Research Article

Cyclic Ether Contaminant Removal from Water Using Nonporous Adaptive Pillararene Crystals via Host-Guest Complexation at the Solid-Solution Interface

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The removal of soluble cyclic ether contaminants, such as dioxane and THF, produced in industrial chemical processes from water is of great importance for environmental protection and human health. Here we report that nonporous adaptive crystals of perethylated pillar[5]arene (EtP5) and pillar[6]arene (EtP6) work as adsorbents for cyclic ether contaminant removal via host-guest complexation at the solid-solution interface. Nonporous EtP6 crystals have the ability to adsorb dioxane from water with the formation of 1:2 host-guest complex crystals, while EtP5 crystals cannot. However, both guest-free EtP5 and EtP6 crystals remove THF from water with EtP5 having a better capacity. This is because EtP5 forms a 1:2 host-guest complex with THF via host-guest complexation at the solid-solution interface while EtP6 forms a 1:1 host-guest complex with THF. EtP6 also shows the ability to selectively remove dioxane from water even in the presence of THF. Moreover, the reversible transitions between nonporous guest-free EtP5 and EtP6 structures and guest-loaded structures make them highly recyclable.

1. Introduction

1,4-Dioxane, a cyclic ether often simply called dioxane, is primarily used as a solvent in industry as well as in the laboratory and a stabilizer for the transport of halogenated hydrocarbons [1]. Dioxane is also a by-product of the polyester manufacturing process, leading to its subsequent occurrence in industrial wastewater streams [2, 3]. Nevertheless, dioxane is also known as a highly stable contaminant and potential carcinogen in water and is becoming a threat for human and animal health [4–6]. There has been severe dioxane pollution in history. During 1976-1985, leakage of dioxane occurred in Ann Arbor, Michigan, and severely damaged the drinking water [7–9]. The removal or degradation of dioxane has not been completed until now. Some efforts have been devoted to increasing control, removal, and remediation of dioxane from sources of pollution. Recent methods involve electrolysis and ozonation [2, 10], phytoremediation [11], advanced oxidation processes (AOPS) [12–15], and so on. However, it is still challenging to completely remove dioxane due to its high miscibility with water, low vapor pressure, and nonbiodegradable nature. Moreover, these current methods are complex, highly energy-consuming, and recyclable. Thus, the search for new and easy strategies or adsorbents for adsorption and subsequent removal of dioxane from water is of great importance.

Pillar[n]arenes are a new and important class of macrocyclic hosts [16, 17]. They are highly symmetrical and rigid, easy to chemically modify, and possess abundant host-guest properties [18–26]. Recently, our group pioneered research on nonporous adaptive crystals (NACs) of pillararenes [27–32]. These nonporous crystals with “intrinsic porosity” can capture specific vaporized guests that have noncovalent interactions with them to form new guest-loaded crystal structures, that is, host-guest chemistry at the solid-gas interface. Based on these unique properties, NACs of pillararenes have been successfully applied in the adsorptive separations of hydrocarbons such as styrene purification and xylene isomer separation [28, 30]. However, the host-guest chemistry of NACs at the solid-solution interface still remains unexplored. The development of such properties for pillararene NACs may broaden their applications in more areas such as liquid-phase separation and water treatment.
Herein, we found that NACs of pillararenes worked as adsorbents to remove cyclic ether contaminants, such as dioxane and THF, from water via host-guest complexation at the solid-solution interface. Two easily obtained pillararenes, perethylated pillar[5]arene (EtP5) and pillar[6]arene (EtP6), were selected and used as adsorbents. Guest-free EtP6 crystals were found to have the ability to adsorb dioxane from water while EtP5 crystals cannot. Adsorption of dioxane from water led to a structural transition of EtP6 from a guest-free EtP6 structure (EtP6) to a dioxane-loaded 1:2 host-guest complex (2(dioxane)@EtP6, Figure 1). However, both guest-free EtP5 and EtP6 crystals removed THF from water via solid-solution host-guest complexation with EtP5 crystals having a better capacity. That is because guest-free EtP5 crystals (EtP5) form a 1:2 host-guest complex with THF (2(THF)@EtP5) at the solid-solution interface while EtP6 crystals only form 1:1 host-guest complex with THF (THF@EtP6). EtP6 also shows the ability to selectively remove dioxane from water even in the presence of THF. Upon removal of guests from the host-guest complex crystals, both EtP5 and EtP6 are transformed back to their original guest-free states and can be recycled many times without degradation.

2. Results

2.1. Preparation of Guest-Free Pillararenes. EtP5 and EtP6 (Figure 1) were synthesized according to previous reports [18, 27–31]. To use EtP5 and EtP6 as adsorbents, guest-free samples of EtP5 and EtP6 were obtained (the detailed method is given in the supplementary file). Powder X-ray diffraction (PXRD) experiments showed that both activated EtP5 and EtP6 were crystalline in the solid state (referred to as EtP5α and EtP6β, respectively). Synchrotron X-ray diffraction experiments were performed to illustrate their single crystal structures. Both EtP5α and EtP6β show rearrangements of the pillar structures and the loss of their cavities (Figures S6–S9) [30]. Meanwhile, the densely packed arrangement of pillararene units leads to nonporosity of EtP5α and EtP6β as confirmed by N₂ sorption experiments (Figures S10–S11).
2.2. Dioxane Removal Experiments. Despite their nonporosity, we investigated the dioxane adsorption abilities of EtP5α and EtP6β from water, respectively. To do so, dioxane was dissolved in D2O (0.600 mL) with a concentration of 0.500 mg mL−1 (5.7 × 10−3 mmol mL−1), and 1.00 mg of water-insoluble EtP5α and EtP6β crystals were added, respectively. As can be seen from the time-dependent 1H NMR spectra, the peak related to dioxane barely changed after addition of EtP5α (Figures S14–S15). However, after addition of EtP6β, the peak of dioxane decreased over time and almost completely disappeared after 24 hours (Figure 2(a)). The final concentration of dioxane after adsorption was calculated to be 4.37 × 10−5 mmol mL−1, about 130 times lower than the original concentration (Figures 2(b), S12). The adsorption efficiency of dioxane reached 99.2%, indicating the highly efficient adsorption capacity of EtP6β (Figures 2(b), S12).
Upon addition of another 5.00 mg of EtP6\(\beta\) into the solution, the final concentration of dioxane was calculated to be \(4.37 \times 10^{-6} \text{ mmol mL}^{-1}\) (0.413 mg L\(^{-1}\)) after 24 hours (Figure S13), which is under the discharge limit for 1,4-dioxane of the Korean Ministry of Environment (5.00 mg L\(^{-1}\)) [8]. This phenomenon indicated that EtP6\(\beta\) instead of EtP5\(\alpha\) can remove dioxane from water effectively.

To understand the adsorption mechanism, both EtP5\(\alpha\) and EtP6\(\beta\) were filtered from the dioxane aqueous solutions 24 hours after they were immersed. \(^1\)H NMR spectra in CDCl\(_3\) showed that no new peaks appeared for EtP5\(\alpha\), while a dioxane peak appeared for EtP6\(\beta\) (Figures S16, S20). The amount of dioxane can be calculated as two dioxane molecules per EtP6 molecule (mole/EtP6). Moreover, compared with the \(^1\)H NMR spectrum of dioxane in CDCl\(_3\), the dioxane peak has no chemical shift change in the presence of EtP6 (Figure S19). This implies that EtP6 does not have host-guest interactions with dioxane in solution due to the presence of CDCl\(_3\) molecules as competitive guests. However, the weak host-guest interactions between EtP6 and dioxane may emerge at the solid-liquid interface because of the absence of competitive guests, thus facilitating EtP6\(\beta\) crystals to capture dioxane from water. Thermogravimetric (TG) analyses also confirmed the results. There is no apparent weight loss below 400\(^\circ\)C for EtP5\(\alpha\) after immersion in the dioxane solution, indicating that no dioxane was adsorbed in EtP5\(\alpha\) (Figure S17). However, an apparent weight loss (13.1\%) below 160\(^\circ\)C for EtP6\(\beta\) occurred after being soaked in the dioxane-water solution, which can also be calculated to be two moles/EtP6 (Figure S21). These results are thus in accordance with NMR.

Powder X-ray diffraction (PXRD) experiments were then performed to monitor the structural information. For EtP5\(\alpha\), the PXRD pattern did not change after immersion in the dioxane solution, meaning no structural transitions (Figure S18). For EtP6\(\beta\), the PXRD pattern after immersion in the dioxane-water solution was different from the original one, but with a reservation of several small original peaks (Figure 2(c), II). Moreover, the PXRD pattern was completely changed after immersion in a higher dioxane-water solution with a concentration of 1.00 mg mL\(^{-1}\) (Figure 2(c), III). These results indicated the occurrence of structural transitions from guest-free EtP6\(\beta\) to a dioxane-loaded new structure after adsorption of dioxane from water.

To reveal the new structure of EtP6, dioxane-loaded EtP6 single crystals were obtained by a solution-growth method and characterized by X-ray crystallography. To our surprise, in the crystal structure of solution-grown dioxane-loaded EtP6 (4(dioxane}@EtP6, Figure 3(a)), four dioxane molecules correspond to one EtP6 molecule with one located in the cavity and three outside the cavity. Meanwhile, the hexagonal shape of EtP6 is deformed to some extent. The deformed hexagonal pillar structure of EtP6 assembles a window-to-window packing mode, leading to the formation of infinite intrinsic 1D channels with dioxane inside and outside the channels (Figure 3(b), right). It should be worth noting that the ratio of dioxane to EtP6 in the single crystal structure is twice of that obtained from EtP6\(\beta\) capturing dioxane from water. Moreover, the PXRD pattern of EtP6\(\beta\)
after capturing dioxane from water is totally different from the one simulated from the single crystal structure of 4(dioxane)@EtP6 (Figure S22I). These results implied that after capturing dioxane from water, EtP6β was transformed into a new structure that is unlike the solution-grown dioxane-loaded EtP6 structure. We then focused on a previously reported cyclohexane (CH)-loaded EtP6 crystal structure (2(CH)@EtP6) with two CH molecules per EtP6 molecule [25], the same ratio as EtP6β after capturing dioxane from water. The PXRD pattern of EtP6β after capturing dioxane matched well with that simulated from 2(CH)@EtP6, manifesting their structural similarities (Figure S22III). Hence, we conclude that after capturing dioxane, EtP6β was transformed into a honeycomb-like structure with two dioxane molecules located in the cavity of one EtP6 molecule.

2.3. Tetrahydrofuran Removal Experiments. Tetrahydrofuran (THF), another cyclic ether pollutant with a smaller molecular size, is also encountered in many chemical processes [33]. THF can react readily with oxygen to produce an unstable hydroperoxide. Distillation of peroxide containing THF increases the peroxide concentration, resulting in a serious risk of explosion. THF also forms an azeotrope with water and the mixture of THF-water needs separation during the manufacture of THF [34, 35]. Although EtP5 cannot remove dioxane from water presumably due to size effect of host-guest complexation at the solid-liquid interface, its potential in the removal of THF was explored. Upon addition of EtP5α crystals (1.00 mg) to 0.600 mL of D2O with a THF concentration of 0.500 mg mL−1 (6.90 × 10−3 mmol mL−1), the time-dependent 1H NMR spectra showed that the peaks of THF decreased over time and almost completely disappeared after 24 hours (Figures S23–S24). The final concentration of THF after adsorption was calculated to be 1.42 × 10−4 mmol mL−1, about 49 times lower than the original concentration (Figure 4(a)). Interestingly, EtP6β also showed the ability to remove THF from water (Supplementary Figure S26). However, the final concentration of THF after treatment with EtP6β was 1.43 × 10−3 mmol mL−1, much higher than that with EtP5α (Figure 4(a)). Upon addition of another 1.00 mg of EtP5α or EtP6β into the respective solutions, the final concentrations of THF after 24 hours were calculated to be 7.15 × 10−6 mmol mL−1 and 1.02 × 10−4 mmol mL−1 (Figures S25, S28), respectively. These results indicate that although both EtP5α and EtP6β can remove THF from water, the efficiency of EtP5α (98.0%) was much higher than that of EtP6β (79.5%).

After filtration from the THF-water solution, both EtP5 and EtP6 crystals were characterized by 1H NMR, TGA, and PXRD. 1H NMR of both crystals dissolved in CDCl3 showed clear peaks related to THF (Figures S29, S32). The molar ratios of THF to EtP5 and EtP6 were calculated to be 2:1 and 1:1, respectively. This suggests the reason why EtP5 had a better performance in the THF removal. Similar to the case in the dioxane removal, the THF peaks in the presence of either EtP5 or EtP6 have no chemical shift changes compared with those of single THF in CDCl3, indicating the absence of host-guest interactions of THF with either EtP5 or EtP6 in solution (Figures S30–S33). Thus, the weak host-guest interactions that happen at the solid-liquid interface without competitive guests may be the driving force for EtP5α and EtP6β crystals to capture THF in water. TG analyses also showed similar results to that obtained by NMR. The weight loss below 120°C can also be calculated as 2 and 1 THF molecules per host molecule, respectively (Figures S31–S34). PXRD experiments showed that both EtP5α and EtP6β underwent structural changes after immersion in the THF-water solution. The PXRD pattern of EtP5α was completely changed to a new one and matched the pattern simulated from the single crystal structure of THF-loaded EtP5 (2(THF)@EtP5, Figure 4(c)) [28], indicating the structural transition from EtP5α to 2(THF)@EtP5 after adsorption of THF from water. Interestingly, the PXRD pattern of EtP6β after adsorption of THF became similar to that of EtP6β after immersion in the dioxane-water solution (Figure 4(d)), manifesting their structural similarities. Thus, it can be deduced that the THF-loaded EtP6 (THF@EtP6) is also a honeycomb-like structure but with 1:1 rather than 1:2 host-guest complex.

2.4. Selective Removal of Dioxane in the Presence of THF. Since EtP6β can remove dioxane and THF individually from water, we wondered whether it could selectively remove THF or dioxane from an aqueous solution containing both THF and dioxane. Upon addition of EtP6β (5.00 mg) to a THF/dioxane/D2O mixture (both the weight concentrations of THF and dioxane were 0.500 mg mL−1; the total volume of the mixture was 0.600 mL), the time-dependent 1H NMR spectra (Figure S35) showed that the concentration of dioxane decreased over time while THF almost remained the same. After 24 hours, the final concentration of dioxane was calculated to be 0.018 mg mL−1 while the concentration of THF remained as high as 0.480 mg mL−1 (Figure 5). These results implied that EtP6β can remove dioxane from water even in the presence of THF with high selectivity.

2.5. Recyclability. One shortcoming of common adsorbents is the decreased performance over time due to fouling. In practical use, an adsorbent must be recycled without any degradation. Upon heating to completely remove dioxane guests from 2(dioxane)@EtP6, the PXRD pattern showed that the desolated 2(dioxane)@EtP6 was transformed back to EtP6β (Figure S43, II and III). Similar phenomena were also observed for 2(THF)@EtP5 and THF@EtP6. PXRD experiments confirmed the complete removal of THF from 2(THF)@EtP5 and THF@EtP6 (Figures S38, S43), respectively. Furthermore, the recovered EtP5α and EtP6β remove THF and dioxane from water again, respectively, without degradation after recycling five times (Figure 6). Thus, we can conclude that reversible host-guest complexation at the solid-liquid interface contributes to the recyclability of pillarene crystals.

3. Discussion

In summary, we found that nonporous adaptive pillarene crystals, EtP5α and EtP6β, can be used as adsorbents to
Figure 4: Investigations on EtP5 and EtP6 adsorption of THF from water. (a) Time-dependent THF concentration change in D_2O upon addition of EtP5α and EtP6β. (b) PXRD patterns: (I) simulated from single crystal structure of 2(THF)@EtP5 [28]; (II) EtP5α after filtration from a 0.500 mg mL\(^{-1}\) THF-D_2O solution; (III) EtP5α. (c) Single crystal structures: 2(THF)@EtP5. (d) PXRD patterns: (I) EtP6β after filtration from a 1.00 mg mL\(^{-1}\) dioxane-D_2O solution; (II) EtP6β after filtration from a 0.500 mg mL\(^{-1}\) THF-D_2O solution; (III) EtP6β. (e) Schematic representation of EtP5α and EtP6β as absorbents to remove THF from water.
remove cyclic ethers from water via host-guest complexation at the solid-solution interface. EtP6β crystals have the ability to adsorb dioxane from water while EtP5α crystals cannot. Adsorption of dioxane leads to a structural transition of EtP6 from EtP6β to a 1:2 host-guest complex 2(dioxane)@EtP6. However, both EtP5α and EtP6β crystals remove THF from water via host-guest complexation at the solid-solution interface with EtP5α having a better capacity. This is due to the formation of a 1:2 host-guest complex of EtP5 with THF (2(THF)@EtP5) rather than the 1:1 host-guest complex of EtP6 with THF (THF@EtP6). EtP6β also shows the ability to selectively remove dioxane from water even in the presence of THF. Compared with current methods to remove dioxane and THF, this approach via host-guest recognition at the solid-liquid interface has several advantages such as the simple and cheap synthesis of pillararenes, solution-processability, and high thermal and chemical stability. Moreover, the reversible transformations between nonporous guest-free structures and guest-loaded structures make pillararenes highly recyclable. Future work will try to expand the applications of pillararene crystals via host-guest complexation at the solid-solution interface such as liquid-phase separation. Other types of hosts with the potential to encapsulate guests at the solid-solution interface are worth exploring for more unique applications.

4. Materials and Methods

4.1. Materials. p-Diethoxybenzene was purchased from JK Chemicals and used as received. All other chemicals,
including tetrahydrofuran (THF) and 1,4-dioxane, were purchased from Sigma-Aldrich and used as received. EtP5 and EtP6 were synthesized as described previously [18]. Desolvated crystalline EtP5 (EtP5x) was recrystallized from acetone and dried under vacuum at 100°C overnight. Desolvated crystalline EtP6 (EtP6β) was recrystallized from acetone and dried under vacuum at 140°C overnight.

4.2. Methods

4.2.1. Solution NMR. Solution 1H NMR spectra were recorded at 400.13 MHz using a Bruker Avance 400 NMR spectrometer.

4.2.2. Thermogravimetric Analysis. TGA analysis was carried out using a Q5000IR analyzer (TA instruments) with an automated vertical overhead thermobalance. The samples were heated at the rate of 10°C/min using N2 as the protective gas.

4.2.3. Powder X-Ray Diffraction. PXRD data before and after vapor sorption were collected in a Rigaku Ultimate-IV X-ray diffractometer operating at 40 kV/30 mA using the Cu Kα line (λ = 1.5418 Å). Data were measured over the range of 5–40° in 5°/min steps over 7 min.

4.2.4. Single Crystal Growth. Single crystals of dioxaneloaded EtP6 were grown by a slow evaporation method: 5 mg of dry EtP6 powder was put in a small vial where 2 mL of 1,4-dioxane was added. The resultant transparent solution was allowed to evaporate slowly to give nice colorless crystals in 2 to 4 days.

4.2.5. Single Crystal X-Ray Diffraction. Single crystal X-ray data sets were measured on a Rigaku MicroMax-007 HF rotating anode diffractometer (Mo-Kα radiation, λ = 0.71073 Å, Kappa 4-circle goniometer, Rigaku Saturn724+ detector). Unless stated, solvated single crystals, isolated from the crystallization solvent, were immersed in a protective oil, mounted on a MiTeGen loop, and flash-cooled under a dry nitrogen gas flow. Empirical absorption corrections, using the multiscan method, were performed with the program SADABS [36]. Structures were solved with SHELXD [37] or SHELXT [38] or by direct methods using SHELXS [39], refined by full-matrix least squares on F2 by SHELXL [40], and interfaced through the programme OLEX2 [41]. Unless stated, all non-H-atoms were refined anisotropically, and all H-atoms were fixed in geometrically estimated positions and refined using the riding model. Supplementary CIFs, which include structure factors, are available free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

4.2.6. Gas Sorption Measurement. Low-pressure gas adsorption measurements were performed on a Micrometrics Accelerated Surface Area and Porosimetry System (ASAP) 2020 surface area analyzer. Samples were degassed under dynamic vacuum for 12 h at 60°C prior to each measurement. N2 isotherms were measured using a liquid nitrogen bath (77 K).

Data Availability

All data needed to evaluate the conclusions in the paper are present in the paper and the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Conflicts of Interest

The authors declare no competing financial interest.

Authors’ Contributions

Yujuan Zhou, Kecheng Jie, and Feihe Huang conceived the project and designed the experiments. Yujuan Zhou, Kecheng Jie, Run Zhao, and Errui Li performed the experiments and analyzed the data. Yujuan Zhou, Kecheng Jie, and Feihe Huang cowrote the paper.

Acknowledgments

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Supplementary Materials

Table S1: experimental single crystal X-ray data for EtP6 structure. Figure S1: ball-stick plots from single crystal structures: 4(dioxane)@EtP6 shown into the cavity (left) and in plane of the aromatic core (right). H-atoms and solvent molecules are omitted for clarity. Not shown on common scale. Figure S2. 1H NMR spectrum (400 MHz, CDCl3, 293 K) of EtP5α. There is a peak related to protons on H2O due to the presence of H2O in CDCl3. Figure S3: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of EtP6β. There is a peak related to protons on H2O due to the presence of H2O in CDCl3. Figure S4: thermogravimetric analysis of desolvated EtP5. Figure S5: thermogravimetric analysis of desolvated EtP6. Figure S6: single crystal structure of guest-free EtP5, which is defined as EtP5α [30]. Figure S7: powder X-ray diffraction pattern: (I) simulated from single crystal structure of guest-free EtP5; (II) activated EtP5 crystals (EtP5α). Figure S8: single crystal structure of thermally stable guest-free EtP6, which is defined as EtP6β [30]. Figure S9: powder X-ray diffraction pattern: (I) activated EtP6 crystals (EtP6β); (II) simulated from single crystal structure of guest-free EtP6. Figure S10. N2 adsorption isotherm of EtP5α. Adsorption, closed symbols; desorption, open symbols. Figure S11. N2 adsorption isotherm of EtP6β. Adsorption, closed symbols; desorption, open symbols. Figure S12: 1H NMR spectrum (400 MHz, D2O, 293 K) of a 0.500 mg mL−1 D2O solution of dioxane after treatment with 1.00 mg of EtP6β for 24 h. Figure S13: 1H NMR spectrum (400 MHz, D2O, 293 K) of the 0.500 mg mL−1 D2O solution of dioxane discussed in
Figure 12 after further treatment with another 5.00 mg of EtP6β for 24 h. Figure S14: time-dependent partial 1H NMR spectra (400 MHz, D2O, 293 K) of the dioxane-D2O solution upon addition of EtP5α. Figure S15: time-dependent dioxane concentration change in D2O upon addition of EtP5α. Figure S16: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of EtP5α after adsorption of dioxane from water. Figure S17: thermogravimetric analysis of EtP5α after adsorption of dioxane from water. Figure S18: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of EtP6α upon removal of THF. Figure S19: 1H NMR spectra (400 MHz, D2O, 293 K) of the THF-D2O solution upon addition of EtP5α. Figure S20: 1H NMR spectrum (400 MHz, D2O, 293 K) of EtP6β upon removal of THF or dioxane. Figure S21: thermogravimetric analysis of EtP6β after adsorption of dioxane from water. The weight loss below 100°C can be calculated as two dioxane molecules per EtP6 molecule. Figure S22: powder X-ray diffraction patterns of EtP6α and EtP6β. (I) EtP6α; (II) EtP6β, filtered from a 1.00 mg mL−1 dioxane-D2O solution; (III) EtP6α and EtP6β after adsorption of dioxane from water; (c) THF. Figure S23: thermogravimetric analysis of EtP6α after adsorption of dioxane from water. The weight loss below 100°C can be calculated as two dioxane molecules per EtP6 molecule. Figure S24: H NMR spectrum of EtP6α after adsorption of dioxane from water. The weight loss below 100°C can be calculated as two dioxane molecules per EtP6 molecule. Figure S25: H NMR spectrum of the THF-D2O solution discussed in Figure S22 after further treatment with another 1.00 mg of EtP5α for 24 h. Figure S26: time-dependent partial 1H NMR spectra (400 MHz, D2O, 293 K) of the dioxane-D2O solution upon addition of EtP5α. Figure S27: 1H NMR spectrum of the dioxane-D2O solution upon addition of EtP5α. Figure S28: 1H NMR spectrum (400 MHz, D2O, 293 K) of the 0.500 mg mL−1 D2O solution of THF after treatment with 1.00 mg of EtP5α for 24 h. Figure S29: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of EtP5α after adsorption of THF from water. Figure S30: partial 1H NMR spectra (400 MHz, CDCl3, 293 K): (a) EtP5α; (b) EtP5α after adsorption of THF from water; (c) THF. Figure S31: thermogravimetric analysis of EtP6β after adsorption of THF from water. The weight loss below 100°C can be calculated as two THF molecules per EtP5 molecule. Figure S32: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of the 0.500 mg mL−1 D2O solution of THF after treatment with 1.00 mg of EtP5α for 24 h. Figure S33: partial 1H NMR spectra (400 MHz, CDCl3, 293 K): (a) EtP6β; (b) EtP6β after adsorption of THF from water; (c) THF. Figure S34: thermogravimetric analysis of EtP6β after adsorption of dioxane from water. The weight loss below 100°C can be calculated as one THF molecule per EtP6 molecule. Figure S35: time-dependent 1H NMR spectra (400 MHz, D2O, 293 K) of a D2O solution (0.600 mL) of 0.500 mg mL−1 THF after treatment with 5.00 mg of EtP6β for 24 h. Figure S36: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of desolvated EtP5 upon removal of THF. Figure S37: thermogravimetric analysis of desolvated EtP5 upon removal of THF. Figure S38: powder X-ray diffraction patterns of EtP5α; (II) desolvated 2(THF)@EtP5 [28]. This implies that upon removal of THF, 2(THF)@EtP5 transforms back to EtP5α. Figure S39: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of desolvated EtP6 upon removal of dioxane. Figure S40: 1H NMR spectrum (400 MHz, CDCl3, 293 K) of desolvated EtP6 upon removal of THF. Figure S41: thermogravimetric analysis of desolvated EtP6 upon removal of dioxane. Figure S42: thermogravimetric analysis of desolvated EtP6 upon removal of THF. Figure S43: powder X-ray diffraction patterns of EtP6α. (I) desolvated THF@EtP6; (II) desolvated 2(dioxane)@EtP6; (III) EtP6β. This implies that upon removal of THF or dioxane, THF@EtP6 and 2(dioxane)@EtP6 transform back to EtP6β [25, 28, 30]. (Supplementary Materials)

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