Electronic Supplementary Material (ESI) for ChemComm.

4-Methylcoumarin-bridged Fluorescent Responsive Cryptand: from [2+2]Photodimerization to Supramolecular Polymer

Ming Cheng,[a] Chenhao Yao,[a] Yihan Cao,[a] Qi Wang,[a] Yi Pan,[b] Juli Jiang,*[a] and Leyong Wang*[a]

[a] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China, Fax: (+86) 25-83597090; [b] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

*Corresponding Author: jjl@nju.edu.cn; lywang@nju.edu.cn

SUPPORTING INFORMATION

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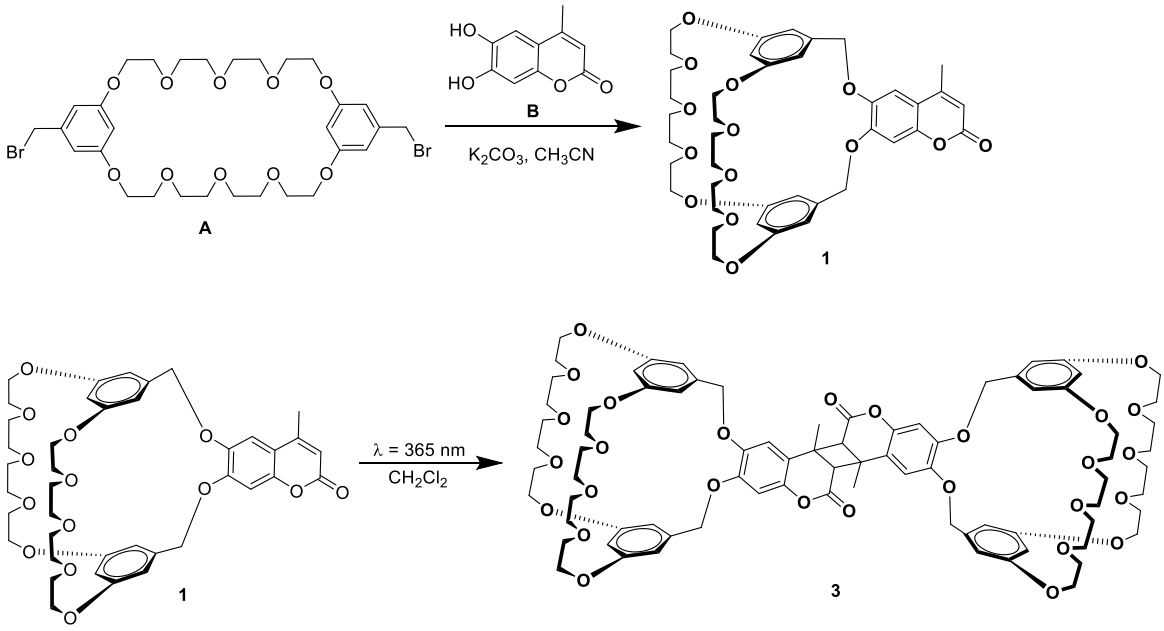
1. Materials and methods

All reactions were performed in open atmosphere unless otherwise stated. All reagents, unless otherwise indicated, were obtained from commercial sources. Anhydrous CH_3CN was obtained by distillation from CaH_2 under N_2 atmosphere. Melting points (M.p.) were determined using a Focus X-4 apparatus and were not corrected. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz or 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan MatTSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

2. Experimental procedures.



Scheme S1. Synthesis of cryptand **1** and dimer-cryptand **3**.

General procedure for the synthesis of cryptand 1: A mixture of **A**[1] (0.20 g, 0.28 mmol) and

compound **B** (0.053 g, 0.28 mmol) in anhydrous CH_3CN was stirred and refluxed for 24 h. The reaction mixture was filtered. The filtrate was removed in vacuum and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by silica-gel column chromatography using (CH_2Cl_2/CH_3OH, 100:1) to afford **1** (0.063 g, 30.0%) as a white solid. M.p.178-180 ^oC ; The ^1H NMR & ^{13}C NMR spectra of **1** are shown in Fig. S1-S2. ^1H NMR (400 MHz, CD_3CN, 298K) δ (ppm): 7.23 (s, 1H), 7.04 (s, 1H), 6.57-6.56 (m, 4H), 6.45-6.42 (m, 2H), 6.15 (s, 1H), 4.89 (s, 4H), 4.13-3.93 (m, 8H), 3.88-3.67 (m, 8H), 3.58-3.54 (m, 16H), 2.42 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.4, 160.0, 159.9, 153.5, 152.4, 150.3, 145.9, 138.9, 137.6, 113.2, 112.6, 111.6, 106.2, 105.8, 102.4, 102.1, 102.0, 73.6, 71.5, 71.1, 70.7, 69.8, 69.7, 67.6, 67.4.; LR-ESI-MS: calcd. for $[\mathbf{1} + H]^+$: 753.31, found *m*/*z* = 753.20; $[\mathbf{1} + \mathbf{N}H_4]^+$: 770.34, found *m*/*z* = 770.20; $[\mathbf{1} + Na]^+$: 775.29, found *m*/*z* = 775.15; HR-MS (ESI): calcd. for $[\mathbf{1} + H]^+$: 753.3117, found *m*/*z* = 753.3119; $[\mathbf{1} + \mathbf{N}H_4]^+$: 770.3382, found *m*/*z* = 770.3387; $[\mathbf{1} + Na]^+$: 775.2936, found *m*/*z* = 775.2940.

General procedure for the synthesis of dimer-cryptand 3: Cryptand **1** (0.7 g, 0.92 mmol) was dissolved in 30 mL dichloromethane. Then the solution was exposed to a 500 W mercury lamp for 96 h. The residue was purified by silica-gel column chromatography using (CH_2Cl_2/CH_3OH, 50:1) to afford **3** (0.030 g, 4.3%) as a white solid. M.p.93-95 ^oC ; The ^1H NMR & ^{13}C NMR spectra of **3** are shown in Fig. S5-S6. ^1H NMR (400 MHz, CD_3CN, 298K) δ (ppm): 7.00 (s, 2H), 6.85 (s, 2H), 6.65-6.49 (m, 8H), 6.44-6.40 (m, 4H), 4.89 (d, *J* = 19.6 Hz, 8H), 4.05-3.92 (m, 16H), 3.71 (br, 16H), 3.55 (br, 32H), 3.42 (s, 2H), 1.36 (s, 6H).; ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ (ppm): 165.9, 159.7, 159.6, 148.9, 145.7, 144.4, 138.6, 138.2, 114.4, 111.6, 107.6, 107.5, 107.5, 107.2, 102.1, 100.3, 100.2, 71.5, 71.0, 70.1, 69.9, 68.9, 67.3, 67.2, 46.7, 44.2, 25.5..; LR-ESI-MS: calcd. for $[\mathbf{3} + H]^+$: 1523.63, found *m*/*z* = 1523.30; $[\mathbf{3} + Na]^+$: 1527.60, found *m*/*z* = 1527.30; HR-MS (ESI): calcd. for $[\mathbf{3} + \mathbf{N}H_4]^+$: 1522.6426, found *m*/*z* = 1522.6422; $[\mathbf{3} + Na]^+$: 1527.5980, found *m*/*z* = 1527.5983.

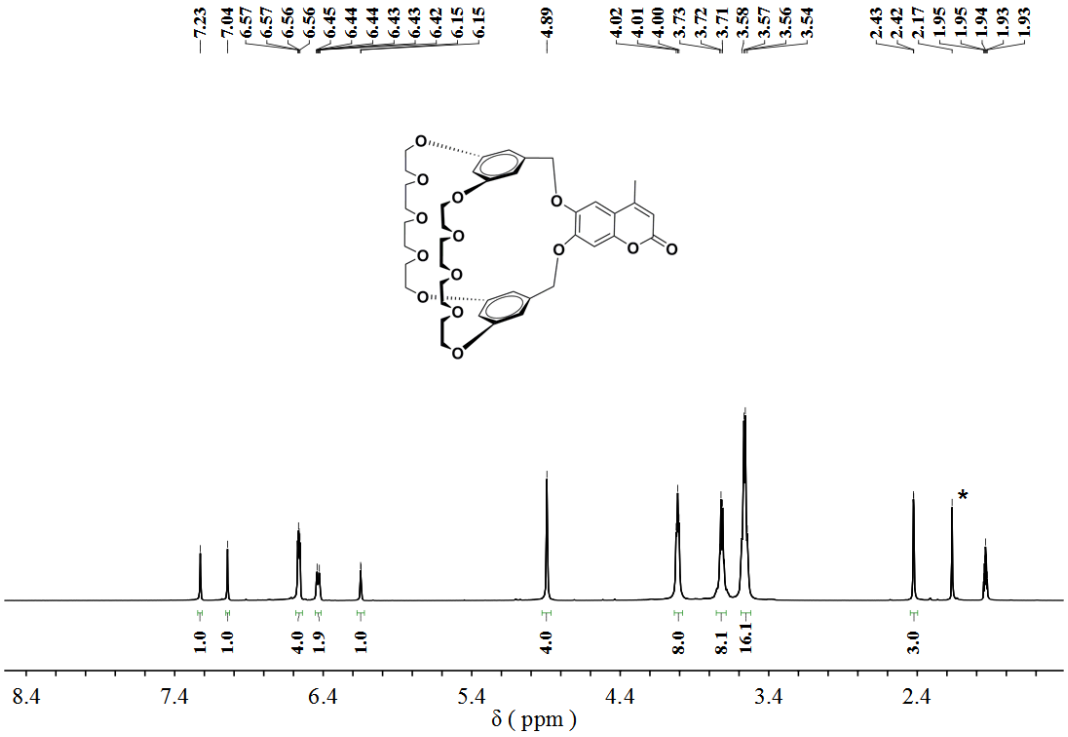


Fig. S1 ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of cryptand **1**. (* signals of H_2O).

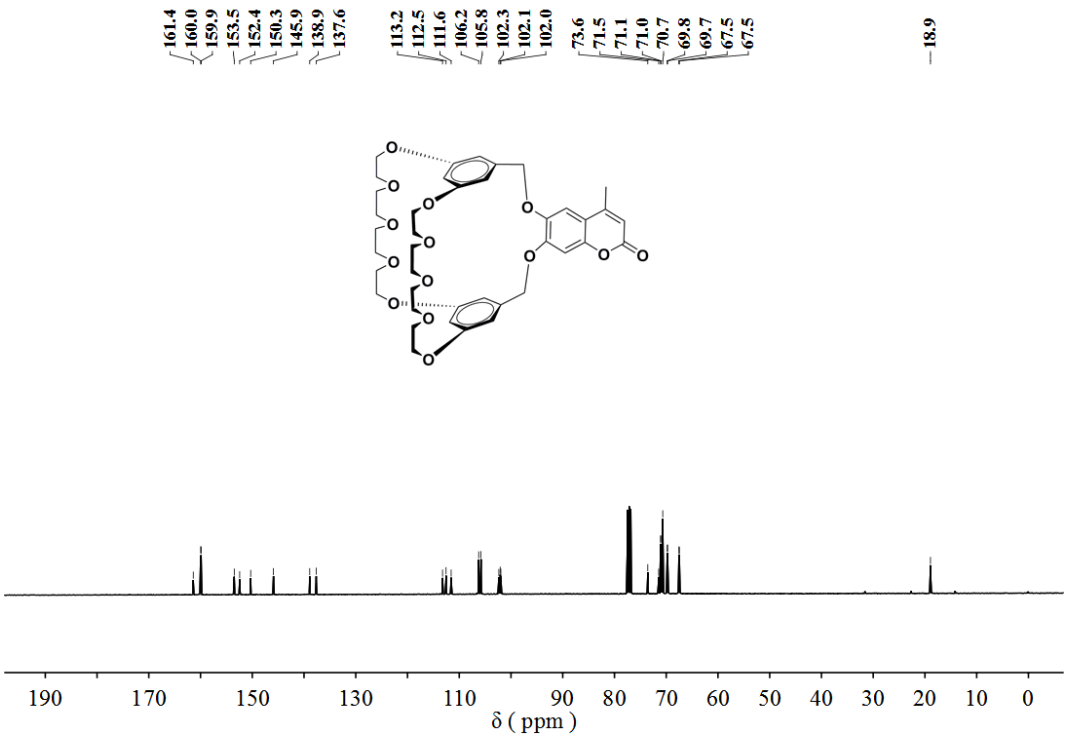


Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of cryptand **1**.

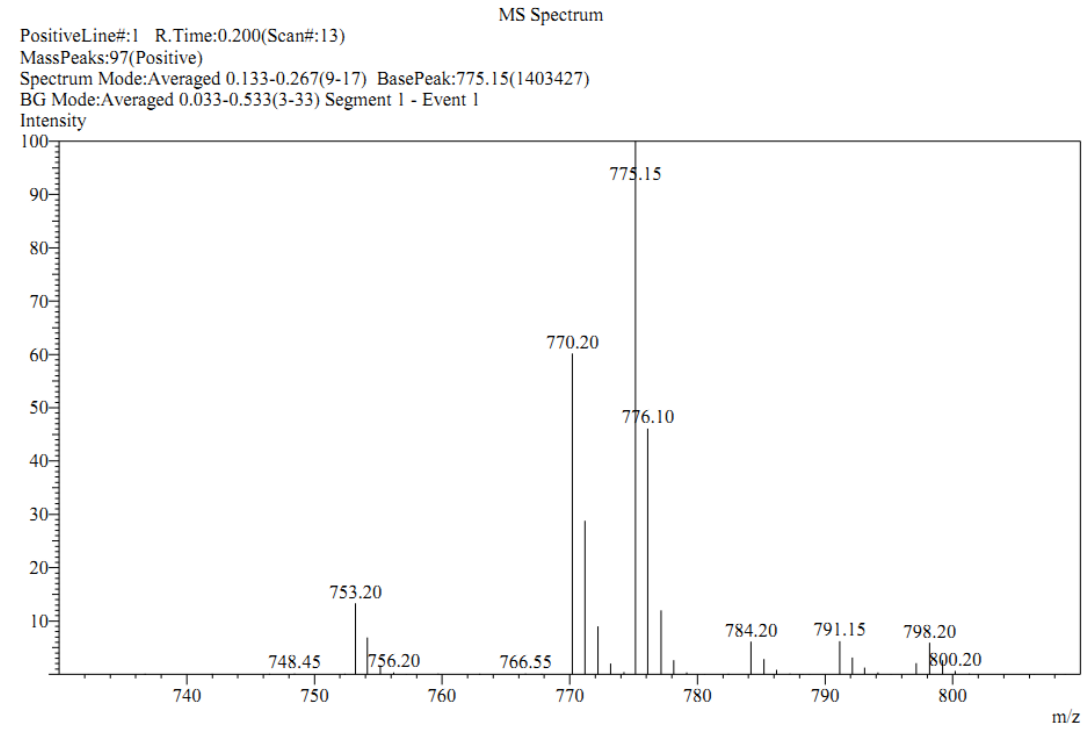


Fig. S3 LR-ESI-MS of cryptand **1**.

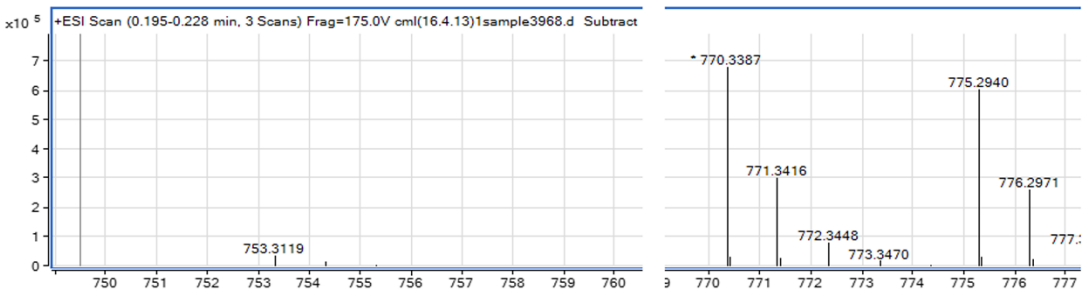


Fig. S4 HR-ESI-MS of cryptand **1**

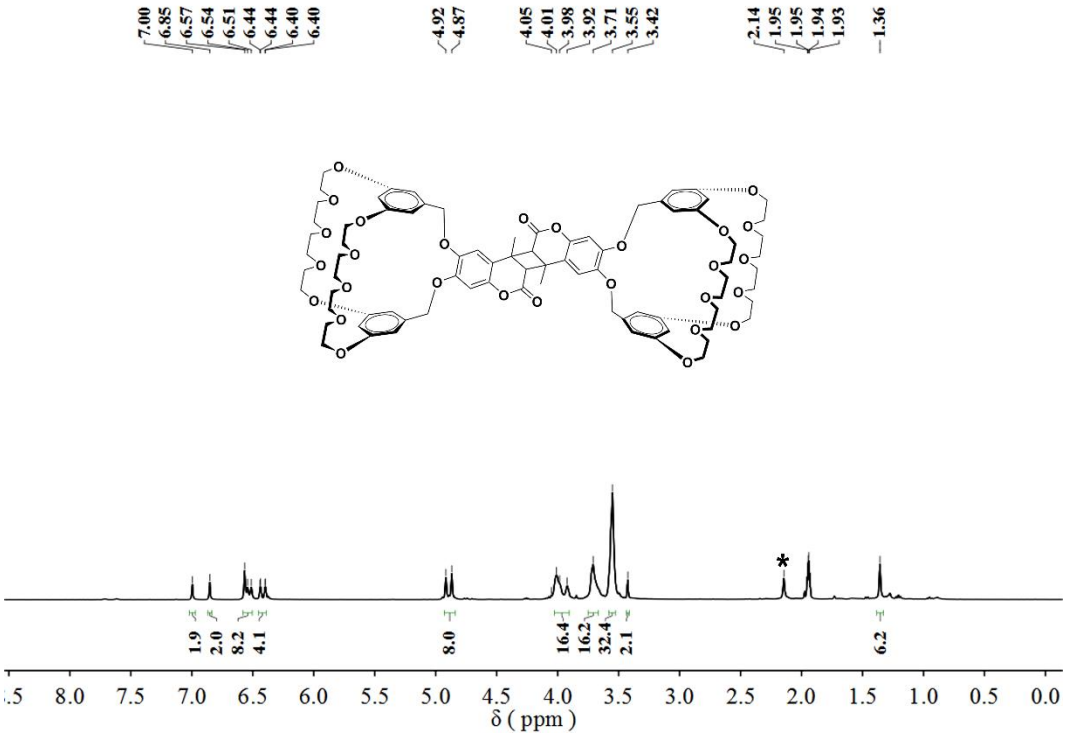


Fig. S5 ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of dimer-cryptand **3**. (* signals of H_2O).

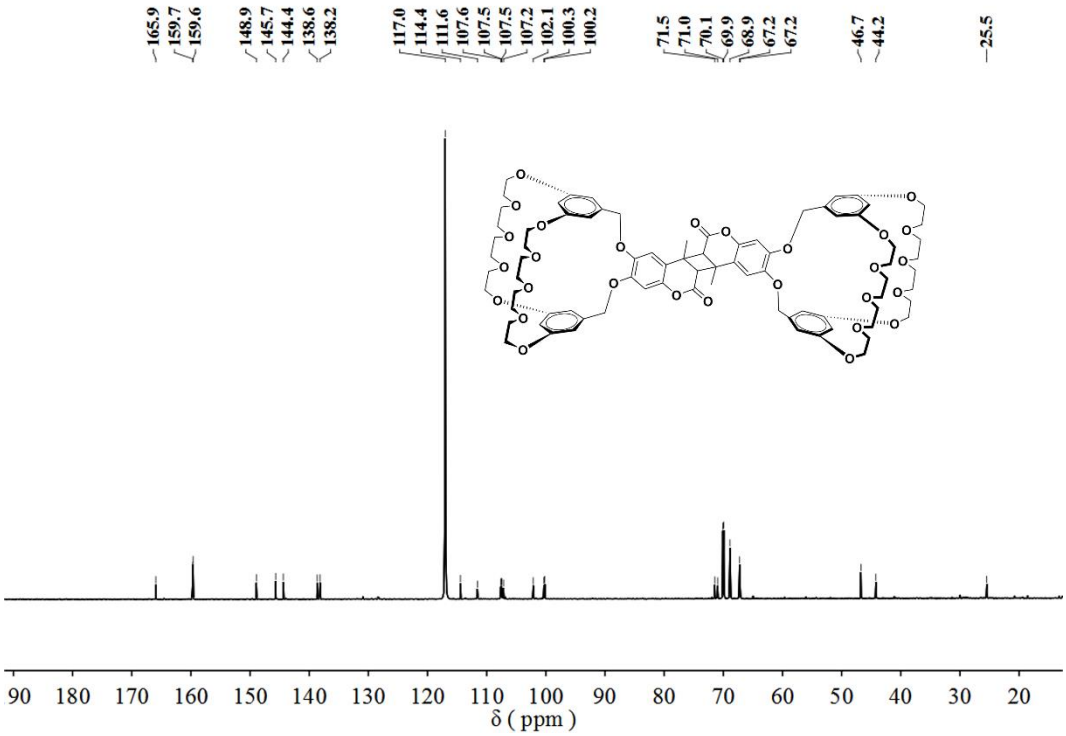


Fig. S6 ^{13}C NMR spectrum (100 MHz, CD_3CN, 298 K) of dimer-cryptand **3**.

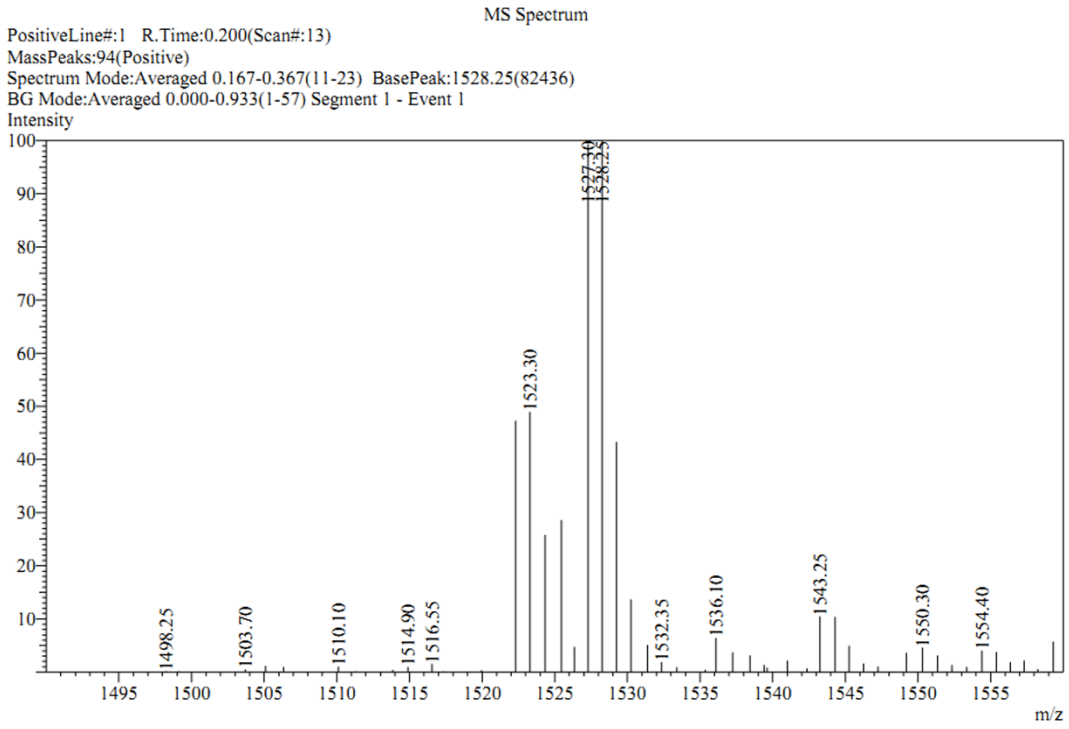


Fig. S7 LR-ESI-MS of dimer-cryptand **3**.

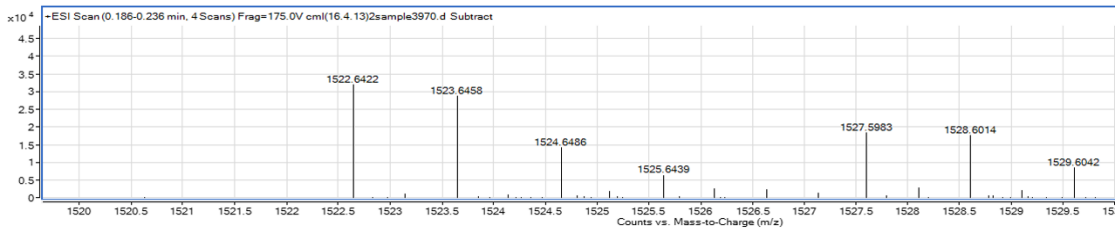
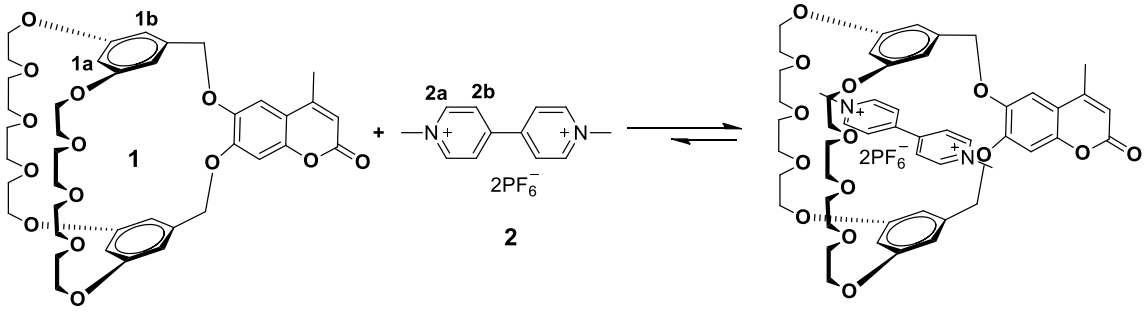


Fig. S8 HR-ESI-MS of dimer-cryptand **3**.

3. Association constants and Job plots of 1 ⊃ 2.



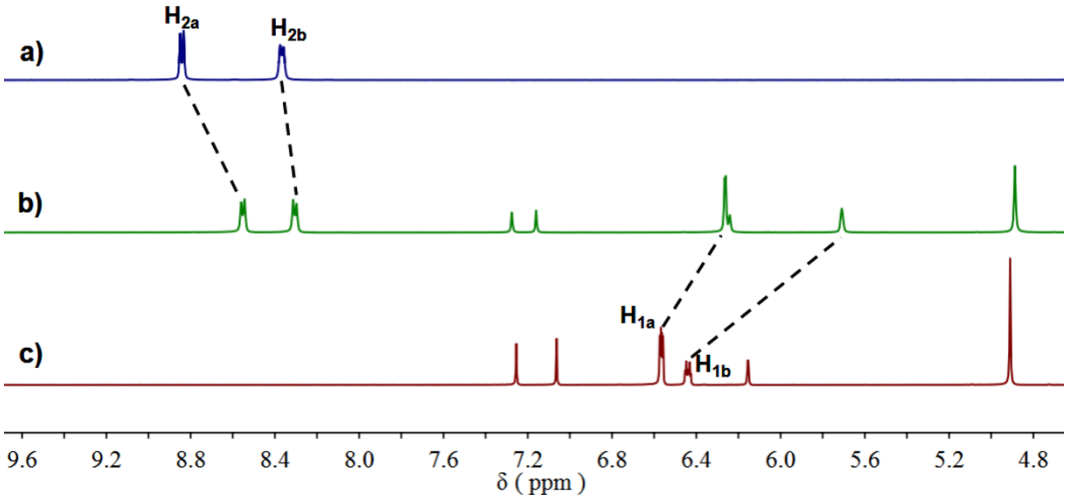


Fig. S9 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K): (a) **2**; (b) 10.00 mM **1** and 10.00 mM **2**; (c) **1**.

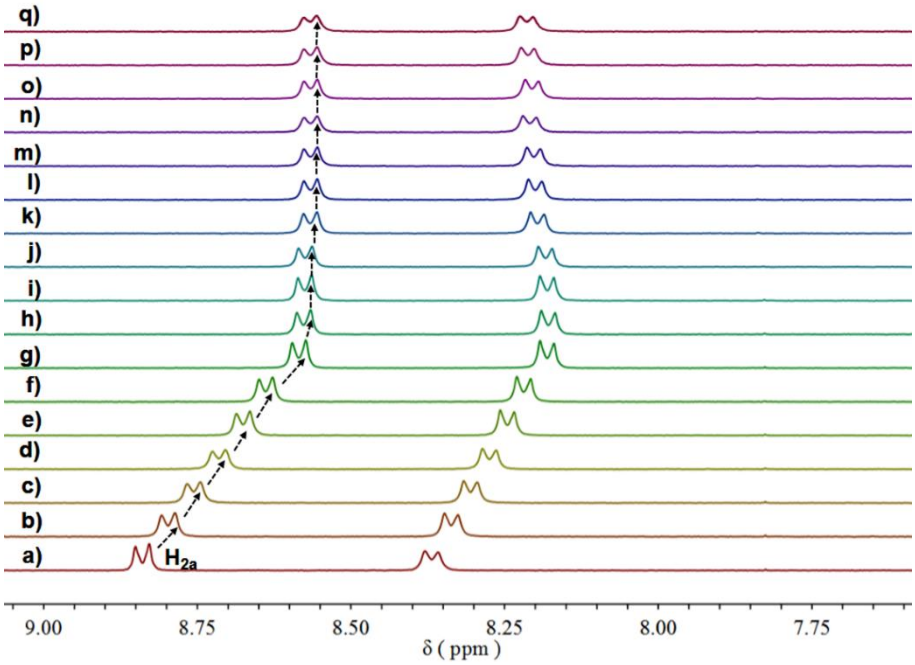


Fig. S10 Partial ^{1}H NMR spectra changes (300 MHz, $CDCl_3/CD_3CN$ = 1/1(v/v), 298 K) of **2** (guest, 2.00 mM) upon addition of **1** (host): (a) 0.00, (b) 0.40, (c) 0.80, (d) 1.20, (e) 1.60, (f) 2.00, (g) 3.00, (h) 5.00, (i) 7.00, (j) 9.00, (k) 13.00, (l) 17.00, (m) 20.00, (n) 24.00, (o) 30.00, (p)36.00, (q)40.00 mM.

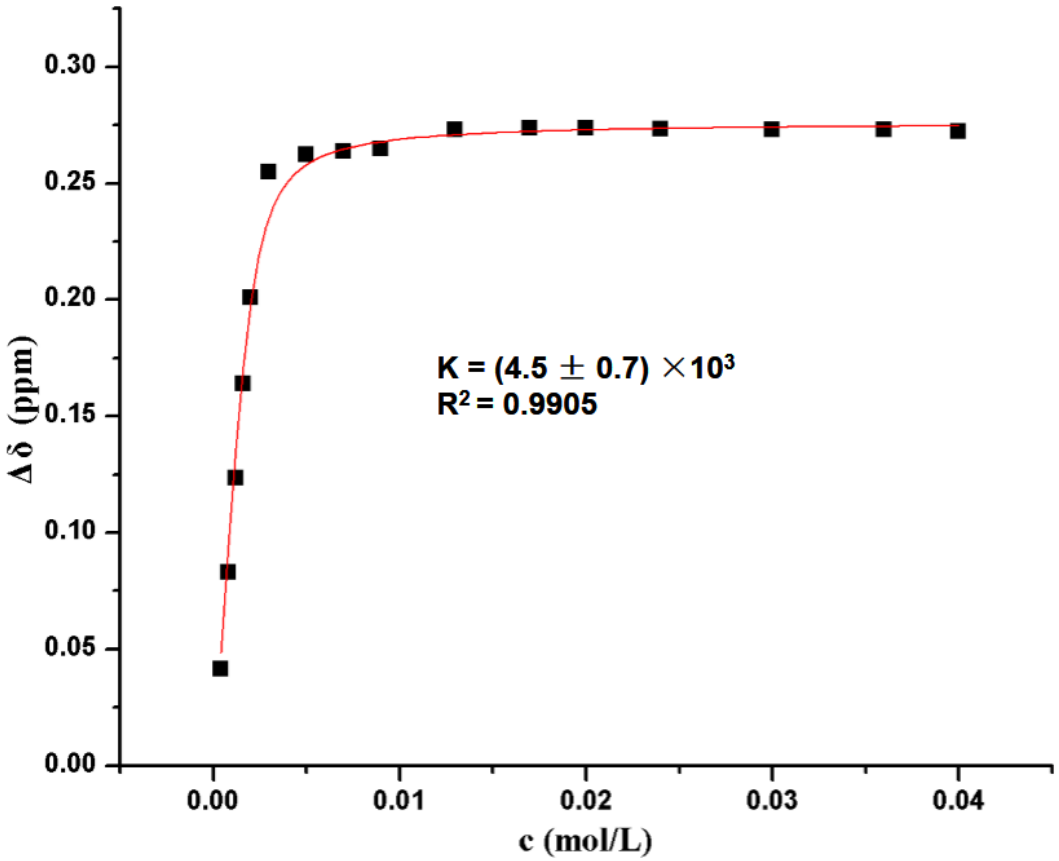


Fig. S11 The non-linear curve-fitting (NMR titrations) for the complexation of **2** (guest) with **1** (host) in $CDCl_3/CD_3CN$ = 1/1 (v/v) at 298 K. Using the signal of **2** at δ 8.8281 (proton H_{2a}) as the reference. The association constant (K_a) of **2** ⊂ **1** in $CDCl_3/CD_3CN$ = 1/1(v/v) was estimated to be about (4.5 ±0.7) × 10^3 M^{-1}.

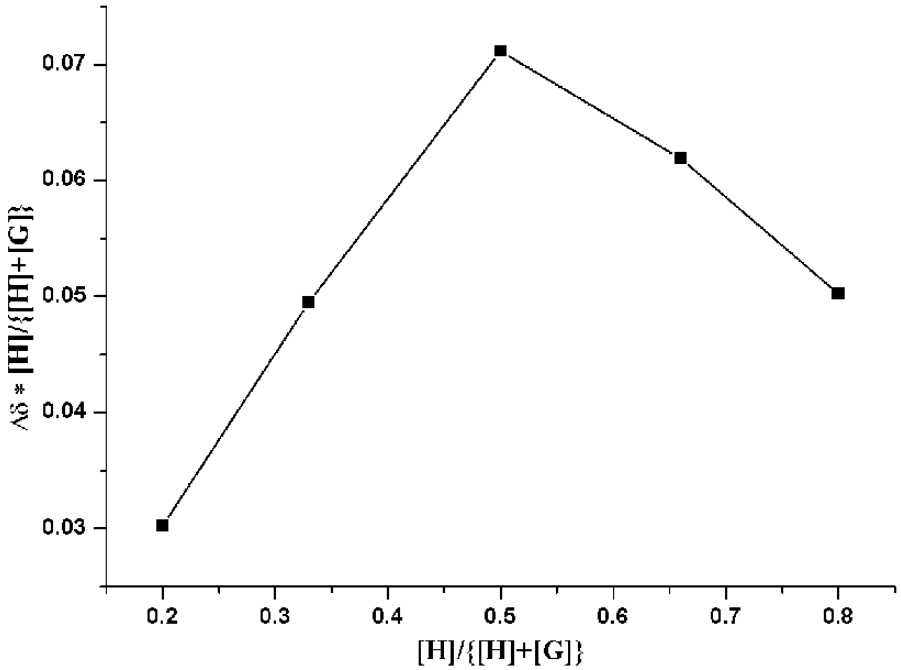


Fig. S12 The Job Plot (NMR titrations) for the complexation of **1** (host) with **2** (guest) in CD_3CN at 298 K. ([H] + [G] = 8 mM).

4. Concentration-dependent ^{1}H NMR spectroscopy of 3 ⊃ 4.

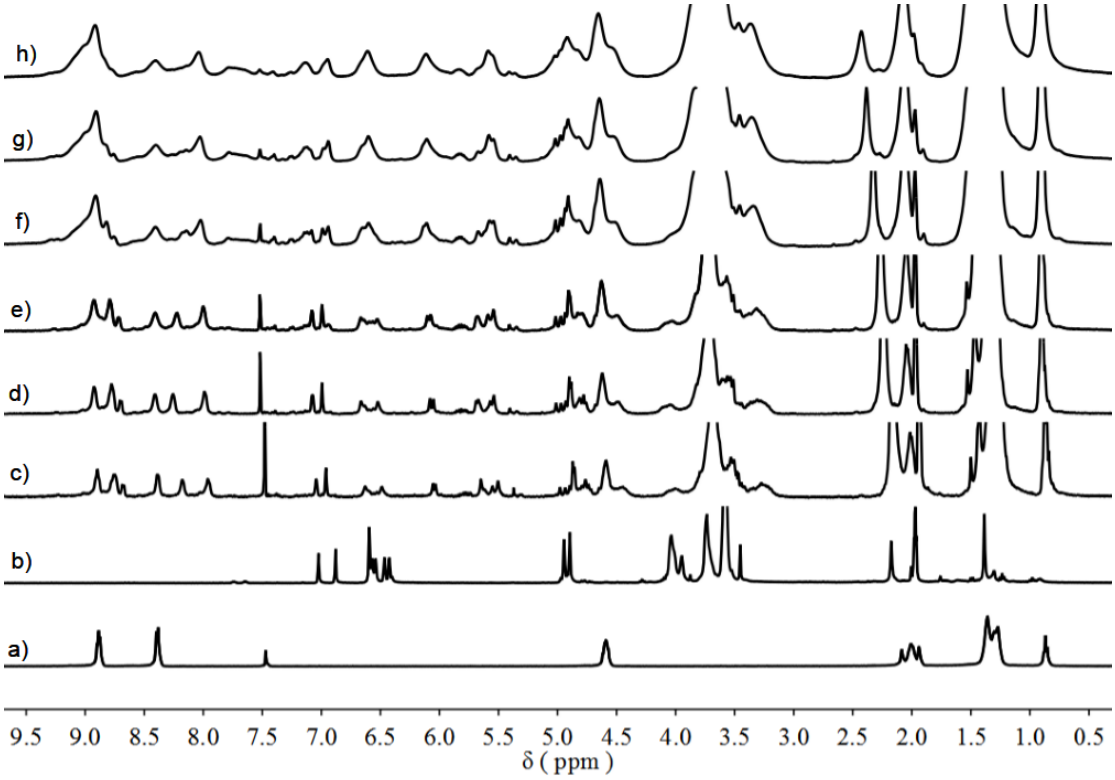


Fig. S13 ^{1}H NMR spectra (400 MHz, 298 K) of (a) individual **4 (**$CDCl_3/CD_3CN$, 1/1, v/v**)**; (b) individual **3 (**CD_3CN**)**; mixtures of **3** and **4** in a 1 : 1 molar ratio at different **3** concentrations ($CDCl_3/CD_3CN$, 1/1, v/v): (c) 5, (d) 10, (e) 20, (f) 40, (g) 60, (h) 74 mM

5. X-ray crystal data for cryptand 1.

Table 1. Crystal data and structure refinement for cryptand **1.**

CCDC number	1449565
Empirical formula	$C_{40}H_{48}O_{14}$
Formula weight	752.81
Temperature	296(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a	13.5950(13) Å
b	20.8235(19) Å
c	23.687(2) Å

α	74.639(2) ^{o}
β	84.656(2) ^{o}
γ	76.364(2) ^{o}
Volume	6280.4(10) $Å^3$
Z	4
Density (calculated)	1.300
Absorption coefficient	0.164
F(000)	2552
Crystal size	0.26 × 0.24 × 0.22 mm^3
Theta range for data collection	2.03 to 25.01 ^{o}
Index ranges	-16 <= h <= 11, -24 <= k <=24, -28 <= l <=28
Reflections collected	39583
Independent reflections	21877 [R(int) = 0.0365]
Completeness to theta = 25.01 °	98.7%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on *F*2	1.184
Final R indices [I > 2sigma(I)]	R1 = 0.0893, wR2 = 0.1740
R indices (all data)	R1 = 0.1375, wR2 = 0.1904
Largest diff. peak and hole	1.440 and -1.021 e $·Å^{-3}$

6. References

1. X. Ji, M. Zhang, X. Yan, J. Li and F. Huang, *Chem. Commun.*, 2013, **49**, 1178-1180.