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Supporting Information

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Supporting Information for

Host-Guest Driven Self-Assembly of Linear and Star Supramolecular Polymers

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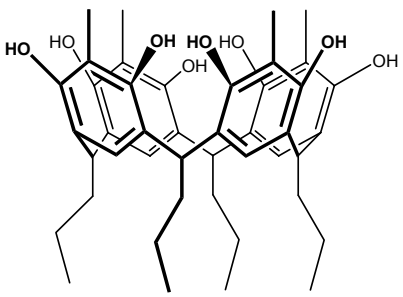
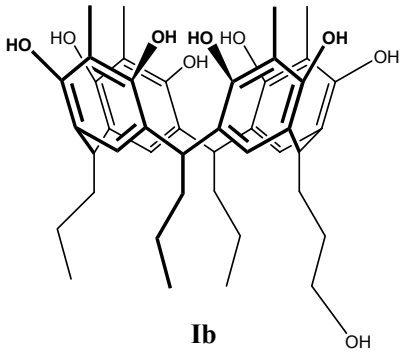
1. General Methods.

^{1}H NMR spectra were obtained using a Bruker AC-300 (300 MHz) or a Bruker AVANCE 300 (300 MHz) spectrometer. All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. ^{31}P NMR spectra were obtained using a Bruker AMX-400 (162 MHz) spectrometer. All chemical shifts (δ) were recorded in ppm relative to external 85% H_3PO_4 at 0.00 ppm. Electrospray ionization ESI-MS experiments were performed on a Waters ZMD spectrometer equipped with an electrospray interface. Column chromatography was performed using silica gel 60 (MERCK 70-230 mesh). All solvents were dried and distilled using standard procedures. All commercial reagents were ACS reagent grade and used as received.

2. Synthesis.



Ia



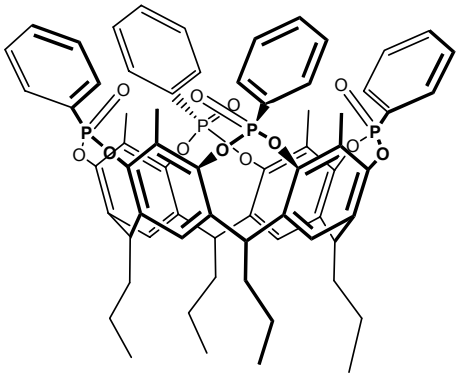
Ib

Synthesis of Ia and Ib.

To a stirred solution of 2-methylresorcinol (9.50 g, 76.50 mmol) in methanol (60 mL) cooled to 0 °C, 2,3-dihydrofuran (1.45 mL, 19.12 mmol) and *n*-butyraldehyde (5.05 mL, 57.4 mmol) were added. HCl (conc) (14.40 mL) was then added dropwise. After 7 days of stirring at 50 °C, the mixture was allowed to cool to room temperature and poured into distilled water (450 mL). A precipitate formed, which was filtered, dried under vacuum and purified by column chromatography (silica, CH_2Cl_2:EtOH, 95:5) to give products **Ia** and **Ib** respectively in 32% and 25% yield (**Ia**: 4.36 g , 6.12 mmol, 32%; **Ib**: 3.50 g, 4.80 mmol, 25%).

Ia: **^{1}H NMR** (300 MHz, 298 K, Acetone-d_6): δ (ppm) 7.94 (s, 8H, ArO**H**); 7.45 (s, 4H, Ar**H**); 4.41 (t, 4H, ArC**H**, J = 7.8 Hz); 2.28 (m, 8H, ArCHC**H_2**); 2.04 (s, 12 H, ArC**H_3**); 1.30 (m, 8H, $CH_2C\mathbf{H_2}CH_3$); 0.94 (t, 12H, $CH_2CH_2C\mathbf{H_3}$, J = 7.3 Hz). **ESI-MS**: *m/z* calcd for $C_{44}H_{56}O_8$ (712.4 Da) $[M-H]^-$: 711.4; found 711.

Ib: **^{1}H NMR** (300 MHz, 298 K, Acetone-d_6): δ (ppm) 7.97 (s, 8H, ArO**H**); 7.46 (s, 2H, Ar**H**); 7.44 (s, 2H, Ar**H**); 4.39 (t, 4H, ArC**H**, J = 7.7 Hz); 3.58 (t, 2H, $CH_2C\mathbf{H_2}OH$, J = 6.3 Hz); 2.36 - 2.23 (m, 8H, ArCHC**H_2**); 2.04 (s, 12 H, ArC**H_3**); 1.49 (m, 2H, $CH_2C\mathbf{H_2}CH_2OH$); 1.28 (m, 6H, $CH_2C\mathbf{H_2}CH_3$); 0.93 (t, 9H, $CH_2CH_2C\mathbf{H_3}$, J = 7.3 Hz). **ESI-MS**: *m/z* calcd for $C_{44}H_{56}O_9$ (729.4 Da) $[M-H]^-$: 728.4; found 728.

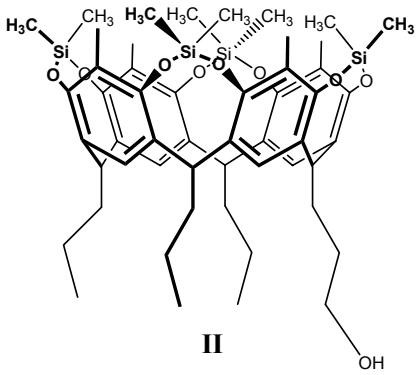


3

Synthesis of 3.

To a solution of **Ia** (0.60 g, 0.80 mmol) in freshly distilled pyridine (20 mL) dichlorophenylphosphine (0.447 mL, 3.39 mmol) was added slowly, at room temperature. After 3 hours of stirring at 80 °C, the solution was allowed to cool at room temperature and 8 mL of a mixture of aqueous 55% H_2O_2 and $CHCl_3$ (1:1) was added. The resulting mixture was stirred for 30 minutes at room temperature, then the solvent was removed under reduced pressure and water added. The precipitate obtained in this way was collected by vacuum filtration, and purified by re-crystallization (H_2O:CH_3CN, 8:2). The product is a fine white powder (0.91 g, 0.76 mmol, 94%)

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 8.09 (m, 8H, P(O)Ar**H**$_o$); 7.62 - 749 (m, 4H + 8H, P(O)Ar**H**$_p$ + P(O)Ar**H**$_m$); 7.15 (s, 4H, Ar**H**); 4.81 (t, 4H, ArC**H**, J = 6.4 Hz); 2.30 (m, 8H, C**H**$_2$$CH_2CH_3$); 2.20 (s; 12H, ArC**H**$_3$); 1.43 (m, 8H, CH_2C**H**$_2$$CH_3$); 1.05 (t, 12H, CH_2CH_2C**H**$_3$, J = 7.3 Hz). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$): δ (ppm) 4.20 (s, P=O). **ESI-MS**: *m/z* calcd for $C_{68}H_{68}O_{12}P_4$ (1200.2 Da) $[M+H]^+$: 1202.2; found 1201.

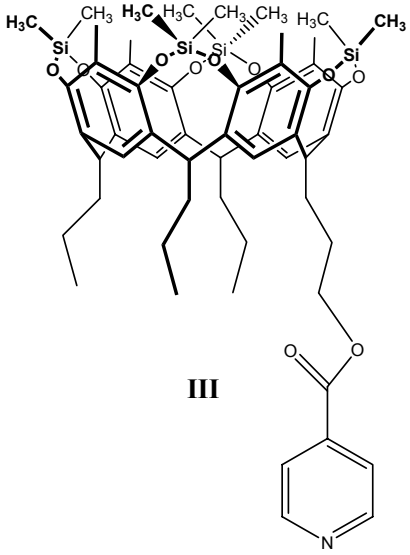


II

Synthesis of II.

To a solution of **Ib** (3.50 g, 4.81 mmol) in dry pyridine (120 mL), cooled to 0 °C, dimethyldichlorosilane (7 mL, 57.75 mmol) was added. The mixture was stirred at 80 °C for 3 hours. The solvent was removed under vacuum and the resulting residue was suspended in methanol (20 mL). The yellow solid obtained after vacuum filtration was purified by column chromatography (silica, CH_2Cl_2:MeOH, 98:2), yielding product **II** as a white powder (4.17 g, 4.37 mmol, 91%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 7.19 (s, 2H, Ar**H**); 7.16 (s, 2H, Ar**H**); 4.60 (t, 4H, ArC**H,** J = 7.9 Hz); 3.71 (t, 2H, C$\mathbf{H_2}$OH, J = 6.3 Hz); 2.31 (m, 2H, C$\mathbf{H_2}$$CH_2CH_2OH$); 2.14 (m, 6H, C$\mathbf{H_2}$$CH_2CH_3$); 1.90 (s, 12H, ArC$\mathbf{H_3}$); 1.56 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2$OH); 1.27 (m, 6H, CH_2C$\mathbf{H_2}$$CH_3$); 0.96 (t, 9H, CH_2CH_2C$\mathbf{H_3}$, J = 7.2 Hz); 0.50 (s, 12H, SiC$\mathbf{H_{3}}$$_{\boldsymbol{out}}$); -0.71 (s, 12H, SiC$\mathbf{H_{3}}$$_{\boldsymbol{in}}$). **ESI-MS**: *m/z* calcd for $C_{52}H_{72}O_9Si_4$ (953.5 Da) $[M+H]^+$: 954.5; found 954.

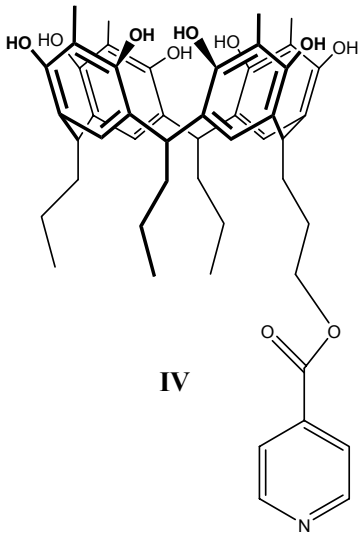


III

Synthesis of III.

To a solution of isonicotinoyl chloride hydrochloride (0.25 g, 1.38 mmol) in pyridine (15 mL), heated at 50 °C, cavitand **II** (0.44 g, 0.46 mmol) was added. The mixture was stirred at 100 °C for 3 hours. After solvent removal, the residue was suspended in distilled water, filtered, to give a solid which was dissolved in CH_2Cl_2 and washed with neutral water. The organic layer was evaporated to dryness, yielding compound **III** as a yellow powder (0.44 g, 0.42 mmol, 90%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 8.74 (d, 2H, **H**$_{\boldsymbol{opy}}$, J = 5.1 Hz); 7.84 (d, 2H, **H**$_{\boldsymbol{mpy}}$, J = 5.1 Hz**)**; 7.16 (s, 4H, Ar**H**); 4.61 (m, 4H, ArC**H**); 4.42 (t, 2H, C$\mathbf{H_2}$OC(O), J = 6.5 Hz); 2.35 (m, 2H, C$\mathbf{H_2}$$CH_2CH_2O$); 2.16 (m, 6H, C$\mathbf{H_2}$$CH_2CH_3$); 1.89 (s, 12H, ArC$\mathbf{H_3}$); 1.78 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2O$); 1.30 (m, 6H, CH_2C$\mathbf{H_2}$$CH_3$); 0.96 (m, 9H, CH_2CH_2C$\mathbf{H_3}$,); 0.49 (s, 12H, SiC$\mathbf{H_{3}}$$_{\boldsymbol{out}}$); -0.70 (s, 12H, SiC$\mathbf{H_{3}}$$_{\boldsymbol{in}}$). **ESI-MS**: *m/z* calcd for $C_{58}H_{75}NO_{10}Si_4$ (1059.5 Da) $[M+H]^+$: 1060.5; found 1060.

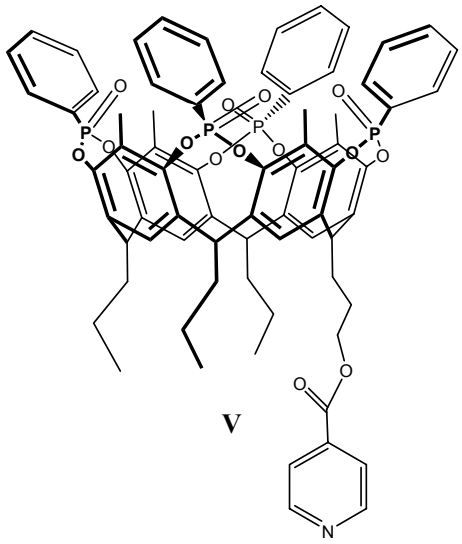


IV

Synthesis of IV.

To compound **III** (1.00 g, 0.95 mmol) dissolved in DMF (20 mL), 0.45 mL of an aqueous 40% HF solution was added. After 18 hours of stirring at 45 °C the solvent was removed under vacuum. The crude product was purified by column chromatography (silica, CH_2Cl_2:MeOH, 95:5) to give resorcinarene **IV** as a pink powder (0.65 g, 0.77 mmol, 82%).

^{1}H NMR (300 MHz, 298 K, Acetone-d_6): δ (ppm) 8.79 (d, 2H, **H**$_{opy,}$ J = 6.4 Hz); 7.96 (s, 4H, ArO**H**); 7.93 (s, 4H, ArO**H**); 7.85 (d, 2H, **H**$_{mpy,}$ J = 6.4 Hz); 7.47 (s, 2H, Ar**H**); 7.41 (s, 2H, Ar**H**); 4.38 (m, 2H + 4H, C**H$_2$**OC(O) + ArC**H**); 2.46 (m, 2H, C**H$_2$**CH_2CH_2O); 2.24 (m, 6H, C**H$_2$**CH_2CH_3); 2.04 (s, 12H, ArC**H$_3$**); 1.76 (m, 2H, CH_2C**H$_2$**CH_2O); 1.26 (m, 6H, CH_2C**H$_2$**CH_3); 0.91 (m, 9H, CH_2CH_2C**H$_3$**). **ESI-MS**: *m/z* calcd for $C_{50}H_{59}NO_{10}$ (834.0 Da) $[M+H]^+$: 835.0; found 835; calcd $[M+Na]^+$: 857.0; found 857.

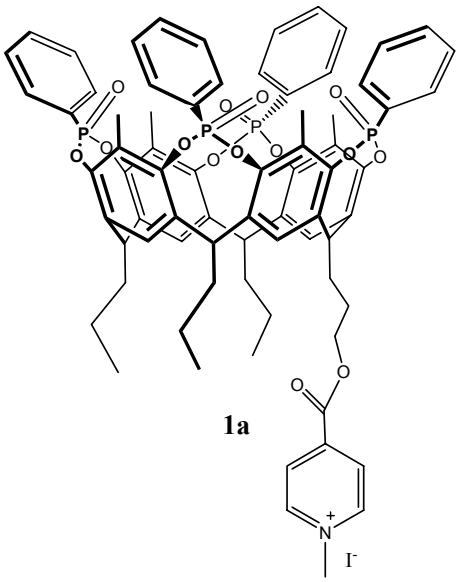


V

Synthesis of V.

To a solution of **IV** (0.5 g, 0.6 mmol) in freshly distilled pyridine (20 mL), dichlorophenylphosphine (0.332 mL, 2.45 mmol) was added slowly, at room temperature. After 3 hours of stirring at 80 °C, the solution was allowed to cool at room temperature and 8 mL of a mixture of aqueous 55% H_2O_2 and $CHCl_3$ (1:1) was added. The resulting mixture was stirred for 30 minutes at room temperature, then the solvent was removed under reduced pressure and water added. The precipitate obtained in this way was collected by vacuum filtration, and purified by re-crystallization (H_2O:CH_3CN, 8:2). The product is a fine white powder (0.753 g, 0.57 mmol, 95%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 8.74 (d, 2H, **H**$_{opy,}$ J = 5.4 Hz); 8.10 (m, 8H, P(O)Ar**H**$_o$); 7.82 (d, 2H, **H**$_{mpy,}$ J = 5.4 Hz); 7.65 - 7.50 (m, 4H + 8H, P(O)Ar**H**$_p$ + P(O)Ar**H**$_m$); 7.12 (s, 4H, Ar**H**); 4.84 (m, 4H, ArC**H**); 4.51 (t, 2H, C**H$_2$**OC(O), J = 6.5 Hz); 2.47 - 2.26 (m, 2H + 6H + 12H, C**H$_2$**CH_2CH_2O + C**H$_2$**CH_2CH_3 + ArC**H$_3$**); 1.91 (m, 2H, CH_2C**H$_2$**CH_2O); 1.43 (m, 6H, CH_2C**H$_2$**CH_3); 1.03 (m, 9H, CH_2CH_2C**H$_3$**). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$) δ (ppm): 4.26 (s, P=O). **ESI-MS**: *m/z* calcd for $C_{74}H_{71}NO_{14}P_4$ (1321.2 Da) $[M+H]^+$: 1322.2; found 1322.2.

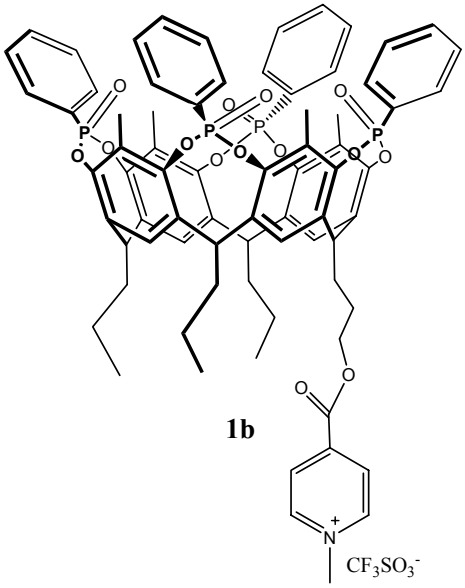


1a

Synthesis of 1a.

To a solution of **V** (0.30 g, 0.23 mmol) in CH_3CN (8 mL), methyl iodide (0.14 mL, 2.30 mmol) was added. The mixture was stirred at reflux for 18 hours. After solvent evaporation the residue was purified by crystallization (H_2O:CH_3CN, 1:1) yielding the product as a yellow powder (0.3 g, 0.21 mmol, 90%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 8.37 (d, 2H, $\mathbf{H}_{opy}$, J = 6.3 Hz); 8.29 (s, 2H, ArH); 8.22 (s, 2H, ArH); 7.99 - 7.91 (m, 2H + 8H, $\mathbf{H}_{mpy}$ + P(O)Ar$\mathbf{H}_o$); 7.60 - 7.51 (m, 4H + 8H, P(O)Ar$\mathbf{H}_p$ + P(O)Ar$\mathbf{H}_m$) ; 4.79 (m, 4H + 2H, ArC**H** + C$\mathbf{H_2}$OC(O)); 3.23 (m, 2H, C$\mathbf{H_2}$$CH_2CH_2O$); 2.98 (m, 6H, C$\mathbf{H_2}$$CH_2CH_3$); 2.15 (s, 12H, ArC$\mathbf{H_3}$); 1.84 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2O$); 1.37 - 1.26 (m, 6H, CH_2C$\mathbf{H_2}$$CH_3$); 1.14 - 1.07 (m, 9H, CH_2CH_2C$\mathbf{H_3}$, J = 7.0 Hz); 0.81 (bs, 12H, C$\mathbf{H}_{3py}$). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$):δ (ppm) 4.20 (s, P=O). **ESI-MS**: *m/z* calcd for $C_{75}H_{74}NO_{14}P_4I$ (1464.2 Da) $[M\text{-}I]^+$: 1337.3; found 1337.

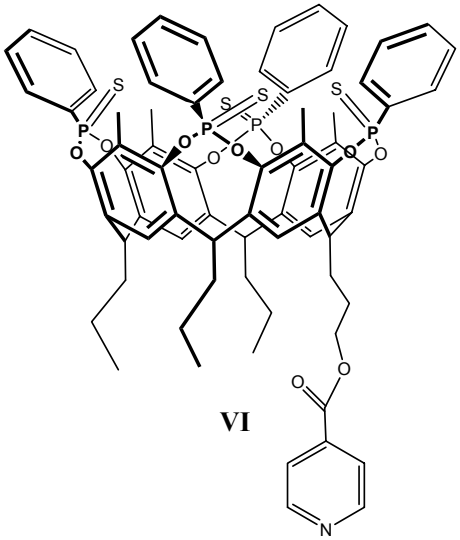


1b

Synthesis of 1b.

To a solution of **V** (0.4 g, 0.30 mmol) in $CHCl_3$ (8 mL), $CH_3SO_3CF_3$ (0.10 mL, 0.91 mmol) was added. The mixture was stirred for 1 hour at room temperature. After solvent evaporation, the residue was purified by crystallization (H_2O:CH_3CN, 1:1) (0.41 g, 0.28 mmol, 92%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 8.35 (bs, 2H, $\mathbf{H}_{opy,}$); 8.06 - 7.96 (m, 2H + 8H, $\mathbf{H}_{mpy}$ + P(O)Ar$\mathbf{H}_o$); 7.59 - 7.50 (m, 4H + 8H + 4H, P(O)Ar$\mathbf{H}_p$ + P(O)Ar$\mathbf{H}_m$ + Ar**H**); 4.75 (m, 4H + 2H, ArC**H** + C$\mathbf{H_2}$OC(O)); 2.82 (m, 2H, C$\mathbf{H_2}$$CH_2CH_2O$); 2.64 (m, 6H, C$\mathbf{H_2}$$CH_2CH_3$); 2.04 (s, 12H, ArC$\mathbf{H_3}$); 1.82 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2O$); 1.60 (m, 6H, CH_2C$\mathbf{H_2}$$CH_3$); 1.01 (m, 9H, CH_2CH_2C$\mathbf{H_3}$); 0,87 (bs, 3H, C$\mathbf{H}_{3py}$). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$): δ (ppm) 4.25 (s, P=O). **ESI-MS**: *m/z* calcd for $C_{76}H_{74}F_3NO_{17}P_4S$ (1486.3 Da) $[M\text{-}CF_3SO_3]^+$: 1337.3; found 1337.

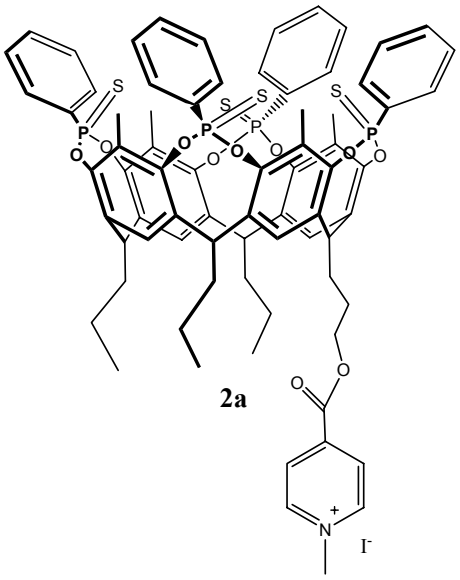


VI

Synthesis of VI.

To a solution of **IV** (0.3 g, 0.36 mmol) in freshly distilled pyridine (15 mL), dichlorophenylphosphine (0.20 mL, 1.47 mmol) was added slowly, at room temperature. After stirring for 3 hours at 80 °C, S_8 (0.11 g, 0.43 mmol) was added and the mixture was stirred again for 2 hours. The solvent was removed under vacuum and the crude was separated in its components by column chromatography (CH_2Cl_2:MeOH, 98:2) (0.3 g, 0.22 mmol, 60%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 8.74 (d, 2H, $\mathbf{H}_{opy}$, J = 4.7 Hz); 8.18 (m, 8H, P(O)Ar$\mathbf{H}_o$); 7.83 (d, 2H, $\mathbf{H}_{mpy}$, J = 4.7 Hz); 7.59 - 7.49 (m, 4H + 8H, P(O)Ar$\mathbf{H}_m$ + P(O)Ar$\mathbf{H}_p$); 7.24 (s, 4H, Ar**H**); 4.72 (m, 4H, ArC**H**); 4.50 (t, 2H, C$\mathbf{H_2}$OC(O), J = 6.6 Hz); 2.46 (m, 2H, C$\mathbf{H_2}$$CH_2CH_2O$); 2.31 (m, 6H, C$\mathbf{H_2}$$CH_2CH_3$); 2.15 (s, 12H, ArC$\mathbf{H_3}$); 1.81 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2O$); 1.40 (m, 6H, CH_2C$\mathbf{H_2}$$CH_3$); 1.03 (m, 9H, CH_2CH_2C$\mathbf{H_3}$). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$): δ (ppm) 72.02 (s, P=S). **ESI-MS**: *m/z* calcd for $C_{74}H_{71}NO_{10}P_4S_4$ (1386.5 Da) $[M+K]^+$ 1425.6; found 1425.

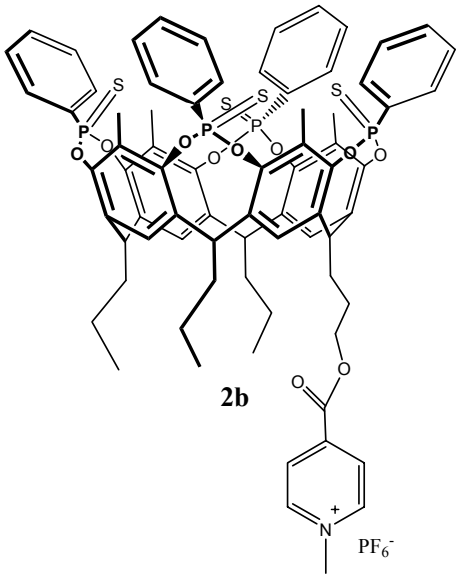


2a

Synthesis of 2a.

To a solution of **VI** (0.30 g, 0.21 mmol) in CH_3CN (8 mL), methyl iodide (0.13 mL, 2.00 mmol) was added. The mixture was stirred at reflux for 18 hours. After solvent removal, the resulting crude product was purified by crystallization (CH_3CN:H_2O, 7:3) (0.30 g, 0.20 mmol, 91%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 9.02 (d, 2H, $\mathbf{H}_{opy}$, J = 5.6 Hz); 8.42 (d, 2H, $\mathbf{H}_{mpy}$ J = 5.6 Hz); 7.94 (m, 8H, P(O)Ar$\mathbf{H}_o$); 7.71 - 7.51 (m, 4H + 8H + 4H, P(O)Ar$\mathbf{H}_p$ + P(O)Ar$\mathbf{H}_m$ + Ar**H**); 4.75 (m, 4H + 3H, ArC**H** + C$\mathbf{H_{3}}_{py}$); 4.60 (bt, 2H, C$\mathbf{H_2}$OC(O)); 3.00 - 2.16 (m, 2H + 6H, C$\mathbf{H_2}$$CH_2CH_2O$ + C$\mathbf{H_2}$$CH_2CH_3$); 2.14 (s, 12H, ArC$\mathbf{H_3}$); 1.86 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2O$); 1.40 (m, 6H, CH_2C$\mathbf{H_2}$$CH_3$); 1.03 (m, 9H, CH_2CH_2C$\mathbf{H_3}$). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$): δ (ppm) 72.54 (s, P=S). **ESI-MS**: *m/z* calcd for $C_{75}H_{74}INO_{10}P_4S_4$ (1528.5 Da) $[M-I]^+$: 1401.5; found 1401.

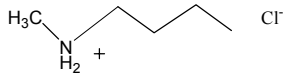


2b

Synthesis of 2b.

A suspension of **2a** (0.35 g, 0.23 mmol) in CH_3CN (2.5 mL) was heated until dissolution. A solution of NH_4PF_6 (0.22 g, 1.42 mmol) dissolved in distilled water (2 mL) was added, and the mixture was stirred at 50 °C for 20 minutes at 50 °C. After cooling at room temperature, a precipitate formed which was stirred for 2 hours and finally collected by vacuum filtration. The obtained white powder was purified by re-crystallization (CH_3CN:H_2O, 1:1) (0.32 g, 0.21 mmol, 91%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 9.13 (d, 2H, $\mathbf{H}_{opy}$, J = 5.5 Hz**)**; 8.48 (d, 2H, $\mathbf{H}_{mpy}$ J = 5.5 Hz); 8.16 (m, 8H, P(O)Ar$\mathbf{H}_o$); 7.69 - 7.52 (m, 4H + 8H + 4H, P(O)Ar$\mathbf{H}_p$ + P(O)Ar$\mathbf{H}_m$ + Ar**H**); 4.77 (m, 4H +3H, ArC**H** + C$\mathbf{H}_{3py}$); 4.60 (bt, 2H, C$\mathbf{H_2}$OC(O)); 2.77 (m, 2H, C$\mathbf{H_2}$$CH_2CH_2O$); 2.55 (m, 6H, C$\mathbf{H_2}$$CH_2CH_3$); 1.15 (s, 12H, ArC$\mathbf{H_3}$); 1.89 (m, 2H, CH_2C$\mathbf{H_2}$$CH_2O$); 1.41 (m, 6H, CH_2C$\mathbf{H_2}$$CH_3$); 1.06 (m, 9H, CH_2CH_2C$\mathbf{H_3}$). **^{31}P NMR** (162 MHz, 298 K, $CDCl_3$): δ (ppm) 72.51 (s, 4P, P=S); -142 (m, 1P, PF_6^-, J = 751.6 Hz). **ESI-MS**: *m/z* calcd for $C_{75}H_{74}F_6NO_{10}P_5S_4$ (1546.5 Da) $[M\text{-}PF_6]^+$: 1401.5; found 1401.



VII

Syntesis of VII.

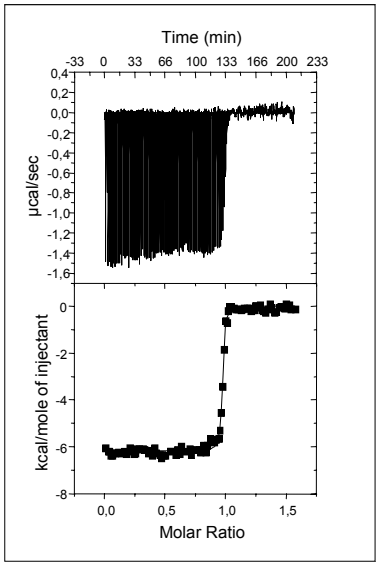
To a solution of N-butylmethylamine (2.00 mL, 16.89 mmol) in diethyl ether (20 mL) an excess of aqueous 36% HCl was added. The resulting mixture was stirred at room temperature for 20 minutes. A precipitate formed, which was collected by vacuum filtration and re-crystallized (Et_2O:CH_3CN, 99:1) yielding product **VII** as white crystals (3.45 g, 1.6 mmol, 95%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ (ppm) 8.50 (bs, 2H, N$\mathbf{H_2}$$CH_3$); 3.00 (m, 2H, $CH_3CH_2CH_2$C$\mathbf{H_2}$N), 2.66 (s, 3H, NH_2C$\mathbf{H_3}$); 1.86 (m, 2H, CH_3CH_2C$\mathbf{H_2}$$CH_2$N); 1.45 (m, 2H, CH_3C$\mathbf{H_2}$$CH_2CH_2$N); 0.95 (t, 3H, C$\mathbf{H_3}$$CH_2CH_2CH_2$N, J = 7.4 Hz). **ESI-MS**: *m/z* calcd for $C_5H_{14}IN$ (215.0 Da) $[M + 2I]^-$ 342.0; found 342.

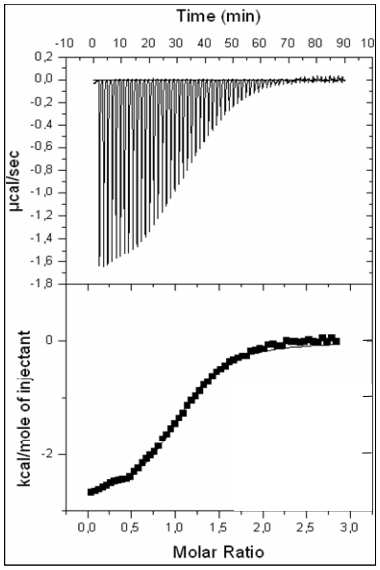
Supporting material for ITC measurements of Table 1.

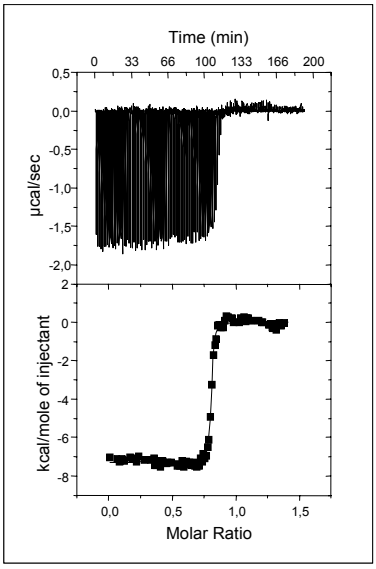
All reported measurements are the average of three independent experiments. Enthalpies of dilution of the hosts and the guests were determined in separate experiments, being negligible.

a) ITC traces of the titration of cavitand **3** with **2a** in CH_2Cl_2. Titration mode: guest (**2a**) into host (**3**) solution; one-site model.

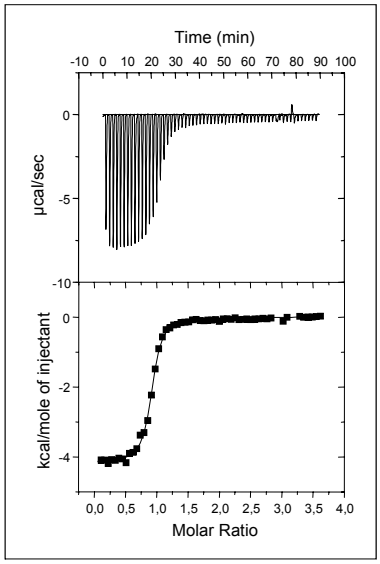


b) ITC traces of the titration of cavitand **3** with **2b** in methanol (left), titration mode: host (**3**) into guest (**2b**) solution; one site-model; ITC traces of the titration of cavitand **3** with **2b** in CH_2Cl_2 (right), titration mode: guest (**2b**) into host (**3**) solution; one-site model.

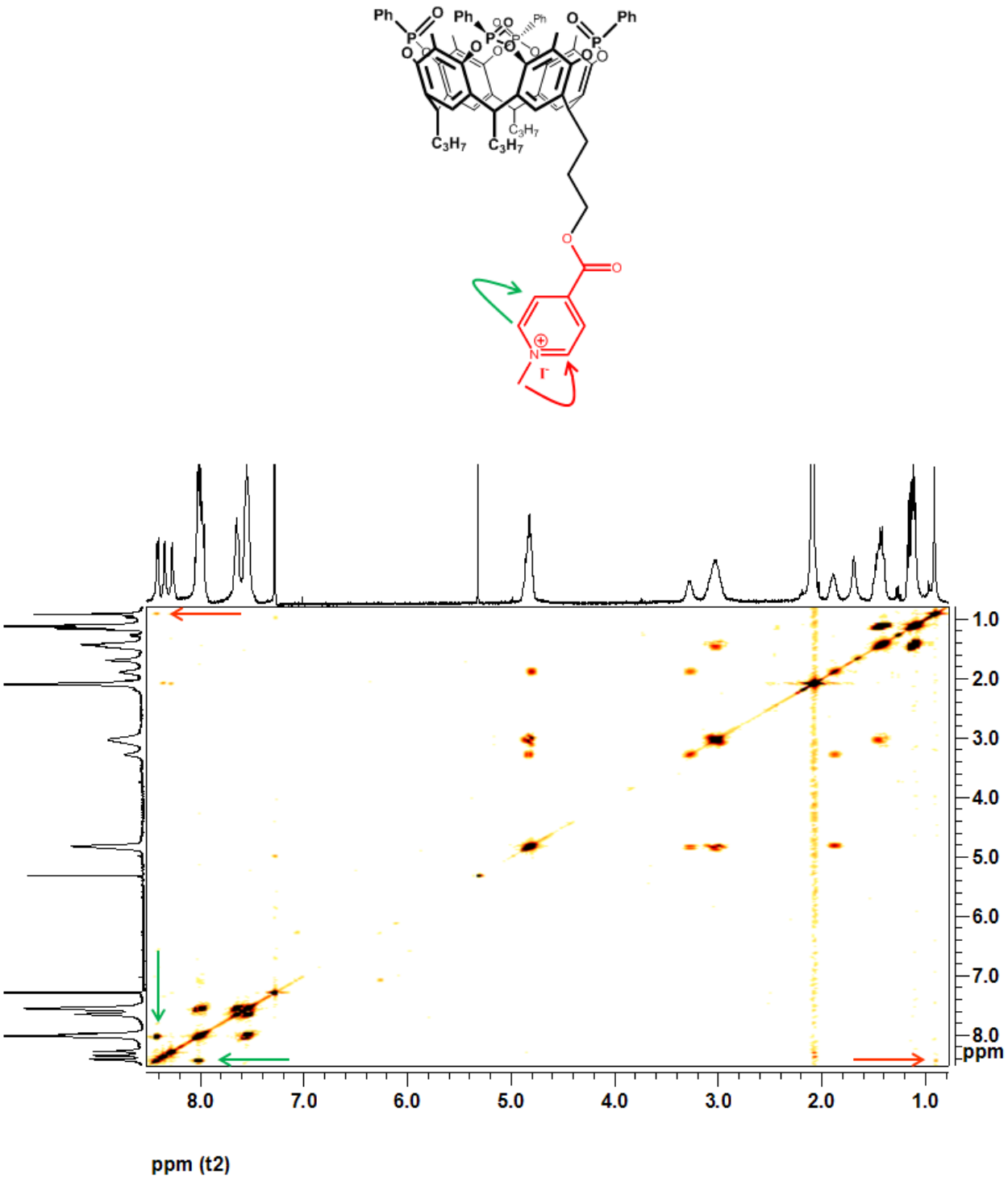




c) ITC traces for the guest exchange from dimer complex **2b●3** with N-butylmethylammonium chloride in methanol. Titration mode: guest (N-butylmethylammonium chloride) into dimer complex (**2b●3**) solution; one-site model.



^{1}H COSY spectrum of homopolymer 1a.



Multi-Angle Laser Light Scattering

The molecular characterization of polymers was performed by static light scattering technique. A multi-angle laser light scattering (MALS) Dawn DSP-F photometer from Wyatt (Santa Barbara, CA, USA) in off-line (batch) mode in freshly distilled chloroform solvent at room temperature was used. All polymeric solutions were accurately filtered through 0.2 μm PTFE filters. The MALS photometer uses a vertically polarized He-Ne laser (wavelength λ=632.8 nm) and simultaneously measures the intensity of the scattered light at 18 angular locations ranging in chloroform solvent from 19.2° to 149.2°. The MALS calibration constant was calculated using toluene as standard assuming a Rayleigh Factor of $1.406 \cdot 10^{-5}$ cm^{-1}. The normalization of the different photodiodes was performed by measuring the scattering intensity of a narrow molecular weight distribution (MWD) polystyrene standards (M_p=10.3 kg/mol, M_w/M_n=1.03, R_g=2.6 nm) in the solvent assumed to act as an isotropic scatterer. Details of the MALS photometer were described elsewhere [1, 2]. The specific refractive index increment, dn/dc, of polymers with respect to the solvent at 25 °C of temperature was measured by a KMX-16 differential refractometer from LDC Milton Roy (Riviera Beach, FL, USA).

References

[1] R. Mendichi, A. Giacometti Schieroni, *Current Trends in Polymer Science*, Pandalai S.G. Ed., TWR Network: Trivandrum India, **2001**, Vol. 6, p 17-32.

[2] P.J. Wyatt, *Anal. Chim. Acta* **1993**, *272*, 1-40.

Tables of Static Light Scattering Results

Polymer 1a dn/dc = 0.152 mL/g	
gL^{-1}	M_W (g/mol)
1.045	11850 ± 150
2.050	13490 ± 230
4.487	16140 ± 90
6.129	17740 ± 190
7.408	19280 ± 270
10.110	22410 ± 320
14.990	26270 ± 80

Polymer disassembly 1a + 2a				
1a (gL^{-1})	2a (gL^{-1})	1a+2a (gL^{-1})	M_W (g/mol)	dn/dc
15.055	1.613	16.667	23720 ± 90	0.151
15.055	3.291	18.344	20160 ± 70	0.150
15.055	4.731	19.786	18230 ± 50	0.149

Crystallographic data for stopper, dimer and homopolymer

CCDC-675445, CCDC-678793 and CCDC- 675446 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

Stopper 2b

Single crystal preparation: Crystals suitable for X-ray diffraction experiments (dimensions 0.5×0.3×0.2 mm^3) of the stopper cavitand **2b** have been obtained by water diffusion in an acetonitrile solution of the compound.

X-ray data, solution, and refinement of structures: Data collection was performed using an in-house conventional X-ray source (monochromatic wavelength λ = 1.5418 Å) and a KappaCCD detector. The crystal of **2b** was mounted on a glass fiber with glue and flash frozen to 100 K with a nitrogen stream. The diffraction data were indexed and integrated using DENZO and scaled with SCALEPACK[1]. The structure was solved in *C*2/c space group by direct methods using SHELXS[2] and Fourier analyses and refined by the full-matrix least-squares based on F^2 using SHELXL-97[3]. The asymmetric unit contains one stopper molecule, one PF_6^- ion and one acetonitrile molecule (Figure S1 up). The acetonitrile molecule is complexed inside the resorcinarene cavity through a CH_3-π H-bond involving the acidic methyl group and the π-basic cavity. The hexafluorophosphate ions are distributed in two crystallographically independent sites: on an inversion centre and along a binary axis. The PF_6^- ions on the inversion centres connect the lower rims of two symmetry related stopper molecules. Each of these molecules mutually interacts with another molecule of cavitand by the methyl-pyridinium group and the upper rim (Figure S1 down).

During the refinement, restraints for pyridyl and phenyl groups have been introduced in the model. In the final refinement, hydrogen atoms were included at calculated positions and non-hydrogen non-disordered atoms were treated anisotropically. Restrains on thermal motion have been introduced using the SIMU card during SHELXL refinement. The experimental data has been corrected empirically for X-ray absorption using XABS2 program[4]. Essential crystal data and refinement details are reported in Table S1.

Table S1. Crystallographic data for 2b.

	Stopper 2b
Formula	$C_{75}H_{74}NO_{10}P_4S_4+PF_6+C_2H_3N$
Formula weight	1546.44
Temperature	298 K
Wavelength	1.5418 Å
Crystal system	Monoclinic
Space Group	C2/c
***a*/Å**	24.4593±0.0875
***b*/Å**	23.8933±0.0359
***c*/Å**	29.3660±0.0456
α/°	90
β/°	108.2344±0.0707
γ/°	90
V/Å^3	16300.1
Z	8
D_c/g cm^{-3}	1.262
F(000)	6432
μ/mm^{-1}	2.569
$\theta_{min,max}$/°	2.65 – 37.38
Resolution	50.0 – 1.25 Å
Reflections collected	12150
Independent reflections	3695
Observed Reflections [F_o>4σ(F_o)]	2942
I/σ(I) (all data)	8.8
I/σ(I) (max resolution)	2.9
Completeness (all data)	98.7%
Completeness (max resolution)	96.2%
Multiplicity (all data)	1.7
Multiplicity (max resolution)	1.3
Data/restraint/parameters	3695/12/653
R[I>2.0σ(I)]	0.1045
R(all data)	0.1204
wR2 [I>2.0σ (I)]	0.3111
Goodness of fit	1.312

Dimer (2b•3)

Single crystal preparation: Crystals suitable for X-ray diffraction experiments (dimensions 0.6×0.2×0.2 mm^3) of the supramolecular complex **2b•3** have been obtained by water diffusion in an acetonitrile solution of the components dissolved in 1:1 ratio.

X-ray data, solution, and refinement of structures: Data collection was performed using an in-house conventional X-ray source (monochromatic wavelength λ = 1.5418 Å) and a KappaCCD detector. The crystal, dipped in paratone, was mounted in a loop and frozen at 100 K in nitrogen.
The diffraction data were indexed and integrated using DENZO and scaled with SCALEPACK[1]. The structure was solved in $P2_1/a$ space group by direct methods using SHELXS[2] and Fourier analyses and refined by the full-matrix least-squares based on F^2 using SHELXL-97[3]. The asymmetric unit contains one crystallographically independent **2b•3** complex, one PF_6^- ion, three acetonitrile molecules and four water molecules. During the refinement, restraints for pyridyl and phenyl groups have been introduced in the model. In the final refinement, hydrogen atoms were included at calculated positions and non-hydrogen non-disordered atoms of monomers and triflates were treated anisotropically. Restrains on thermal motion have been introduced using the SIMU card during SHELXL refinement. The experimental data has been corrected empirically for X-ray absorption using XABS2 program[4]. Essential crystal data and refinement details are reported in Table S2.

Homopolymer (1b)

Single crystal preparation: The supramolecular homopolymer **1b** was crystallized by the vapor diffusion method with sitting-drops at 20°C using Linbro multi-well tissue plates as containers of reservoir solutions. The stock monomer solution used contained 15 mg/mL in TFE (A). Crystals of 1 were obtained in drops formed by mixing solution A (2 μL) and a reservoir solution (2 μL) containing trifluoroethanol solutions of methanol and ethanol as precipitants and allowing this to equilibrate against the reservoir (1 mL). Crystals suitable for X-ray diffraction experiments (dimensions 0.2×0.1×0.1 mm^3) were obtained from a solution containing ethanol and methanol concentrations between 20% and 40% v/v.

X-ray data, solution, and refinement of structures: Preliminary in-house diffraction experiments using a conventional X-ray source with crystals frozen at 100 K permitted only the determination of the unit cell parameters (maximum resolution limit=3.5 Å). Therefore, data collection was performed using synchrotron radiation (XRD1 diffraction beam-line of Elettra, Trieste) with a monochromatic X-ray beam

(monochromatic wavelength λ = 1.2000 Å) and MarCCD detector. The crystals, dipped in glycerol, were mounted in a loop and frozen at 100 K in nitrogen.

The diffraction data were indexed and integrated using DENZO and scaled with SCALEPACK[1]. The structure was solved in $P2_1/n$ space group by direct methods using SHELXS[2] and Fourier analyses and refined by the full-matrix least-squares based on F^2 using SHELXL-97[3]. The asymmetric unit contains two crystallographically independent monomer molecules, two triflate ions. During the refinement, restraints for pyridyl and phenyl groups and for triflate ions have been introduced in the model. In the final refinement, hydrogen atoms were included at calculated positions and non-hydrogen atoms of monomers and triflates were treated anisotropically. Restrains on thermal motion have been introduced using the SIMU card during SHELXL refinement. The experimental data has been corrected empirically for X-ray absorption using XABS2 program[4]. The SQUEEZE function of the program PLATON[5] reveals a residual electron density of 1045 electrons/cell (corresponding to 14.5 methanol molecules in the asymmetric unit) in cell-remaining voids (32.6 % of cell volume). A refinement using reflections modified by the SQUEEZE procedure behaved well, and the R-factors were significantly reduced from 0.287 to 0.192. Essential crystal data and refinement details are reported in Table S2.

References

[1] Z. Otwinowski, W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode. Methods in Enzymology **1997**; 276: Macromolecular Crystallography, part A:307-326.

[2] G. M. Sheldrick, Phase annealing in SHELX-90: direct methods for larger structures. *Acta Cryst. Sect. A* **1990**; *46*:467-473.

[3] G. M. Sheldrick, T. R. Schneider, SHELXL: high resolution refinement. *Methods in Enzymology* **1997**; 277: Macromolecular Crystallography, part B:319-343.

[4] S. Parkin, B. Moezzi, H. Hope, XABS2: an empirical absorption correction program. *J. Appl. Cryst.* **1995**; *28,* 53-56.

[5] A. L. Spek, *Acta Cryst.* **1990**; A46(C-34).

Table S2. Crystallographic data for 2b•3 dimer and 1b homopolymer.

	Dimer	Homopolymer
Formula	$C_{143}H_{142}NO_{22}P_8S_4+PF_6+3C_2H_3N$	$C_{75}H_{74}NO_{14}P_4+CF_3SO_3$
Formula weight	2861.64	1486.30
Temperature	100 K	100 K
Wavelength	1.5418 Å	1.0 Å
Crystal system	Monoclinic	Monoclinic
Space Group	$P2_1/a$	$P2_1/n$
***a*/Å**	15.9619±0.0011	26.2499 1±0.0005
***b*/Å**	49.5064±0.0031	28.3296±0.0008
***c*/Å**	21.2934±0.0009	27. 1469±0.0007
α/°	90	90
β/°	107.0161±0.0039	111.5976±0.0017
γ/°	90	90
V/Å^3	16089.47	18770.42
Z	4	8
D_c/g cm^{-3}	1.181	1.052
F(000)	5972	6208
μ/mm^{-1}	1.955	0.42
$\theta_{min,max}$/°	1.78 – 36.30	0.57 24.62
Resolution	50.0 – 1.30 Å	50.0 – 1.2 Å
Reflections collected	39524	379973
Independent reflections	7458	12912
Observed Reflections [$F_o>4\sigma(F_o)$]	4876	7353
I/σ(I) (all data)	9.6	5
I/σ(I) (max resolution)	2.0	1.1
Completeness (all data)	98.1%	99.4%
Completeness (max resolution)	90.1%	98.3%
Multiplicity (all data)	3.8	7.2
Multiplicity (max resolution)	1.7	5.2
Data/restraint/parameters	7458/0/754	11144/1346/1638
R[I>2.0σ(I)]	0.1248	0.1911
R(all data)	0.1880	0.2124
wR2 [I>2.0σ (I)]	0.2415	0.4171
Goodness of fit	1.559	1.838

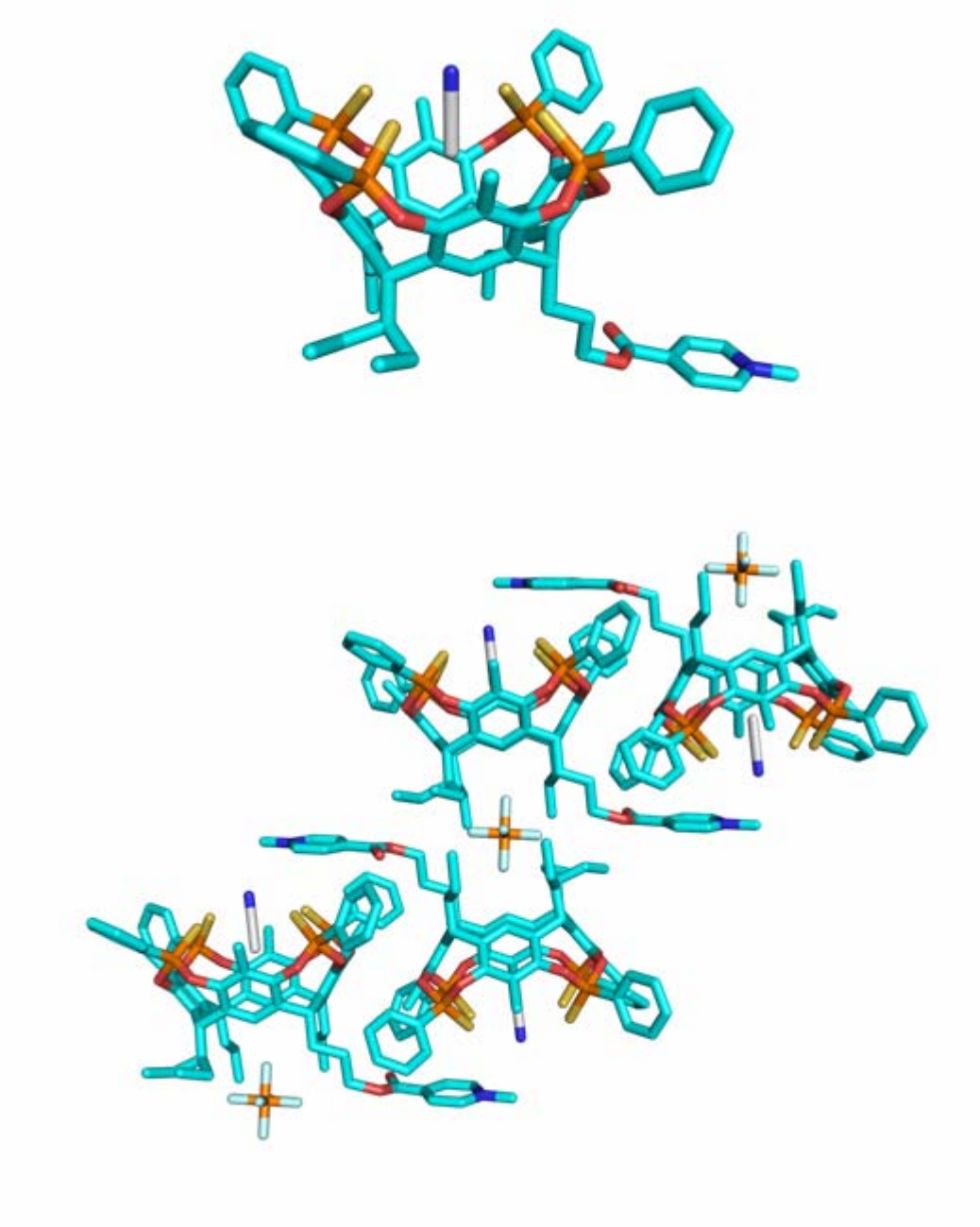


Figure S1: Crystal structure of Stopper **2b**: Up: Asymmetric Unit content; Down: crystal packing in the solid state.

Guest-driven assembly/disassembly of 1a homopolymer monitored by ^{31}P NMR

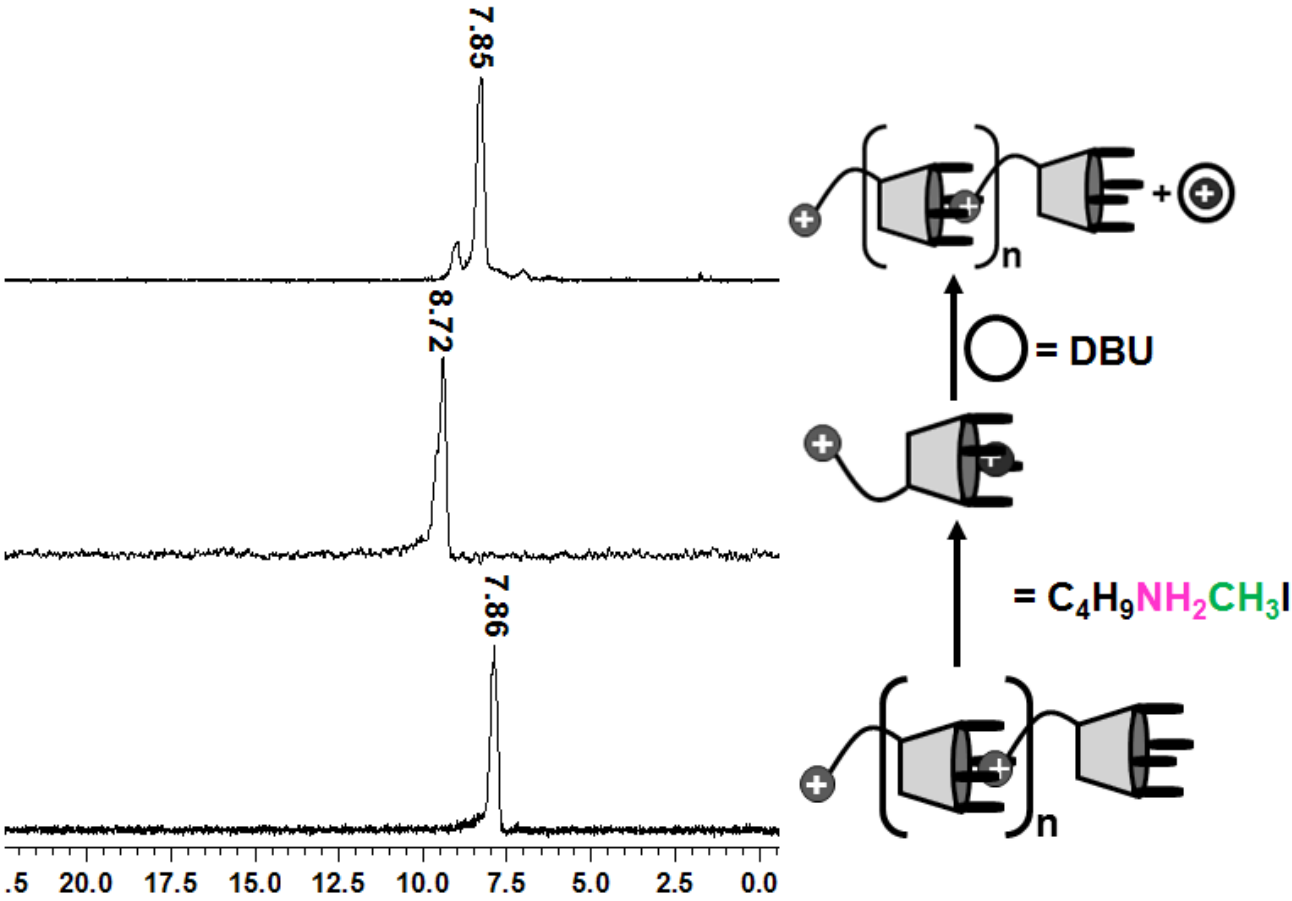


Figure S2: (a) homopolymer **1a**; (b) **1a•N-butylmethylammonium iodide** complex; (c) restored homopolymer **1a**