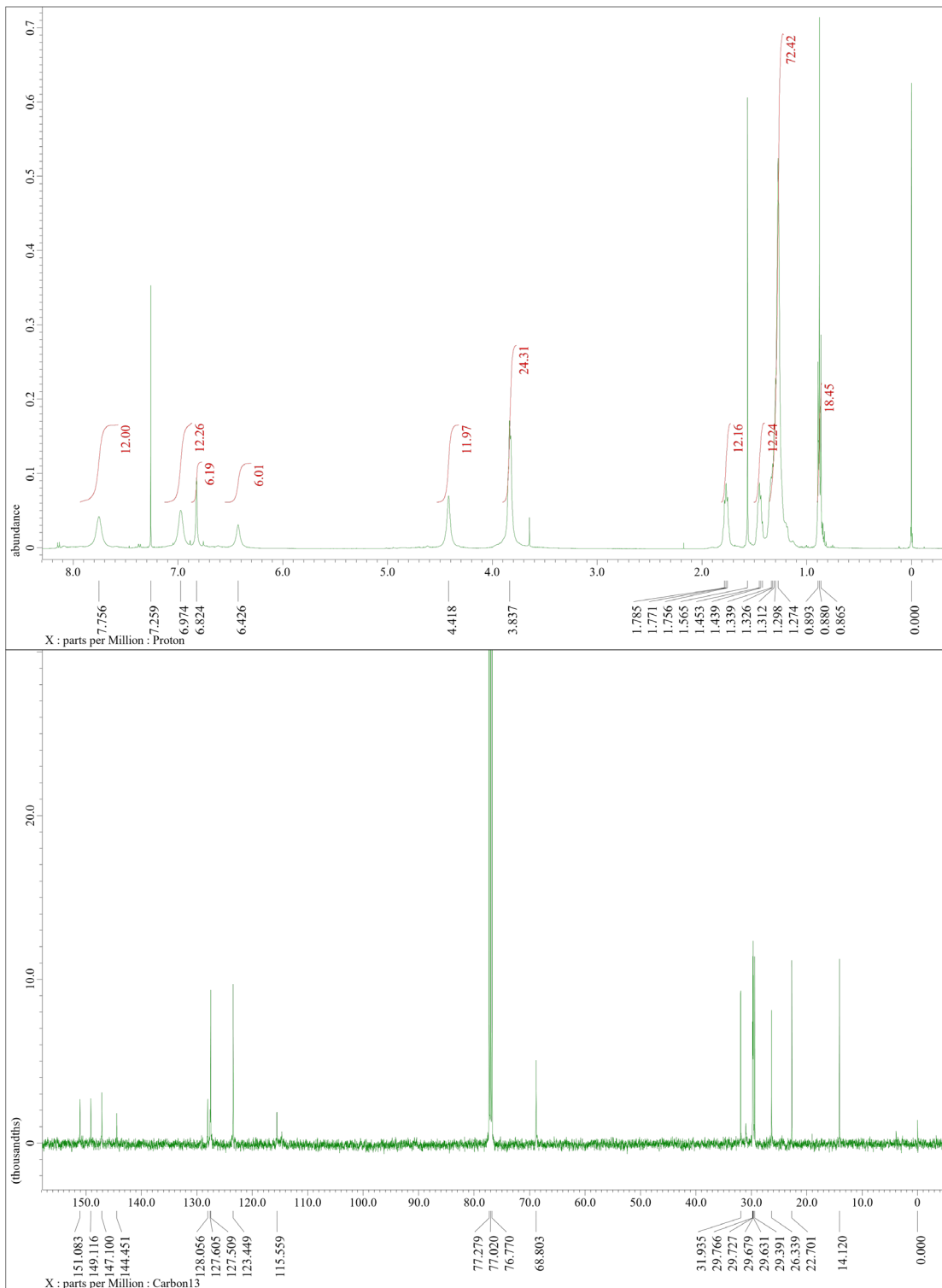
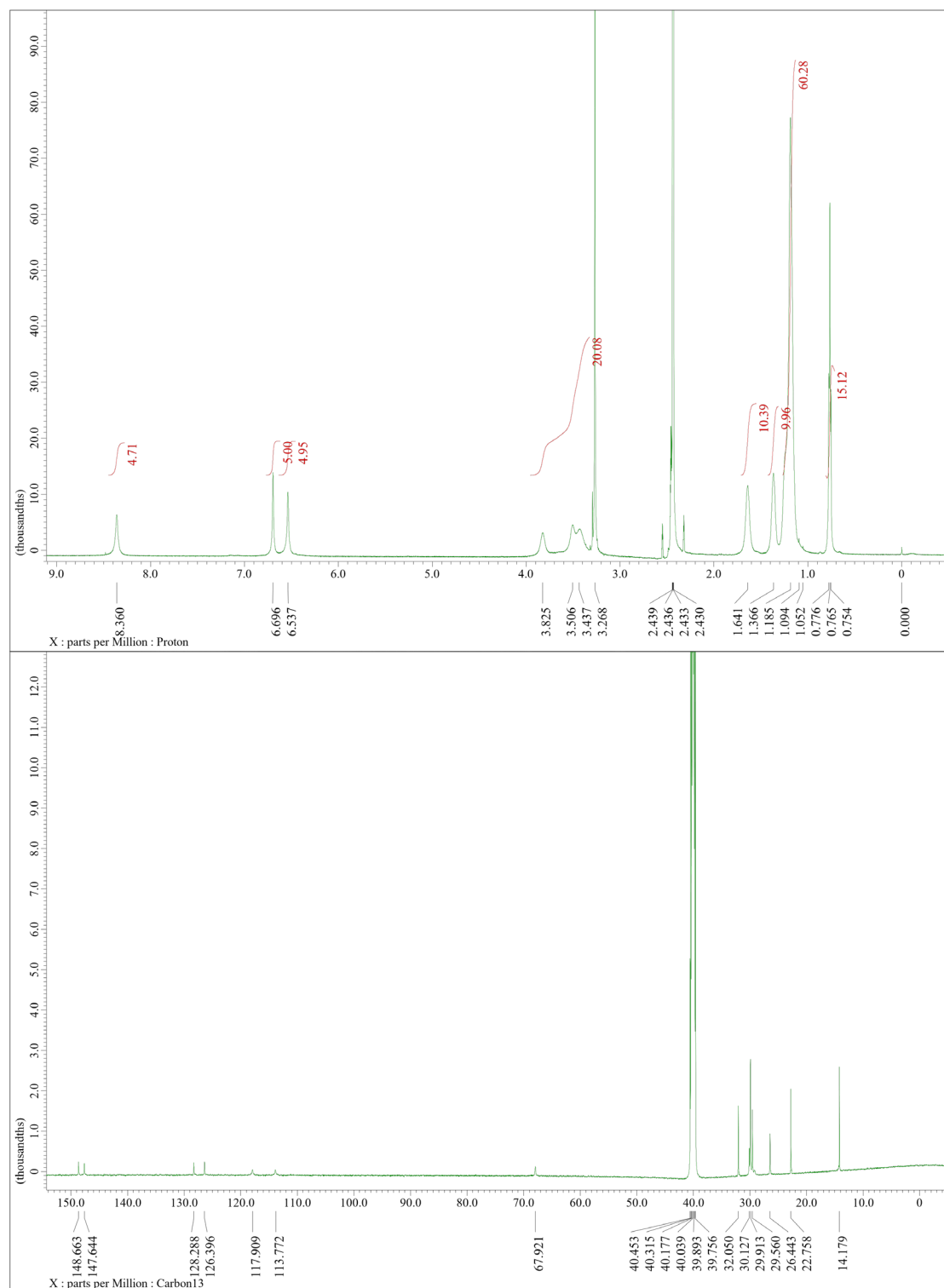


Figure S80. ^1H and ^{13}C NMR spectra of **2b-C10** (500 MHz, CDCl_3 , 298 K).



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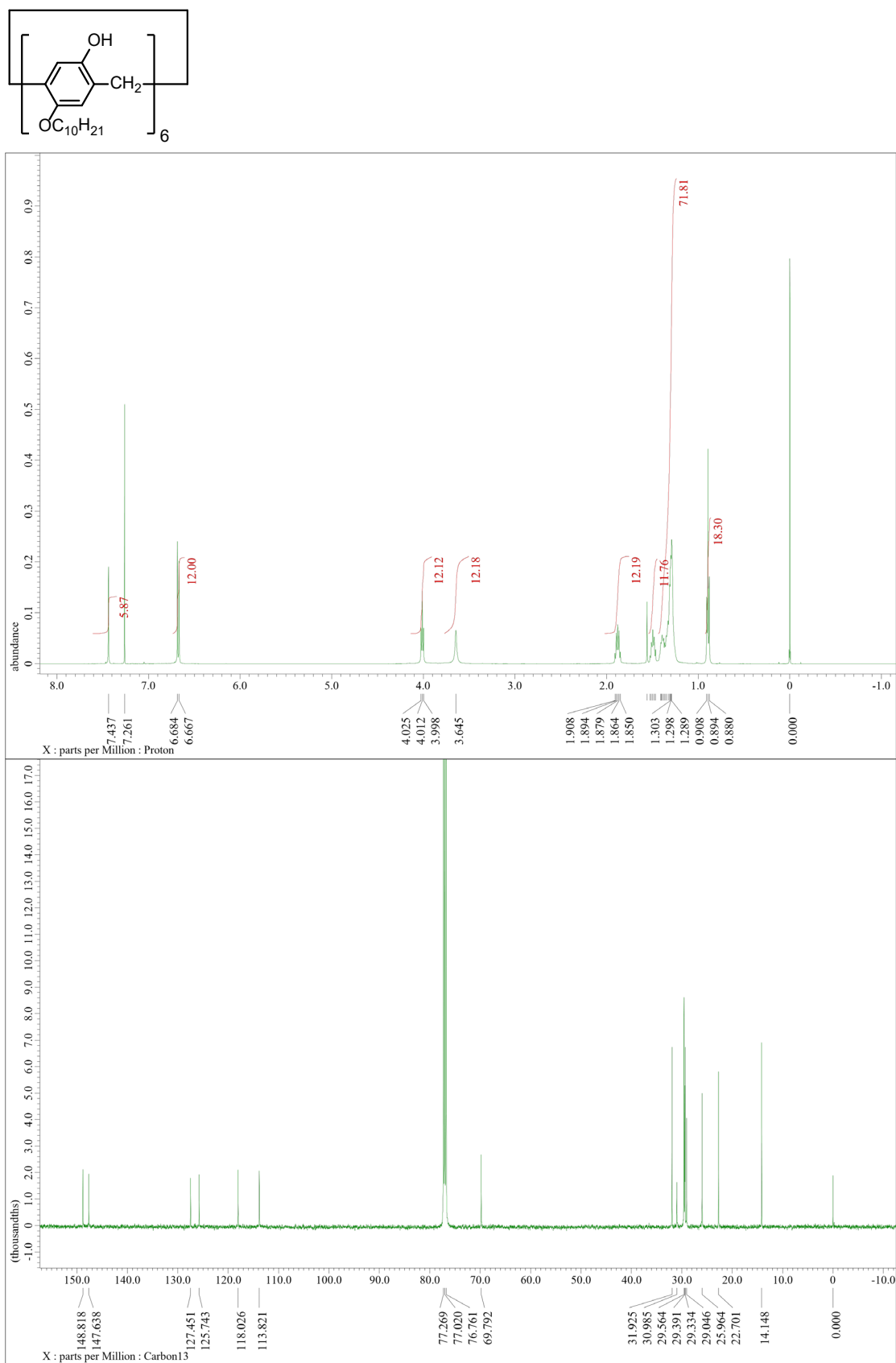


Figure S82. ¹H and ¹³C NMR spectra of **3b-C10** (500 MHz, CDCl₃, 298 K).

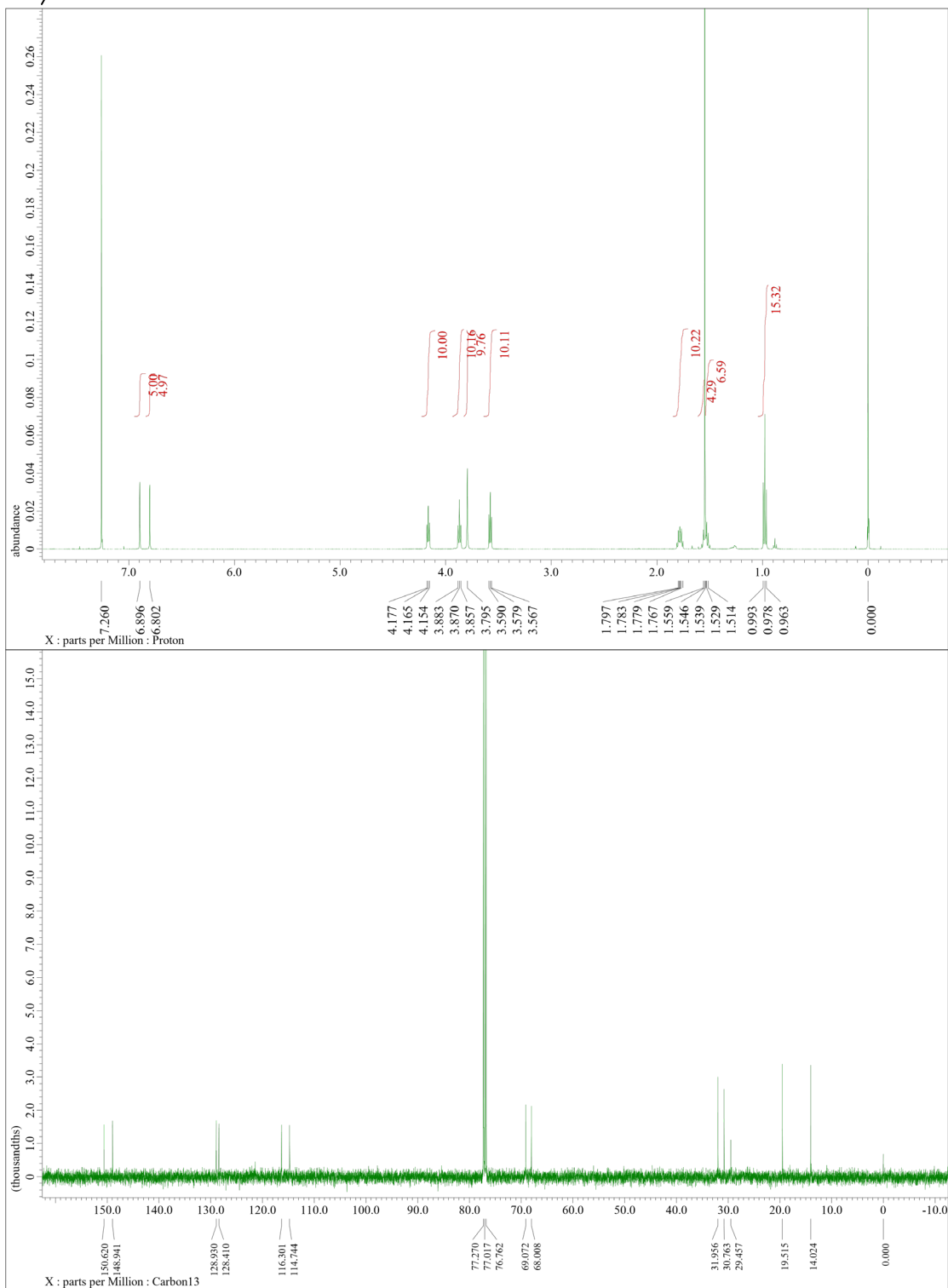


Figure S83. ^1H and ^{13}C NMR spectra of **4a** (500 MHz, CDCl_3 , 298 K).

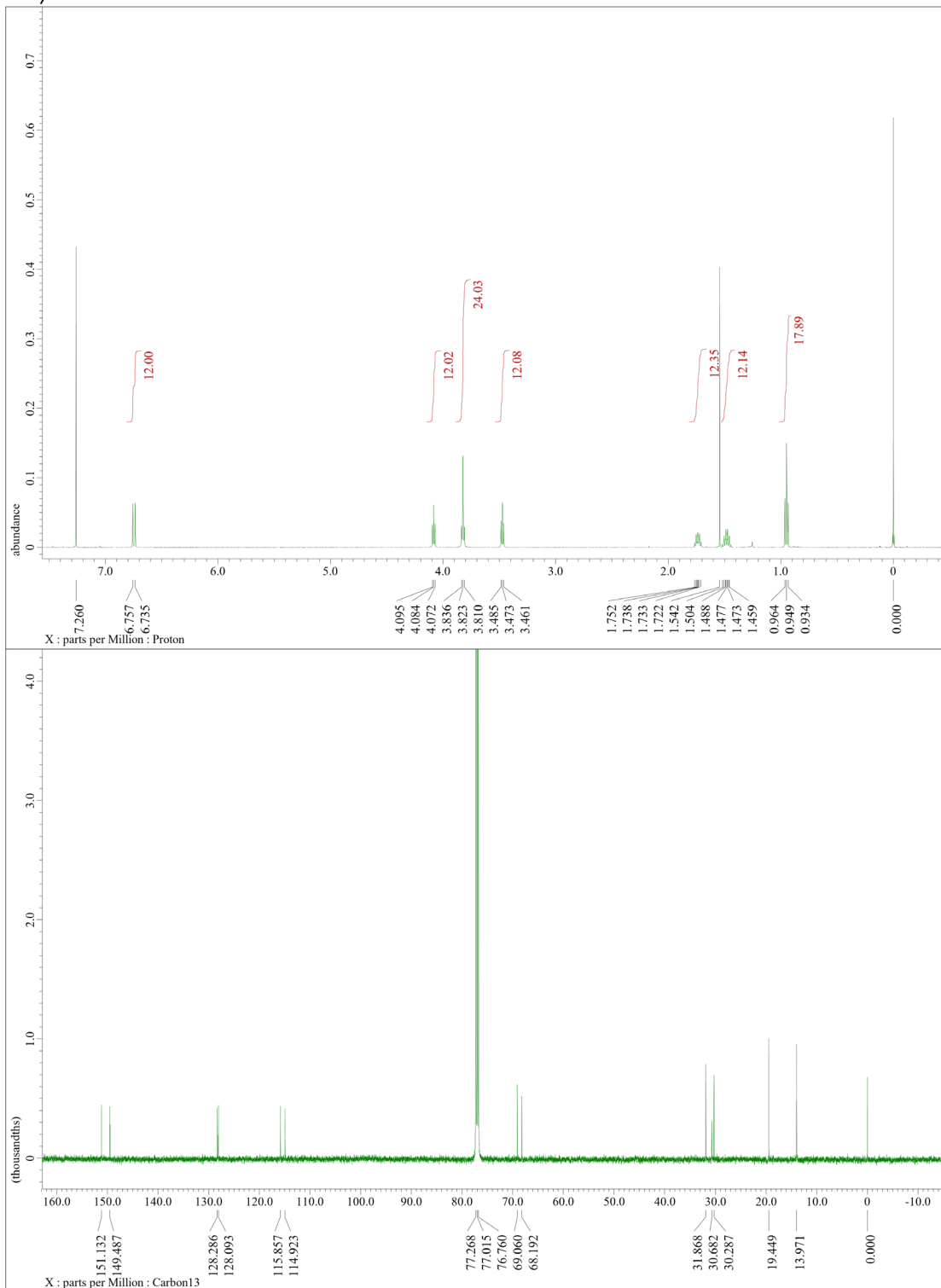


Figure S84. ^1H and ^{13}C NMR spectra of **4b** (500 MHz, CDCl_3 , 298 K).

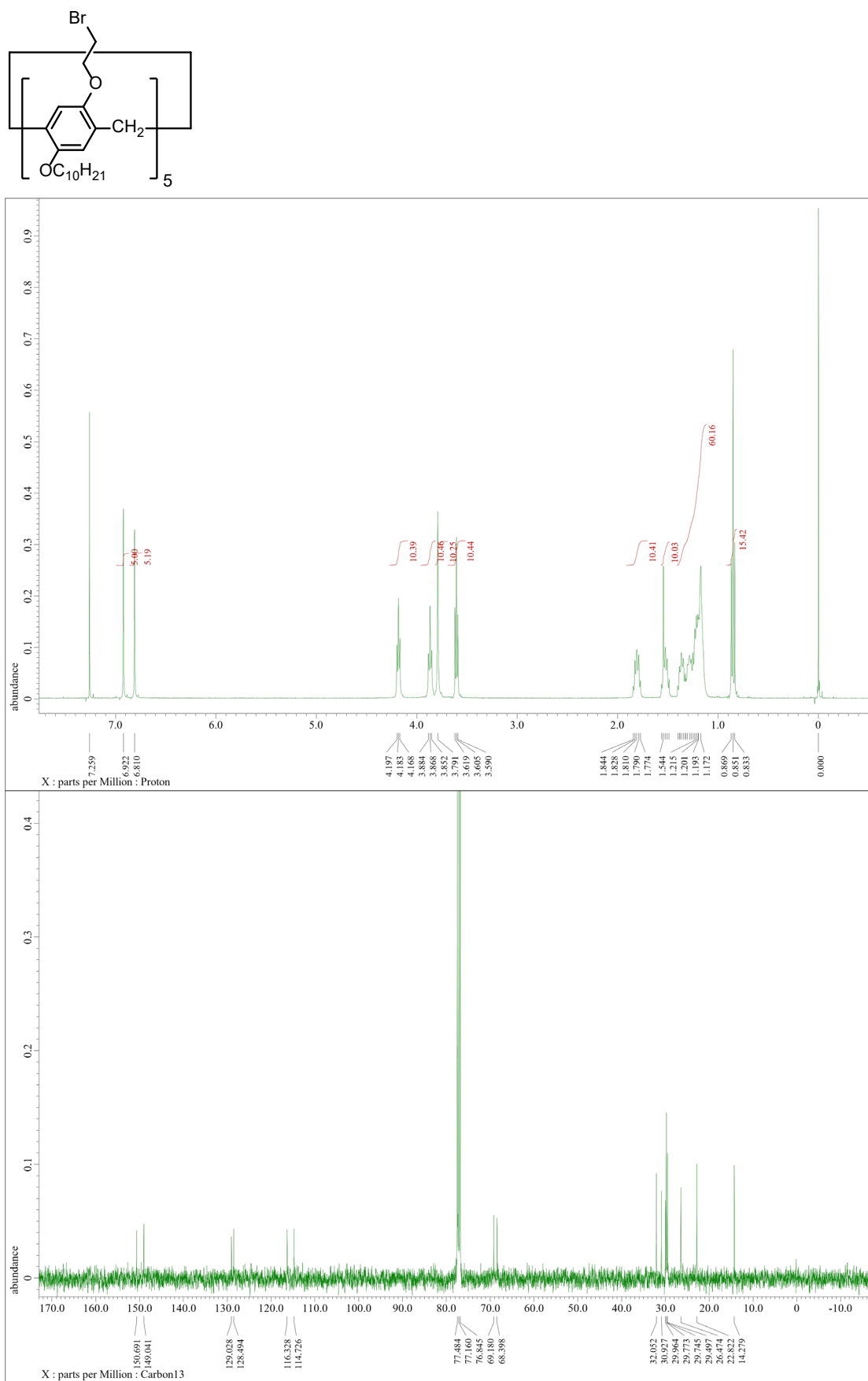


Figure S85. ¹H and ¹³C NMR spectra of **4a-C10** (400 MHz, CDCl₃, 298 K).

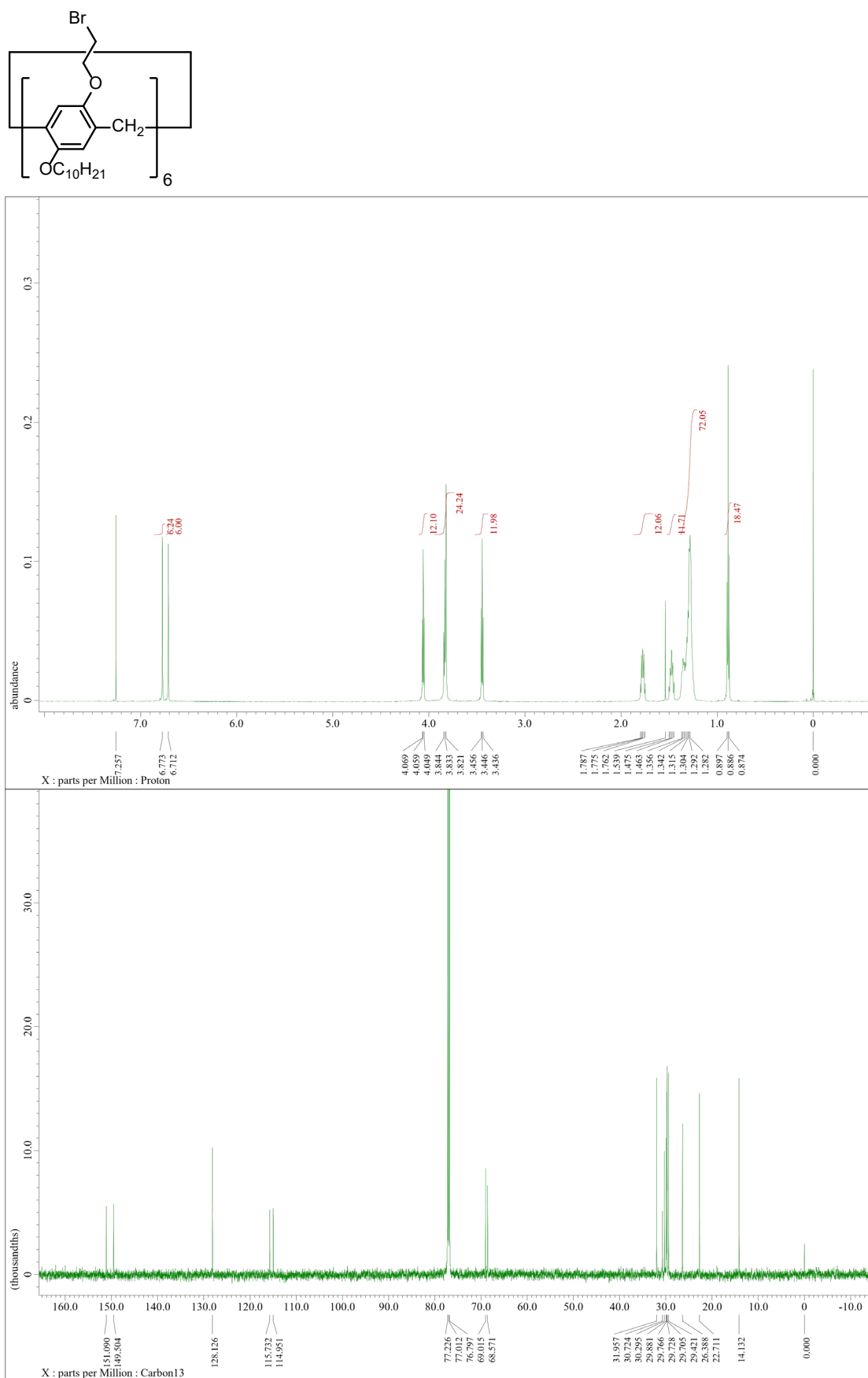


Figure S86. ¹H and ¹³C NMR spectra of **4b-C10** (600 MHz, CDCl₃, 298 K).

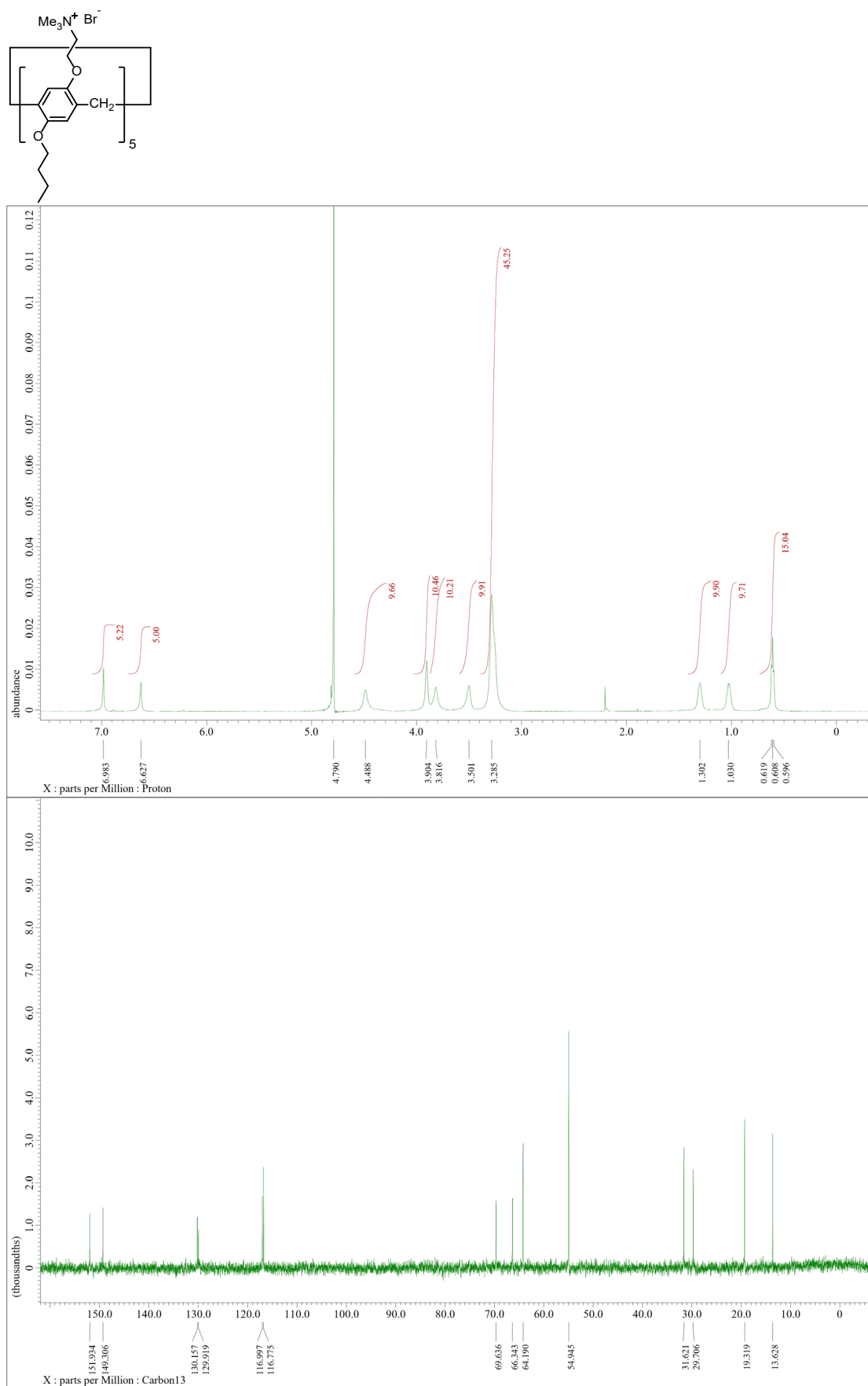


Figure S87. ¹H and ¹³C NMR spectra of AP-P5A (600 MHz, D₂O, 298 K).

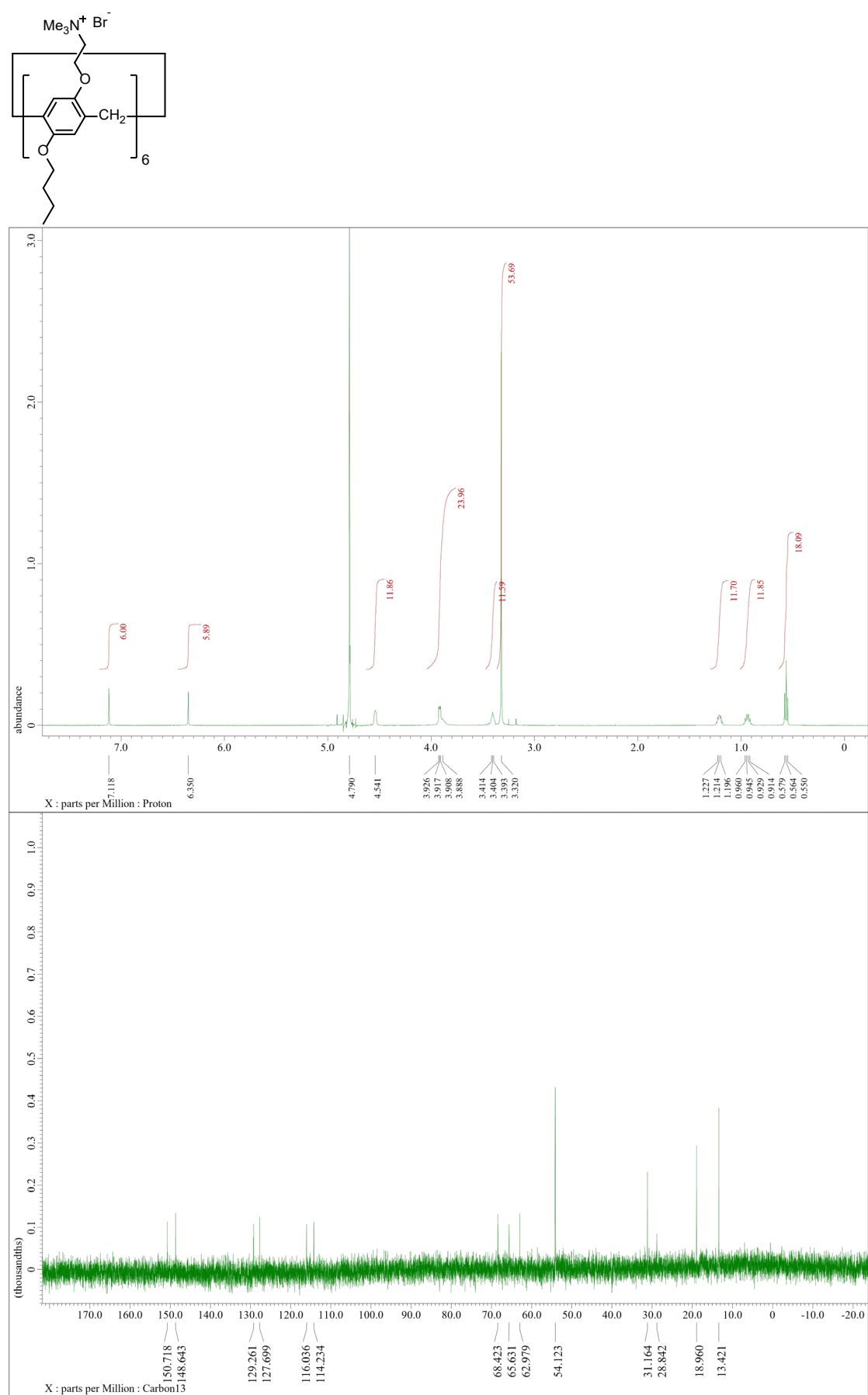


Figure S88. ^1H and ^{13}C NMR spectra of AP-P6A (600 MHz, D_2O , 298 K).

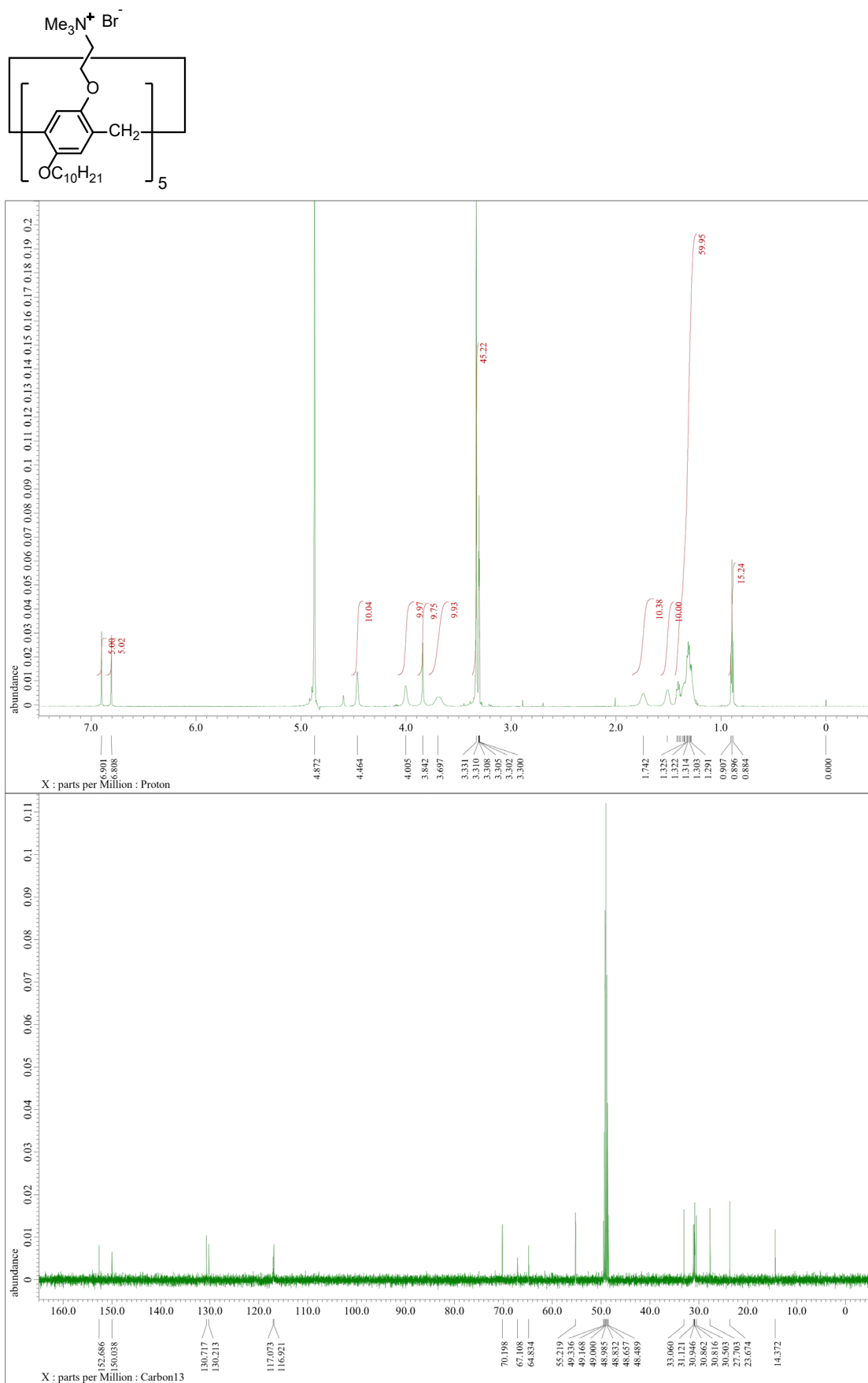


Figure S89. ^1H and ^{13}C NMR spectra of **AP-P5A-C10** (600 MHz, CD_3OD , 298 K).

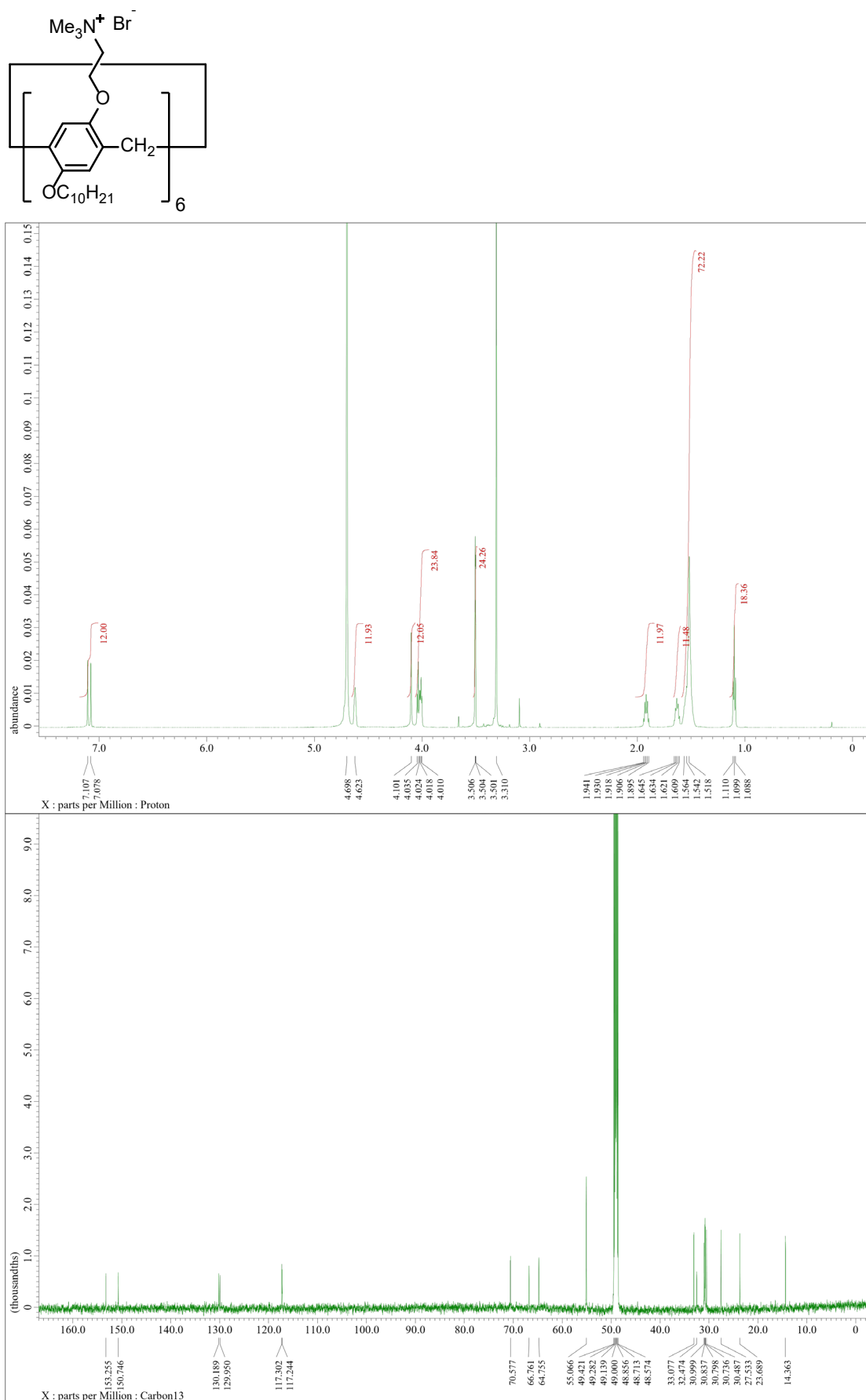


Figure S90. ^1H and ^{13}C NMR spectra of AP-P6A-C10 (600 MHz, CD_3OD , 298 K).

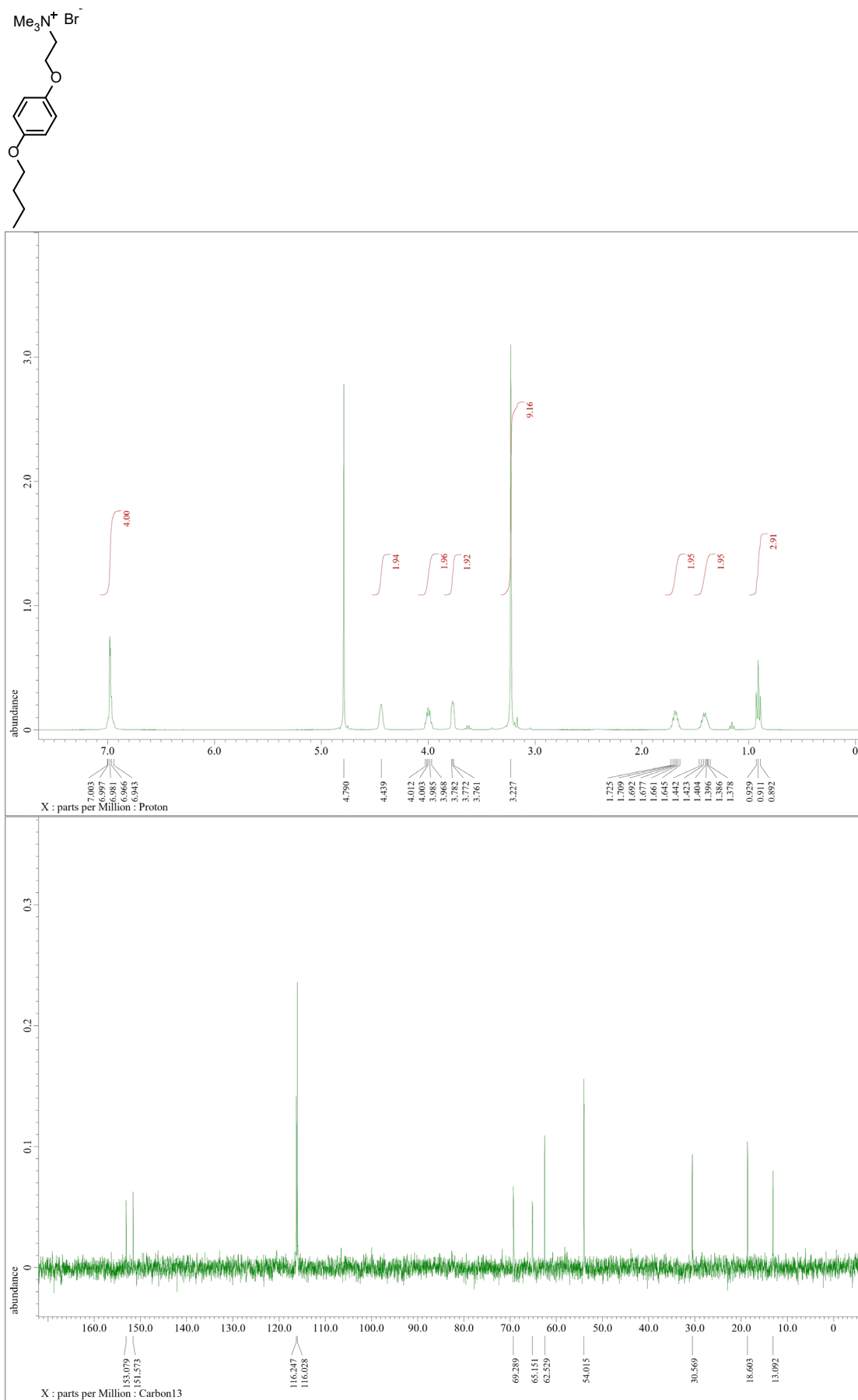


Figure S91. ¹H and ¹³C NMR spectra of **AP-monomer** (400 MHz, D₂O, 298 K).

9. References

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- [S2] Shi, T.-H.; Fa, S.; Nagata, Y.; Wada, K.; Ohtani, S.; Kato, K.; Ogoshi, T. Discrete chiral organic nanotubes by stacking pillar[5]arenes using covalent linkages. *Cell Rep. Phys. Sci.* **2022**, *3*, 101173.
- [S3] Fang, Y.; Li, C.; Wu, L.; Bai, B.; Li, X.; Jia, Y.; Feng, W.; Yuan, L. A non-symmetric pillar[5]arene based on triazole linked 8-oxyquinolines as a sequential sensor for thorium(IV) followed by fluoride ions. *Dalton Trans.* **2015**, *44*, 14584–14588.