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## Assembly of a Self-Complementary Monomer: Formation of Supramolecular Polymer Networks and Responsive Gels

### Yong-Sheng Su, Jia-Wei Liu, Yi Jiang, and Chuan-Feng Chen<sup>\*[a]</sup>

Abstract: Self-complementary monomer 1, which combines a macrotricyclic polyether and two dibenzylammonium ions together, was synthesized, and its self-assembly into supramolecular polymer networks by host-guest interactions was studied. For the purpose of comparative study, two model molecules 2 and 3 were also prepared. It was found that model molecule 2 and dibenzylammonium ion 4 form a 1:2 complex in solution and in the solid state, which afforded a model system for the investigation of the assembly behavior of monomer 1. Consequently, the <sup>1</sup>H NMR spectrum of **1** in  $CD_3CN$ showed characteristic proton signals similar to the model system, which suggested that **1** self-assembles into a supramolecular polymer network. Formation of the supramolecular polymer was further evidenced by the MALDI-TOF MS spectrum, viscometry, and dynamic light-scattering (DLS) experiments. Moreover, it was found that the

**Keywords:** gels • molecular recognition • polymers • self-assembly • supramolecular chemistry decomposition and re-formation of the supramolecular polymer could be chemically controlled by the use of triethylamine and trifluoroacetic acid. Interestingly, the supramolecular polymer forms an organogel both in  $CD_3CN$  and in 1:1 (v/v)  $CDCl_3/CD_3CN$ , and reversible thermo- and pH-induced gel-sol transitions were also found. The presented work will provide a new strategy for the construction of supramolecular polymers with specific structures and properties.

### Introduction

Supramolecular polymers,<sup>[1]</sup> a new field formed by the combination of supramolecular chemistry and polymer science, has currently attracted great interest. Consequently, chemists have developed a variety of strategies for constructing supramolecular polymers over the past years,<sup>[2,3]</sup> in which host-guest interaction<sup>[4]</sup> has become one of the most important and convenient approaches. In particular, crown ether based molecular recognition has been successfully utilized in the construction of supramolecular polymers with linear,<sup>[5]</sup> star,<sup>[6]</sup> hyperbranched,<sup>[7]</sup> and dendronized<sup>[8]</sup> topologic structures. Some of the supramolecular polymers with specific structures also form supramolecular gels,<sup>[9]</sup> which have received significant and current attention because of their wide potential application in materials science, drug delivery, and chemical sensors. Recently, Huang and Liu et al.<sup>[10]</sup> reported the fabrication of responsive supramolecular gels with a network structure based on the molecular recognition between dibenzo[24]crown-8 (DB24C8)-terminated four-

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arm star poly(ε-caprolactone) (PCL) and dibenzylammonium-terminated two-arm star PCL. Although the integration of molecular recognition with polymers results in the crosslinkage of polymers for the formation of supramolecular networks,<sup>[11]</sup> to the best of our knowledge, no supramolecular polymer networks based on host–guest interactions of self-complementary low-molecular-weight monomers without polymeric backbones have hitherto been reported.

Recently, we reported a triptycene-derived macrotricyclic polyether that contained two DB24C8 moieties, a powerful host for complexation with different guests in different topology.<sup>[12]</sup> In particular, we found that the macrocycle forms a 1:2 complex with 2 equiv dibenzylammonium ions (Scheme 1a),<sup>[13]</sup> which inspired us to further design and synthesize a self-complementary monomer 1 that combines a macrotricyclic polyether (host units) and two dibenzylammonium ions (guest units) together (Scheme 1b). In this paper, we report the synthesis of the monomer 1 and its self-assembly into supramolecular polymer networks, which represent the first example of supramolecular polymer networks formed by the assembly of self-complementary lowmolecular-weight monomers based on intermolecular hostguest interactions. Interestingly, it was also found that the supramolecular polymers showed gel properties in acetonitrile or acetonitrile/chloroform solution, and the supramolecular gels exhibited reversible thermo- and pH-induced gel-sol transitions.

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Scheme 1. a) Formation of the 1:2 complex between the macrotricyclic host and dibenzylammonium salts; b) Structures and proton designations of self-complementary monomer 1, model molecules 2 and 3, and guest 4.

### **Results and Discussion**

Synthesis of monomer 1 and model molecules 2 and 3: The synthetic methodology for monomer 1 and model molecules 2 and 3 is depicted in Scheme 2. Firstly, we prepared dibenzylammonium derivative 8 by the reaction of 4-nitrobenzaldehyde and benzylamine in toluene, reduction with NaBH<sub>4</sub> in 1:1 THF/CH<sub>3</sub>OH, protection of the amine group, and then catalytic hydrogenation in the presence of Pd/C. Under the same conditions, compound 14 was prepared from 4-nitrobenzaldehyde and 3,5-dimethoxylbenzylamine. Starting from anthracene derivative 10, macrotricyclic polyether 5 that contained two DB24C8 moieties was synthesized in three steps according to a method described before.<sup>[14]</sup> Then, Diels-Alder cycloaddition between 5 and dimethyl acetylenedicarboxylate afforded the macrotricyclic derivative 6, which was hydrolyzed, followed by heating it to reflux in acetic anhydride to give acid anhydride 7. t-Butyloxycarbonvl (Boc)-protected precursor 9 was obtained by the reaction of compound 7 with Boc-protected compound 8 (2 equiv). Finally, monomer 1 that contained complementary molecular recognition moieties was produced in 95% yield by hydrolysis of precursor 9 with aqueous HPF<sub>6</sub>. Similarly, model molecule 2 was prepared in 95% yield by the reaction of acid anhydride 7 and aniline. Model molecule 3 was conveniently obtained by the reaction of 7 and 14, followed the hydrolysis by aqueous HPF<sub>6</sub>. Compound 2 was designed to study its complexation with dibenzylammonium ions, and subsequently afforded a model system for further study of the assembly behavior of monomer 1. In the case of model molecule 3, it has a similar structure to monomer 1 except for the sterically hindered end groups in "guest moieties," which prevent its threading through the cavity of DB24C8 to form supramolecular polymers.

**Complexation between model molecule 2 and guest 4**: We first tested the complexation between model molecule **2** and dibenzylammonium ion **4** by NMR spectroscopy. As shown in Figure 1b, the <sup>1</sup>H NMR spectrum of a 1:2 mixture of **2** 



Figure 1. Partial <sup>1</sup>H NMR spectra (300 MHz,  $CDCl_3/CD_3CN = 1:1, 298 \text{ K}$ ) for a) guest **4**; b) complexation between **2** and 2.0 equiv **4**; and c) host **2**. c2 and c1 denote the 1:2 and 1:1 complex between the macrotricyclic host and the dibenzylammonium ion, respectively.  $[2]_0 = 4.0 \text{ mM}$ .

and 4, recorded in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v), revealed the characteristic complexed signals of both the host and the guest. Since the complexation between host 2 and guest 4 showed a slow exchange process, the weak resonances for the 1:1 complex and uncomplexed species in addition to those strong resonances for 1:2 complex  $2.4_2$  were also shown. It was found that the benzyl protons of guest 4 located outside the cavity of host 2 showed downfield signals, whereas the signals of the benzyl protons H<sub>a</sub>, H<sub>b</sub>, and H<sub>c</sub> located inside the cavity of 2 shifted upfield strikingly. In particular, the signal of the benzylic methylene proton H<sub>a</sub> adjacent to the NH<sub>2</sub><sup>+</sup> center exhibited a large downfield shift, which was attributed to the hydrogen-bond interactions and the deshielding effect of the aromatic rings in 2. Moreover, an upfield shift for aromatic proton  $H_1$  of 2 and significant changes in the chemical shifts of the protons in crown ether

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Scheme 2. Schematic illustrations for the preparation of a) compound 8, b) compound 14, and c) monomer 1, and model molecules 2 and 3.

units were also observed. These observations were similar to the cases of the complexation between the triptycene-derived cylindrical macrotricyclic host and the dibenzylammonium ions,<sup>[13]</sup> which suggested that an expected 1:2 complex **2-4**<sub>2</sub> was formed in solution.

Formation of complex  $2\cdot 4_2$  was also confirmed by its ESI-MS spectrum (see the Supporting Information). Consequently, strong peaks at m/z 868.2 and 1538.5 for  $[2\cdot 4_2-2 PF_6^{-}]^{2+}$  and  $[2\cdot 4-PF_6^{-}]^{+}$ , respectively, were found. Further support for the formation of the complex  $2\cdot 4_2$  came from its X-ray analysis (see the Experimental Section). As shown in Figure 2, two dibenzylammonium ions were threaded symmetrically through the center of the DB24C8 cavities of host 2, which resulted in a novel [3]pseudoro-



Figure 2. a) Top view and b) side view of the crystal structure of complex  $2.4_2$ . Solvent molecules and hydrogen atoms were omitted for clarity.

taxane-type complex in the solid state. Moreover, there existed multiple noncovalent interactions not only between the host and the guest, but also between the two guests, which played an important role in the formation of the 1:2 complex.<sup>[13]</sup> Formation of the expected 1:2 complex **2**·**4**<sub>2</sub> provided a model system for further study of the assembly of **1** with the self-complementary moieties.

Assembly of self-complementary monomer 1: The self-assembly of monomer 1 was first investigated by NMR spectroscopy. As shown in Figure 3a, the <sup>1</sup>H NMR spectrum of monomer 1 in CD<sub>3</sub>CN revealed characteristic complexed signals between the host and the guest moieties. It was found that the resonances for protons  $H_A$ ,  $H_B$ , and  $H_C$  of the guest moieties strikingly shifted upfield, which indicated that they were located inside the cavities of the host moiety. Moreover, besides the resonances for 1:2 complexation between the macrotricyclic host moiety and the dibenzylammonium ions, the resonances for 1:1 complexed and uncomplexed species were also observed. All of these complexation behaviors of 1 were very similar to the case of the model system described above. Since the short and rigid linkers avoided self-recognition between the host and the guest moieties of 1, it was thus implied that monomer 1 has self-assembled into an expected supramolecular polymer network based on the intermolecular host-guest interac-

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Figure 3. Partial <sup>1</sup>H NMR spectra (300 MHz, 298 K, 4 mM) of a) the supramolecular polymer formed by the self-assembly of **1** in CD<sub>3</sub>CN; b) complexation between **2** and 2.0 equiv **4** in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v); c) **1** in [D<sub>6</sub>]DMSO; and d) **3** in CD<sub>3</sub>CN. c2 and c1 denote the 1:2 and 1:1 complex between the host moiety and the dibenzylammonium ion, respectively.

tions. Comparatively, we found that model molecule **3** only showed the uncomplexed signals (Figure 3d) because the sterically hindered end groups in the "guest moieties" prevent their complexation. Since the complex between DB24C8 and dibenzylammonium ions completely decomposed in DMSO,<sup>[13]</sup> it was found that monomer **1** showed clear uncomplexed signals in [D<sub>6</sub>]DMSO (Figure 3c), which also enabled us to obtain its characteristic NMR spectroscopic data.

The association and disassociation of the complex between DB24C8 and the dibenzylammonium ion can be chemically controlled by the pH value,<sup>[12b]</sup> which inspired us to further investigate the reversible formation of the supramolecular polymer from **1** by NMR spectroscopy (see the Supporting Information). Consequently, we found that in the presence of triethylamine (TEA), the characteristic proton signals for the complexation between the host and the guest moieties of monomer **1** completely disappeared, which implied that the decomposition of the supramolecular polymer networks occurred. Interestingly, it was found that the addition of an excess amount of trifluoroacetic acid (TFA) to the above system leads to the re-formation of the supramolecular polymer.

The MALDI-TOF mass spectrum provided another piece of evidence for the formation of the supramolecular polymer (see the Supporting Information). As a result, the strongest peak at m/z 3155 (100%) was shown, which corresponds to the dimer  $[\mathbf{1}_2 - 3 \text{HPF}_6 - \text{PF}_6]^+$ . Moreover, a strong peak at m/z 4879 for  $[\mathbf{1}_3 - 4 \text{HPF}_6 - \text{PF}_6]^+$  was also observed, which is consistent with the trimer. Although higher units in the supramolecular polymer could not be found, probably because of the restriction of their "fly" abilities and the experimental conditions, the higher intensities for the dimer trimer than the monomer (m/z)1599 and for  $[1-2HPF_6+Na]^+$ ) implied that monomer 1 showed strong self-assembling abilities.

Viscometry provides a convenient and simple technique to characterize the growth of supramolecular polymers with increasing concentrations of the monomer. As shown in Figure 4, the reduced viscosity of the acetonitrile solutions



Figure 4. Variation of reduced viscosities,  $V_{R}$  (CH<sub>3</sub>CN, 298 K) as a function of the concentrations of the supramolecular polymers obtained by the intermolecular host–guest complexation of monomer 1 ( $\blacksquare$ ) and the model molecule 3 ( $\triangle$ ).

of compound 1 varied exponentially with its concentrations, thereby suggesting the formation of supramolecular polymer networks. On the contrary, under the same conditions, the reduced viscosity of 3 varied linearly with its concentrations because of the sterically hindered end groups in the guest moieties of 3 that prevented its thread through the cavity of DB24C8. This observation indicated that no significant physical entanglements or noncovalent intermolecular interactions in 3 occurred, which is also in accordance with its monomer structure.

Formation of the supramolecular polymer was further supported by the dynamic light-scattering (DLS) experiments (see the Supporting Information). As a result, a 15 mM solution of compound **1** in acetonitrile showed an average hydrodynamic radius of 53.6 nm, which implied its great aggregation. However, under the same conditions, no aggregation could be detected for a solution of **3** per our expectation.

Formation of a responsive supramolecular gel: Interestingly, it was found that the supramolecular polymer could form a supramolecular gel at high concentrations. Consequently, when an acetonitrile solution of **1** with a concentration higher than 20 mM cooled from 80 to 25 °C, a transparent supramolecular gel formed. Heating the gel resulted in recovery of the fluid solution again (Figure 5a). Formation of the gel at lower temperatures could be ascribed to the restoration of the supramolecular polymer from **1**, which was partially disrupted at elevated temperatures. Moreover, we also found that the supramolecular gel could form at lower concentration ( $\approx 5$  mM) of 1 in 1:1 (v/v) CDCl<sub>3</sub>/CD<sub>3</sub>CN. Besides

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Figure 5. Supramolecular gel formed from 1 a) in CH<sub>3</sub>CN and its thermoinduced gel-sol transitions, and b) in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v) and its pHinduced gel-sol transitions.

the temperature response, the gel also showed pH-induced gel-sol transitions. As shown in Figure 5b, the gel could be converted into a fluid solution upon the addition of TEA (2.2 equiv), which resulted in the deprotonation of the dibenzylammonium ions, and thus disrupted the supramolecular polymer. It was also interestingly noted that the addition of TFA (about 2.4 equiv) to the above solution led to the re-formation of the supramolecular gel. These completely reversible thermo- and pH-induced gel-sol transitions further supported the formation of supramolecular polymer networks, and also reflected their dynamic nature as typical supramolecular systems.

#### Conclusion

In summary, we have synthesized a self-complementary monomer that combined a cylindrical macrotricyclic polyether and two dibenzylammonium moieties together, and demonstrated that the low-molecular-weight monomer self-assembles into chemically controlled supramolecular polymer networks by intermolecular host–guest recognition. Interestingly, we also found that the supramolecular polymers showed gel properties in acetonitrile or acetonitrile/chloroform solutions, and the supramolecular gels exhibit reversible thermoand pH-induced gel–sol transitions. We believe that the work presented here can provide a strategy for the construction of the supramolecular polymers with specific structures and properties.

### **Experimental Section**

**General:** Melting points, taken using an electrothermal melting point apparatus, are uncorrected. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using a Bruker DMX300 NMR spectrometer. 2D COSY experiments were measured using a Bruker DMX600 NMR spectrometer. MALDI-TOF MS were obtained using a Bruker BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Chemistry, CAS. Measurements of the reduced viscosities of

the solution of the supramolecular polymer and model molecule **3** as a function of concentrations were conducted using an Ubbelohde viscometer at  $(25\pm0.05)$ °C. Hydrodynamic radii of solutions of **1** and **3** were measured after solutions were filtered through a Teflon filter (pore size 0.2 µm) and using Wyatt DynaPro NanoStar dynamic light-scattering (DLS) detectors.

Compound 11: K<sub>2</sub>CO<sub>3</sub> (14.8 g, 107 mmol) was added to a stirred solution of compound 10<sup>[15]</sup> (3.60 g, 13.3 mmol) and tri(ethylene glycol) monotosylate (17.8 g, 58.6 mmol) in dried CH<sub>3</sub>CN (300 mL). The reaction mixture was stirred while heating to reflux for 24 h, cooled to ambient temperature, and then filtered. The filtrate was concentrated to give a residue, which was dissolved in dried CH<sub>2</sub>Cl<sub>2</sub> (250 mL), and 4-toluene sulfonyl chloride (TsCl) (13.4 g, 70.3 mmol), Et<sub>3</sub>N (8.80 g, 87.1 mmol), and 4-dimethylaminopyridine (DMAP) (0.360 g, 3.00 mmol), respectively, were added to the solution. The reaction mixture was heated to reflux for 10 h, cooled to ambient temperature, and then washed with HCl (2M) and water successively. The organic layer was dried over anhydrous Na2SO4, and then concentrated to afford a crude product, which was further purified by flash column chromatography with CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH (3:1 v/v) as eluent to afford 11 (12.2 g, 65%) as a colorless oil. <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{CDCl}_3): \delta = 7.77 \text{ (d}, J = 8.3 \text{ Hz}, 8 \text{ H}), 7.45 \text{ (s}, 4 \text{ H}), 7.28 \text{ (d}, J = 8.3 \text{ Hz}, 8 \text{ H})$ 8.3 Hz, 8H), 4.33 (t, J=4.9 Hz, 8H), 4.19-4.10 (m, 8H), 3.95 (t, J= 4.9 Hz, 8H), 3.77-3.56 (m, 24H), 2.89 (s, 6H), 2.38 ppm (s, 12H);  $^{13}\text{C}\,\text{NMR}$  (75 MHz, CDCl<sub>3</sub>):  $\delta\!=\!148.3,\,144.8,\,133.0,\,129.8,\,127.9,\,126.1,\,$ 124.1, 105.1, 70.9, 70.9, 70.8, 69.7, 69.3, 68.7, 68.4, 21.6, 14.7 ppm; MALDI-TOF MS: m/z: 1414.5 [M]+, 1437.5 [M+Na]+, 1453.6 [M+K]+; elemental analysis calcd (%) for  $C_{68}H_{86}O_{24}S_4$ : C 57.69, H 6.12; found: C 57.49, H 6.30.

Compound 5: A mixed solution of 11 (0.90 g, 3.3 mmol) and 10 (4.72 g, 3.33 mmol) in DMF (180 mL) was slowly added through a funnel into a suspension that contained cesium carbonate (8.70 g, 26.7 mmol) in DMF (130 mL) at 110°C over 36 h. After being stirred at 110°C for 3 d, the reaction mixture was cooled to ambient temperature. Removal of DMF under reduced pressure gave a residue, which was dissolved in chloroform and then filtered. The filtrate was washed with water twice, dried over anhydrous Na2SO4, and concentrated to afford a crude product, which was purified by flash column chromatography with CH2Cl2 and methanol (80:1 v/v) as eluent to afford 5 (0.80 g, 24%) as a yellow solid. M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 6.83$  (s, 8H), 4.38–4.17 (m, 8H), 4.19-3.95 (m, 32H), 3.94-3.74 (m, 8H), 2.30 ppm (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 147.0$ , 125.0, 123.0, 103.0, 71.4, 69.02, 67.6, 14.1 ppm; MALDI-TOF MS: m/z: 996.6 [M]+, 1019.6 [M+Na]+, 1035.6  $[M+K]^+$ ; elemental analysis calcd (%) for  $C_{56}H_{68}O_{16} \cdot 0.5H_2O$ : C 66.85, H 6.91; found: C 66.62, H 6.90.

**Compound 6**: Compound **5** (0.60 g, 0.60 mmol) was suspended in dimethyl acetylenedicarboxylate (10 mL), which was heated at approximately 180 °C for 30 min. Removal of volatile constituents under reduced pressure gave a residue, which was washed with methanol. The collected solid was recrystallized in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH to afford **6** (0.68 g, 89%) as a white solid. M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =6.81 (s, 8H), 4.21–3.92 (m, 16H), 3.94–3.74 (m, 28H), 3.75–3.56 (m, 16H), 2.09 ppm (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =166.1, 150.7, 145.7, 141.5, 109.2, 71.0, 69.9, 51.9, 49.1, 13.8 ppm; MALDI-TOF MS: *m*/*z*: 1303.5 [*M*+Na]<sup>+</sup>, 1319.5 [*M*+K]<sup>+</sup>; elemental analysis calcd (%) for C<sub>68</sub>H<sub>80</sub>O<sub>24</sub>: C 63.74, H 6.29; found: C 63.62, H 6.33.

**Compound 6**': NaOH (0.31 g, 7.8 mmol) and H<sub>2</sub>O (2 mL) were added to a suspension of **6** (0.50 g, 0.39 mmol) in CH<sub>3</sub>OH (30 mL). The reaction mixture was heated at reflux for 10 h, and then concentrated under reduced pressure to give a residue, which was dissolved in H<sub>2</sub>O (15 mL). After the solution was acidified to pH < 3, the resultant precipitate was filtered, washed with water, and then dried under vacuum to yield **6'** (0.48 g, 100%) as a white solid. M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =12.87 (s, 4H), 6.87 (s, 8H), 3.98 (s, 16H), 3.79–3.42 (m, 32H), 2.06 ppm (s, 12H); <sup>13</sup>C NMR (75 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =167.0, 149.1, 144.9, 141.6, 108.9, 70.3, 69.1, 48.4, 13.6 ppm; MALDI-TOF MS: *m/z*: 1247.7 [*M*+Na]<sup>+</sup>; elemental analysis calcd (%) for C<sub>64</sub>H<sub>72</sub>O<sub>24</sub>: C 62.74, H 5.92; found: C 62.69, H 5.85.

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Compound 9: A solution of 6' (0.41 g, 0.33 mmol) in acetic anhydride (10 mL) was heated to reflux under Ar for 4 h. Removal of the solvent under reduced pressure gave 7 as a yellow solid, which was used without further purification. Compound 12 (452 mg, 1.32 mmol) was dissolved in 1:1 (v/v) CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (20 mL) and 10% Pd(C) (50 mg) was added. The mixture was stirred under an  $H_2$  atmosphere for 3 h, filtered, and then solvent was removed. The mixture of 7 and 8 obtained above was dissolved in CHCl<sub>3</sub> (15 mL) and stirred at 50 °C overnight, then solvent was removed under reduced pressure. The residue was suspended in acetic anhydride (15 mL), NaOAc (54 mg, 0.66 mmol) was added and then stirred under N2 at 100°C for 3 h. Removal of solvent under reduced pressure gave a crude product, which was purified by flash column chromatography with  $CH_2Cl_2$  and methanol (60:1 v/v) as eluent, then recrystallized in CH2Cl2/Et2O to afford 9 (0.54 g, 92%) as a yellow solid. M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.38-7.09$  (m, 18H), 6.90 (s, 8H), 4.45-4.25 (m, 8H), 4.18-4.07 (m, 8H), 4.07-3.97 (m, 8H), 3.91-3.77 (m, 24H), 3.78-3.66 (m, 8H), 2.30 (s, 12H), 1.48 ppm (s, 18H);  $^{13}\text{C}\,\text{NMR}$  (75 MHz, CDCl<sub>3</sub>):  $\delta\!=\!165.3,\ 163.6,\ 163.4,\ 157.4,\ 155.9,\ 145.9,$ 141.6, 140.9, 137.9, 130.8, 128.5, 127.7, 127.3, 126.5, 109.7, 104.9, 86.0, 80.2, 71.1, 70.0, 69.9, 48.6, 28.4, 22.9, 12.1 ppm; MALDI-TOF MS: m/z: 1799.9  $[M+Na]^+$ ; elemental analysis calcd (%) for  $C_{102}H_{112}N_4O_{24}H_2O$ : C 68.56, H 6.37, N 3.14; found: C 68.51, H 6.40, N 3.09.

**Monomer 1**: In a suspension of **9** (0.20 g, 0.11 mmol) in CH<sub>3</sub>CN (15 mL), an excess amount of HPF<sub>6</sub> (0.5 mL) was added and stirred at 0°C for 1 h. Removal of the solvent under reduced pressure gave a residue, which was washed with water. The solid was collected and dried under vacuum to yield pure **1** (195 mg, 95%) as a yellow solid. M.p. > 300°C; <sup>1</sup>H NMR (300 MHz, DMSO):  $\delta = 9.06$  (s, 4H), 7.64–7.38 (m, 14H), 7.31 (d, J = 8.3 Hz, 4H), 6.98 (s, 8H), 4.23–4.12 (m, 8H), 4.00 (s, 16H), 3.84–3.41 (m, 32H), 2.25 ppm (s, 12H); <sup>13</sup>C NMR (75 MHz, DMSO):  $\delta = 164.7$ , 164.3, 156.8, 149.4, 145.1, 143.7, 141.2, 139.5, 132.2, 131.8, 130.3, 129.9, 128.9, 128.7, 127.3, 127.1, 112.7, 109.5, 99.5, 70.3, 69.2, 65.3, 50.4, 49.8, 48.3, 46.2, 23.7, 11.9 ppm; MALDI-TOF MS: m/z: 1599 [M–2HPF<sub>6</sub>+Na]<sup>+</sup>, 3155 [2M–3HPF<sub>6</sub>–PF<sub>6</sub><sup>-</sup>]<sup>+</sup>, 4879 [3M–4HPF<sub>6</sub>–PF<sub>6</sub><sup>-</sup>]<sup>+</sup>; elemental analysis calcd (%) for C<sub>92</sub>H<sub>98</sub>F<sub>12</sub>N<sub>4</sub>O<sub>20</sub>P<sub>2</sub>·H<sub>2</sub>O: C 58.54, H 5.34, N 2.97; found: C 58.51, H 5.40, N 3.09.

**Compound 2**: According to a similar procedure for the synthesis of **9**, compound **2** as a yellow solid was obtained in 95% yield by the reaction of acid anhydride **7** and aniline. M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.35$  (d, J = 7.8 Hz, 4H), 7.28 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.5 Hz, 4H), 6.89 (s, 8H), 4.17–4.06 (m, 9H), 4.06–3.97 (m, 8H), 3.94–3.77 (m, 24H), 3.77–3.67 (m, 8H), 2.29 ppm (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 165.3$ , 157.4, 145.8, 141.6, 131.7, 128.9, 127.4, 126.5, 109.6, 71.1, 70.0, 69.9, 48.6, 12.1 ppm; MALDI-TOF MS: m/z: 1361.6 [*M*+Na]<sup>+</sup>; elemental analysis calcd (%) for C<sub>76</sub>H<sub>78</sub>N<sub>2</sub>O<sub>20</sub>: C 68.15, H 5.87, N 2.09; found: C 67.93, H 5.91, N 2.09.

Compound 12: A mixture of 4-nitrobenzaldehyde (1.51 g, 10.0 mmol) and benzylamine (1.07 g, 10.0 mmol) in toluene (65 mL) was heated at reflux for 24 h, and then concentrated under reduced pressure. The residue was dissolved in 1:1 (v/v) THF/CH<sub>3</sub>OH (40 mL), and NaBH<sub>4</sub> (1.11 g, 30.0 mmol) was added in batches. After the mixture was stirred at room temperature overnight, an excess amount of NaBH4 was decomposed by adding water slowly, and the mixture was extracted three times by CH2Cl2. The organic layer was dried over anhydrous Na2SO4, and then concentrated to afford a residue, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (45 mL). After adding di-tert-butyl dicarbonate (Boc2O) (4.36 g, 20.0 mmol) and DMAP (122 mg, 1.00 mmol), the mixture was stirred at room temperature overnight. Removal of the solvent under reduced pressure gave a crude product, which was purified by flash column chromatography with petroleum and EtOAc (30:1 v/v) as eluent to afford 12 (2.12 g, 62 %) as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.17$  (d, J = 8.1 Hz, 2H), 7.65-6.88 (m, 7H), 4.68-4.25 (m, 4H), 1.50 ppm (s, 9H); <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 155.8, 147.2, 145.8, 137.4, 128.7, 128.4, 128.1, 127.6,$ 123.8, 80.7, 50.2, 48.9, 28.4 ppm; ESI-MS: m/z: 365.2 [M+Na]+; elemental analysis calcd (%) for  $C_{19}H_{22}N_2O_4$ : C 66.65, H 6.48, N 8.18; found: C 66.48. H 6.48. N 8.02.

**Compound 13:** According to a similar procedure for the synthesis of **12**, compound **13** as a colorless oil was obtained in 66% yield starting from

3,5-dimethoxylbenzylamine and 4-nitrobenzaldehyde.<sup>[16]</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.18 (d, *J*=8.6 Hz, 2H), 7.43–7.29 (m, 2H), 6.38 (s, 2H), 6.33 (s, 1H), 4.63–4.19 (m, 4H), 3.77 (s, 6H), 1.62–1.32 ppm (m, 10H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =161.1, 155.8, 147.2, 145.8, 139.8, 128.4, 127.8, 123.8, 105.9, 105.4, 99.2, 80.7, 55.3, 50.3, 49.3, 48.9, 28.4 ppm; ESI-MS: *m*/*z*: 425.2 [*M*+Na]<sup>+</sup>; elemental analysis calcd (%) for C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>: C 62.67, H 6.51, N 6.96; found: C 62.61, H 6.49, N 6.79.

**Compound 15**: According to a similar procedure for the synthesis of **9**, compound **15** as a yellow solid was synthesized in 92 % yield by the reaction of acid anhydride **7** and compound **14** (obtained from the reduction of **13**, and used without further purification). M.p. >300°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  =7.33–7.07 (m, 8H), 6.90 (s, 8H), 6.35 (s, 6H), 4.46–4.19 (m, 8H), 4.18–3.95 (m, 16H), 3.95–3.59 (m, 44H), 2.30 (s, 12H), 1.47 ppm (s, 18H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  =165.3, 161.0, 157.4, 155.9, 145.8, 141.6, 140.4, 130.8, 128.6, 127.8, 126.5, 109.7, 105.3, 99.3, 80.2, 71.1, 70.0, 69.9, 55.3, 49.4, 48.6, 28.4, 12.1 ppm; MALDI-TOF MS: *m*/z: 1919.9 [*M*+Na]<sup>+</sup>, 1936.0 [*M*+K]<sup>+</sup>; elemental analysis calcd (%) for C<sub>106</sub>H<sub>120</sub>N<sub>4</sub>O<sub>28</sub>: C 67.07, H 6.37, N 2.95; found: C 67.35, H 6.40, N 3.06.

**Compound 3**: According to a similar procedure for the synthesis of **1**, compound **3** as a yellow solid was obtained in 93% yield from **15**. M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$ =7.45 (d, *J*=8.2 Hz, 4H), 7.26 (d, *J*=8.2 Hz, 4H), 7.00 (s, 8H), 6.61 (d, *J*=2.0 Hz, 4H), 6.57 (d, *J*=2.0 Hz, 2H), 4.22–4.12 (m, 8H), 4.12–3.96 (m, 16H), 3.81 (s, 12H), 3.78–3.53 (m, 32H), 2.33 ppm (s, 12H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN):  $\delta$ = 164.8, 161.0, 157.2, 145.1, 141.3, 133.0, 132.6, 130.3, 129.5, 127.0, 117.0, 109.2, 107.4, 100.7, 70.3, 69.3, 69.1, 54.9, 51.3, 50.7, 48.4, 11.3 ppm; MALDI-TOF MS: *m/z*: 1720.8 [*M*–2HPF<sub>6</sub>+Na]<sup>+</sup>; elemental analysis calcd (%) for C<sub>96</sub>H<sub>106</sub>F<sub>12</sub>N<sub>4</sub>O<sub>24</sub>P<sub>2</sub>-3H<sub>2</sub>O: C 56.41, H 5.52, N 2.74; found: C 56.40, H 5.52, N 2.93.

**Crystal data for 2-4;-2CH<sub>3</sub>CN**:  $C_{108}H_{116}F_{12}N_6O_{20}P_2$ ;  $M_r$ =2108.01; triclinic;  $P\bar{1}$ ; a=14.724(4), b=15.238(4), c=15.251(5) Å;  $\alpha$ =104.069(3),  $\beta$ = 106.313(3),  $\gamma$ =104.044(3)°; V=3002.5(15) Å<sup>3</sup>; Z=1;  $\rho$ =1.166 gcm<sup>-3</sup>; T=173(2) K;  $R_1$ =0.1088,  $wR_2$ =0.2632 (all data),  $R_1$ =0.0881,  $wR_2$ = 0.2455 ( $I > 2\sigma(I)$ ). CCDC-782052 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data\_request/cif.

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