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Supporting Information (13 pages)

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1. Materials and methods

All commercial reagents were used as received. Solvents were either employed as purchased or dried according to procedures described in the literature. $^1$H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. $^{13}$C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometry at 100 MHz. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. High resolution mass spectra were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). MALDI-TOF-MS spectra were performed on a AXIMA Performance-MALDI TOF/TOF (Matrix: 2,5-dihydroxy-benzoic acid).
2. Synthesis of $4^{E1}$

A mixture of dibromobutane (77.7 g, 360 mmol), hydroquinone (9.90 g, 90 mmol), and potassium carbonate (37.26 g, 0.27 mol) in 60 mL acetone was refluxed under N$_2$ for 24 h. The reaction mixture was concentrated in vacuo and the resulting residue was partitioned between 150 mL water and 150 mL chloroform. The organic layer was evaporated to dryness and the precipitate was washed with sodium hydroxide solution (3×50 mL, 1 N), water (2×50 mL), and $n$-hexane (2×50 mL), and dried in vacuo to give 4 as a white solid 18.8 g (55 %). $^1$H NMR (400 MHz, chloroform-$d$, room temperature) $\delta$ (ppm): 6.81 (s, 4H), 3.94 (t, $J = 6$ Hz, 4H), 3.48 (t, $J = 6$ Hz, 4H), 2.03–2.10 (m, 4H), 1.88–1.95 (m, 4H).

Figure S1. $^1$H NMR spectrum (100 MHz, chloroform-$d$, room temperature) of 4.
3. Synthesis of 2 and 3

To a solution of 4 (1.95 g, 5.00 mmol) in 1, 2-dichloroethane (50 mL), paraformaldehyde (0.181 g, 6.00 mmol) was added at 20 °C. Then, boron trifluoride diethyl etherate (BF₃•(OC₂H₅)₂, 0.71 g, 5.00 mmol) was added to the solution and the mixture was stirred at 20 °C for 10 min. Then saturated NaHCO₃ aqueous solution (50 mL) was added. The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/dichloromethane (v/v = 2:1) as the eluent to give the product, 2 and 3. 2 was a colorless oil (0.110 g, 6%). 3 was a white solid (0.52 g, 27 %, Mp: 91.2–93.1 °C). 3 was separated firstly, and then was 2 eluted out. 2: ¹H NMR (400 MHz, chloroform-d, room temperature) δ (ppm): 6.67 (s, 12H), 3.79–3.83 (m, 36H), 3.40 (t, J = 6.4 Hz, 24H), 1.93–1.99 (m, 24H), 1.82–1.87 (m, 24H). ¹³C NMR (100 MHz, chloroform-d, room temperature) δ (ppm): 150.39, 127.94, 114.90, 67.70, 33.85, 29.73, 29.61, 28.33. MALDI-TOF-MS: m/z calcd for [M]+ C₉₀H₁₂₀Br₁₂O₁₂, 2351.8858 (100.0%), 2353.8837 (83.4%), found 2353.2. 3: ¹H NMR (400 MHz, chloroform-d, room temperature) δ (ppm): 6.84 (s, 10H), 3.95 (s, 20H), 3.76 (s, 10H), 3.47 (t, J = 6.1 Hz, 20H), 2.08 (s, 20H), 1.96 (m, 20H). ¹³C NMR (100 MHz, chloroform-d, room temperature) δ (ppm): 150.39, 127.94, 114.90, 67.70, 33.85, 29.73, 29.61, 28.33. MALDI-TOF-MS: m/z calcd for [M]+ C₇₅H₁₀₀Br₁₀₀O₁₀₀, 1959.9048 (100.0%), 1960.9081 (81.1%), found 1960.7.
**Figure S2.** $^1$H NMR spectrum (400 MHz, chloroform-$d$, room temperature) of 2.

**Figure S3.** $^{13}$C NMR spectrum (100 MHz, chloroform-$d$, room temperature) of 2.
**Figure S4.** MALDI-TOF-MS of 2.

**Figure S5.** ¹H NMR spectrum (400 MHz, chloroform-§, room temperature) of 3.
Figure S6. $^{13}$C NMR spectrum (100 MHz, chloroform-$d$, room temperature) of 3.

Figure S7. MALDI-TOF-MS of 3.
4. Synthesis of 1

\[ \text{Compound 2 (1.30 g, 0.556 mmol) and trimethylamine (33 \% in ethanol, 9 mL, 3.33 mmol) were added to ethanol 20 mL. The solution was refluxed overnight. Then the solvent was removed by evaporation, deionized water 20 mL was added. After filtration, a clear solution was got. Then the water was removed by evaporation to obtain 1 as a colorless solid (1.65 g, 97 \%). Mp 210-212 °C.} \]

\[ ^1\text{H NMR (400 MHz, D}_2\text{O, room temperature) } \delta \text{ (ppm): } 6.83 \text{ (s, 12H), 3.91 (t, } J = 4.0 \text{ Hz, 24H), 3.82 (s, 12H), 3.19 (t, } J = 4.0 \text{ Hz, 24H), 2.95 (s, 108H), 1.71 (m, 48H).} \]

The \[ ^{13}\text{C NMR spectrum of 4 is shown in Figure S7.} \]

\[ ^{13}\text{C NMR (125 MHz, D}_2\text{O, room temperature) } \delta \text{ (ppm): 150.25, 129.31, 116.85, 68.76, 66.13, 52.94, 30.14, 25.87, 19.55.} \]

LRESIMS is shown in Figure S10: \[ m/z 532.45 \text{ [M - 5Br]}^{5+}. \]

HRESIMS is shown in Figure S11: \[ m/z \text{ of } C_{126}H_{228}Br_{12}N_{12}O_{12} 532.45 \text{ [M - 5Br]}^{5+}. \]
**Figure S8.** $^1$H NMR spectrum (400 MHz, D$_2$O, room temperature) of 1

**Figure S9.** $^{13}$C NMR spectrum (125 MHz, D$_2$O, room temperature) of 1.
Figure S10. Electrospray ionization mass spectrum of 1.

Figure S11. High resolution electrospray ionization mass spectroscopy of 1.

5. Synthesis of G2

To a solution of sodium 6-hydroxynaphthalene-2-sulfonate (2.95 g, 12.0 mmol) in water (50 mL), 1-bromododecane (5.98 g, 24.0 mmol), NaOH (0.96 g, 24 mmol) and ethanol (50 mL) were added. The mixture was refluxed overnight and then filtrated to get a yellow solid. After washed with dichloromethane and ethanol, a white solid was
obtained (2.6 g, 52%). $^1$H NMR (400 MHz, DMSO-$d_6$, room temperature) $\delta$ (ppm): 8.04 (s, 1H), 7.86 (d, $J$ = 8.9 Hz, 1H), 7.72 (d, $J$ = 8.5 Hz, 1H), 7.64 (d, $J$ = 8.3 Hz, 1H), 7.29 (s, 1H), 7.15 (d, $J$ = 8.8 Hz, 1H), 4.08 (t, $J$ = 6.4 Hz, 2H), 1.77 (t, $J$ = 6.4 Hz, 2H), 1.45 (m, 2H), 1.25 (m, 16H), 0.84 (t, $J$ = 6.4 Hz, 3H).

*Figure S12.* $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, room temperature) of G2.
6. Determination of association constant for the complex between 1 and \( \text{G}_1 \) by fluorescence titration experiments.

**Figure S13.** Fluorescence emission spectra of \( \text{G}_1 \) \((1.00 \times 10^{-4} \text{ M}, \lambda_{\text{ex}} = 274 \text{ nm})\) in water at 298 K with different concentrations of 1 (from 0 to \( 1.77 \times 10^{-4} \text{ M} \)) (top) and the plot of the Stern-Volmer equation \( \ln \left( \frac{F_0 - F}{F} \right) = \ln K + n \ln [I] \)\(^{S2}\) for the complexation using the fluorimetric titration data at \( \lambda_{\text{em}} = 339 \text{ nm} \). \( F_0 \) is the initial fluorescent emission intensity of \( \text{G}_1 \) and \( F \) is the fluorescent emission intensity of \( \text{G}_1 \) in the presence of different concentrations of 1 (bottom).
References:
