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COMMUNICATION

Cross-linked Supramolecular Polymer Constructed from Pillar[5]arene and Porphyrine *via* the Host-Guest Interactions

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A novel supramolecular polymer DMeP5@TImPor was successfully constructed between host molecule bis-(methoxy-pillar[5]arene) (DMeP5) and guest molecule 5,10,15,20-tetrakis(butoxy-4-(1H-imidazol-1-yl))porphyrine (TImPor) depending on the host-guest interactions and characterized by the combination of various techniques including NMR, DLS, SEM, TEM, and AFM. Addition of competitive guest adiponitrile (ADN) led to effective dissociation of the complex DMeP5@TImPor and re-formation of original guest species, giving additional support for the host-guest interaction-based supramolecular polymer nature of the present system. Interestingly, exposure of this supramolecular polymer thin film to the acidic gas led to the complete quenching of the fluorescence, endowing the system with an application potential in acidic gas detection.

Supramolecular polymers combine supramolecular chemistry and traditional polymer chemistry together in a perfect manner by holding monomers together depending on directional and reversible non-covalent interactions.^[1] The polymeric structure and dynamic non-covalent interactions render supramolecular polymers polymer-like nature in addition to their multiple stimuli-responsiveness, recycling, self-healing, adaption, and degradability properties.^[1a,2] These fascinating features have attracted significant research attention in diverse fields including optoelectronic materials, molecular recognition systems, catalysts, and memory in the past several decades.^[1b,3] Hydrogen bonding, metal-ligand coordination, and π - π stacking interactions have been employed to fabricate linear or cross-linked supramolecular polymers,^[4] while the host-guest interactions were widely utilized to construct macrocyclic host-based supramolecular polymers with unique mechanical and stimuli-responsive properties.^[1m,2b,5]

Pillar[n]arenes, as a new class of macrocyclic hosts, have found a wide range of application potentials in molecular switches, drug delivery, sensors, metal-organic frameworks.^[6,7] In particular, pillar[n]arene derivatives with appropriately sized cavity exhibit good host-guest supramolecular polymer formation property due to their high binding ability with the guest molecules.^[5d,8] On the other hand, due to their interesting photophysical, electrochemical, and catalytic properties,^[9] quite recently a number of porphyrin derivatives have been fabricated into host-guest supramolecular polymers with different macrocyclic compounds including calix[n]arenes,^[10] cucurbit[n]urils,^[11] and cyclodextrins.^[12] In 2009, Liu and co-workers employed dicationic and tetracationic porphyrins as model guests to construct two supramolecular polymers with 1D linear and 2D netlike topological structures upon complexation with bis(*p*-sulfonatocalix[5]arene).^[10a] In 2013, our group demonstrated the construction of a supramolecular polymer from 5,10,15,20-tetrakis(N-carboxymethyl-4-pyridinium)porphyrin tetrabromide and tetramethylcucurbit[6]uril on the basis of single crystal X-ray diffraction analysis.^[11a] In 2014, Zhang reported the hyperbranched supramolecular polymers formed from cucurbit[8]uril and porphyrin derivatives containing four naphthalene groups.^[11c] Very lately, a linear supramolecular polymer made from dithienylethene-bridged bis(permethyl- β -cyclodextrin) and 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin was reported.^[12b] However, there seems to still lack report over the porphyrin-involved pillar[n]arenes host-guest supramolecular polymers. But it is worth noting that just after the submission of the present paper, Stoddart and co-workers described the porphyrinic supramolecular daisy chains incorporating pillar[5]arene-viologen host-guest interactions.^[13]

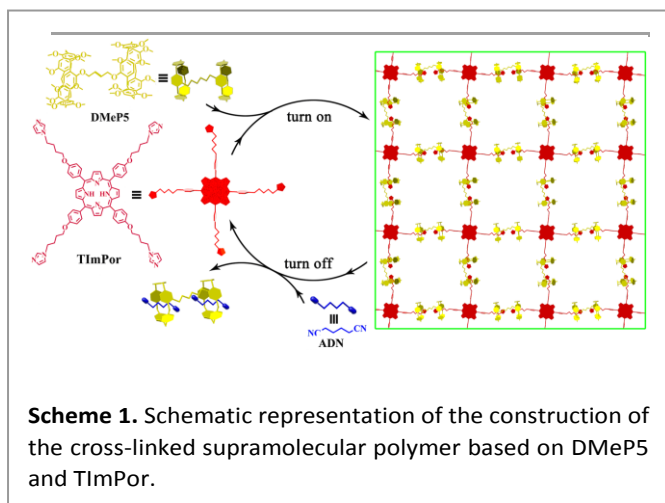
In the present paper, we describe preparation and characterization of a novel host-guest supramolecular polymer formed by host molecule bis-(methoxy-pillar[5]arene) (DMeP5) and four-arm guest molecule 5,10,15,20-tetrakis(butoxy-4-(1H-imidazol-1-yl))porphyrin (TImPor), Scheme 1. Nevertheless, addition of competitive guest adiponitrile (ADN) led to effective dissociation of the complex DMeP5@TImPor and re-formation of original guest molecular TImPor, giving additional support for the host-guest interaction-based supramolecular polymer nature of the present system.

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Due to the effective cooperative effect, macrocycle dimers often form more stable complexes with guests through the intramolecular cooperative binding compared with monomers.^[14] For the purpose of achieving effective supramolecular polymerization of the pillar[n]arene host molecules with guests, a dimeric host molecule bis(methoxy-pillar[5]arene) (DMeP5) was prepared by introducing an alkyl chain as a bridge to link two pillar[5]arenes in the present case. Reaction of 1 equiv. of 1,4-bis(4-methoxyphenoxy)butane and 16 equiv. of 1,4-dimethoxybenzene with paraformaldehyde promoted by anhydrous FeCl₃ in 1,2-dichloroethane led to the formation of the host compound DMeP5. Meanwhile, a four-arm guest compound, namely 5,10,15,20-tetrakis(butoxy-4-(1H-imidazol-1-yl))porphyrin (TImPor), was also designed and synthesized, Scheme 1. The four *meso*-attached butoxy-4-(1H-imidazol-1-yl) moieties of TImPor are expected to interact with the host molecule and the rigid-bulky porphyrin linker to suppress the formation of cyclic species. Simple mixing DMeP5 and TImPor in chloroform led to the formation of supramolecular polymer DMeP5@TImPor depending on strong host-guest interactions between the two species of molecules. The newly formed supramolecular polymer was characterized by NMR spectroscopy, dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Nevertheless, the key intermediate and target compounds were also characterized by mass, ¹H and ¹³C NMR spectroscopies, Fig. S1-S6 (ESI[†]).



The formation of the inclusion complex DMeP5@TImPor can be conveniently monitored by ¹H NMR spectroscopy in CDCl₃. Fig. 1 compares the ¹H NMR spectrum of the free guest species of TImPor with that for the mixture of DMeP5 and TImPor in the ratio of 2:1 in CDCl₃. As can be seen from this figure, adding DMeP5 into the CDCl₃ solution of TImPor, the imidazole protons H₁ and H₃ as well as the alkyl chain protons H₄-H₇ of TImPor experience significantly up-field shift due to the shielding effect of the electron-rich cavities of DMeP5, suggesting the deep inclusion of the alkyl chain and partial imidazole moiety of guest TImPor in the cavity of DMeP5 due to the formation of complex DMeP5@TImPor. This is further confirmed by the NOESY cross-signals between methyl proton H_a of DMeP5 and methylene proton H₅ of TImPor in the NOESY spectrum of the mixture between DMeP5 and TImPor in the ratio of 2:1 in CDCl₃, Fig.

S7 (ESI[†]). In order to investigate the binding affinity of DMeP5 with TImPor, a model compound 1,4-dimethoxypillar[5]arene (MeP5) (actually one of the two pillararenes in DMeP5) and 1-butylimidazole (Bulm) (actually one of the four arms in TImPor) were applied for the ¹H NMR titration experiments.^[8a,8e] According to the experimental result, Fig. S8 (ESI[†]), the association constant (*K*_a) for the formation of the complex MeP5@Bulm was calculated to be 1.62 × 10² M⁻¹ in CDCl₃.

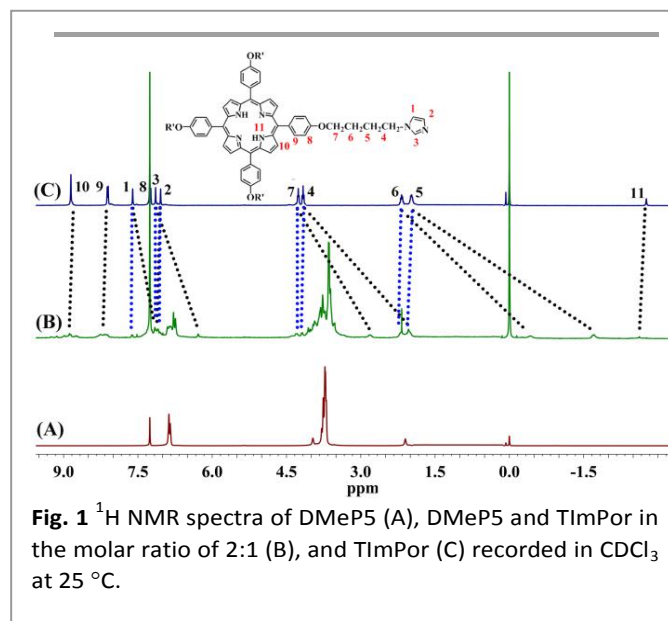


Fig. 1 ¹H NMR spectra of DMeP5 (A), DMeP5 and TImPor in the molar ratio of 2:1 (B), and TImPor (C) recorded in CDCl₃ at 25 °C.

Both electronic absorption and fluorescence emission spectroscopy were utilized to collect further information about the binding between DMeP5 and TImPor. According to the electronic absorption spectroscopic results, Fig. S9 (ESI[†]), upon gradual addition of DMeP5 into TImPor, the porphyrin Soret absorption underwent slight bathochromic shift due to the formation of the complex DMeP5@TImPor. Further support for this conclusion comes from the fluorescence spectroscopic result and the observation of a slight decrease in the emission intensity, accompanied by a slight bathochromic shift in the porphyrin Q band, after adding DMeP5 into the solution of TImPor, Fig. S9 (ESI[†]).

Diffusion-ordered NMR spectroscopy (DOSY) was usually employed to correlate the ¹H NMR signals with the diffusion coefficient (*D*) in solution and therefore successfully used to characterize the formation of supramolecular polymer.^[5c,15] In the present case, the DOSY spectra of a series of samples with different molar ratios between DMeP5 and TImPor in CDCl₃ were recorded, Fig. 2A. Along with increase in the molar ratio of DMeP5 and TImPor, the average diffusion coefficient of the complex decreased from 4.33 × 10⁻¹⁰ to 2.79 × 10⁻¹⁰ m²s⁻¹. Obviously, the complexation between DMeP5 and TImPor leads to such a dramatic decrease in the diffusion coefficient as compared with that of TImPor, suggesting that the host-guest building blocks diffuse as one entity and indicating the formation of large polymeric species between these two building blocks. Nevertheless, the DOSY experiments were also performed to investigate the formation of concentration-dependent supramolecular polymer in solution. As shown in Fig. 2B, a plot of diffusion coefficient *versus* concentration suggests that as

the concentration of TImPor increases from 2.5×10^{-4} to 4.0×10^{-3} M, the average diffusion coefficient of supramolecular polymer DMeP5@TImPor gets decreased from 4.70×10^{-10} to $2.95 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which further reveals the formation of high molecular weight polymer structures at relatively high concentrations.

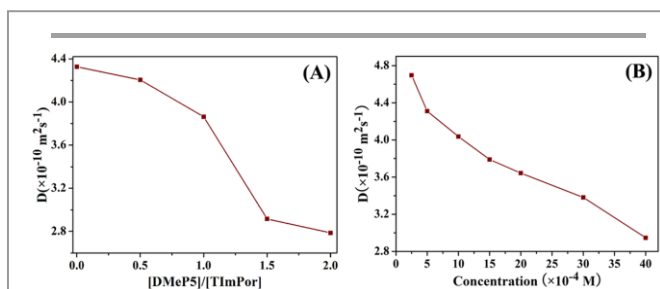


Fig. 2 Diffusion coefficient of TImPor with different ratios of DMeP5 (A), and 2.0 equiv. DMeP5 with different concentrations of TImPor (B) recorded in CDCl_3 at 25°C .

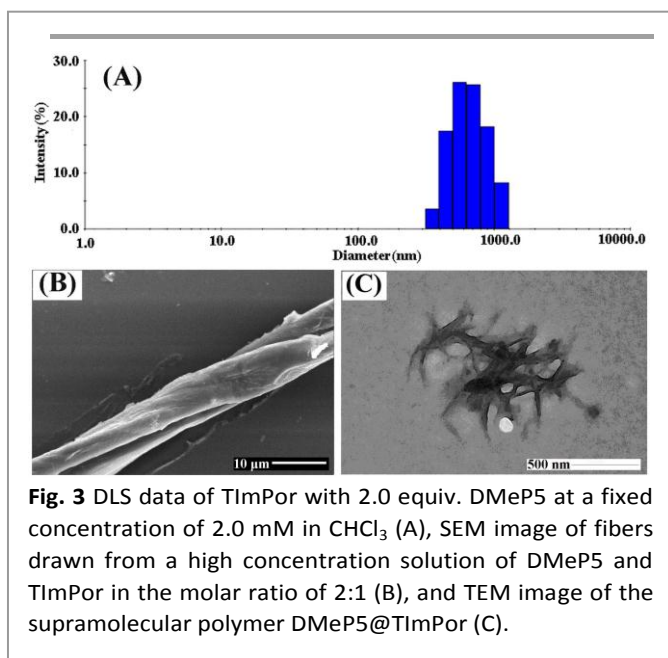


Fig. 3A and S11 (ESI[†]) show the Dynamic light scattering (DLS) data of supramolecular polymer DMeP5@TImPor in CHCl_3 . As can be found, mixing DMeP5 and TImPor at the molar ratio of 2:1 leads to the observation of one peak at 690 nm, indicating the formation of the aggregates with the average diameter of this size in CHCl_3 solution. This gives unambiguous evidence for the formation of supramolecular polymer architectures between DMeP5 and TImPor.

Furthermore, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to provide further insight into the size and morphology of the supramolecular aggregates formed from DMeP5 and TImPor. The microscopic fibers drawn from a high concentration solution were observed by SEM for the supramolecular polymer, Fig. 3B, giving a direct evidence for the formation of supramolecular polymer with high molecular weight. In addition, after evaporating the solution of DMeP5 and

TImPor on copper grid, cross-linked network structures were observed by TEM image, Fig. 3C, which is in line with the typical morphology observed for the cross-linked supramolecular polymers. This phenomenon was further confirmed by atomic force microscopy (AFM) image, Fig. S12 (ESI[†]), in which a number of crossing network structures were observed, affording further direct physical evidence for the formation of such supramolecular polymer due to the entanglement of cross-linked macro-sized aggregates.^[16]

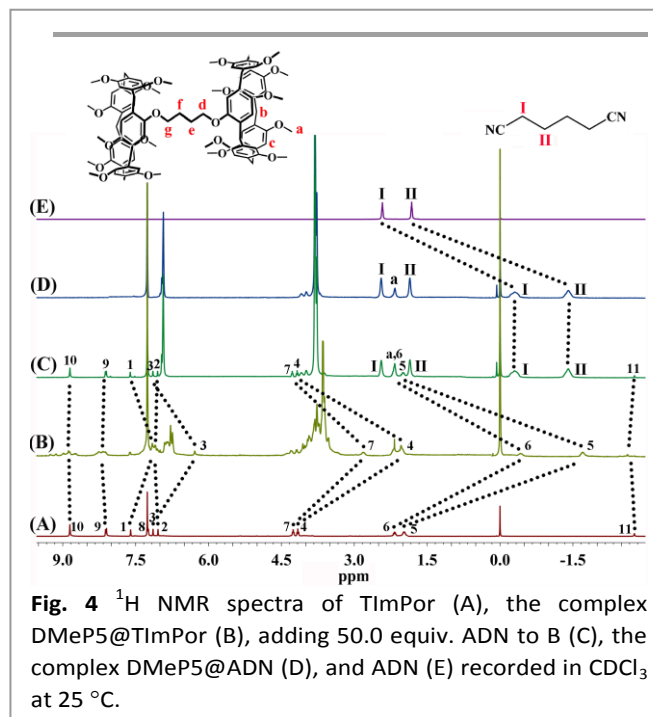


Fig. 4 ^1H NMR spectra of TImPor (A), the complex DMeP5@TImPor (B), adding 50.0 equiv. ADN to B (C), the complex DMeP5@ADN (D), and ADN (E) recorded in CDCl_3 at 25°C .

Reversible transformation to and from the starting building block, in particular for the guest species under certain conditions, is one of the primary features of supramolecular polymers.^[17] This is also true in the present case. As shown in Fig. 4, upon gradual addition of 50.0 equiv. adiponitrile (ADN) as the competitive guest (which possesses stronger binding ability with 1,4-dimethoxypillar[5]arene)^[1n,8e,18] into the DMeP5@TImPor supramolecular polymer solution in CDCl_3 , the signals for the methylene protons H_I and H_{II} of ADN exhibited obviously upfield shifts ($\Delta\delta = -2.73$ and -3.23 ppm, respectively) compared to the free competitive guest ADN. At the same time, the signals of TImPor in the DMeP5@TImPor system returned to the original state of the free TImPor molecule, indicating the effective dissociation of the original inclusion complex DMeP5@TImPor with the re-formation of guest TImPor species and concomitant formation of the new inclusion complex between DMeP5 and ADN.

To have further evidence for the disassembly of supramolecular polymer DMeP5@TImPor along with the addition of competitive guest ADN, the DOSY and DLS measurements were also carried out. As shown in Fig. S13 (ESI[†]), upon addition of 100.0 equiv. ADN to the CDCl_3 solution of DMeP5@TImPor, the average diffusion coefficient of the assemblies increases pronouncedly from 2.90×10^{-10} to $4.68 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Furthermore, the DLS experiment results

show that only small sized aggregates with the average diameter of either 3 or 42 nm could be observed when 100.0 equiv. competitive guest ADN was added into the CHCl_3 solution of DMeP5@TImPor, Fig. S14 (ESI[†]), indicating the disassembly of supramolecular polymer and the formation of new inclusion complex with small volume based on the complexation between pillar[5]arene and ADN. As a result, the above host-guest competition investigation gives clear evidence for the destruction of cross-linked supramolecular polymer by adding a competitive guest, which also affords a successful example of the supramolecular transformation from cross-linked supramolecular polymer to the inclusion complex DMeP5@ADN.

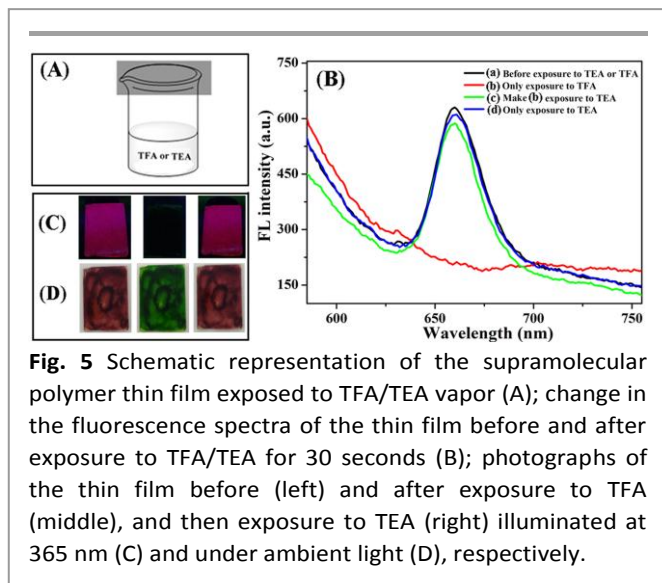


Fig. 5 Schematic representation of the supramolecular polymer thin film exposed to TFA/TEA vapor (A); change in the fluorescence spectra of the thin film before and after exposure to TFA/TEA for 30 seconds (B); photographs of the thin film before (left) and after exposure to TFA (middle), and then exposure to TEA (right) illuminated at 365 nm (C) and under ambient light (D), respectively.

In order to explore the application of the supramolecular polymer for detecting acidic/alkaline gases, a thin film of the supramolecular polymer was prepared by drop-casting the high concentration solution of the polymer in CHCl_3 onto quartz slides. Interestingly, as long as the thin film is exposed to trifluoroacetic acid (TFA) vapor, the fluorescence gets completely quenched at once, Fig. 5B, accompanied by a visually clear color change from purplish red to green under ambient light due to the protonation of porphyrin.^[19] When this TFA-treated film is re-exposed to triethylamine (TEA) vapor, the protonated porphyrin units in the supramolecular polymer get deprotonated again, leading to a complete recovery of the fluorescence for the thin film. As shown in Fig. 5, if the thin film is only exposed to TEA gas, the fluorescence intensity of the thin film does not change and certainly shows no visually color change behavior. These results seem to suggest the potential application of this supramolecular polymer as the acidic gas sensor.

In summary, a novel supramolecular polymer was successfully constructed between bis-(methoxy-pillar[5]arene) (DMeP5) and 5,10,15,20-tetrakis{butoxy-4-(1H-imidazol-1-yl)}porphyrine (TImPor) depending on the host-guest interactions and characterized by a wide range of techniques. Addition of competitive guest adiponitrile led to effective dissociation of supramolecular polymer DMeP5@TImPor and re-formation of original guest species, giving additional

support for the host-guest interaction-based supramolecular polymer nature of the present system. In particular, exposure of this supramolecular polymer thin film to the acidic gas led to complete quenching in the fluorescence accompanied by a visually color change from purplish red to green under ambient light, endowing the system with an application potential in acidic gas detection.

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