Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information (ESI)

Redox Controlled Reversible Transformation of a Supramolecular Alternating Copolymer to Radical Cation Containing Homo-polymer

Sahnawaz Ahmed, Nilotpal Singha, Bapan Pramanik, Julfikar Hassan Mondal and Debapratim Das*
Department of Chemistry, Indian Institute of Technology Guwahati, North Guwahati, Kamrup, Assam 781039, India

Syntheses:

2-amino-N-(6-(2-amino-3-(1H-indol-2-yl)propanamido)hexyl)-3-(1H-indol-3-yl)propanamide (1): To a stirring solution of 1,6-diaminohexane (0.3 g, 2.6 mmol) in dichloromethane (DCM), Boc-Trp-OH (2g, 6.6 mmol) was added and the temperature was maintained around 0°C using an ice-bath; followed by the successive addition of EDC.HCl (1.25g, 6.6 mmol), DIPEA (2.1g, 16.2 mmol) and HOBT (0.89 g, 6.6 mmol). The reaction mixture was brought to room temperature and stirred for 24 h. It was then washed with saturated $NaHCO_3$ solution (twice), 10% citric acid solution (twice), again with saturated $NaHCO_3$ and finally with brine. The reaction mixture was then extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was removed on a rotary evaporator. The crude mixture was subjected to column chromatography on a 60-120 mesh silica gel column using ethyl acetate/hexane as the mobile phase (yield: 1.34g, 75%). The product obtained was then subjected to deprotection of the Boc group by trifluoroacetic acid (TFA, 2 ml) containing 1% triethylsilane (TES). After 2 h of stirring, solvents were removed on a rotary evaporator followed by precipitation from diethyl ether. The precipitate was washed with dry diethyl ether several times. The solid was then dried under vacuum, dissolved in water and lyophilized. The purity of the sample was checked by HPLC, NMR and ESI-MS techniques (yield: 1.2g, 65%). ^{1}H NMR (600 MHz, D_2O) δ = 7.59-7.58 (d, *J* = 7.8 Hz, 2H), 7.45-7.44 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 2H), 7.22-7.20 (t, *J* = 7.2 Hz, 2H) , 7.16-7.13 (t, *J* = 7.2 Hz, 2H), 4.13-4.11 (t, *J* = 6 Hz, 2H), 3.37-3.27 (m, 4H), 3.06-3.04(m, 2H), 2.80-2.78 (m, 2H), 0.95-0.92 (m, 4H), 0.61-0.59 (m, 4H) ppm. ^{13}C NMR (100 MHz, D_2O) δ 169.20, 136.19, 126.69, 125.06, 122.33, 118.27, 115.59, 112.03, 106.78, 54.09, 39.49, 30.04, 27.09, 25.09 ppm; HRMS (ESI) m/z calcd. for $C_{28}H_{36}N_6O_2$: 488.2978; found 489.2972 [$M+H^+$].

1',1''-((ethane-1,2-diylbis(oxy)-2,1-diyl))bis(1-ethyl-[4,4'-bipyridine]-1,1'-diium)dibromide dichloride (2): A mixture of 1,2-bis(2-chloroethoxy)ethane (1.6 g, 8.6 mmol) and 4,4'-dipyridyl (4.7 g, 30.1 mmol) in 15 ml DMF was heated at 110°C with constant stirring for 24 h. After cooling, diethyl ether was added to the mixture to get a brown precipitate. The solid was filtered and washed several times with diethyl

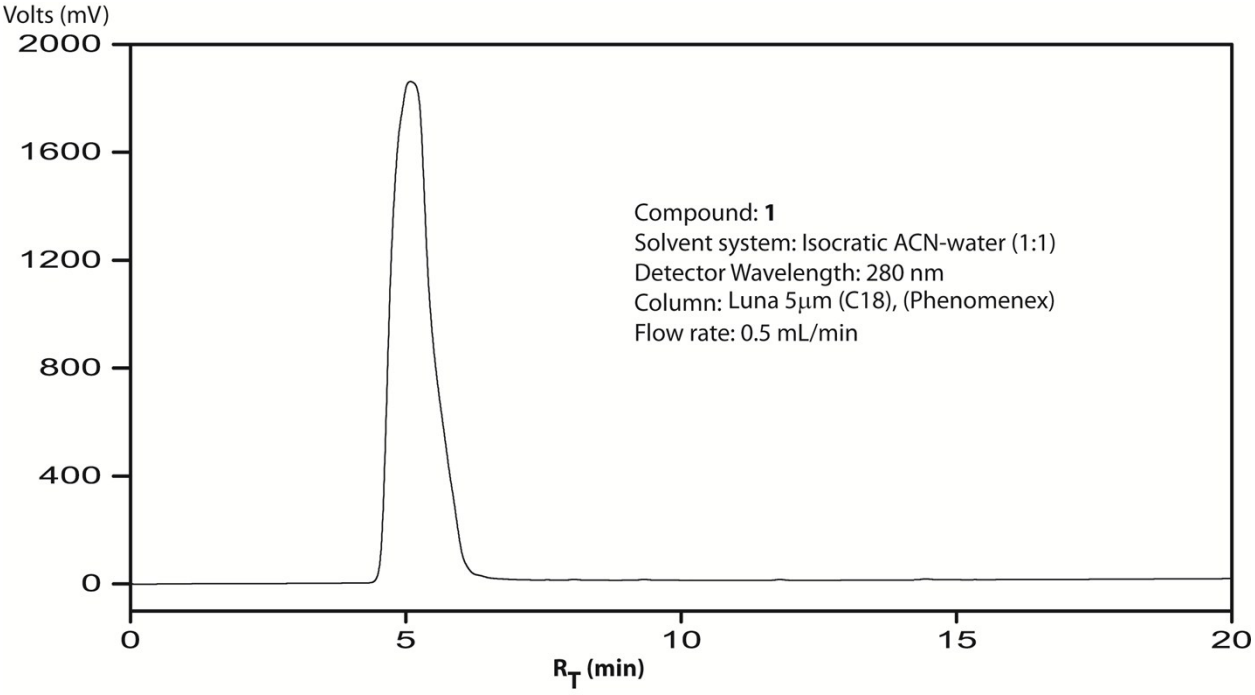
ether and dried under reduced pressure. The solid was taken in 20 ml MeOH-acetonitrile mixture (3:7) and excess ethyl bromide was added. The reaction mixture was refluxed for 24 h when extra ethyl bromide was added time to time. The solvent was removed under reduced pressure and the material washed with diethyl ether several times and finally dried under reduced pressure to get the pure product (yield: 2.4g, 39%). ^{1}H NMR (600 MHz, D_2O) δ = 9.12-9.10 (t, *J* = 7.2 Hz, 8H), 8.55-8.53 (t, *J* = 6.6 Hz, 8H), 4.91-4.86 (q, *J* = 9.2 Hz, 4H), 4.76-4.74 (t, *J* = 7.8 Hz, 4H), 4.07 (t, *J* = 6.0 Hz, 4H), 3.67 (s, 4H), 1.69-1.66 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, D_2O) δ = 150.71, 150.07, 146.31, 145.62, 127.66, 127.46, 70.45, 69.25, 61.77, 58.18, 16.35 ppm. HRMS (ESI) m/z calcd. for $C_{30}H_{38}Br_3N_4O_2$: 727.0524; found 725.0521 $[M+Br^{-}-2Cl]^{+}$.

1-butyl-1'-ethyl-[4,4'-bipyridine]-1,1'-diium bromide (3): 4, 4'-dipyridyl (2g, 12.8 mmol) was dissolved in DCM followed by the addition of excess ethyl bromide (11 g, 101 mmol) and continuous stirring at room temperature for 24 h. The yellow precipitate was filtered and washed with diethyl ether several times before drying it under reduced pressure to get mono-ethylviologen (yield 2.5 g, 73%). The yellow product was dissolved in 20 ml MeOH-acetonitrile mixture (3:7) and to it n-butyl bromide (2.6 g 18.9 mmol) was added. The reaction mixture was refluxed for 24 h when extra ethyl bromide was added time to time. The solvents were removed under reduced pressure and the solid was suspended in diethyl ether and filtered. The solid was washed several times with diethyl ether and dried under reduced pressure to get the yellow colored title compound. (yield: 2.6 g, 68%). ^{1}H NMR (400 MHz, D_2O) δ = 9.15-9.12 (t, *J* = 6.4 Hz, 4H), 8.56-8.53 (t, *J* = 6.4 Hz, 4H), 4.77-4.72 (merged with solvent peak, 2H), 4.54 -4.48 (t, *J* = 6.0 Hz, 2H), 2.11-2.03 (m, 2H), 1.73-1.69 (t, *J* = 7.6 Hz, 3H), 1.46-1.37 (m, 2H), 0.99-0.95 (t, *J* = 7.2Hz, 3H) ppm. ^{13}C NMR (100 MHz, D_2O) δ = 150.19, 145.09, 127.26, 62.24, 57.90, 32.83, 19.01, 15.87, 12.66 ppm. HRMS (ESI) m/z calcd. for $C_{16}H_{22}N_{22}$: 121.0886; found 121.0884 $[M-2Br]^{2+}$.

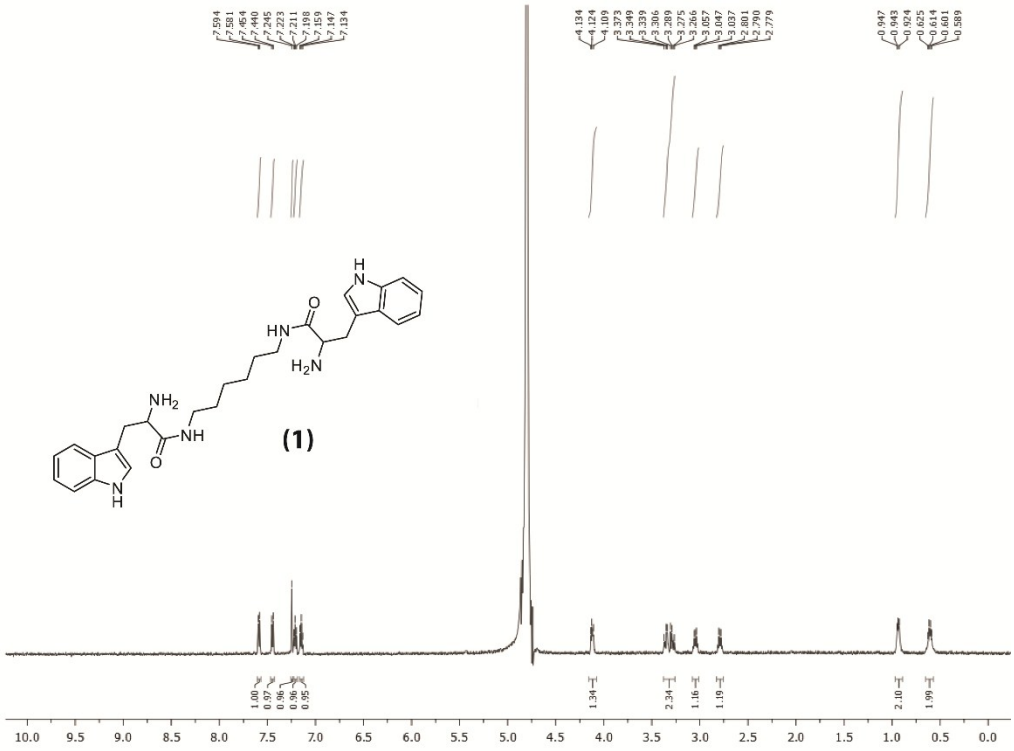
2-amino-N-butyl-3-(1H-indol-3-yl)propanamide (4) : Boc-Trp-OH (0.5 g, 1.64 mmol), HOBt (0.083 mg, 1.8 mmol), HBTU (0.685 g, 1.8 mmol), were dissolved in DCM. Triethylamine (343 µL, 2.47 mmol) was added to the mixture and stirred vigorously. Finally, *n*-butylamine (326.5 µL, 3.28 mmol) was added. The reaction

mixture was allowed to stir for 24 h. The reaction mixture was diluted with DCM and washed with brine. The organic layers were combined together and dried over anhydrous sodium sulfate and filtered. The solvent was removed on a rotary evaporator. The residue was further treated with TFA containing 1% TES for 2h. TFA was removed under reduced pressure and the mixture was subjected to column chromatography on a 60-120 mesh silica gel column. The pure product obtained as an oily liquid after eluting the column with 5% MeOH-DCM solvent mixture. (yield: 0.2 g, 47%). ^{1}H NMR (600 MHz, D_2O) δ = 7.62-7.60 (d, *J* = 8.4 Hz, 1H), 7.52-7.51 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 7.26-7.24 (t, *J* = 6 Hz, 1H), 7.19-7.16 (t, *J* = 7.2 Hz, 1H) , 4.17-4.14 (t, *J* = 8.4 Hz, 1H), 3.39-3.29 (m, 2H), 3.11-3.08 (t, *J* = 6.6 Hz, 1H), 2.92-2.87 (m, 1H), 1.12-1.09 (m, 2H), 0.94-0.87 (m, 2H), 0.74-.72 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, D2O) δ = 169.03, 136.53, 126.74, 125.11, 122.19, 119.56, 118.26, 112.10, 106.72, 54.04, 38.13, 30.09, 27.12, 19.25, 13.02 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{21}N_3O$: 259.1763; found 260.1766 $[M+H]^+$.

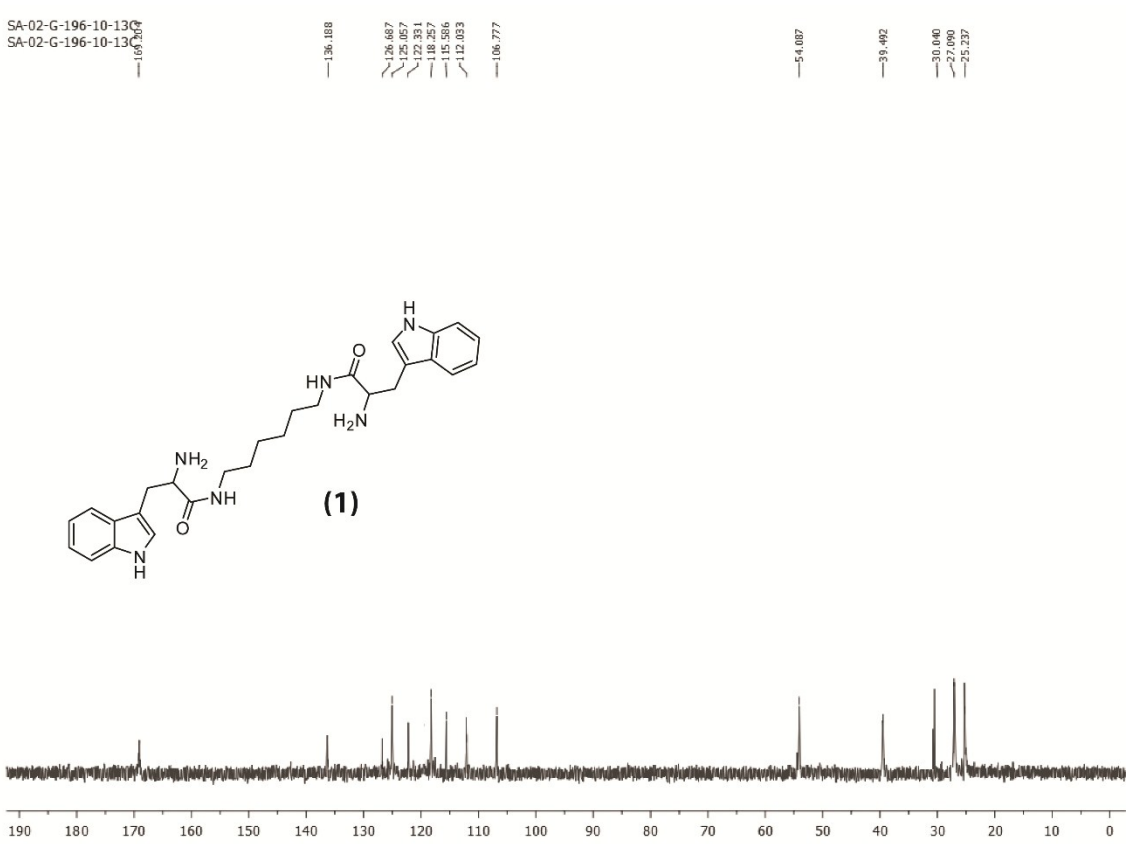
Cucurbit[8]uril (CB[8]): Cucurbit[8]uril (CB[8]) was synthesized following previously published protocol.[1] ^{1}H NMR (600 MHz, $D_2O/CF_3CO_2D/D_2SO_4$ (1:1:0.15)): $\delta =$ 4.25 (d, 16H), 5.55 (s, 16H), 5.86 (d, 16H) ppm; MS (ESI): m/z 1461.41 $(CB[8] + Cs)^+$.



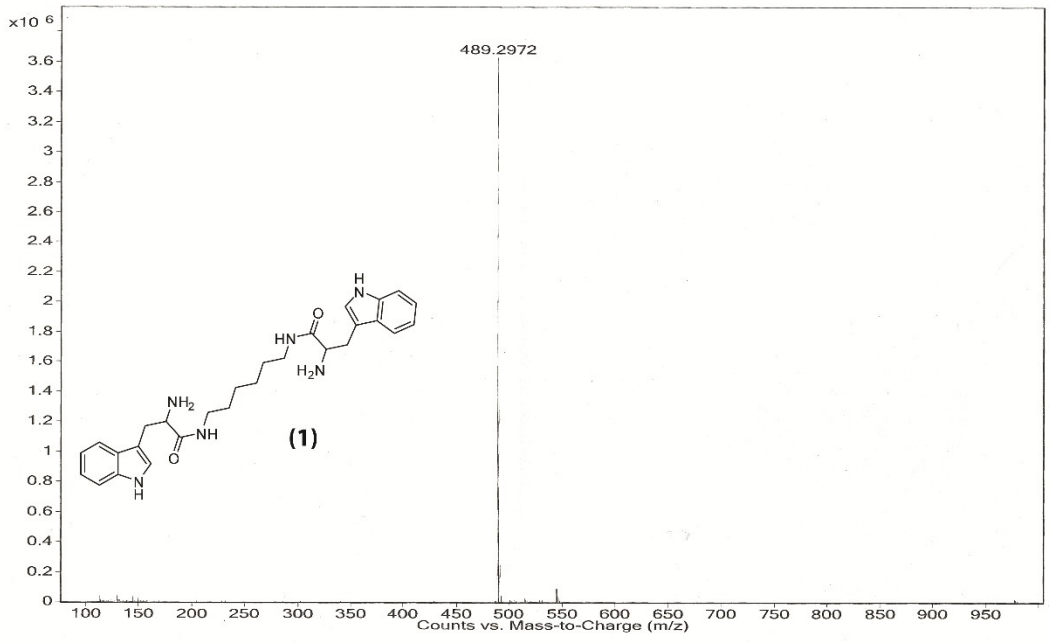
S1.Chromatogram of purified **1**.



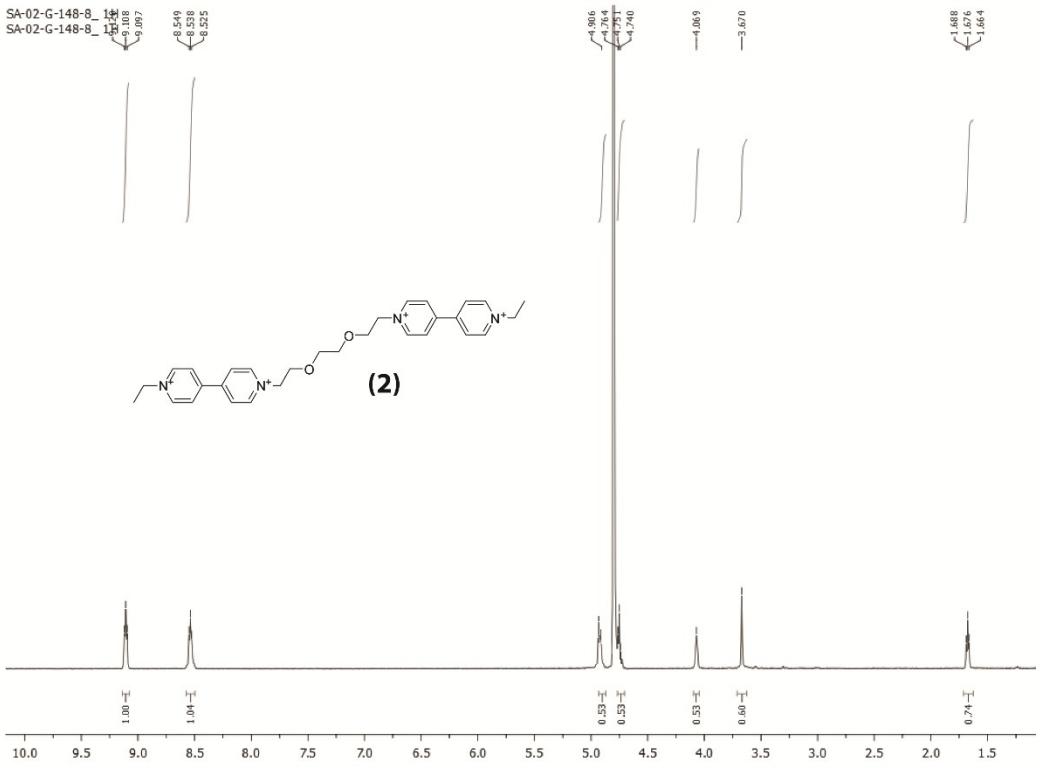
S2. ^{1}H NMR spectrum of **1**.



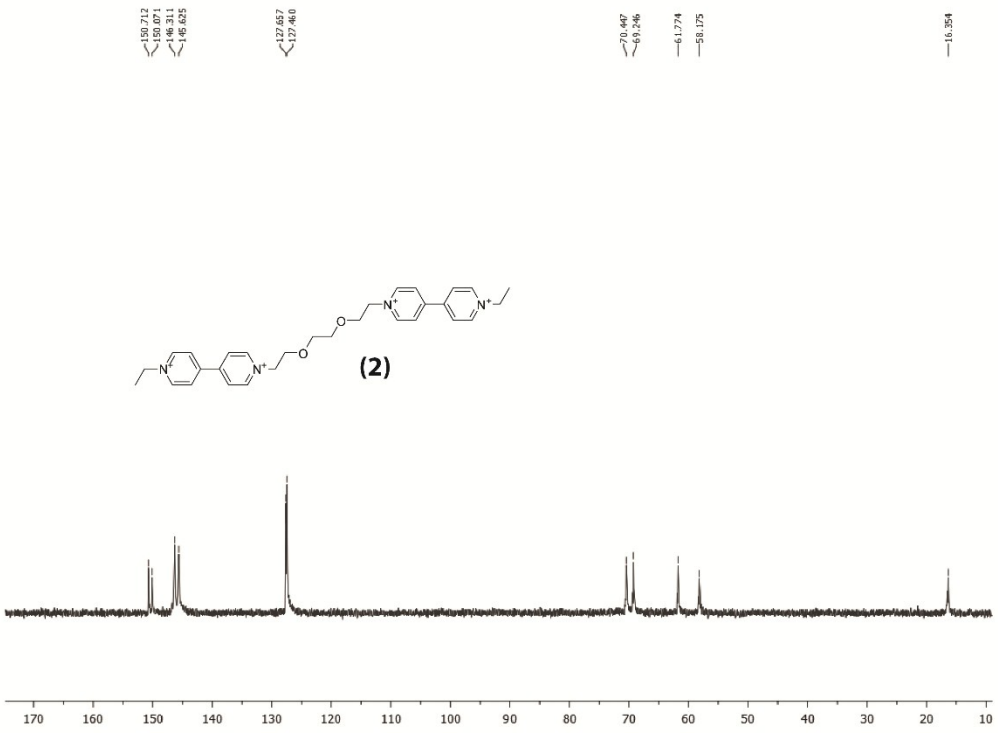
S3. ^{13}C NMR spectrum of **1**.



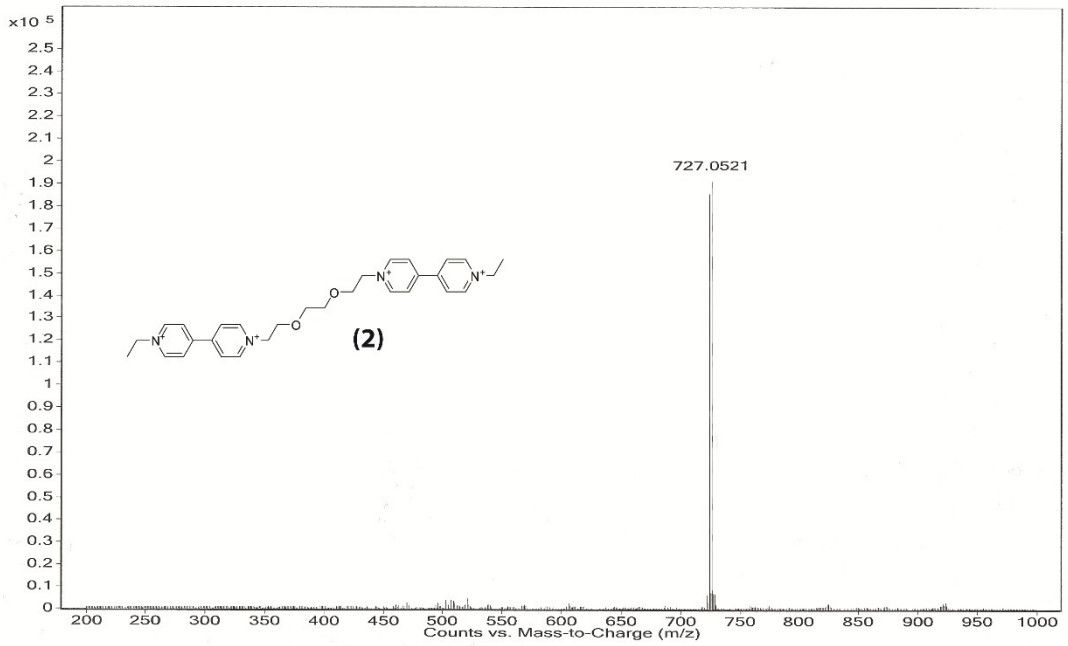
S4. ESI-MS spectrum of **1**.



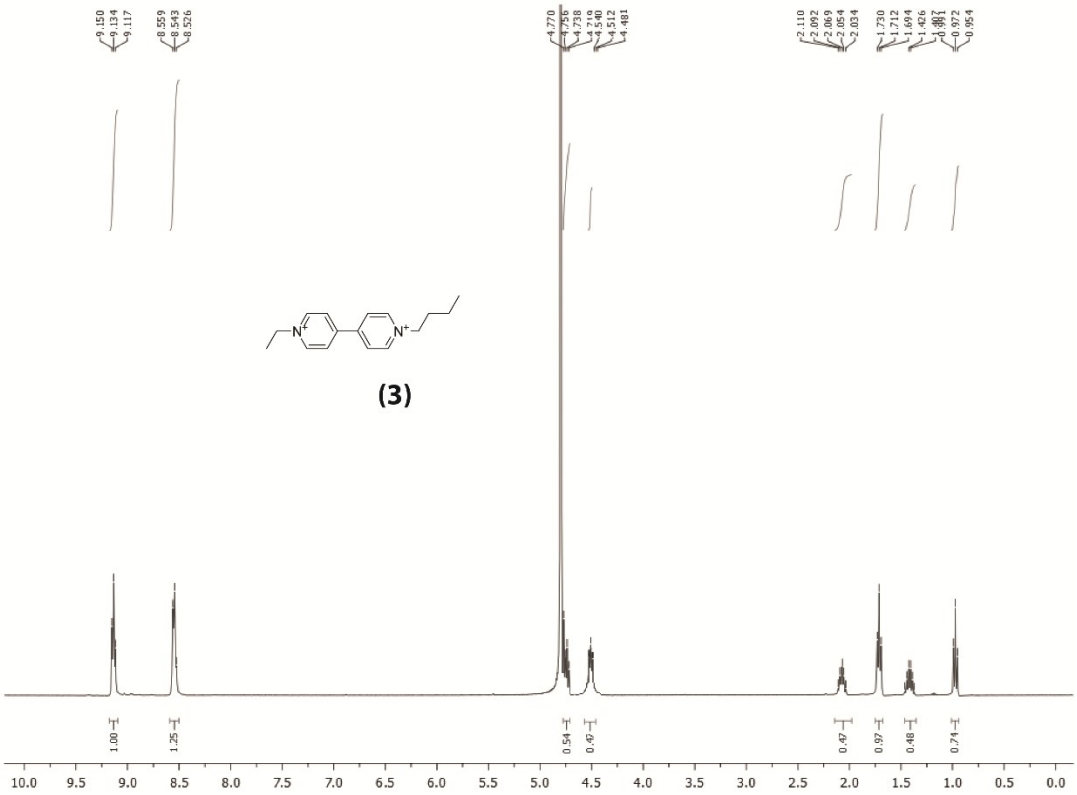
S5. ^{1}H NMR spectrum of **2**.



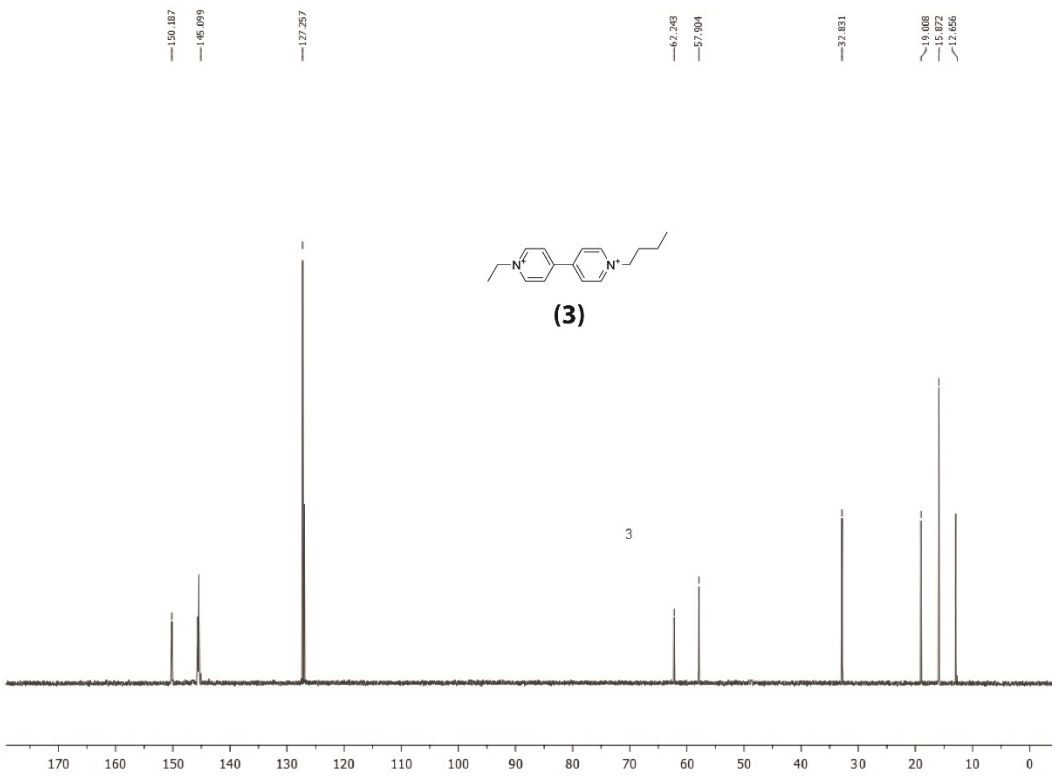
S6. ^{13}CNMR spectrum of **2**.



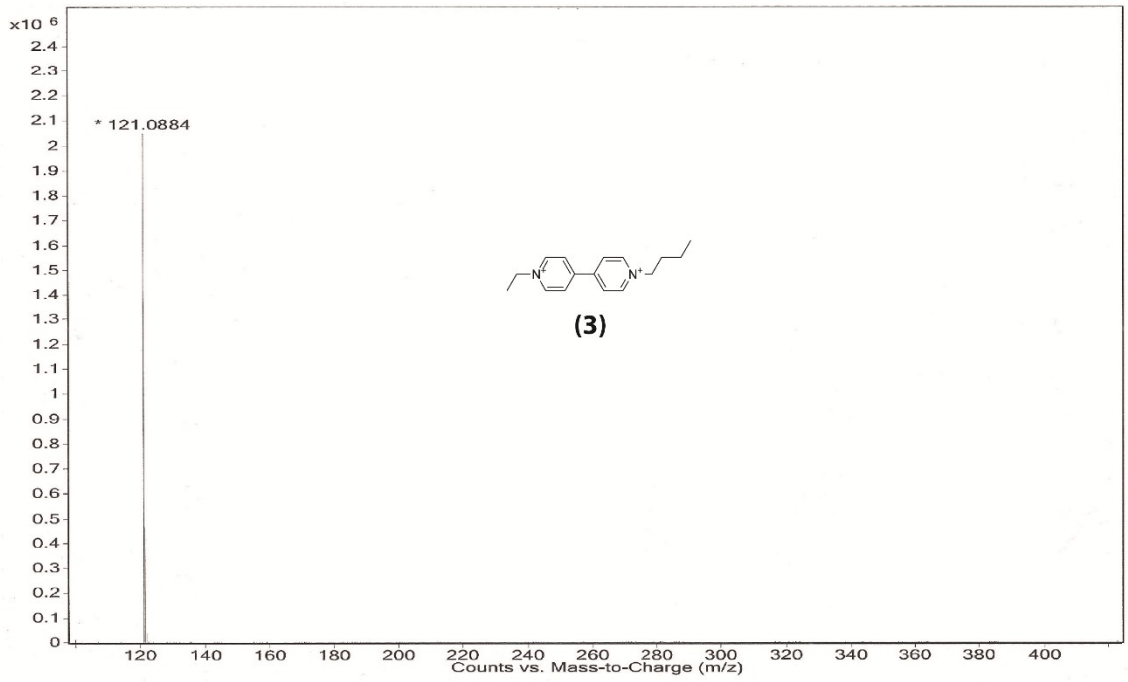
S7. ESI-MS spectrum of **2**.



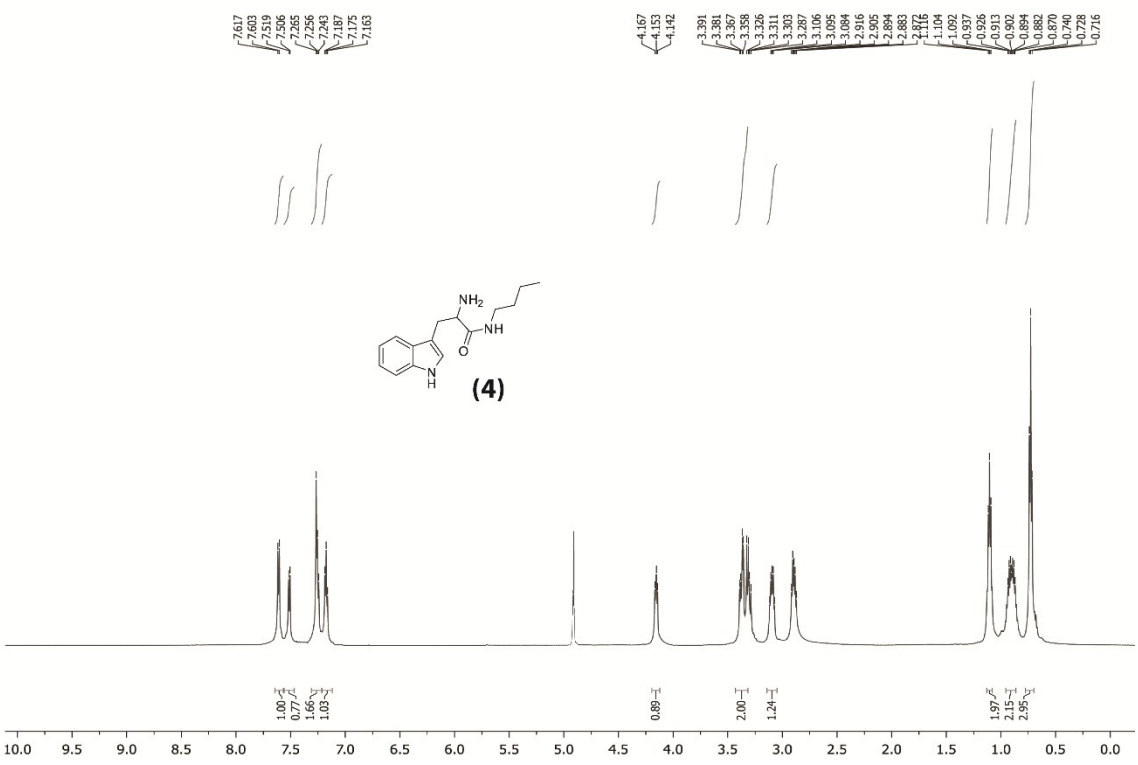
S8. ^{1}H NMR spectrum of **3**.



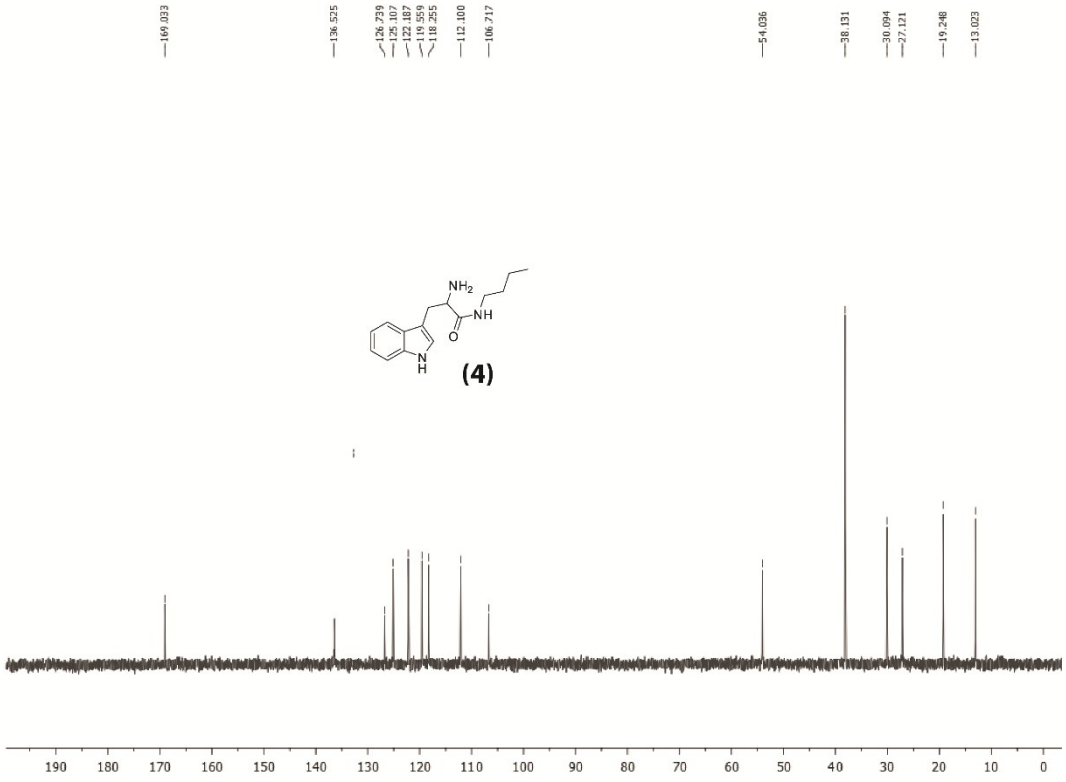
S9. ^{13}C NMR spectrum of **3**.



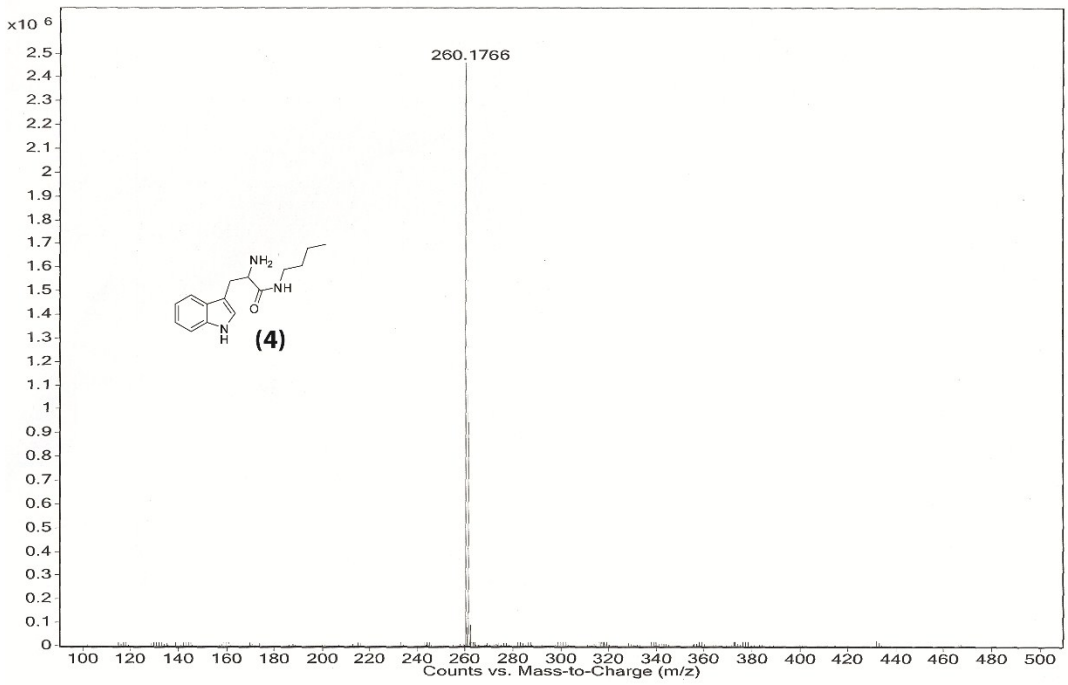
S10. ESI-MS spectrum of **3**.



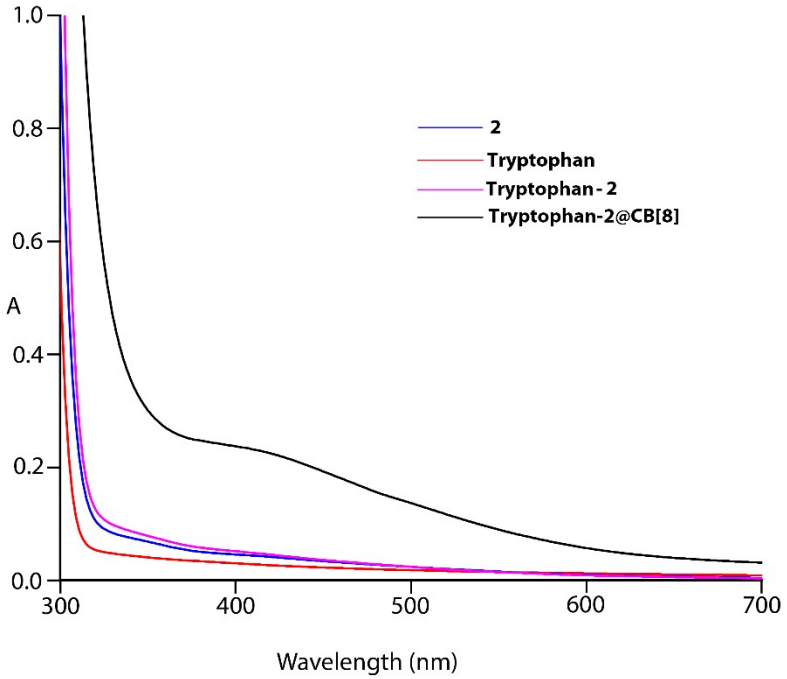
S11. ^{1}H NMR spectrum of **4**.



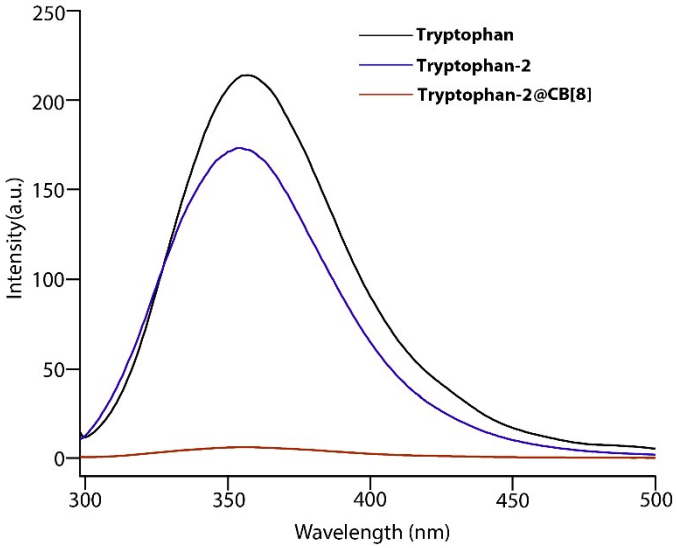
S12. ^{13}C NMR spectrum of **4**.



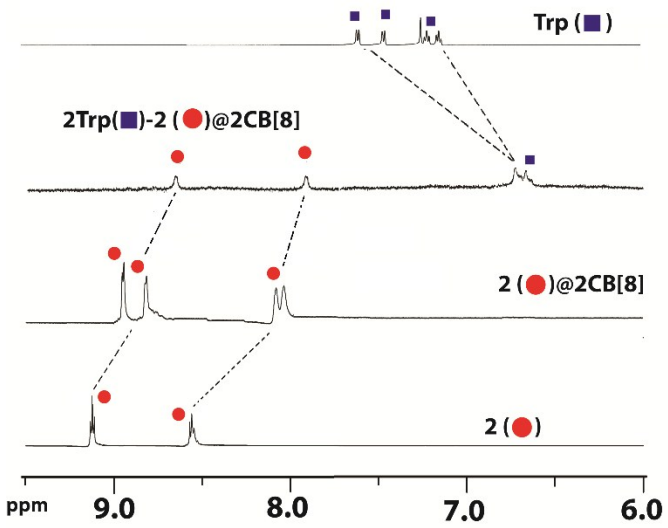
S13. ESI-MS spectrum of **4**.



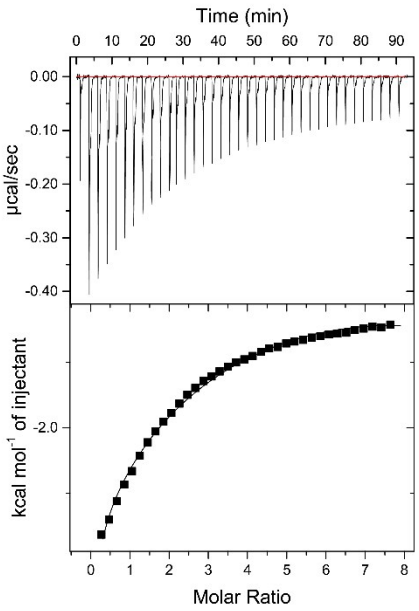
S14. UV-Visible spectra of aqueous solutions of various compositions of Tryptophan, **1** and CB[8] showing the appearance of the CT band upon formation of the ternary complex of Tryptophan-**2**@2CB[8]; [**2**] = 0.5mM. [Tryptophan] = 1mM, [CB[8]] = 1mM.



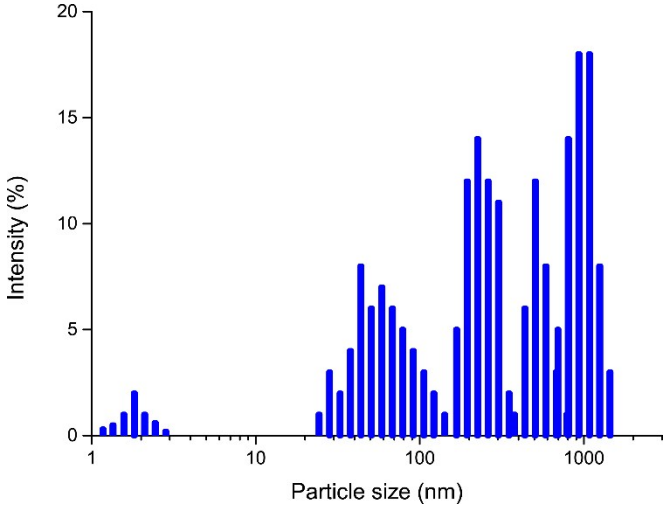
S15. Emission spectra of aqueous solutions of various compositions of Tryptophan, **1** and CB[8] showing the significant quenching of Tryptophan fluorescence upon formation of the ternary complex of Tryptophan-**2**@2CB[8]; [**2**] = 0.5mM. [Tryptophan] = 1mM, [CB[8]] = 1mM. (λ_{ex}= 279nm).



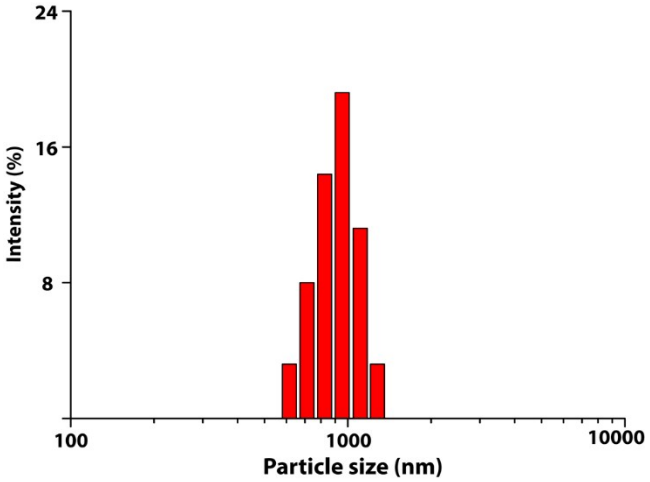
S16. ^{1}H NMR spectra of tryptophan, **2**, CB[8] and their mixtures showing the up-field shifts of the aromatic protons upon inclusion complexation.



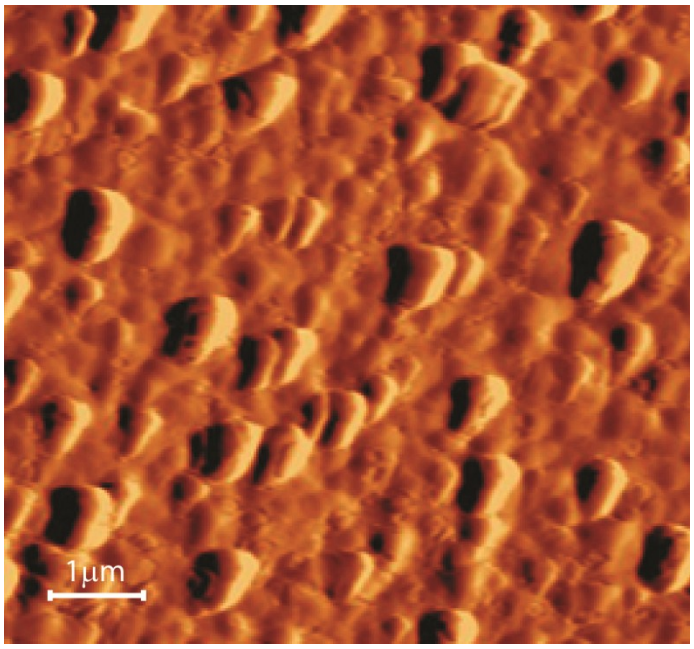
S17. Thermograms (top) and binding isotherms (bottom) of Tryptophan with **2**@CB[8] (1:2) showing 2:1 binding.



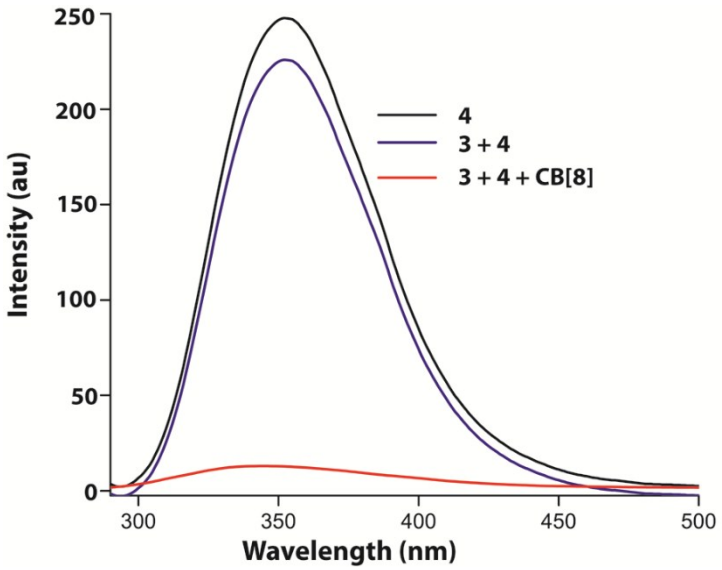
S18. DLS profile of the solution of **1**-**2**@2CB[8] (1:1:2) immediately after the hydrazine hydrate treatment.



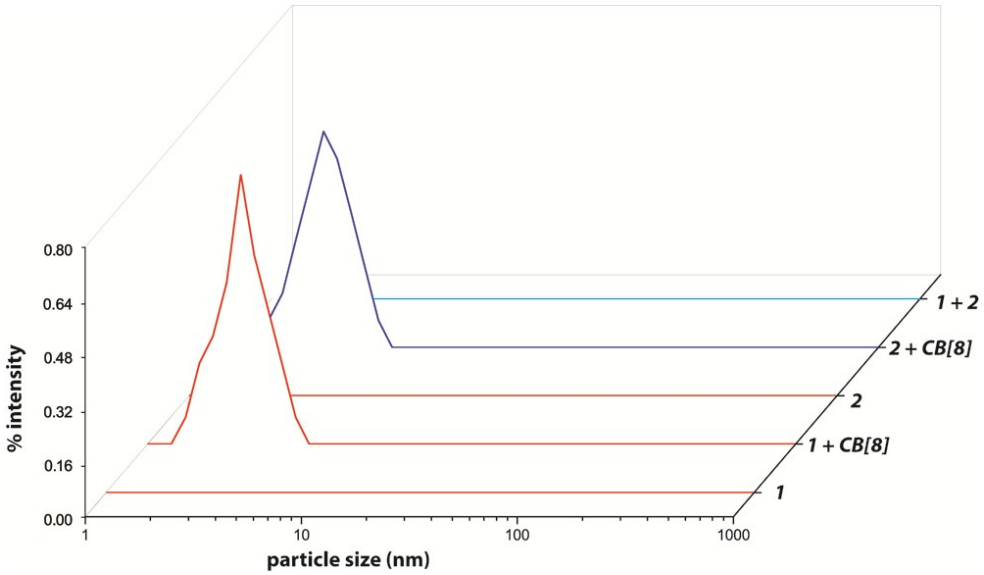
S19. DLS profile of the solution of **1**-**2**@2CB[8] (1:1:2) 6 h after the hydrazine hydrate treatment.



S20. AFM image of the hydrazine hydrate treated **1**-**2**-CB[8] (1:1:2) solution.



S21. Emission spectra of aqueous solutions of various compositions of **3**, **4** and CB[8] showing the significant quenching of Tryptophan fluorescence upon formation of the ternary complex of **3-4**@CB[8]; [**3**] = 0.5mM. [**4**] = 0.5 mM, [CB[8]] = 0.5 mM. (λ_{ex}= 279nm).



S22. DLS profile of the solutions of **1** and **2** in absence and presence of CB[8] showing extremely negligible distributions without CB[8].

Table S1. Diffusion coefficients obtained from DOSY spectroscopy.

Sample (0.25 mM for guests)	D_{av}[a] (10^{-10} m^2s^{-1})	Degree of polymerization (calculated)
1	4.31	-
2	4.09	-
CB[8]	2.91	-
3	4.25	-
4	4.38	-
1-**2**-CB[8] (1:1:2)	0.54	127
3-**4**-CB[8] (1:1:1)	2.72	-
1-**2**-CB[8] (1:1:2)+ N_2H_4	0.38	354
2-CB[8] (1:2)	2.82	-
3-CB[8] (1:2) + N_2H_4	2.69	-
2-CB[8] (1:2) + N_2H_4 (*ie.* **5**@CB[8] (1:2))	0.39	328

[a] only the diffusion coefficients for the complexes mentioned in case of multiple D_{av} values in the same sample.

Table S2. Solution binding constants and related thermodynamic parameters obtained from ITC experiments.

System titrated	Titrant	N (sites)	K_a (M^{-1})	ΔH (cal/mol)	ΔS (cal/mol/deg)
CB[8]	**2**	0.486 ± 0.0026	(2.02 ± 0.201) × 10^6	-9259 ± 78.02	-2.21
2-CB[8] (1:2)	**1**	0.94 ± 0.0011	(5.12 ± 0.348) × 10^5	-13640 ± 145.1	-19.60
2-CB[8] (1:2)	Trp	2.08 ± 0.034	(1.07 ± 0.266) × 10^4	-6453± 1393	-3.21

Reference

1 J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.* 2000, **122**, 540−541.