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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LRESI-MS) were obtained on a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization mass spectra (HRESI-MS) were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer 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). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. The critical aggregation concentration (CAC) values of $G$ and $H\rightarrow G$ were determined on a DDS-307 instrument. Transmission electron microscopy (TEM) investigations were carried out on a JEM-1200EX instrument. Dynamic light scattering measurements were performed on a goniometer ALV/CGS-3 using a UNIPHASE He-Ne laser operating at 632.8 nm. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

**Scheme S1.** Synthetic route to cationic water-soluble biphen[3]arene H.

A mixture of 1,2-dibromoethane (18.8 g, 100 mmol), 4,4'-biphenol (1.86 g, 10.0 mmol), and K$_2$CO$_3$ (5.52 g, 40.0 mmol) in 150 mL CH$_3$CN was refluxed under N$_2$ for 24 h. Then the reaction mixture was cooled to room temperature and filtered. The filter cake was washed with dichloromethane (2 x 60 mL). The filtrate was concentrated under vacuum, and then the residue was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1 v/v) as the eluent to get product 1 as a white solid (1.60 g, 40%). The $^1$H NMR spectrum of 1 is shown in Fig. S1. $^1$H NMR (400 MHz, chloroform-$d$, 293 K) $\delta$(ppm): 7.48 (d, $J = 8$ Hz, 4H), 6.97 (d, $J = 8$ Hz, 4H), 4.33 (t, $J = 6$ Hz, 4H), 3.67 (t, $J = 6$ Hz, 4H).
2.2. Synthesis of compound 2

To the solution of 1 (1.00 g, 2.50 mmol) in 1, 2-dichloroethane (50 mL), paraformaldehyde (0.0750 g, 2.50 mmol) was added. The suspension was stirred at 25 °C for 30 min to crush the large paraformaldehyde particles. Then boron trifluoride diethyl etherate (BF$_3$·O(C$_2$H$_5$)$_2$, 0.355 g, 2.50 mmol) was added to the solution. After continuing stirred at 25 °C for 3.5 h, the reaction was quenched by addition of water. The organic phase was separated and the crude product was purified by column chromatography (petroleum ether/dichloromethane, v/v 1:1) to get 2 as a white solid (0.206 g, 20 %), mp: 235.2–236.5 °C. The $^1$H NMR spectrum of 2 is shown in Fig. S2. $^1$H NMR (400 MHz, chloroform-$d$, 293 K) $\delta$ (ppm): 7.29 (d, $J$ = 8 Hz, 6H), 7.06 (s, 6H), 6.84 (d, $J$ = 8 Hz, 6H), 4.26 (t, $J$ = 6 Hz, 12H), 4.04 (s, 6H), 3.56 (t, $J$ = 6 Hz, 12H). The $^{13}$C NMR spectrum of 2 is shown in Fig. S3. $^{13}$C NMR (100 MHz, chloroform-$d$, 293 K) $\delta$ (ppm): 155.09, 134.08, 130.17, 128.93, 125.55, 112.32, 68.46, 29.41 and 29.04.
MALDI-TOF-MS is shown in Fig. S4: m/z calcd for [M + H]^+ C_{51}H_{40}Br_{6}O_{6}, 1236.8568; found 1236.857. HRESIMS: m/z of C_{51}H_{42}O_{18}Na 1258.8547 [M + Na]^+, 619.5259 [M + 2H]^2+.

Fig. S2 ^1H NMR spectrum (400 MHz, chloroform-d, 293K) of 2.

Fig. S3 ^13C NMR spectrum (100 MHz, chloroform-d, 293K) of 2.
Fig. S4 MALDI-TOF-MS of 2. Assignment of the main peak: m/z 1236.857 [M + H]+.

2.3. Synthesis of compound H

Compound 2 (0.124 g, 0.100 mmol) and trimethylamine (33 % in methanol, 5 mL, 18.5 mmol) were added to methanol (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. Water was then removed by rotary evaporation to gain H as a white powder (143 mg, 90 %), mp: > 300 °C. The 1H NMR spectrum of H is shown in Fig. S5. 1H NMR (400 MHz, D2O, 293 K) δ (ppm): 7.42 (d, J = 8 Hz, 6H), 7.06 (d, J = 8 Hz, 6H), 7.01 (s, 6H), 4.45 (s, 12H), 3.95 (s, 6H), 3.74 (s, 12H), 3.05 (s, 54H). The 13C NMR spectrum of H is shown in Fig. S6. 13C NMR (100 MHz, D2O, 293 K) δ (ppm): 157.35, 137.00, 132.04, 131.79, 129.31, 115.14, 68.18, 65.01, 62.54 and 56.79. LRESIMS is shown in Fig. S7: m/z 318.3 [M – 4Br]+. MALDI-TOF-MS: m/z of C69H102Br5N6O6 1510.778 [M − Br]+. HRESIMS: m/z of 318.2960 [M – 4Br]+.
**Fig. S5** $^1$H NMR spectrum (400 MHz, D$_2$O, 293K) of H.

**Fig. S6** $^{13}$C NMR spectrum (100 MHz, D$_2$O, 293K) of H.
**Fig. S7** Electrospray ionization mass spectrum of H. Assignment of the main peak: m/z 318.3 [M – 4Br]+.

3. **$^1$H NMR investigations between H and compounds G2, G3**

**Fig. S8** $^1$H NMR spectra (400 MHz, D$_2$O, 293 K) of (a) 2.00 mM G2; (b) 2.00 mM G2 and 2.00 mM H; (c) 2.00 mM H. (The asterisk represents the protons related to methanol)
**Fig. S9** $^1$H NMR spectra (400 MHz, D$_2$O, 293 K) of (a) 2.00 mM G3; (b) 2.00 mM G3 and 2.00 mM H; (c) 2.00 mM H. (The asterisk represents the protons related to methanol)

4. 2D NOESY spectrum between H and compounds G1, G2, G3

**Fig. S10** 2D NOESY NMR (500 MHz, D$_2$O, 293 K) spectrum of a solution of H (10.0 mM) and G1 (10.0 mM). (The asterisk represents the protons related to methanol)
**Fig. S11** Partial 2D NOESY NMR (500 MHz, D$_2$O, 293 K) spectrum of a solution of H (10.0 mM) and G1 (10.0 mM).

**Fig. S12** Partial 2D NOESY NMR (500 MHz, D$_2$O, 293 K) spectrum of a solution of H (10.0 mM) and G1 (10.0 mM).
**Fig. S13** 2D NOESY NMR (500 MHz, D$_2$O, 293 K) spectrum of a solution of H (10.0 mM) and G2 (10.0 mM). (The asterisk represents the protons related to methanol)

**Fig. S14** Partial 2D NOESY NMR (500 MHz, D$_2$O, 293 K) spectrum of a solution of H (10.0 mM) and G2 (10.0 mM). (The asterisk represents the protons related to methanol)
Fig. S15 2D NOESY NMR (500 MHz, D₂O, 293 K) spectrum of a solution of H (10.0 mM) and G3 (10.0 mM). (The asterisk represents the protons related to methanol)

Fig. S16 Partial 2D NOESY NMR (500 MHz, D₂O, 293 K) spectrum of a solution of H (10.0 mM) and G3 (10.0 mM). (The asterisk represents the protons related to methanol)
5. Association constant and stoichiometry determination for the complexation between \( H \) and compounds \( G_1, G_2, G_3 \)

To determine the association constant and stoichiometry for the complexation between \( H \) and \( G_1 \) (or \( G_2 \) or \( G_3 \)), \(^1\)H NMR titration was done with solutions which had a constant concentration of the host \( H \) (1.00 mM) and varying concentrations of the guest \( G_1 \) (or \( G_2 \) or \( G_3 \)). By a non-linear curve-fitting method, the association constant \( (K_a) \) of \( H \rightarrow G_1 \) (or \( H \rightarrow G_2 \) or \( H \rightarrow G_3 \)) was determined. By a mole ratio plot, 1:1 stoichiometry was obtained for the complexation between \( H \) and \( G_1 \) (or \( G_2 \) or \( G_3 \)).

The non-linear curve-fitting was based on the equation:\[^{[82]}\]

\[
\Delta \delta = \left( \Delta \delta_\infty/[H]_0 \right) (0.5[G]_0 + 0.5([H]_0+1/K_a) - (0.5 ([G]_0^2 + (2[G]_0 (1/K_a - [H]_0)) + (1/K_a + [H]_0)^{0.5})) \]  
(Eq. S1)

Where \( \Delta \delta \) is the chemical shift change of \( H_a \) (or \( H_d \)) on \( H \), \( \Delta \delta_\infty \) is the chemical shift change of \( H_a \) (or \( H_d \)) when the host \( H \) is completely complexed, \([G]_0\) is the initial concentration of the guest \( G_1 \) (or \( G_2 \) or \( G_3 \)), and \([H]_0\) is the fixed initial concentration of the host \( H \).

**Fig. S17** Partial \(^1\)H NMR spectra (400 MHz, D\(_2\)O, 293K) of \( H \) at a concentration of 1.00 mM upon addition of \( G_1 \):  
(a) 0.00 mM; (b) 0.031 mM; (c) 0.071 mM; (d) 0.189 mM; (e) 0.307 mM; (f) 0.418 mM; (g) 0.465 mM; (h) 0.568 mM; (i) 0.821 mM; (j) 1.21 mM; (k) 1.61 mM; (l) 2.41 mM; (m) 3.47 mM.
**Fig. S18** The chemical shift changes of H\(_a\) on H upon addition of G1. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

\[ R^2 = 0.99 \]
\[ K_a = (1.56 \pm 0.07) \times 10^3 \]

**Fig. S19** Mole ratio plot for H and G1, indicating a 1:1 stoichiometry.
**Fig. S20** Partial $^1$H NMR spectra (400 MHz, D$_2$O, 293K) of H at a concentration of 1.00 mM upon addition of G2:
(a) 0.00 mM; (b) 0.198 mM; (c) 0.449 mM; (d) 0.678 mM; (e) 0.951 mM; (f) 1.31 mM; (g) 1.61 mM; (h) 1.88 mM; (i) 2.25 mM; (j) 3.01 mM; (k) 3.93 mM; (l) 4.96 mM.

**Fig. S21** The chemical shift changes of H$_d$ on H upon addition of G2. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.
Fig. S22 Mole ratio plot for H and G2, indicating a 1:1 stoichiometry.

Fig. S23 Partial $^1$H NMR spectra (400 MHz, D$_2$O, 293K) of H at a concentration of 1.00 mM upon addition of G3:
(a) 0.00 mM; (b) 0.420 mM; (c) 0.730 mM; (d) 1.01 mM; (e) 1.24 mM; (f) 1.59 mM; (g) 1.92 mM; (h) 2.24 mM; (i) 2.68 mM; (j) 3.08 mM; (k) 3.52 mM; (l) 4.35 mM; (m) 5.27 mM.
**Fig. S24** The chemical shift changes of H_d on H upon addition of G3. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

**Fig. S25** Mole ratio plot for H and G3, indicating a 1:1 stoichiometry.

6. Electrospray ionization mass spectrum of a solution of H and model compound G1 in water
Fig. S26 Electrospray ionization mass spectrometry of a solution of H with G1 in water. Assignment of main peaks: m/z 274.3 [H ⇒ G1 − 5Br]^{5+}.

7. Critical aggregation concentration (CAC) determination of G and H ⇒ G

Some parameters such as the conductivity, fluorescence intensity, osmotic pressure and surface tension of the solution change sharply around the critical aggregation concentration. The dependence of the solution conductivity on the solution concentration is used to determine the critical aggregation concentration. Typically, the slope of conductivity versus the concentration below CAC is steeper than the slope above the CAC. Therefore, the junction of the conductivity-concentration plot represents the CAC value. To measure the CAC values of G and H ⇒ G, the conductivities of the solutions at different concentrations (from 0 to 0.171 mM) were determined. By plotting the conductivity versus the concentration, we estimated the CAC values of G and H ⇒ G.

Fig. S27 The concentration-dependent conductivity of G. The critical aggregation concentration was determined to be 1.24 × 10^{-5} M.
Fig. S28 The concentration-dependent conductivity of $H \rightarrow G$. The critical aggregation concentration (CAC) was determined to be $1.69 \times 10^{-6}$ M.

8. Dynamic light scattering (DLS) results of $G$ and $H \rightarrow G$

Fig. S29 DLS result of $G$ with an aqueous solution of $5.00 \times 10^{-4}$ M.
9. Zeta potential results of G and H→G

Fig. S31 Zeta potential result of G with an aqueous solution of 5.00 × 10⁻⁴ M.

Fig. S32 Zeta potential result of H→G with an aqueous solution of 3.33 × 10⁻⁴ M.

10. Fluorescence spectroscopy study of the aggregation behavior
**Fig. S33** (a) Fluorescence emission spectra of pyrene in aqueous solutions of G (80.0 μM) by increasing the concentration of H from 0 to 240 μM (0–3 equiv) at room temperature. (b) Dependence of the relative fluorescence intensity of pyrene on H concentration with a fixed concentration of G (80.0 μM) at room temperature. [pyrene] = 1.00 μM.

**References:**
