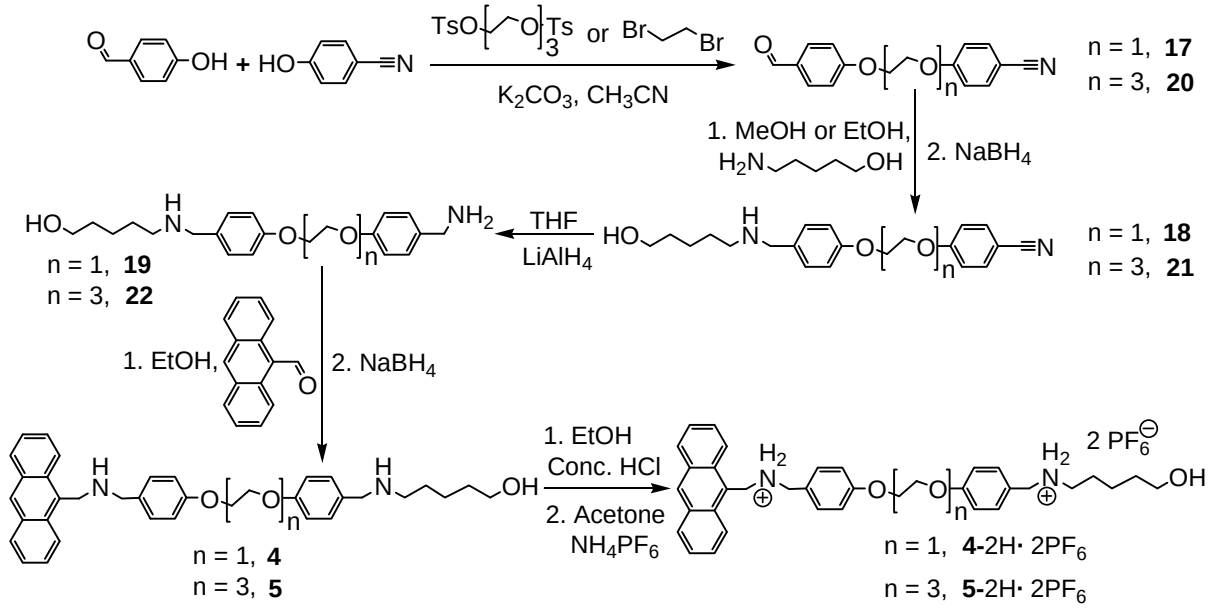
# Supporting Information for "Integrative Self-Sorting: A Programming Language for High Level Self-Assembly"

Wei Jiang, Christoph A. Schalley

*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, 14195 Berlin, Germany*

## SI Appendix



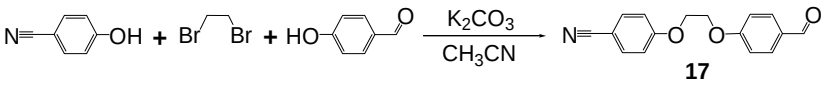

***Scheme S1*** the synthetic procedures for extended divalent guests **4**-2H·2$PF_6$ and **5**-2H·2$PF_6$.

## Supporting Text

**General Methods.** All reagents (including dibenzo-24-crown-8 (**C8**)) were purchased from ACROS, Alfa Aesar, or Aldrich and used without further purification. Solvents were either employed as purchased or dried prior to use by usual laboratory methods. Column chromatography was performed on silica gel 60 (Merck 40 – 60 nm, 230 – 400 mesh). Melting points were determined on a Reichert Thermovar apparatus and are reported uncorrected. $^{1}$H and $^{13}$C NMR spectra were recorded on Bruker ECX 400 MHz and Jeol Eclipse 500 MHz NMR spectrometers. The $^{1}$H NMR signal assignment for all assemblies was

made through 2D NMR experiments. Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) experiments were conducted on an Agilent 6210 ESI-TOF, Agilent Technologies. Benzo-21-crown-7 (**C7**) (1, 2), **1**-2H·2$PF_6$ (3), **2**-2H·2$PF_6$ (2), 1,8-ditosyloxy-3,6-dioxaoctane (4), and **23** (5) were synthesized according to literature procedures. The synthesis and characterization of **3**-2H·2$PF_6$ has been reported elsewhere (6). The synthetic procedures for **6**, **7**, and **8** were modified from literature (7).

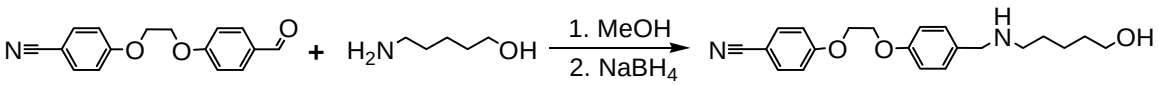
**4-(2-(4-cyanophenoxy)ethoxy)benzaldehyde (17)**




**17**

1,2-dibromoethane (5.16 mL, 60 mmol), 4-hydroxybenzaldehyde (7.32 g, 60 mmol), 4-hydroxybenzonitrile (7.14 g, 60 mmol), and $K_2CO_3$ (33.00 g, 240 mol) were suspended in anhydrous MeCN (300 mL). The reaction mixture was heated to reflux under Argon atmosphere and stirred for 2 days. After cooling down to room temperature, the reaction mixture was filtered off and washed with $CH_2Cl_2$ (100 mL). The filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography ($SiO_2$: hexane/dichloromethane 1:2) to yield **17** as white solid (1.45 g, 9%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.36-4.44 (m, 4H), 6.95-7.05 (m, 4H), 7.57 (d, *J* = 9.2 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 9.87 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 66.5, 66.6, 104.7, 115.0, 115.4, 119.1, 130.5, 132.1, 134.1, 161.8, 163.4, 190.8; ESI-TOF-HRMS: *m/z* calcd for $[M+Na]^+$ $C_{16}H_{13}NO_3Na$, 290.0788; found, 290.0784.

**4-(2-(4-((5-hydroxypentylamino)methyl)phenoxy)ethoxy)benzonitrile (18)**

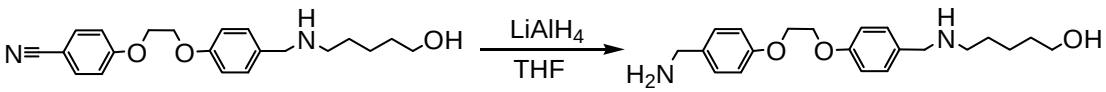



**17** **18**

**17** (1.45 g, 5.4 mmol) and 5-amino-1-pentanol (0.71 mL, 6.5 mmol) were refluxed for 24 h in MeOH (200 ml). After cooling down to room temperature, $NaBH_4$ (2.80 g, 74 mmol) was then added and the resulting solution stirred at room temperature for a further 24 h. The

solvent was removed in *vacuo*. The resulting residue was treated with water and the compound was repeatedly extracted with $CH_2Cl_2$ (three times 60 ml). The organic phase was dried with anhydrous $Na_2SO_4$, and the solvent was evaporated to give the crude product, which was subjected to column chromatography over silica gel (eluent, $CH_2Cl_2$:MeOH, 100:1 to 12:1) to afford **18** (1.40 g, 73%) as a white solid. $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K): δ = 1.20-1.40 (m, 4H), 1.44-1.54 (m, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 4H), 4.26-4.40 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 9.2 Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K): δ = 23.6, 27.8, 32.7, 47.9, 51.3, 61.0, 66.6, 67.5, 103.6, 114.8, 116.2, 119.6, 129.3, 130.9, 134.8, 158.3, 162.3; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{21}H_{27}N_2O_3$, 355.2016; found, 355.2006.

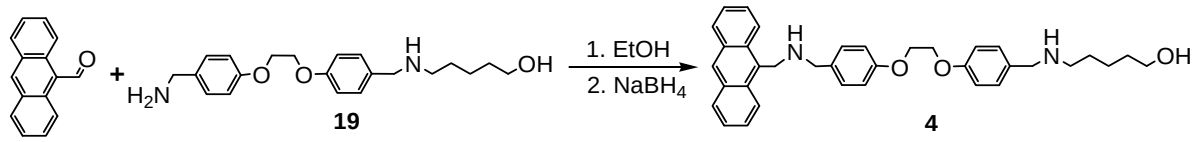
**5-(4-(2-(4-(aminomethyl)phenoxy)ethoxy)benzylamino)-1-pentanol (19)**




**18** **19**

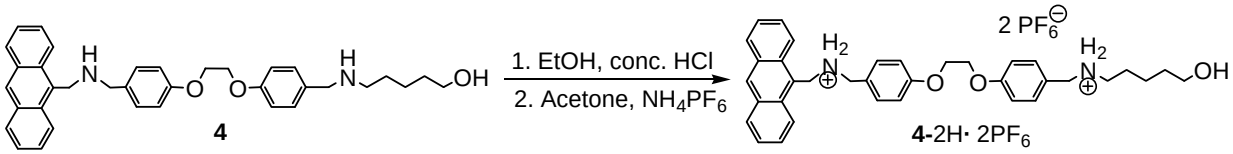
$LiAlH_4$ (1.07 g, 28 mmol) was added in portion to the solution of **18** (1.37 g 3.9 mmol) in dry THF (150 mL) at 0 °C, and the mixture was refluxed for 24 h. Minimum saturated aqueous $Na_2SO_4$ solution was added to neutralize superfluous $LiAlH_4$, The precipitate was filtered off, and washed with $CH_2Cl_2$ (50 mL). The combined filtrate was dried over $Na_2SO_4$, and concentrated in *vacuo* to give **19** as a yellowish solid (0.98 g, 70%), which was used for the next step without further purification. $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K): δ = 1.20-1.29 (m, 2H), 1.31-1.42 (m, 4H), 2.35-2.43 (m, 2H), 3.29-3.36 (m, 4H), 3.53-3.63 (m, 4H), 4.20-4.25 (m, 4H), 6.83-6.90 (m, 4H), 7.15-7.22 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K): δ = 23.9, 29.8, 33.1, 45.6, 49.2, 53.0, 61.2, 66.9, 114.6, 114.7, 128.7, 129.6, 133.9, 137.2, 157.4, 157.5; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{21}H_{31}N_2O_3$, 359.2329; found, 359.2329.

**5-(4-(2-(4-(((9-anthracenyl)methylamino)methyl)phenoxy)ethoxy)benzylamino)-1-pentanol (4)**




9-Anthracenecarboxaldehyde (0.56 g, 2.74 mmol) and **19** (0.98 g, 2.74 mmol) were refluxed for 24 h in absolute ethanol (100 ml). After cooling down to room temperature, $NaBH_4$ (2.8 g, 74 mmol) was then added and the resulting solution stirred at room temperature for a further 24 h. The solvent was removed in *vacuo*. The resulting residue was treated with water and the compound was repeatedly extracted with $CH_2Cl_2$ (60 mL, three times). The organic phase was dried with anhydrous $Na_2SO_4$, and the solvent was evaporated to give the crude product, which was subjected to column chromatography over silica gel (eluent, $CH_2Cl_2$ : MeOH : ammonium hydroxide solution (25wt%), 100:2:0.2 to 100:10:0.2) to afford **4** (0.40 g, 27%) as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.35-1.52 (m, 4H), 1.69-1.81 (m, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 3.53 (t, *J* = 5.8 Hz, 2H), 3.87-3.97 (m, 4H), 4.20-4.29 (m, 4H), 4.64 (s, 2H), 6.87-6.95 (m, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.40-7.50 (m, 6H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.18 (m, *J* = 8.8 Hz, 2H), 8.36 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 23.0, 26.1, 31.6, 44.7, 46.5, 50.9, 53.6, 61.7, 66.6, 66.7, 114.7, 115.1, 124.2, 125.0, 126.2, 127.4, 129.2, 129.8, 130.4, 131.4, 131.6, 131.7, 132.8, 157.9, 159.2; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{36}H_{41}N_2O_3$, 549.3112; found, 549.3138.

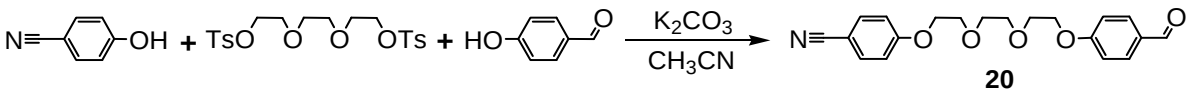
**Divalent Guest 4**-2H·2$PF_6$




To the solution of **4** (0.40 g, 0.73 mmol) in EtOH (50 mL) was added conc. HCl to adjust pH < 2, and the solvent was then evaporated off under reduced pressure. The residue was suspended in acetone (50 mL). Saturated aqueous $NH_4PF_6$ solution was added until the

suspension became clear. The solvent was removed in *vacuo*, and water (100 mL) was added to the residue. The resulting mixture was stirred at ambient temperature overnight. The mixture was then filtered, washed with copious amounts of $H_2O$, and dried to yield **4**-2H·2$PF_6$ as a yellow solid (0.23 g, 38%). m.p. 134-136 °C; $^1$H NMR (400 MHz, $CD_3CN$, 298 K): δ = 1.31-1.40 (m, 4H), 1.58-1.68 (m, 2H), 2.96 (t, *J* = 7.8 Hz, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 4.06 (s, 2H), 4.32-4.39 (m, 4H), 4.42 (s, 2H), 5.16 (s, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.53-7.65 (m, 4H), 8.02-8.07 (m, 2H), 8.10-8.15 (m, 2H), 8.70 (s, 1H); $^{13}$C NMR (100 MHz, $CD_3CN$, 298 K): δ = 22.5, 25.4, 31.5, 47.5, 50.9, 51.5, 61.1, 66.7, 115.0, 115.2, 121.2, 122.7, 123.1, 125.7, 127.7, 129.6, 130.8, 131.4, 131.8, 132.3, 159.7, 159.9; ESI-TOF-HRMS: *m/z* calcd for $[M-2PF_6-H]^+$ $C_{36}H_{41}N_2O_3$, 549.3112; found, 549.3115; calcd for $[M-PF_6]^+$ $C_{36}H_{42}F_6N_2O_3P$, 695.2832; found, 695.2792.

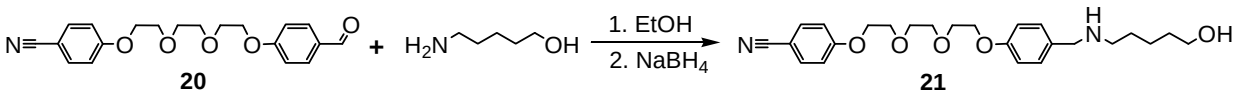
**4-(2-(2-(2-(4-cyanophenoxy)ethoxy)ethoxy)ethoxy)benzaldehyde (20)**




**20**

1,8-ditosyloxy-3,6-dioxaoctane (9.20 g, 20 mmol), 4-hydroxybenzaldehyde (2.44 g, 20 mmol), 4-hydroxybenzonitrile (2.38 g, 20 mmol), and $K_2CO_3$ (11.00 g, 80 mol) were suspended in anhydrous MeCN (150 mL). The reaction mixture was heated to reflux under Argon atmosphere and stirred for 2 days. After cooling down to room temperature, the reaction mixture was filtered off and washed with $CH_2Cl_2$ (100 mL). The filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography (SiO2: hexane/dichloromethane 1:4) to yield **20** as white solid (1.50 g, 21%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.72-3.76 (m, 4H), 3.84-3.90 (m, 4H), 4.12-4.22 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 9.87 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 67.8, 69.58, 69.64, 71.0, 104.3, 114.9, 115.4, 119.2, 130.2, 132.0, 134.0, 162.1, 163.9, 190.8; ESI-TOF-HRMS: *m/z* calcd for $[M+Na]^+$ $C_{20}H_{21}NO_5Na$, 378.1312; found, 378.1315.

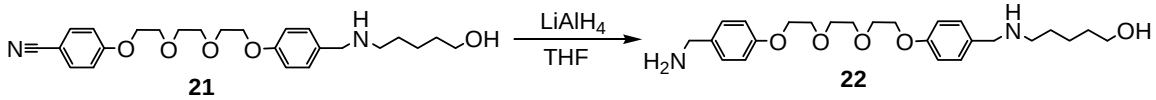
**4-(2-(2-(2-(4-((5-hydroxypentylamino)methyl)phenoxy)ethoxy)ethoxy)ethoxy)-benzonitrile (21)**




**20** **21**

The solution of **20** (1.50 g, 4.2 mmol) and 5-amino-1-pentanol (0.55 mL, 5.0 mmol) in absolute ethanol (150 ml) were refluxed for 24 h. After cooling down to room temperature, $NaBH_4$ (2.20 g, 58 mmol) was then added and the resulting solution stirred at room temperature for a further 24 h. The solvent was removed in *vacuo*. The resulting residue was treated with water and the compound was repeatedly extracted with $CH_2Cl_2$ (three times 60 ml). The organic phase was dried with anhydrous $Na_2SO_4$, and the solvent was evaporated to give the crude product, which was subjected to column chromatography over silica gel (eluent, $CH_2Cl_2$ : MeOH, 100:1 to 12:1) to afford **21** (1.04 g, 56%) as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ = 1.36-1.54 (m, 4H), 1.69-1.79 (m, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 3.56 (t, *J* = 5.8 Hz, 2H), 3.69-3.72 (m, 4H), 3.78-3.87 (m, 4H), 3.92 (s, 2H), 4.02-4.07 (m, 4H), 4.12-4.16 (m, 4H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 9.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ = 23.1, 26.3, 31.6, 46.6, 51.0, 53.5, 61.8, 67.5, 67.9, 69.5, 69.8, 70.9, 71.0, 104.1, 115.0, 115.4, 119.3, 124.5, 131.5, 134.0, 159.3, 162.2; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{25}H_{35}N_2O_5$, 443.2541; found, 443.2549.

**5-(4-(2-(2-(2-(4-(aminomethyl)phenoxy)ethoxy)ethoxy)ethoxy)benzylamino)-1-pentanol (22)**

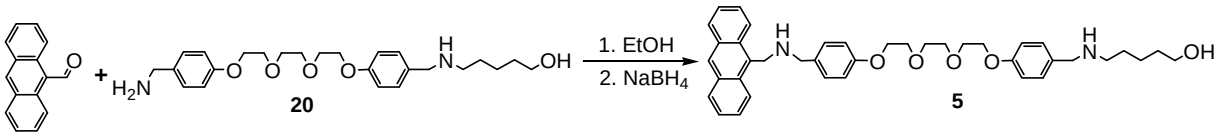



**21** **22**

$LiAlH_4$ (0.43 g, 11.3 mmol) was added in portion to the solution of **21** (1.00 g 2.26 mmol) in dry THF (100 mL) at 0 °C, and the mixture was refluxed for 24 h. Minimum saturated aqueous $Na_2SO_4$ solution was added to neutralize superfluous $LiAlH_4$, The precipitate was filtered off, and washed by $CH_2Cl_2$ (50 mL). The combined filtrate was dried over $Na_2SO_4$,

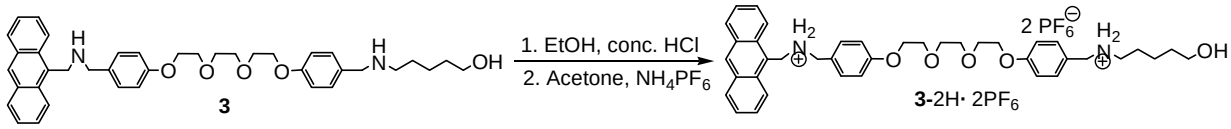
and concentrated in *vacuo* to give **22** as a yellowish solid (0.90 g, 89%), which was used for the next step without further purification. $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.35-1.44 (m, 2H), 1.48-1.60 (m, 4H), 2.61 (t, *J* = 7.0 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 3.69 (s, 2H), 3.72-3.75 (m, 4H), 3.77 (s, 2H), 3.82-3.87 (m, 4H), 4.07-4.13 (m, 4H), 6.82-6.89 (m, 4H), 7.15-7.21 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 23.5, 29.7, 32.6, 45.9, 49.2, 53.5, 62.6, 67.5, 67.6, 69.9, 71.0, 114.6, 114.8, 128.3, 129.4, 132.7, 135.7, 157.8, 157.9; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{25}H_{39}N_2O_5$, 447.2854; found, 447.2851; calcd for $[M+Na]^+$ $C_{25}H_{38}N_2O_5Na$, 469.2673; found, 469.2674.

**5-(4-(2-(2-(2-(4-(((9-anthracenyl)methylamino)methyl)phenoxy)ethoxy)ethoxy)-ethoxy)benzylamino)-1-pentanol (5)**




9-Anthracenecarboxaldehyde (0.43 g, 2.09 mmol) and **22** (0.90 g, 2.02 mmol) were refluxed for 24 h in absolute ethanol (150 ml). After cooling down to room temperature, $NaBH_4$ (1.00 g, 26.3 mmol) was then added and the resulting solution stirred at room temperature for a further 24 h. The solvent was removed in *vacuo*. The resulting residue was treated with water and the compound was repeatedly extracted with $CH_2Cl_2$ (80 mL, three times). The organic phase was dried with anhydrous $Na_2SO_4$, and the solvent was evaporated to give the crude product, which was subjected to column chromatography over silica gel (eluent, $CH_2Cl_2$ : MeOH : ammonium hydroxide solution (25wt%), 100:2:0.2 to 100:10:0.2) to afford **5** (0.98 g, 76%) as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.33-1.51 (m, 4H), 1.65-1.74 (m, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 3.52 (t, *J* = 6.0 Hz, 2H), 3.70-3.76 (m, 4H), 3.79-3.88 (m, 6H), 3.94 (s, 2H), 4.01-4.06 (m, 2H), 4.10-4.15 (m, 2H), 4.66 (s, 2H), 6.83-6.94 (m, 4H), 7.28-7.52 (m, 8H), 7.97 (d, *J* = 7.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H) , 8.38 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 23.1, 26.4, 31.7, 44.7, 46.7, 51.1, 53.6, 61.8, 67.5, 67.6, 69.8, 69.9, 70.9, 114.7, 115.0, 124.2, 125.0, 126.2, 127.4, 129.2, 129.7, 130.4, 131.3, 131.6, 132.4, 158.1, 159.2; ESI-TOF-HRMS: *m/z* calcd for $[M+H]^+$ $C_{40}H_{49}N_2O_5$, 637.3636; found, 637.3646.

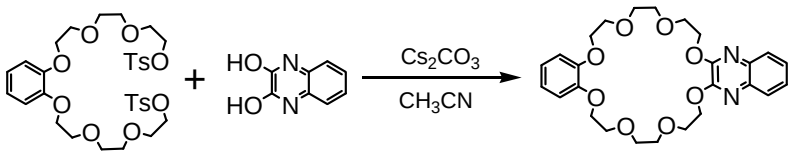
**Divalent Guest 5-**2H·2$PF_6$




**3** **3-**2H· 2$PF_6$

To the solution of **5** (0.98 g, 1.54 mmol) in EtOH (50 mL) was added conc. HCl to adjust pH < 2, and the solvent was then evaporated off under reduced pressure. The residue was suspended in acetone (50 mL). Saturated aqueous $NH_4PF_6$ solution was added until the suspension became clear. The solvent was removed in vacuo, and water (100 mL) was added to the residue. The resulting mixture was stirred at ambient temperature overnight. The mixture was then extracted with ethyl acetate (50 mL × 2), and the solvent was evaporated until dryness to give **5-**2H·2$PF_6$ as a yellow solid (0.90 g, 63%). m.p. 89-91 °C; $^1$H NMR (400 MHz, $CD_3CN$, 298 K): δ = 1.30-1.49 (m, 4H), 1.58-1.68 (m, 2H), 2.93-3.02 (m, 2H), 3.45 (t, *J* = 6.2 Hz, 2H), 3.62-3.67 (m, 4H), 3.74-3.81 (m, 4H), 4.03-4.16 (m, 6H), 4.45 (t, *J* = 5.6 Hz, 2H), 5.16-5.22 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.53-7.66 (m, 4H), 8.02-8.08 (m, 2H), 8.09-8.15 (m, 2H), 8.70 (s, 1H); $^{13}$C NMR (100 MHz, $CD_3CN$, 298 K): δ = 22.5, 25.4, 31.5, 47.5, 51.0, 51.6, 61.2, 67.6, 67.7, 69.3, 70.4, 114.9, 115.2, 121.1, 122.3, 122.8, 123.1, 125.7, 127.7, 129.5, 130.8, 131.3, 131.7, 132.3, 159.8, 160.1; ESI-TOF-HRMS: *m/z* calcd for $[M\text{-}2PF_6\text{-}H]^+$ $C_{40}H_{49}N_2O_5$, 637.3636; found, 637.3636; $[M\text{-}PF_6]^+$ $C_{40}H_{50}F_6N_2O_5P$, 764.3372; found, 764.3392.

**Crown Ether 24**

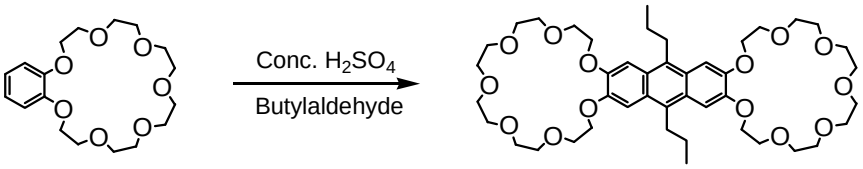



**23** **24**

While stirring vigorously under argon atmosphere, a suspension of $Cs_2CO_3$ (5.00 g, 15.3 mmol) and 2,3-dihydroxyquinoxaline (0.49 g, 3.0 mmol) in anhydrous $CH_3CN$ (150 mL) was heated to reflux. To the suspension was added dropwise a solution of **23** (2.05 g, 3.0 mmol) in anhydrous $CH_3CN$ (150 mL) during 24 h. The resulting reaction mixture was stirred under

reflux for another 3d. Upon cooling down to ambient temperature, the suspension was filtered and washed with $CH_2Cl_2$ (100 mL). The filtrate was concentrated under vacuum. The residue was partitioned between $CH_2Cl_2$ (100 mL) and water (100 mL), and the aqueous phase was extracted twice by $CH_2Cl_2$ (100 mL). The combined organic phase was dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure to give the crude product, which was purified by column chromatography over silica gel (eluent: ethyl acetate/MeOH, 100:1 to 50:1) to afford **24** (0.38 g, 25%) as a white solid. m.p. 115-116 °C; $^1$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.81-3.85 (m, 8H), 3.90-3.94 (m, 4H), 3.95-3.99 (m, 4H), 4.12-4.16 (m, 4H), 4.63-4.67 (m, 4H), 6.85-6.89 (m, 4H), 7.42-7.48 (m, 2H), 7.68-7.74 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 67.3, 69.4, 69.6, 70.1, 71.4, 71.6, 114.3, 121.5, 126.5, 126.7, 137.2, 149.1, 149.6; ESI-TOF-HRMS: *m/z* calcd for $[M+Na]^+$ $C_{26}H_{32}N_2O_8Na$, 523.2051; found, 523.2046.

**Anthracene Bis-21-Crown-7 7**

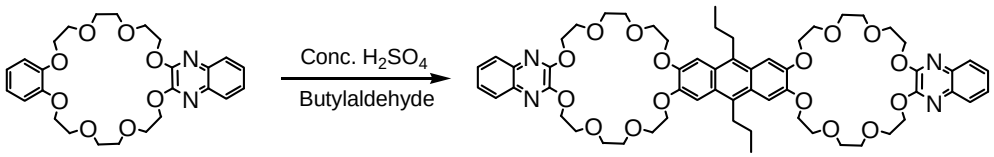



**Benzo-21-Crown-7** **7**

To the vigorously stirred solution of conc. sulfuric acid (13.0 mL, 84%) under argon atmosphere in ice-water bath was added slowly a solution of butylaldehyde (0.20 mL, 2.00 mmol) and Benzo-21-Crown-7 (200 mg 0.56 mmol) in dichloromethane (2 ml). The resulting mixture was stirred vigorously for another 5h. The reaction solution was poured into ice-water mixture (200 mL), and neutralized with ammonium hydroxide solution (25wt%). The water phase was extracted by dichloromethane (100 mL×3). The combined organic phase was dried over anhydrous $Na_2SO_4$, and concentrated in *vacuo* to give a solid residue. Pure **7** (184 mg, 80%) was obtained after column chromatography on silica gel (eluent: $CH_2Cl_2$/MeOH, 100:1 to 20:1) as a yellow solid. m.p. 168-169 °C; $^1$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.11 (t, *J* = 7.4 Hz, 6H), 1.74-1.85 (m, 4H), 3.34 (t, *J* = 7.8 Hz, 4H), 3.64-3.71 (m, 16H), 3.74-3.80 (m, 8H), 3.85-3.90 (m, 8H), 4.01-4.06 (m, 8H), 4.29-4.35 (m, 8H), 7.40 (s, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 15.0, 23.8, 30.8, 68.9, 69.7, 70.6, 71.0, 71.1, 71.2, 71.3, 100.0,

104.8, 125.7, 129.5, 148.4; ESI-TOF-HRMS: *m/z* calcd for $[M+Na]^+$ $C_{44}H_{66}O_{14}Na$, 841.4345; found, 841.4334.

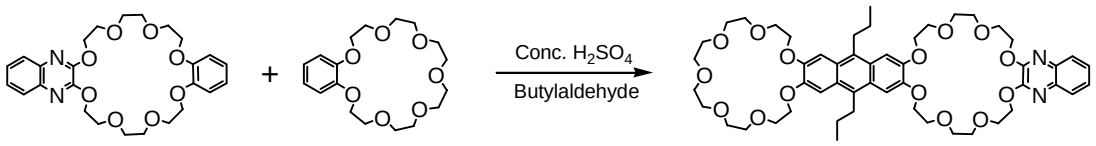
**Anthracene Bis-24-Crown-8 8**




**24** **8**

To the vigorously stirred solution of conc. sulfuric acid (6.5 mL, 84%) under argon atmosphere in ice-water bath was added slowly a solution of butylaldehyde (0.05 mL, 0.5 mmol) and crown ether **24** (100 mg 0.2 mmol) in dichloromethane (1 ml). The resulting mixture was stirred vigorously for another 5h. The reaction solution was poured into ice-water mixture (100 mL), and neutralized with ammonium hydroxide solution. The water phase was extracted by dichloromethane (60 mL×3). The combined organic phase was dried over anhydrous $Na_2SO_4$, and concentrated in *vacuo* to give a solid residue. Pure **8** (80 mg, 72%) was obtained after column chromatography on silica gel (eluent: $CH_2Cl_2$/MeOH, 100:1 to 50:1) as a yellow solid. m.p. 206-208 °C; $^1$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.10 (t, *J* = 7.2 Hz, 6H), 1.73-1.84 (m, 4H), 3.31 (t, *J* = 8.0 Hz, 4H), 3.85-3.94 (m, 16H), 3.96-4.06 (m, 16H), 4.28-4.33 (m, 8H), 4.63-4.68 (m, 8H), 7.36 (s, 4H), 7.40-7.45 (m, 4H), 7.66-7.71 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 15.0, 23.8, 30.8, 67.4, 69.3, 69.5, 70.0, 71.6, 104.7, 125.7, 126.4, 126.6, 129.5, 137.2, 148.4, 149.6; ESI-TOF-HRMS: *m/z* calcd for $[M+Na]^+$ $C_{60}H_{74}N_4O_{16}Na$, 1129.4992; found, 1129.4991.

**Hetero-Crown Ether dimer 6**




**24** **Benzo-21-Crown-7** **6**

To the vigorously stirred solution of conc. sulfuric acid (13.0 mL, 84%) under argon atmosphere in ice-water bath was added slowly a solution of butylaldehyde (0.10 mL, 1.00 mmol), **24** (100 mg 0.20 mmol) and Benzo-21-Crown-7 (71 mg 0.20 mmol) in dichloromethane (3 ml). The resulting mixture was stirred vigorously for another 5h. The reaction solution was poured into ice-water mixture (200 mL), and neutralized with ammonium hydroxide solution. The water phase was extracted by dichloromethane (100 mL×3). The combined organic phase was dried over anhydrous $Na_2SO_4$, and concentrated in *vacuo* to give a solid residue. Pure **6** (61 mg, 32%) was obtained after column chromatography on silica gel (eluent: $CH_2Cl_2$/MeOH, 100:1 to 20:1) as a yellow solid. m.p. 166-168 °C; $^1$H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.10 (t, *J* = 7.4 Hz, 6H), 1.73-1.85 (m, 4H), 3.32 (t, *J* = 7.8 Hz, 4H), 3.60-4.10 (m, 36H), 4.28-4.34 (m, 8H), 4.62-4.68 (m, 4H), 7.35-7.45 (m, 6H), 7.66-7.71 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): δ = 15.0, 23.8, 30.8, 53.5, 67.4, 69.0, 69.3, 69.5, 69.8, 70.0, 70.6, 71.1, 71.2, 71.4, 71.6, 104.7, 125.7, 126.4, 126.6, 129.5, 137.2, 148.4, 149.6; ESI-TOF-HRMS: *m/z* calcd for $[M+Na]^+$ $C_{52}H_{70}N_2O_{15}Na$, 985.4668; found, 985.4661. Meanwhile, two homodimers **7** (65 mg, 58% based on **24**) and **8** (50 mg, 61% based on Benzo-21-Crown-7) were also isolated.

## Additional Material Mentioned in the Main Text

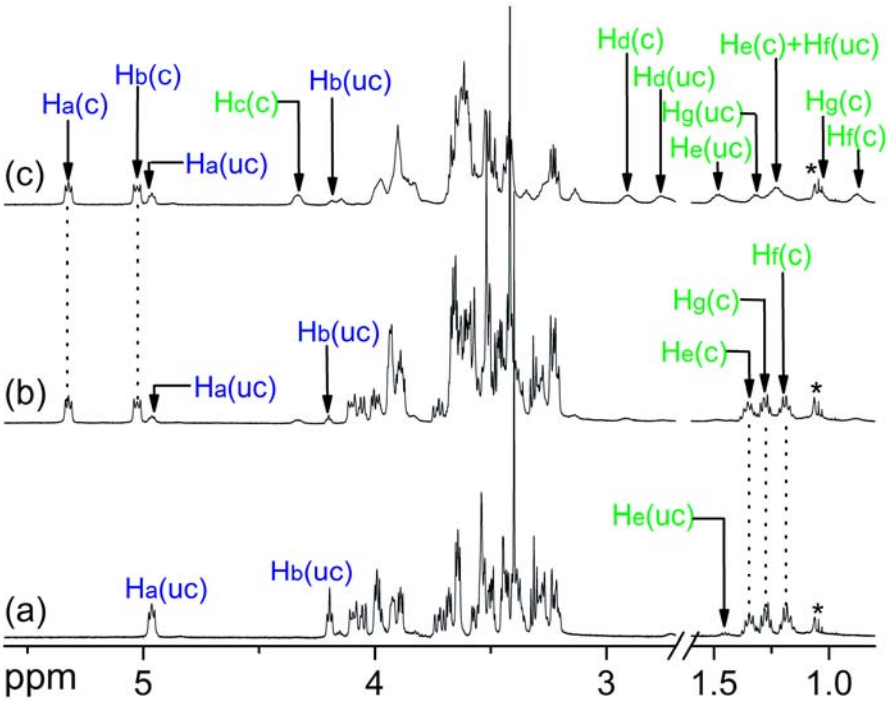



**Fig. S1.** Partial $^{1}$H NMR spectra (500 MHz, 298 K, $CDCl_3$:$CD_3CN$ = 2:1, 10.0 mM) of equimolar mixtures of (a) **5**-2H·2$PF_6$ and **C7**; (c) **5**-2H·2$PF_6$ and **C8**; and (b) **5**-2H·2$PF_6$, **C7**, and **C8**. Asterisks: solvent impurities. The NMR spectra show similar shifts as those found for the equimolar mixture of **4**-2H·2$PF_6$, **C7**, and **C8**, indicating **11**-2H·2$PF_6$ is the predominant species in the equimolar mixture of **5**-2H·2$PF_6$, **C7**, and **C8**.

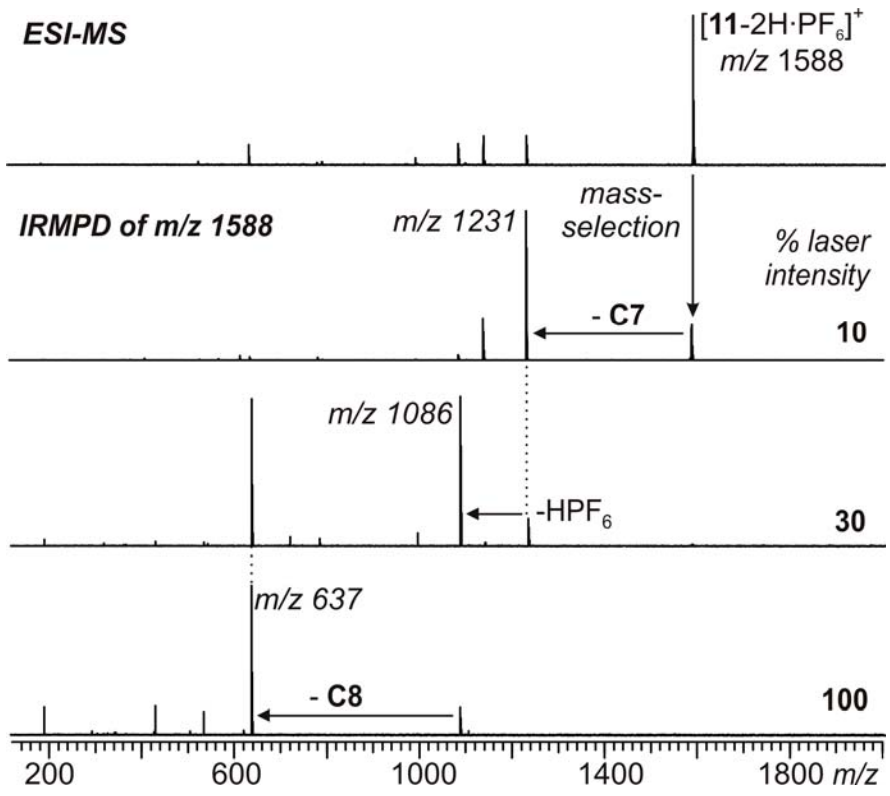



**Fig. S2.** Mass spectra of **11**-2H·2$PF_6$. Top: Electrospray-ionization Fourier-transform ion-cyclotron-resonance (ESI-FTICR) mass spectrum of a 1:1:1 DCM solution of **5**-2H·2$PF_6$, **C7**, and **C8**. Bottom: Infrared-Multiphoton Dissociation (IRMPD) experiments (MS/MS) of mass-selected [**11**-2H·$PF_6$]$^+$. The most intense peak in the mass spectrum of the mixture **5**-2H·2$PF_6$, **C7**, and **C8** is at *m/z* 1588 which is readily assigned to [**11**-2H·$PF_6$]$^+$, and then the sequential loss of **C7**, $HPF_6$, and **C8** during the MS/MS of mass-selected [**11**-2H·$PF_6$]$^+$ with increasing laser intensity confirm the sequence of **C7** and **C8** in **11**-2H·2$PF_6$.

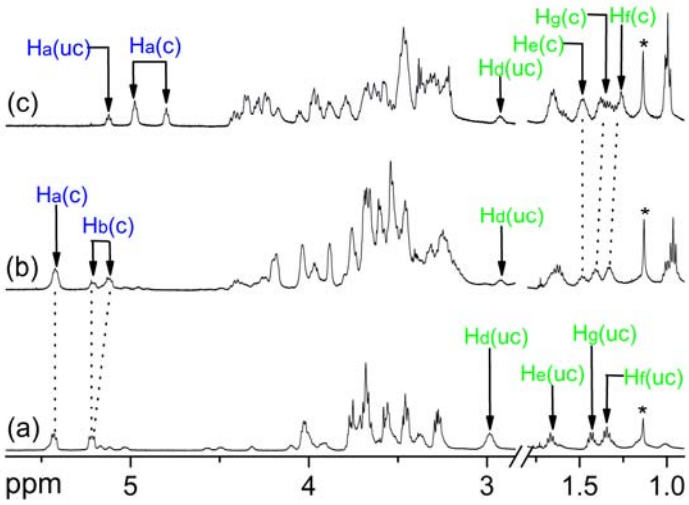



**Fig. S3.** Partial $^1$H NMR spectra (500 MHz, 298 K, $CDCl_3$:$CD_3CN$ = 5:1) of (a) 1:1 mixtures of **C8** and **3**-2H·2$PF_6$; (c) 1:2 mixtures of **7** and **3**-2H·2$PF_6$; and (b) 1:2:2 mixtures of **7**, **C8**, and **3**-2H·2$PF_6$. [**C8**] = 2[**7**] = 10.0 mM. Complexed and uncomplexed species are denoted by "c" and "uc" in the parentheses, respectively. Asterisks: solvent impurities.

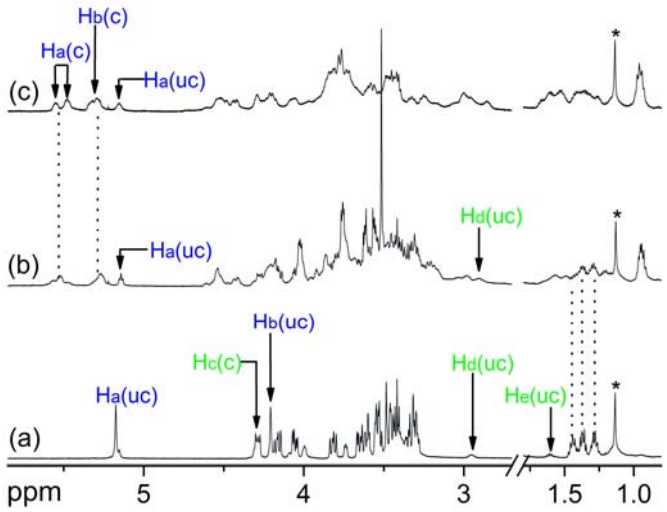



**Fig. S4.** Partial $^1$H NMR spectra (500 MHz, 298 K, $CDCl_3$:$CD_3CN$ = 5:1) of (a) 1:1 mixtures of **C7** and **3**-2H·2$PF_6$; (c) 1:2 mixtures of **8** and **3**-2H·2$PF_6$; and (b) 1:2:2 mixture of **8**, **C7**, and **3**-2H·2$PF_6$. [**C7**] = 2[**8**] = 10.0 mM. Complexed and uncomplexed species are denoted by "c" and "uc" in the parentheses, respectively. Asterisks: solvent impurities. According the changes of $H_a$, $H_b$, $H_d$, and $H_e$ on **3**-2H·2$PF_6$ in Fig. S4b, site **A** and **B** of most of **3**-2H·2$PF_6$ are bound by **C7** and **8**, respectively. However, the structure of the predominant species in the 1:2:2 mixture of **8**, **C7**, and **3**-2H·2$PF_6$ cannot be concluded only from NMR experiments.

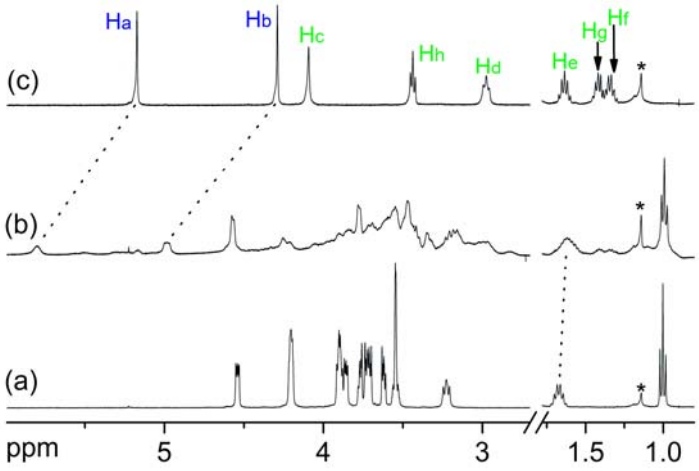



**Fig. S5.** Partial $^1$H NMR spectra (500 MHz, 298 K, $CDCl_3$:$CD_3CN$ = 5:1, 2 mM) of (a) **3**-2H·2$PF_6$; (b) 1:1 mixtures of **6** and **3**-2H·2$PF_6$; and (c) **6**. Asterisks: solvent impurities. Because of the complexity of the resulting complex **15**-4H·4$PF_6$, the $^1$H NMR spectra are too complicated to give any useful information about the predominance of **15**-4H·4$PF_6$ in this solution and the relative location of every component in **15**-4H·4$PF_6$.

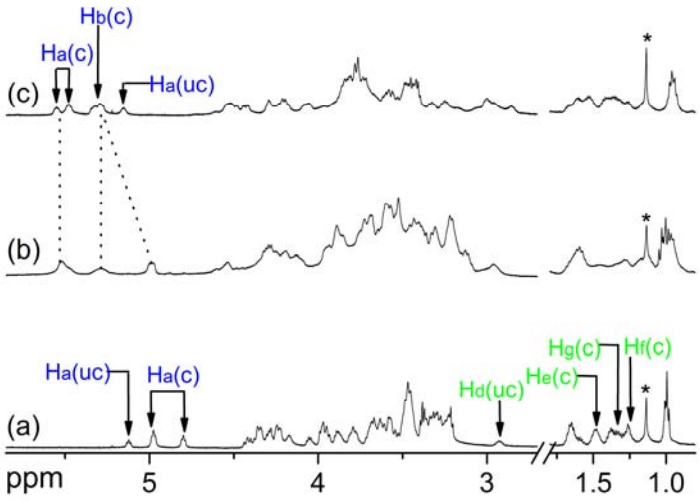



**Fig. S6.** Partial $^1$H NMR spectra (500 MHz, 298 K, $CDCl_3$:$CD_3CN$ = 5:1) of (a) 1:2 mixtures of **7** and **3**-2H·2$PF_6$; (c) 1:2 mixtures of **8** and **3**-2H·2$PF_6$; and (b) 1:1:2 mixtures of **7**, **8**, and **3**-2H·2$PF_6$. [**3**-2H·2$PF_6$] = 2[**7**] = 10.0 mM. Complexed and uncomplexed species are denoted by "c" and "uc" in the parentheses, respectively. Asterisks: solvent impurities. Similar problem as **15**-4H·4$PF_6$ exists here.

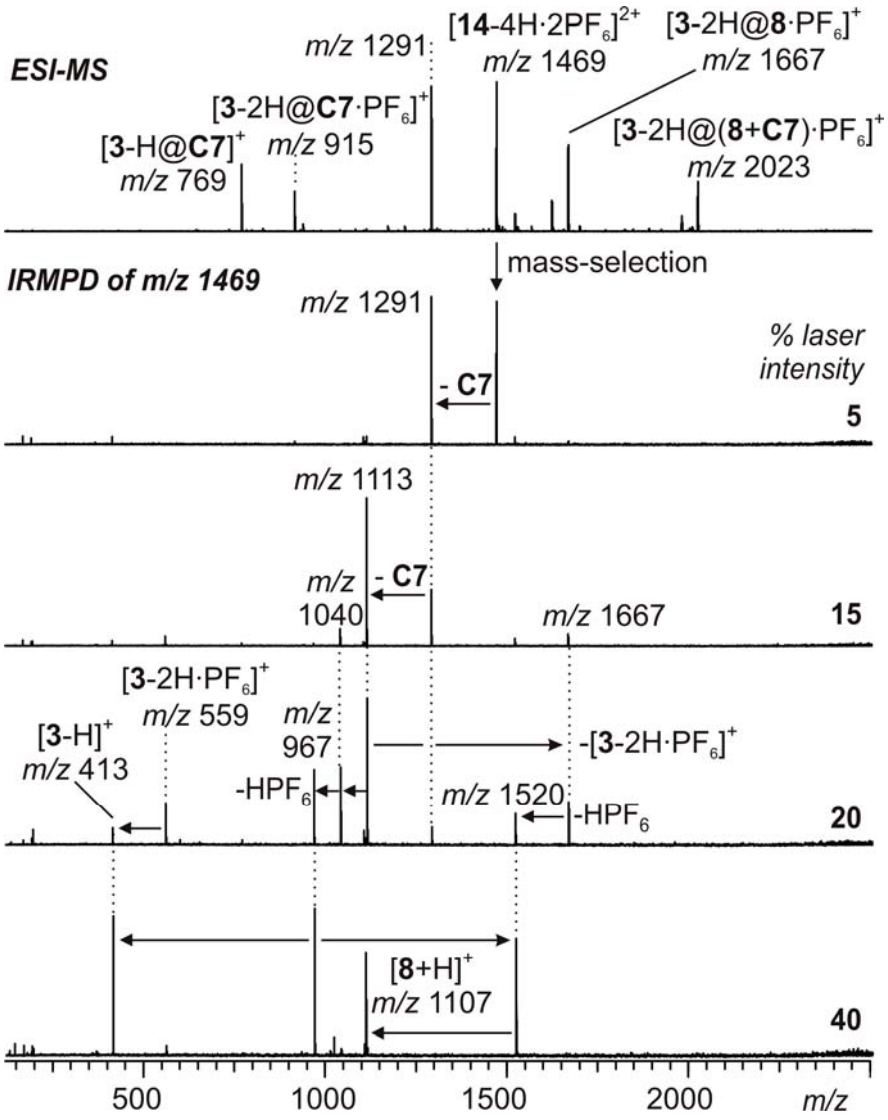



**Fig. S7.** Mass spectra of **14**-4H·4$PF_6$. Top: ESI-FTICR mass spectrum of a 1:2:2 DCM solution of **8**, **C8**, and **3**-2H·2$PF_6$. Bottom: IRMPD experiments (MS/MS) of mass-selected [**14**-4H·2$PF_6$]$^{2+}$. The peaks at *m/z* 1291 and 1667 in the mass spectrum of the mixture of **8**, **C8**, and **3**-2H·2$PF_6$ are the fragments from [**14**-4H·2$PF_6$]$^{2+}$ (*m/z* 1469) during ionization process of five-component assembly based on weak interactions. With this respect, **14**-4H·4$PF_6$ is predominant in the 1:2:2 DCM solution of **8**, **C8**, and **3**-2H·2$PF_6$. The sequence information in **14**-4H·4$PF_6$ can also be revealed by MS/MS experiments of mass-selected [**14**-4H·2$PF_6$]$^{2+}$.

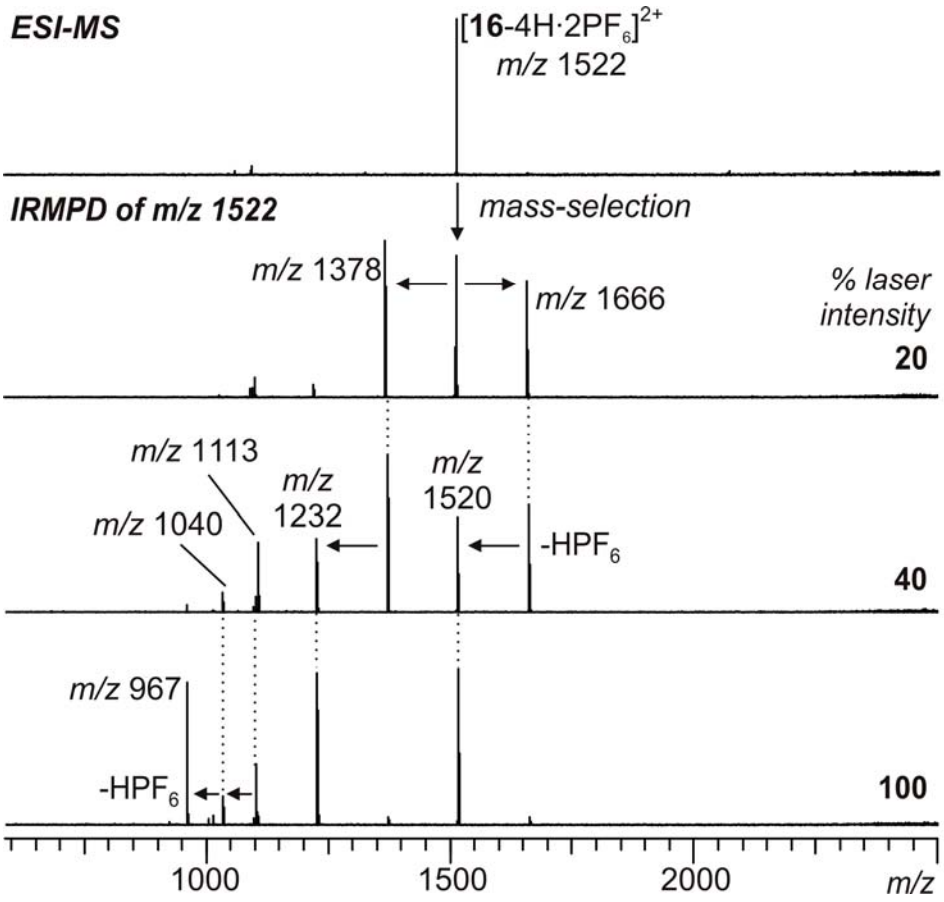



**Fig. S8.** Mass spectra of **16**-4H·4$PF_6$. Top: ESI-FTICR mass spectrum of a 1:1:2 DCM solution of **7**, **8**, and **3**-2H·2$PF_6$. Bottom: IRMPD experiments (MS/MS) of mass-selected [**16**-4H·2$PF_6$]$^{2+}$. The absence of oligomer peak in the mass spectrum of **16**-4H·4$PF_6$ suggests the closed structure in **16**-4H·4$PF_6$, otherwise oligomer peak should be very easy to form in solution and readily detected by ESI-MS. Two fragmentation pathways are involved in the MS/MS experiments of mass-selected [**16**-4H·2$PF_6$]$^{2+}$. The easiest one at lower laser intensity is breaking the macrocycle of 24-crown-8 in **8** to distribute two charges to two fragments at *m/z* 1666 and 1378, which is probably driven by charged repulsion. The second one occurs only at higher laser intensity by losing neutral **7**, which is perfectly in line with the structure of **16**-4H·4$PF_6$.

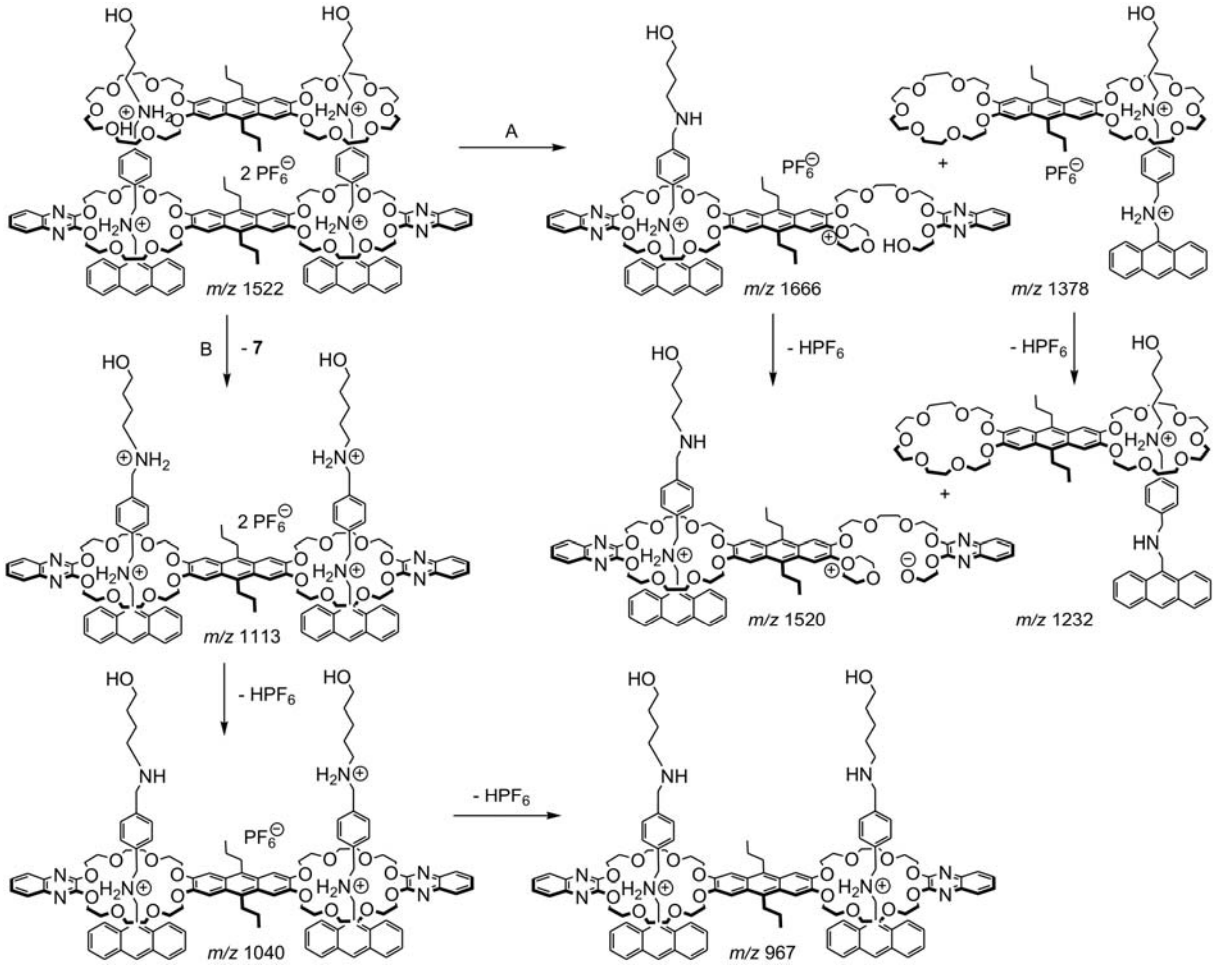



**Fig. S9.** Two fragmentation pathways of $[\mathbf{16}\text{-}4H\cdot 2PF_6]^{2+}$ during IRMPD (MS/MS) experiments. Pathway **A** is remarkable in that it shows, how the complex can realize a charge-separating fragmentation by cleaving a crown ether, if no other low energy pathway is available. Instead, pathway **B** generates a neutral and a dicationic fragment, which still suffers from charge repulsion. One should also consider that the ionic hydrogen bond can be quite strong in the absence of competing solvent, so that the cleavage along pathway **B** is not necessarily much lower than **A**. The structures of the fragments at *m/z* 1232, 1378, 1520, and 1666 are only suggestions. Alternative structures are possible, e.g. different distributions of protons or other oxonium ions.

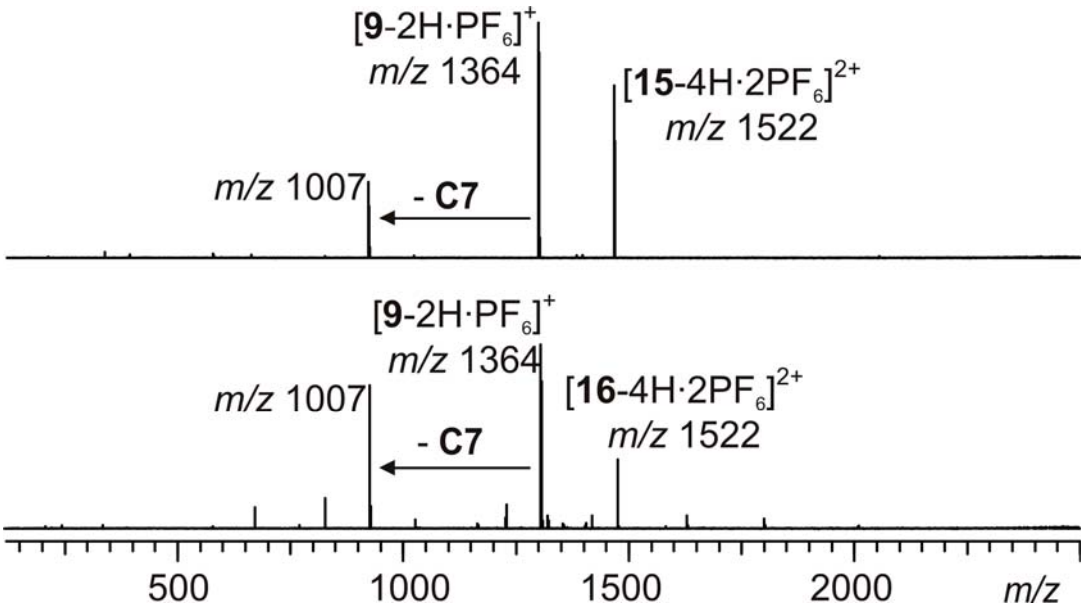



**Fig. S10.** Mass spectra obtained from the mixture of **9**-2H·2$PF_6$ and **15**-4H·4$PF_6$ or **16**-4H·4$PF_6$. Top: ESI-FTICR mass spectrum of a 2:1 DCM solution of **9**-2H·2$PF_6$ and **15**-4H·4$PF_6$. Bottom: ESI-FTICR mass spectrum of a 2:1 DCM solution of **9**-2H·2$PF_6$ and **16**-4H·4$PF_6$. From these two spectra, we know [**9**-2H·$PF_6$]$^+$ (*m/z* 1364) and [**15**-4H·2$PF_6$]$^{2+}$ or [**16**-4H·2$PF_6$]$^{2+}$ (*m/z* 1522) are the most dominant species in the corresponding solution (the peak at *m/z* 1364 is fragment of [**9**-2H·$PF_6$]$^+$ during ionization process by losing neutral **C7**), which strongly suggest the closed structures of **15**-4H·4$PF_6$ and **16**-4H·4$PF_6$. Otherwise, the more complex and bigger assemblies should be detected by ESI-MS.

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