Electronic Supplementary Information


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1. Experimental Section

1.1 General Method. All the reagents involved in this research were commercially available and used without further purification unless otherwise noted. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. 

$^1$H NMR, $^{13}$C NMR, and $^1$H-$^1$H ROESY NMR spectra were recorded on Bruker Avance-400 or 500 spectrometers. All chemical shifts are reported in ppm with residual solvents or TMS (tetramethylsilane) as the internal standards. Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) experiments were conducted on an applied Q EXACTIVE mass spectrometry system. Molecular simulations were performed at the Semi-Empirical PM6 level of theory by using Spartan’14 (Wavefunction, Inc.). Isothermal Titration Calorimetry (ITC) titration experiments were carried out in 1,2-dichloroethane/CH$_3$CN 3 : 2 (v/v) at 25 °C on a NanoITC LV – 190 µL (Waters GmbH, TA Instruments, Eschborn, Germany). Scanning electron microscope (SEM) images were obtained from the field emission SEM (FESEM, ZEISS Merlin). Transmission electron microscopy investigations were carried out on a HITACHI HT-7700 instrument. Powder XRD measurement was performed on a Smartlab (9 kW, Rigaku, Japan). The synthesis of 1a has been reported.$^1$
1.2 Synthetic Procedures

**Compounds S1b-1d**

**General procedure for S1b-1d:** The mixture of 2,6-dihydroxynaphthalene (16.0 g, 100 mmol), 1-bromo-hydrocarbon (300 mmol), and K₂CO₃ (69.0 g, 500 mmol) in dry DMF (300 mL) were stirred overnight at 100 °C under Argon protection. After cooling to room temperature, the mixture was poured into water (500 mL). The precipitate was filtered and washed with copious H₂O and MeOH. The filter cake was collected and dried in vacuum to give the target compound.

**S1b** was obtained in 62% yield as a white solid. ¹H NMR (400 MHz, CDCl₃, 25 °C):
\[ \delta [ppm] = 7.64 (d, J = 8.8 Hz, 2H), 7.17 - 7.09 (m, 4H), 4.07 (t, J = 6.6 Hz, 4H), 1.85 (q, J = 7.1 Hz, 4H), 1.52 (t, J = 7.7 Hz, 4H), 1.41 - 1.27 (m, 16H), 0.97 - 0.88 (m, 16H) \]
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of compound S1b
\(^{13}\)C NMR spectrum (101 MHz, CDCl\(_3\), 25 °C) of compound S1b

\[ \delta [ppm] = 155.54, 129.70, 128.02, 119.20, 106.93, 68.08, 31.87, 29.44, 29.34, 29.30, 29.30, 26.16, 22.71, 14.15. \]

ESI-HRMS: m/z calcd for [M+H]\(^+\) C\(_{34}\)H\(_{57}\)O\(_2\), 497.4353; found 497.4356 (error = 0.6 ppm).

S1c was obtained in 92% yield as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta [ppm] = \delta 7.64 (d, J = 8.8 \text{ Hz}, 2H), 7.16 – 7.10 (m, 4H), 4.06 (t, J = 6.6 \text{ Hz}, 4H), 1.86 (dd, J = 8.3, 6.5 \text{ Hz}, 4H), 1.55 – 1.49 (m, 4H), 1.43 – 1.29 (m, 32H), 0.91 (t, J = 6.7 \text{ Hz}, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), 25 °C): \(\delta [ppm] = 155.54, 129.70, 128.02, 119.20, 106.93, 68.08, 31.87, 29.44, 29.34, 29.30, 26.16, 22.71, 14.15. \)

ESI-HRMS: m/z calcd for [M+H]\(^+\) C\(_{34}\)H\(_{57}\)O\(_2\), 497.4353; found 497.4356 (error = 0.6 ppm).
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of compound S1c

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of compound S1c
ESI mass spectrum of compound S1c

S1d was obtained in 94% yield as a white solid. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C):
$\delta$ [ppm] = 7.63 (d, $J = 8.8$ Hz, 2H), 7.14 (d, $J = 8.7$, 2.4 Hz, 2H), 7.10 (s, 2H), 4.06 (t, $J = 6.6$ Hz, 4H), 1.88 – 1.82 (m, 4H), 1.50 (q, $J = 7.5$ Hz, 4H), 1.41 – 1.28 (m, 48H), 0.90 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 155.52, 129.68, 128.01, 119.19, 106.91, 68.07, 31.95, 29.72, 29.69, 29.64, 29.62, 29.46, 29.39, 29.33, 26.14, 22.72, 14.16. ESI-MS: m/z calcd for [M+H]$^+$ C$_{42}$H$_{73}$O$_2$, 609.5605; found 609.5593 (error = -2.0 ppm).
$^{1}$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of compound S1d

$^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 25 °C) of compound S1d
Dibromides S2b-2d

General procedure for S2b-2d: the corresponding compound S1 (30 mmol) and paraformaldehyde (6.0 g, 300 mmol) were dissolved in HBr/AcOH (30% w/w, 400 mL). The resulting mixture was heated to 50 °C and stirred for 5 h. The solution was cooled to room temperature. The light purple precipitate was filtered off and washed with copious AcOH and MeOH, and then dried to afford the target product.

S2b was obtained in 61% yield as an off-white solid. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ [ppm] = 8.05 (d, J = 9.3 Hz, 2H), 7.36 (d, J = 9.4 Hz, 2H), 5.09 (s, 4H), 4.20 (t, J = 6.5 Hz, 4H), 1.90 (p, J = 6.8 Hz, 4H), 1.57 (d, J = 6.6 Hz, 4H), 1.36 (dt, J = 26.9, 6.5 Hz, 16H), 0.98 – 0.86 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ [ppm] = 153.29, 127.83, 125.49, 119.07, 115.56, 69.54, 31.84, 29.55, 29.36, 29.28, 26.10,
25.27, 22.69, 14.14. ESI-HRMS: m/z calcd for [M-Br]+ C$_{28}$H$_{42}$O$_2$Br, 489.2363; found 489.2369 (error = 1.4 ppm).

$^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of dibromide S2b

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of dibromide S2b
**ESI mass spectrum of dibromide S2b**

S2b was obtained in 62% yield as an off-white solid. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 8.05 (d, $J = 9.3$ Hz, 2H), 7.36 (d, $J = 9.4$ Hz, 2H), 5.09 (s, 4H), 4.20 (t, $J = 6.5$ Hz, 4H), 1.90 (p, $J = 6.8$ Hz, 4H), 1.57 (d, $J = 6.6$ Hz, 4H), 1.36 (dt, $J = 26.9$, 6.5 Hz, 16H), 0.98 – 0.86 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 153.29, 127.83, 125.49, 119.07, 115.56, 69.54, 31.84, 29.55, 29.36, 29.28, 26.10, 25.27, 22.69, 14.14. ESI-HRMS: m/z calcd for [M-Br]$^+$ C$_{36}$H$_{58}$O$_2$Br, 601.3615; found 601.3594 (error = -3.5 ppm).
$^{1}H$ NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of dibromide S2c

$^{13}C$ NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of dibromide S2c
S2c was obtained in 56% yield as an off-white solid. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 8.04 (d, $J$ = 9.3 Hz, 2H), 7.36 (d, $J$ = 9.4 Hz, 2H), 5.09 (s, 4H), 4.19 (t, $J$ = 6.5 Hz, 4H), 1.94 – 1.86 (m, 4H), 1.28 (s, 48H), 0.90 (t, $J$ = 6.8 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 153.29, 127.82, 125.49, 119.06, 115.56, 69.54, 31.94, 29.71, 29.68, 29.62, 29.54, 29.39, 26.09, 25.28, 22.71, 14.15. ESI-HRMS: m/z calcd for [M-Br]$^+$ C$_{44}$H$_{74}$BrO$_2$, 713.4872; found 713.4850 (error = -2.3 ppm).

S2d was obtained in 56% yield as an off-white solid. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 8.04 (d, $J$ = 9.3 Hz, 2H), 7.36 (d, $J$ = 9.4 Hz, 2H), 5.09 (s, 4H), 4.19 (t, $J$ = 6.5 Hz, 4H), 1.94 – 1.86 (m, 4H), 1.28 (s, 48H), 0.90 (t, $J$ = 6.8 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 153.29, 127.82, 125.49, 119.06, 115.56, 69.54, 31.94, 29.71, 29.68, 29.62, 29.54, 29.39, 26.09, 25.28, 22.71, 14.15. ESI-HRMS: m/z calcd for [M-Br]$^+$ C$_{44}$H$_{74}$BrO$_2$, 713.4872; found 713.4850 (error = -2.3 ppm).
$^{1}$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of dibromide S2d

$^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 25 °C) of dibromide S2d
Compounds S3b-3d

General procedure for S3b-3d: To a stirred mixture of corresponding dibromide S2 (10 mmol) in CH₃COOH (250 mL), CH₃COONa (3.3 g, 40 mmol) was added. The reaction mixture was stirred and heated at 110 ºC for 5h. The reaction mixture was cooled to room temperature and the resulting precipitate was washed with ethanol and dried to afford the target compound.

S3b was obtained in 91% yield as a white solid. ¹H NMR (400 MHz, CDCl₃, 25 ºC): δ [ppm] = 7.97 (d, J = 9.3 Hz, 2H), 7.34 (d, J = 9.3 Hz, 2H), 5.67 (s, 4H), 4.14 (t, J = 6.5 Hz, 4H), 2.08 (s, 6H), 1.87 – 1.81 (m, 4H), 1.49 (q, J = 7.3 Hz, 4H), 1.33 (m, 16H), 0.90 (d, J = 7.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, 25 ºC): δ [ppm] = 171.39, 154.12, 128.94, 125.94, 117.06, 116.06, 69.91, 57.41, 31.83, 29.51, 29.35,
29.28, 26.04, 22.67, 21.08, 14.11. ESI-HRMS: m/z calcd for [M+Na]+ C_{32}H_{48}O_6Na, 551.3343; found 551.3356 (error = 2.4 ppm).

\[ \text{H NMR spectrum (400 MHz, CDCl}_3, 25 \, ^\circ\text{C) of compound S3b} \]

\[ \text{1H NMR spectrum (400 MHz, CDCl}_3, 25 \, ^\circ\text{C) of compound S3b} \]
$^{13}$C NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of compound S3b

[Image of $^{13}$C NMR spectrum]

ESI mass spectrum of compound S3b

S3c was obtained in 94% yield as a white solid. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 7.97 (d, $J = 9.3$ Hz, 2H), 7.34 (d, $J = 9.3$ Hz, 2H), 5.67 (s, 4H), 4.14 (t, $J = 6.5$ Hz, 4H), 2.09 (s, 6H), 1.87 – 1.81 (m, 4H), 1.49 (q, $J = 7.3$ Hz, 4H), 1.32 (m, 32H), 0.90 (d, $J = 7.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25 °C): $\delta$ [ppm] = 171.39, 154.12, 128.94, 125.94, 117.06, 116.06, 69.91, 57.41, 31.83, 29.51, 29.35, 29.28, 26.04, 22.67, 21.08, 14.11. ESI-HRMS: m/z calcd for [M+Na]$^+$ C$_{40}$H$_{64}$O$_6$Na, 663.4595; found 663.4592 (error = -0.4 ppm).
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of compound S3c

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of compound S3c
ESI mass spectrum of compound S3e

S3d was obtained in 98% yield as a white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C): \(\delta\) [ppm] = 7.97 (d, \(J = 9.3\) Hz, 2H), 7.34 (d, \(J = 9.4\) Hz, 2H), 5.67 (s, 4H), 4.13 (t, \(J = 6.5\) Hz, 4H), 2.08 (s, 6H), 1.84 (p, \(J = 6.8\) Hz, 4H), 1.49 (p, \(J = 7.1\) Hz, 4H), 1.28 (s, 48H), 0.90 (t, \(J = 6.8\) Hz, 6H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\), 25 °C): \(\delta\) [ppm] = 171.41, 154.12, 128.93, 125.94, 117.02, 116.05, 69.90, 57.41, 31.94, 29.71, 29.70, 29.68, 29.64, 29.58, 29.52, 29.41, 29.38, 26.04, 22.71, 21.09, 14.15. ESI-HRMS: \(m/z\) calcd for [M+Na]\(^+\) C\(_{48}\)H\(_{80}\)O\(_6\)Na, 775.5853; found 775.5825 (error = -2.8 ppm).
H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of compound S3d

$^1$H NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of compound S3d

$^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 25 °C) of compound S3d
ESI mass spectrum of compound S3d

Diol S4b-4d

General procedure for S4b-4d: the corresponding compound S3 (10 mmol) was added to a solution of 3.9 g potassium hydroxide in 250 mL ethanol and refluxed for 2 h. Upon cooling, the product precipitates and was filtered off and dried in vacuum to give the target product.

S4b was obtained in 92% yield as white solid. $^1$H NMR (400 MHz, CDCl$_3$, 25 ºC): $\delta$ [ppm] = 8.13 (d, $J = 9.4$ Hz, 2H), 7.34 (d, $J = 9.4$ Hz, 2H), 5.20 (d, $J = 5.8$ Hz, 4H), 4.15 (t, $J = 6.5$ Hz, 4H), 2.05 (t, $J = 6.2$ Hz, 2H), 1.90 – 1.83 (m, 4H), 1.54 – 1.48 (m, 4H), 1.43 – 1.27 (m, 16H), 0.94 – 0.89 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25 ºC): $\delta$ [ppm] = 152.99, 128.55, 125.10, 122.01, 115.56, 69.69, 56.15, 31.84, 29.62, 29.39, 29.27, 26.15, 22.68, 14.12. ESI-MS: m/z calcd for [M-OH]$^+$ C$_{28}$H$_{43}$O$_3$, 423.3207; found 427.3216 (error = 2.1 ppm).
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of diol S$_{4b}$

$^{13}$C NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of diol S$_{4b}$
ESI mass spectrum of diol S4b

**S4c** was obtained in 98% yield as a white solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): δ [ppm] = 8.11 (d, $J$ = 9.3 Hz, 2H), 7.32 (d, $J$ = 9.3 Hz, 2H), 5.17 (s, 4H), 4.13 (t, $J$ = 6.5 Hz, 4H), 1.86 – 1.81 (m, 4H), 1.49 (d, $J$ = 7.9 Hz, 4H), 1.26 (s, 32H), 0.87 (d, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25 °C): δ [ppm] = 153.01, 128.54, 125.08, 122.01, 115.56, 69.67, 56.18, 31.94, 29.69, 29.66, 29.64, 29.62, 29.44, 29.38, 26.15, 22.72, 14.15. ESI-HRMS: m/z calcd for [M-OH]$^+$ C$_{36}$H$_{59}$O$_3$, 539.4459; found 539.4473 (error = 2.7 ppm).
$^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of diol S4c

$^1$C NMR spectrum (101 MHz, CDCl$_3$, 25 °C) of diol S4c
**S4c** was obtained in 82% yield as a white solid. $^1$H NMR (500 MHz, CDCl$_3$, 25 ºC): $\delta$ [ppm] = 8.13 (d, $J = 9.3$ Hz, 2H), 7.33 (d, $J = 9.4$ Hz, 2H), 5.19 (d, $J = 6.2$ Hz, 4H), 4.15 (s, 4H), 1.86 (dd, $J = 8.5$, 6.4 Hz, 4H), 1.54 – 1.48 (m, 4H), 1.28 (s, 48H), 0.90 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 ºC): $\delta$ [ppm] = 153.04, 128.52, 125.06, 122.03, 115.58, 69.66, 56.22, 31.94, 29.71, 29.68, 29.63, 29.61, 29.43, 29.38, 26.15, 22.71, 14.15. ESI-HRMS: $m/z$ calcd for [M-OH]$^+$ C$_{44}$H$_{75}$O$_3$, 651.5716; found 651.5698 (error = -2.0 ppm).
$^{1}H$ NMR spectrum (500 MHz, CDCl$_3$, 25 °C) of diol S$_4$d

$^{13}C$ NMR spectrum (126 MHz, CDCl$_3$, 25 °C) of diol S$_4$d
ESI mass spectrum of diol S4d

**General procedure for 1b-d:** To the mixture of NaH (2.0 g, 50 mmol) and Cs₂CO₃ (4.9 g, 15 mmol) in dry THF (500 mL) at reflux was added the solution of dibromide S2 (5.0 mmol) and diol S4 (5.0 mmol) in dry warm THF (60 mL) dropwise through a syringe pump. The resulting mixture was stirred at reflux for another 30h. The solvent was removed under reduced pressure. The residue was suspended in H₂O (100 mL), and then extracted with CH₂Cl₂ (100 mL × 3). The combined organic phase was washed with saturated NaCl and dried over anhydrous Na₂SO₄. Then, the solvent was removed with rotary evaporator to give the crude product which was purified by column chromatography (SiO₂, petroleum ether: ethylacetate = 100:1 ~ 10:1) to give pure TA4 as white solid.
**1b** was obtained in 13% yield as a white solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ [ppm] = 7.73 (s, 8H), 6.92 (d, $J = 9.2$ Hz, 8H), 5.03 (s, 16H), 3.79 – 3.59 (m, 16H), 1.38 – 1.30 (m, 96H), 0.93 (t, $J = 6.4$ Hz, 24H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ [ppm] = 153.14, 129.22, 125.72, 119.90, 115.28, 69.65, 31.95, 29.56, 29.54, 29.45, 26.23, 22.74, 13.91. ESI-HRMS: $m/z$ calcd for [M+TMA]$^+$ C$_{116}$H$_{180}$NO$_{12}$+, 1779.3500; found 1779.3552 (error = 2.9 ppm). Tetramethylammonium (TMA) Hexafluorophosphate was added to facilitate the ionization of **1b**.

![1H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 25 °C) of **1b**.](image)
$^{13}$C NMR spectrum (101 MHz, CD$_2$Cl$_2$, 25 °C) of 1b

ESI-TOF mass spectrum of TMA$^+$@1b
1c was obtained in 14% yield as a white solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): δ [ppm] = 7.73 (s, 8H), 6.92 (d, $J = 9.2$ Hz, 8H), 5.03 (s, 16H), 3.79 – 3.59 (m, 16H), 1.38 – 1.30 (m, 96H), 0.93 (t, $J = 6.4$ Hz, 24H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 25 °C): δ [ppm] = 153.14, 129.22, 125.72, 119.90, 115.28, 69.65, 31.95, 29.56, 29.54, 29.45, 26.23, 22.74, 13.91. ESI-HRMS: $m/z$ calcd for [M+TMA]$^+$ C$_{148}$H$_{244}$NO$_{12}$+, 2227.8508; found 2227.8579 (error = 3.2 ppm). Tetramethylammonium (TMA) Hexafluorophosphate was added to facilitate the ionization of 1c.
$^{13}$C NMR spectrum (101 MHz, CD$_2$Cl$_2$, 25 °C) of 1c

ESI-TOF mass spectrum of TMA$^+$@1c
1d was obtained in 11% yield as a white solid. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C): δ [ppm] = 7.78 (s, 8H), 6.96 (s, 8H), 5.05 (s, 16H), 3.80 (s, 16H), 1.32 (m, 224H), 0.91 (m, 24H). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 25 °C): δ [ppm] = 153.15, 129.23, 125.74, 115.28, 69.67, 61.91, 31.96, 29.85, 29.83, 29.81, 29.78, 29.72, 29.67, 29.41, 26.27, 22.72, 13.90; ESI-HRMS: $m/z$ calcd for [M+TMA]$^+$ C$_{180}$H$_{308}$NO$_{12}$, 2676.3516; found 2676.3509 (error = 2.1 ppm). Tetramethylammonium (TMA) Hexafluorophosphate was added to facilitate the ionization of 1d.

$^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 25 °C) of 1d
$\text{C NMR spectrum (126 MHz, CD}_2\text{Cl}_2, 25^\circ\text{C) of 1d}$

$\text{ESI-TOF mass spectrum of TMA}^+@1d$

Chemical Formula: $C_{110}H_{100}NO_{12}^+$

Exact Mass: 2227.8508

Figure S1 Partial $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 1.0 mM, 25 °C) of 1d.

Fig. S2. $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 25 °C) of 1d at various concentrations. Numbers of scan: 512 (0.1 mM), 512 (0.2 mM), 256 (0.4 mM), 64 (0.8 mM), 32 (1.0 mM). The peak shapes are exactly the same, suggesting the peak broadening of 1d is not due to aggregation in solution but because of slower conformational interconversion.
Figure S3. TEM images of 1a, 1b, 1c and 1d. At the nanoscale, the structures of 1a and 1b appear to be spherical nanodisks with diameters of about 400 nm. 1c and 1d self-assemble into ribbon-like structures with smaller size and less regular shapes. These indicate that the self-assembly of 1a and 1b are more organized than 1c and 1d. The sample for TEM experiments for 1a-1d was prepared by as follows: 0.1 mL dichloromethane solution of the corresponding compound (20 mM) was dispersed into 1.0 mL acetone and sonicated for 1 min. Then a drop of above dispersion was put on carbon-supported film and dried.
Figure S4. Powder XRD diffraction patterns and energy-minimized structures of 1a-1d. The diffraction signals of 1a and 1b are stronger than those of 1c and 1d, suggesting the higher ordering and closer packing of 1a and 1b in the solid state.
3. NMR Spectra of Host-Guest Complexes

![NMR Spectra of Host-Guest Complexes](image)

**Fig. S5** Partial $^1$H, $^1$H-ROESY NMR spectra (500 MHz, CD$_2$Cl$_2$:CD$_3$CN =5:1, 2.0 mM, 25 °C) of 1D1$^{2+}$@1b and Energy-minimized structures.
**Fig. S6** Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$:CD$_3$CN =5:2, 1.0 mM, 25 °C) of 
a) D$_2$D$_2^{2+}$@1a, b) D$_2$D$_2^{2+}$@1b, c) D$_2$D$_2^{2+}$@1c, d) D$_2$D$_2^{2+}$@1d.
Fig. S7 Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$:CD$_3$CN =5:2, 1.0 mM, 25 °C) of a) MeV$^{2+}@1a$, b) MeV$^{2+}@1b$, c) MeV$^{2+}@1c$, d) MeV$^{2+}@1d$. 
Fig. S8 Partial $^1$H, $^1$H-ROESY NMR spectra (500 MHz, CD$_2$Cl$_2$:CD$_3$CN =5:2, 2.0 mM, 25 °C) of D2D$_{2+}$@1b and Energy-minimized structures.
4. Binding Constants Determined by ITC

Fig. S9 Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of 1a (0.15 mM) with \textbf{D2D-2PF}_6 (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH$_3$CN.
**Fig. S10** Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of 1b (0.15 mM) with D2D-2PF₆ (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH₃CN.
**Fig. S11** Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of 1c (0.10 mM) with D2D-2PF$_6$ (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH$_3$CN.
**Fig. S12** Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of 1a (0.15 mM) with MeV-2PF$_6$ (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH$_3$CN.
**Fig. S13** Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of 1b (0.15 mM) with MeV-2PF$_6$ (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH$_3$CN.
**Fig. S14** Titration plots (heat rate versus time and heat versus guest/host ratio) obtained from ITC experiments of 1c (0.10 mM) with MeV-2PF$_6$ (1.00 mM) in the 3:2 mixture of 1,2-dichloroethane and CH$_3$CN.
5. TEM and Powder XRD Experiments

**Figure S15.** TEM images of the host-guest complexes of 1b-1d with 1D1^{2+}, D2D^{2+} or MeV^{2+}. At the nanoscale, the complexes of 1d existed as nano-rod or nanosheets with a width of ca. 200 nm. The complexes of 1c appear to be nano-rod or membrane-like assemblies. The structures of the complexes of 1b appear to be irregular. Generally, the addition of guests induced drastic structural changes of the oxatub[4]arenes. But different guests and the same oxatub[4]arene show rather similar structure.

The samples of the complexes for TEM experiments were prepared using the following steps: the corresponding host-guest complexes (5.0 mg) was dispersed to 1.0 mL ether and sonicated for 1 minute. Then a drop of the above suspension was put on carbon-supported film and dried.
**Figure S16.** Powder XRD diffraction patterns and energy-minimized structures of the complexes of 1d with three guests. The similar diffraction peaks (002, 003 and 004) indicate similar molecular packing for the three complexes in solid state. This result support the conclusion that different guests and thus the induced different conformation of oxatub[4]arene result in rather similar structures in the solid state.
6. X-Ray Single Crystal Structure of 1a

Crystal of 1a was obtained by slow evaporation of 1:1 CH₂Cl₂-MeCN solution. The reflections were collected at 120 K with an Agilent Super-Nova dual wavelength diffractometer with a micro-focus X-ray source and multilayer optics monochromatized Mo-Kα (λ=0.71073 Å) radiation for 1a. CrysAlisPro² was used for both data collection and processing. The intensities were corrected for absorption using analytical face index absorption correction method.³ The structures were solved by Direct method with SHELXT⁴ and refined by full-matrix least-squares methods using the OLEX2⁵ which utilizes the SHELXL-2015 module⁶. All non-hydrogen atoms in the structures were refined with anisotropic thermal parameters.

Crystal data for 1a: C₈₀H₁₀₄O₁₂, M = 1257.63, monoclinic, a = 18.8502(5) Å b = 9.25277(17) Å c = 20.4322(5) Å, α = 90.00°, β = 106.169(3)°, γ = 90.00°, V = 3422.75(15) Å³, T = 120.15(10) K, space group P2₁/n, Z = 2, 20660 reflections measured, 7487 independent reflections (R_int = 0.0317). The final R₁ value was 0.0470 (I > 2σ(I)). The final wR(F²) value was 0.0998 (I > 2σ(I)). The final R₁ value was 0.0756 (all data). The final wR(F²) value was 0.1123 (all data). The goodness of fit on F² was 1.025. CCDC-1577176 contains the supplementary data for this structure. 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.
7. References


