Electronic Supplementary Information

Novel pseudo[2]rotaxanes constructed by self-assembly of dibenzyl tetramethylene bis-carbamate derivatives and per-ethylated pillar[5]arene

Shuhan Xiong, Xiaoning Zhang, Lu-Bo Meng, Juli Jiang, Chen Lin,* Leyong Wang

State Key Laboratory of Coordination Chemistry, Center for Multimolecular Organic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China.

Fax: +86 25-83597090; Tel: +86 25-83592529;

E-mail: linchen@nju.edu.cn.

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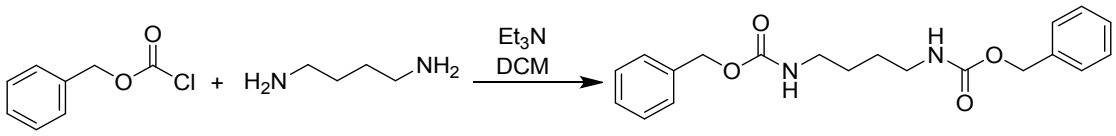
1. Materials and methods

All reactions were performed in atmosphere unless noted. All reagents were commercially available and use as supplied without further purification. Solvents were either employed as purchased or dried according ti procedures described in the literature. Compound **EtP[5]A** was prepared by published literature procedures.[S1] NMR spectra were collected on either a Bruker Avance DMX 300 MHz spectrometer or a Bruker Avance DMX 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and signals as internal references, and the chemical shifts (δ) were expressed in ppm. 2D COSY and NOESY experiments were performed on a Bruker DPX 400 MHz spectrometer. 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. Synthesis of Guest



Scheme S1 Synthesis of **G1**

Synthesis of **G1**: 1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.02 g, 10 mmol) were added in dichloromethane (50 mL). Then benzyl chloroformate (1.71 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by Na_2SO_4. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 160/1, *v/v*) to afford **G1** (1.64 g, 92.0 %), m.p. 146−147 °C. ^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ (ppm): 7.35−7.37 (m, 10H, ArH), 5.10 (s, 4H, CH_2), 4.79 (s, 2H, NH), 3.20 (s, 4H, CH_2), 1.53 (s, 4H, CH_2). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ (ppm): 156.5, 136.6, 128.5, 128.1, 66.7, 40.6, 27.2. LR-ESI-MS is: *m/z* calcd for $[M + H]^+$, 357.18, found 357.15; calcd for $[M + Na]^+$, 379.16, found 379.15. HR-ESI-MS is: *m/z* calcd for $[M + Na]^+$, $C_{20}H_{24}N_2O_4Na^+$, 379.1628, found 379.1631.

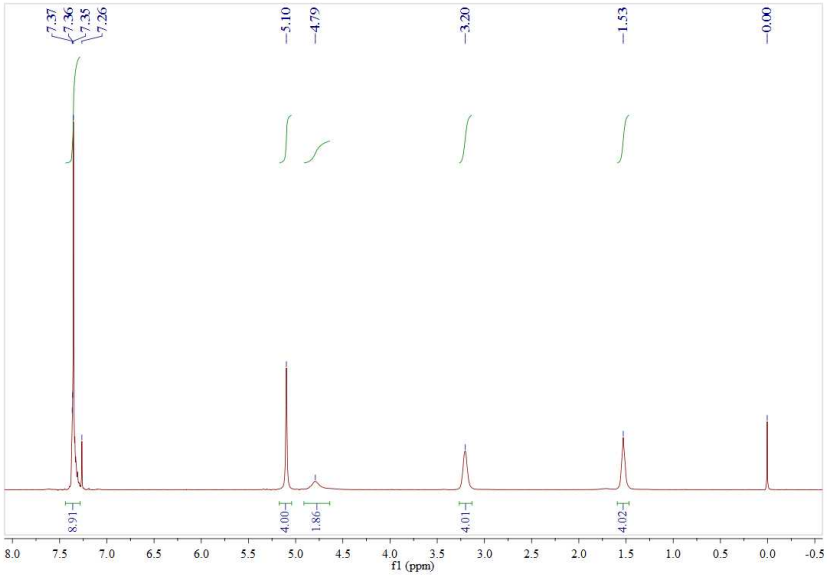


Fig. S1 ^{1}H NMR spectrum (300 MHz, chloroform-*d*, 298 K) of **G1**

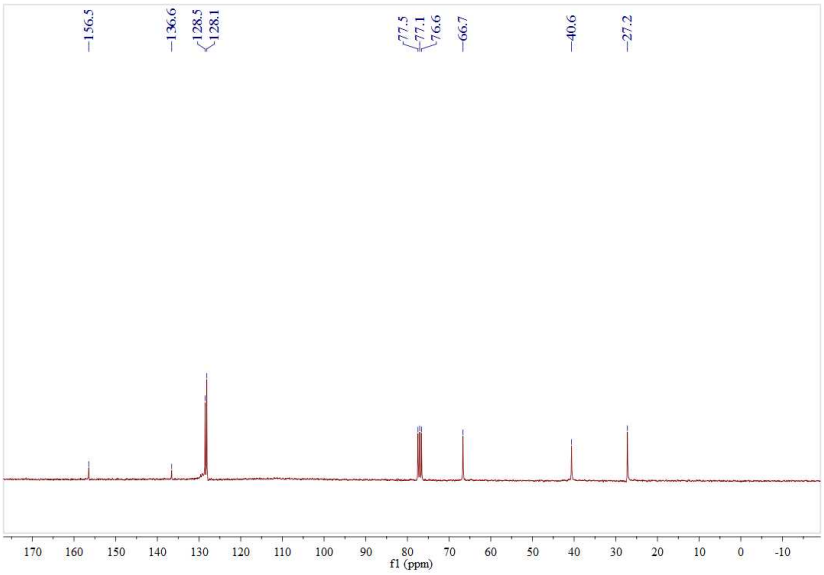
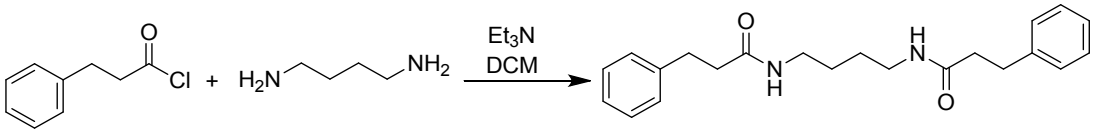


Fig. S2 ^{13}C NMR spectrum (75 MHz, chloroform-*d*, 298 K) of **G1**



Scheme S2 Synthesis of **G2**

Synthesis of **G2**: 1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.52 g, 15 mmol) were added in dichloromethane (50 mL). Then hydrocinnamoyl chloride (2.53 g, 15 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by Na_2SO_4. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 60/1, *v/v*) to afford **G2** (1.28 g, 72.7 %), m.p. 176−178 °C. ^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ (ppm): 7.31−7.19 (m, 10H, ArH), 5.78 (s, 2H, NH), 3.18 (d, J = 5.66 Hz, 4H, CH_2), 2.97 (t, J = 7.59 Hz, 4H, CH_2), 2.50 (t, J = 7.62 Hz 4H, CH_2), 1.35 (t, J = 6.24 Hz, 4H, CH_2). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ (ppm): 172.4, 140.9, 128.5, 128.4, 126.2, 38.9, 38.5, 31.8, 26.6. LR-ESI-MS is: *m/z* calcd for $[M + H]^+$, 353.22, found 353.15; calcd

for $[M + Na]^+$, 375.20, found 375.15. HR-ESI-MS is: *m/z* calcd for $[M + Na]^+$, $C_{22}H_{28}N_2O_2Na^+$, 375.2043, found 375.2044.

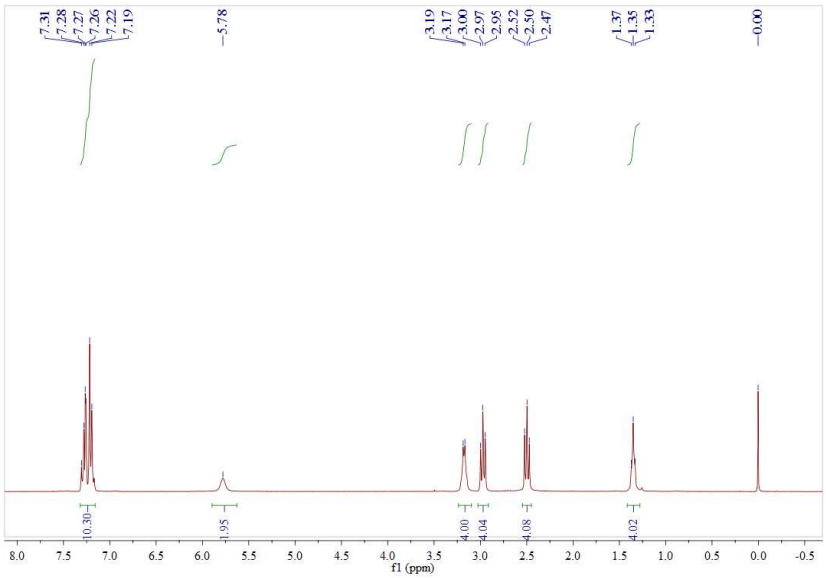


Fig. S3 ^{1}H NMR spectrum (300 MHz, chloroform-*d*, 298 K) of **G2**

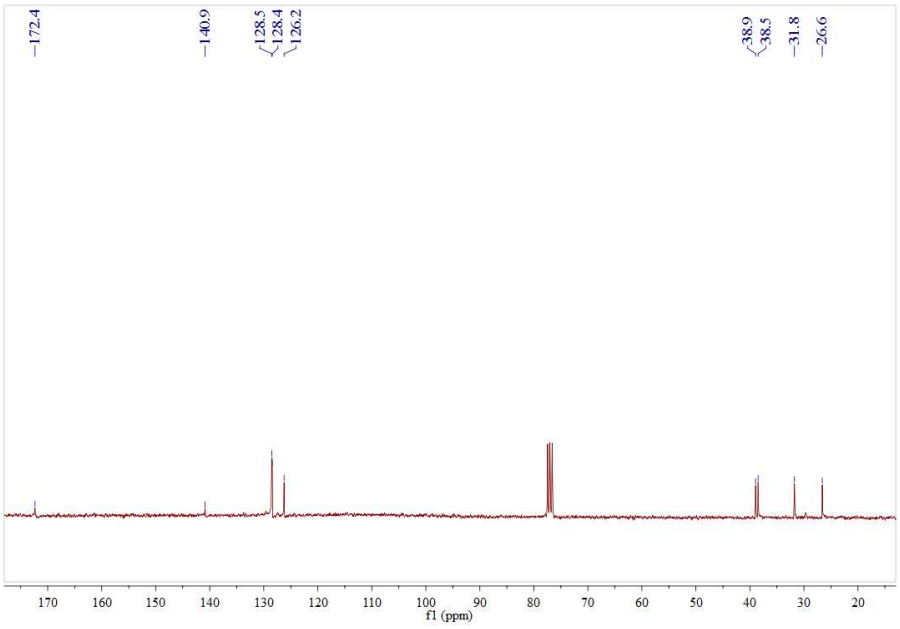
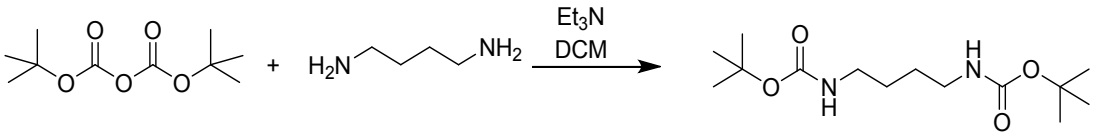


Fig. S4 ^{13}C NMR spectrum (75 MHz, chloroform-*d*, 298 K) of **G2**



Scheme S3 Synthetic route to **G3**

Synthesis of **G3**: 1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.01 g, 10 mmol) were added in dichloromethane (50 mL). Then di-tert-butyl dicarbonate (2.18 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by Na_2SO_4. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 80/1, *v/v*) to afford **G3** (1.34 g, 92.9 %), m.p. 139−140 °C. ^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ (ppm): 4.53 (s, 2H, NH), 3.12 (s, 4H, CH_2), 1.50 (m, 4H, CH_2), 1.44 (s, 18H, CH_3). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ (ppm): 156.0, 79.2, 40.3, 28.4, 27.4. LR-ESI-MS is: *m/z* calcd for $[M + H]^+$, 289.21, found 289.15; calcd for $[M + Na]^+$, 311.19, found 311.15. HR-ESI-MS is: *m/z* calcd for $[M + Na]^+$, $C_{14}H_{28}N_2O_4Na^+$, 311.1941, found 311.1943.

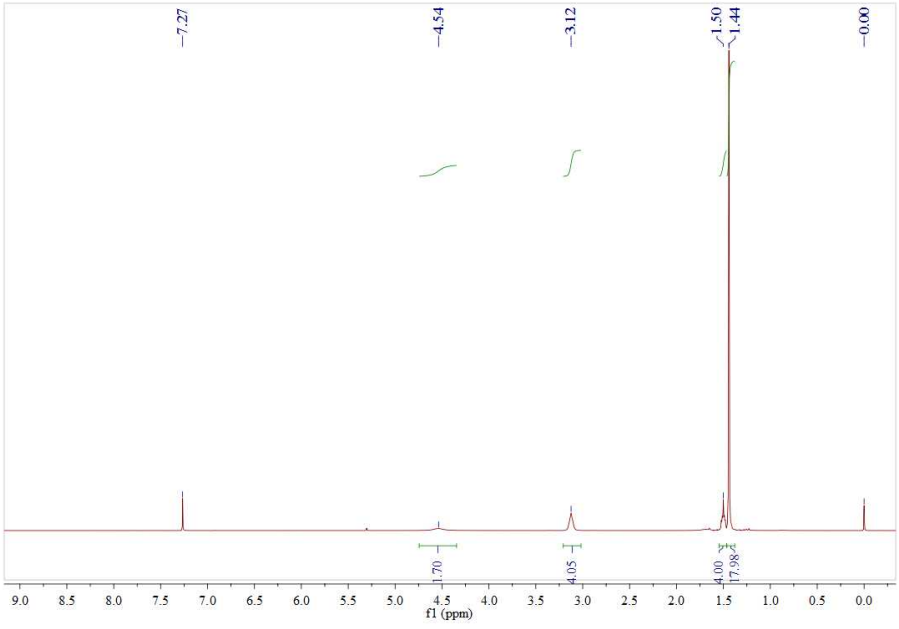


Fig. S5 ^{1}H NMR spectrum (300 MHz, chloroform-*d*, 298 K) of **G3**

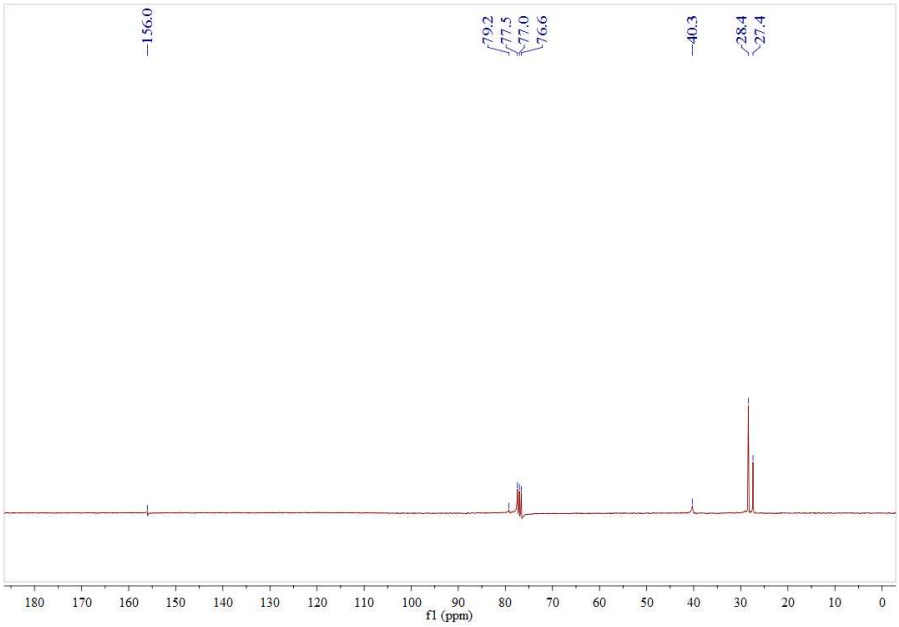


Fig. S6 ^{13}C NMR spectrum (75 MHz, chloroform-*d*, 298 K) of **G3**

Scheme S4. Synthetic route to **G4**

Synthesis of **G4**: 1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.52 g, 15 mmol) were added in dichloromethane (50 mL). Then butyryl chloride (1.60 g, 15 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by Na_2SO_4. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 40/1, *v/v*) to afford **G4** (0.46 g, 40.3 %), m.p. 164−165 °C. ^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ (ppm): 5.85 (s, 2H, NH), 3.28 (d, J = 5.95 Hz, 4H, CH_2), 2.16 (t, J = 7.48 Hz, 4H, CH_2), 1.73−1.63 (m, 4H, CH_2), 1.56−1.52 (m, 4H, CH_2), 0.95 (t, 6H, CH_3). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ (ppm): 173.4, 39.0, 38.6, 26.9, 19.2, 13.8. LR-ESI-MS is: *m/z* calcd for $[M + H]^+$, 229.19, found 229.15; calcd for $[M + Na]^+$, 251.17, found 251.15. HR-ESI-MS is: *m/z* calcd for $[M + Na]^+$, $C_{12}H_{24}N_2O_2Na^+$, 251.1730, found 251.1729.

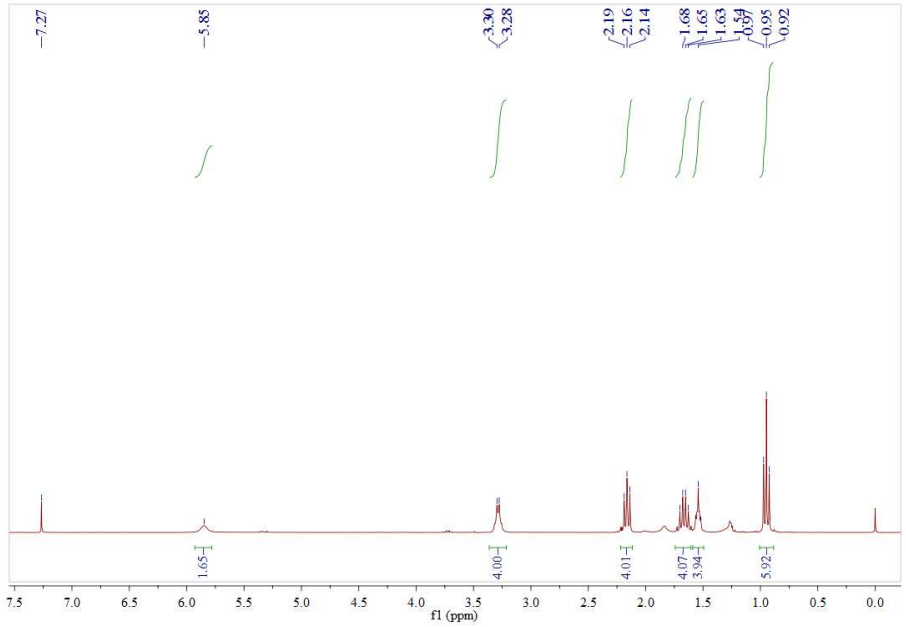


Fig. S7 ^{1}H NMR spectrum (300 MHz, chloroform-*d*, 298 K) of **G4**

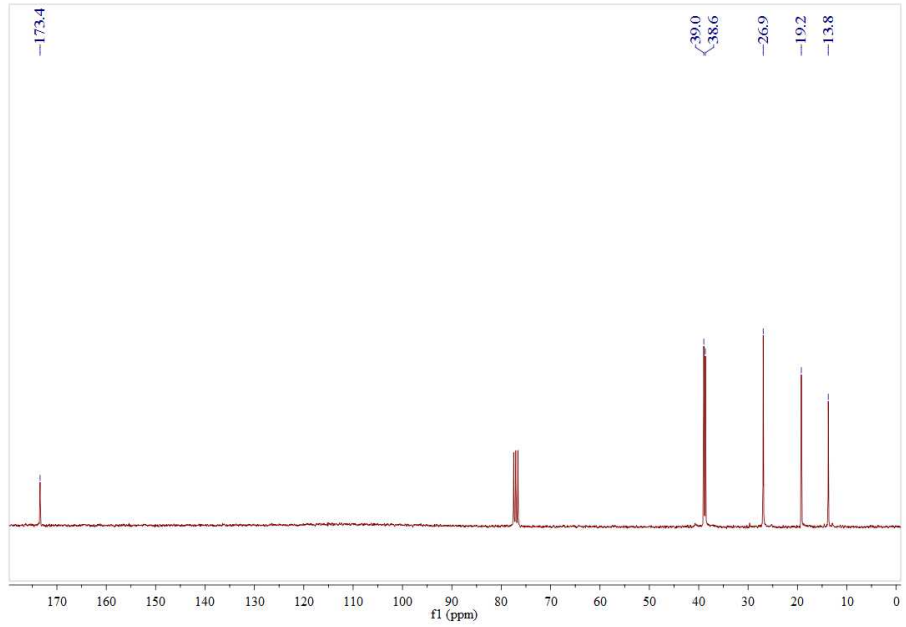
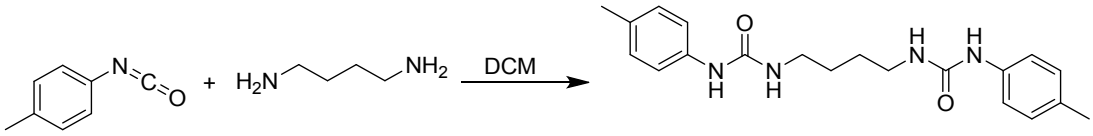


Fig. S8 ^{13}C NMR spectrum (75 MHz, chloroform-*d*, 298 K) of **G4**



Scheme S5. Synthetic route to **G5**

Synthesis of **G4**: 1,4-butanediamine (0.44 g, 5 mmol) were added in dichloromethane (50 mL). Then *p*-tolyl isocyanate (1.33 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 2 hours. The reaction mixture was filtrated. The filter cake was washed by dichloromethane and water. Dry the cake to afford **G5** (1.56 g, 88.0 %), m.p. 277−279 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ (ppm): 8.26 (s, 2H, NH), 7.25 (d, J =8.47 Hz, 4H, ArH), 7.00 (d, J =8.45 Hz, 4H, ArH), 6.07 (t, J =5.62 Hz, 2H, NH), 3.07 (d, J =5.61 Hz, 4H, CH_2), 1.30−1.23 (m, 4H, CH_2), 0.87 (t, J =7.29 Hz, 6H, CH_3). The clear ^{13}C NMR spectrum of **G5** could not be obtained, because it is not well soluble in DMSO-d_6. LR-ESI-MS is: *m/z* calcd for $[M + H]^+$, 355.21, found 355.15; calcd for $[M + Na]^+$, 377.19, found 377.15. HR-ESI-MS is: *m/z* calcd for $[M + Na]^+$, $C_{20}H_{26}N_4O_2Na^+$, 377.1948, found 377.1951.

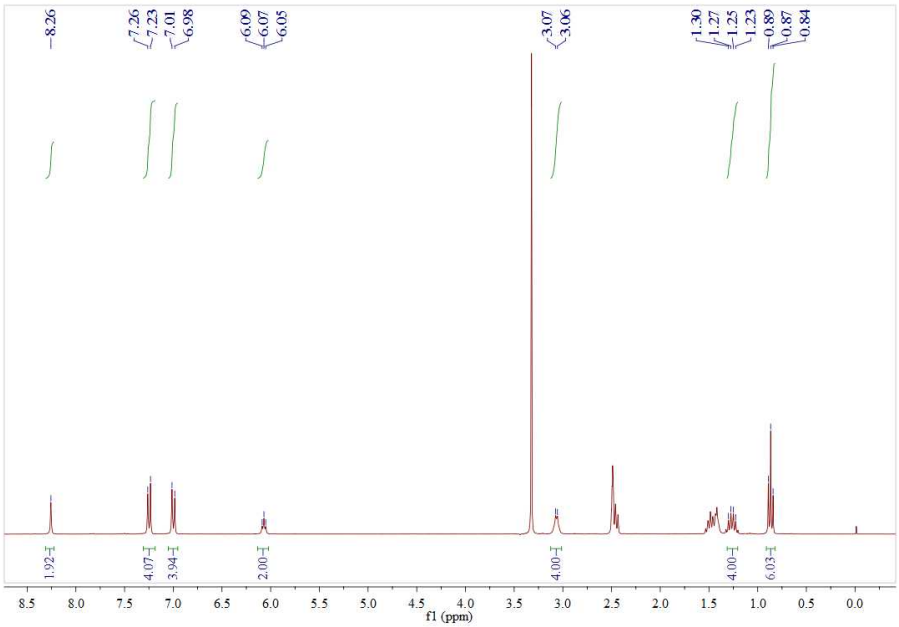
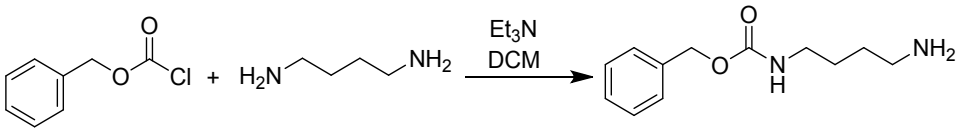


Fig. S9 ^{1}H NMR spectrum (300 MHz, DMSO-d_6, 298 K) of **G5**



Scheme S6. Synthetic route to **G7$_P$**

Synthesis of **G7$_p$**: 1,4-butanediamine (0.88 g, 10 mmol) and triethylamine (1.21 g, 12 mmol) were added in dichloromethane (170 mL). Then benzyl chloroformate (1.70 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. Some precipitates were observed from the reaction solution, and the resulting reaction mixture was extracted by water (20 mL), ethyl acetate (40 mL), and methanol (1 mL). The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 40/1, *v/v*) to afford **G7$_P$** (0.54 g, 24.3 %). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 7.77 (s, 2H, NH), 7.37−7.31 (m, 5H, ArH), 5.01 (s, 2H, CH_2), 3.03−2.98 (m, 2H, CH_2), 2.79−2.74 (m, 2H, CH_2), 1.55−1.42 (m, 4H, CH_2).

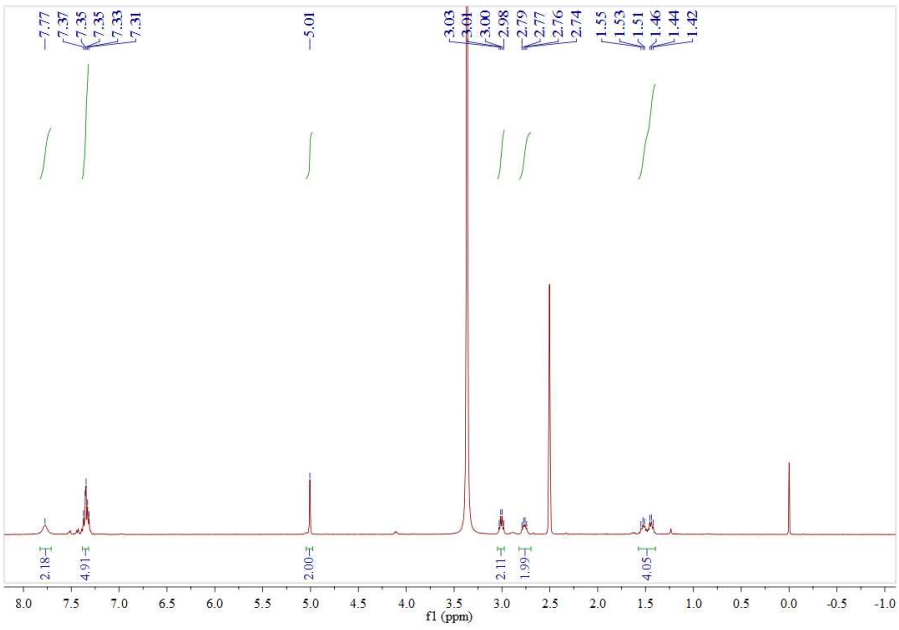
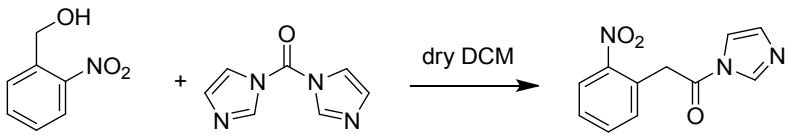


Fig. S10 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **G7$_p$**



Scheme S7. Synthetic route to **Gs**

Synthesis of **Gs**: 2-Nitrobenzyl alcohol (0.766 g, 5 mmol) and 1,1-CarbonyldiiMidazole (1.62 g, 10 mmol) were added in dichloromethane (100 mL). The mixture was stirred at room temperature for 5 hours. The reaction mixture was washed by brine and dried by Na_2SO_4. The organic layer was evaporated under vacuum to afford **Gs** (1.13 g, 91.8 %). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ (ppm): 8.36 (s, 1H, CH), 8.19 (d, J = 8.12 Hz, 1H, ArH), 7.91−7.83 (m, 2H, CH), 7.71−7.68 (m, 2H, ArH), 7.12 (s, 1H, ArH), 5.79 (s, 2H, CH_2).

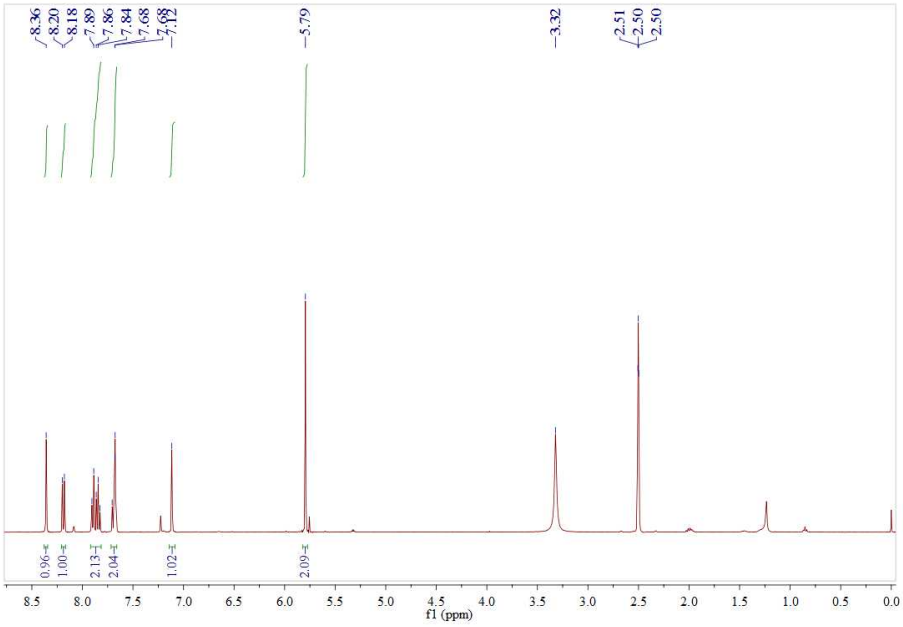
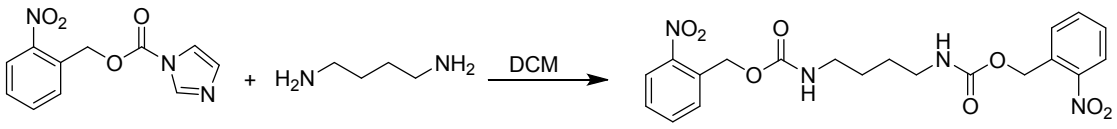


Fig. S11 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **Gs**



Scheme S8. Synthetic route to **G6**

Synthesis of **G6**: 1,4-butanediamine (0.088 g, 1 mmol) was added in dichloromethane (30 mL). Then **Gs** (0.49 g, 2 mmol) was dropped to the mixture. The mixture was stirred at room

temperature for 12 hours. The reaction mixture was washed by brine and dried by Na_2SO_4. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 60/1, *v/v*) to afford **G6** (0.21 g, 47.0%), m.p. 174−175 °C. ^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ (ppm): 8.08 (d, J =8.10 Hz, 2H, ArH), 7.65−7.60 (m, 4H, ArH), 7.48 (t, J =7.54 Hz, 2H, ArH), 5.51 (s, 4H, CH_2), 4.94 (s, 2H, NH), 3.23(s, 4H, CH_2), 1.58 (s, 4H, CH_2, overlapped with the solvent peak of water). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K) δ (ppm): 156.1, 134.5, 129.4, 125.2, 62.3, 27.1. LR-ESI-MS is: *m/z* calcd for $[M + H]^+$, 447.15, found 447.05; calcd for $[M + Na]^+$, 469.13, found 469.05. HR-ESI-MS is: *m/z* calcd for $[M + Na]^+$, $C_{20}H_{22}N_4O_8Na^+$, 469.1330, found 469.1332.

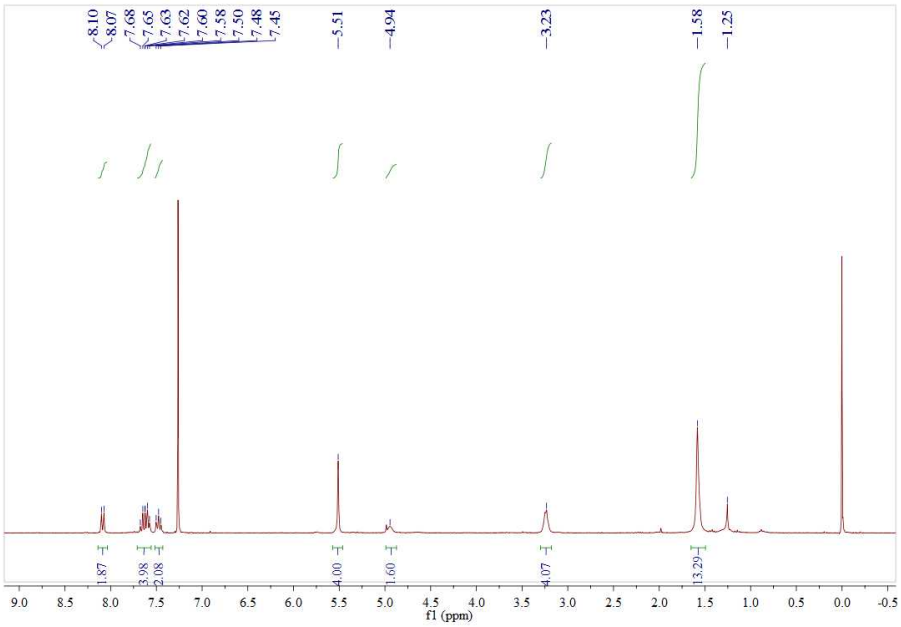


Fig. S12 ^{1}H NMR spectrum (300 MHz, chloroform-*d*, 298 K) of **G6**

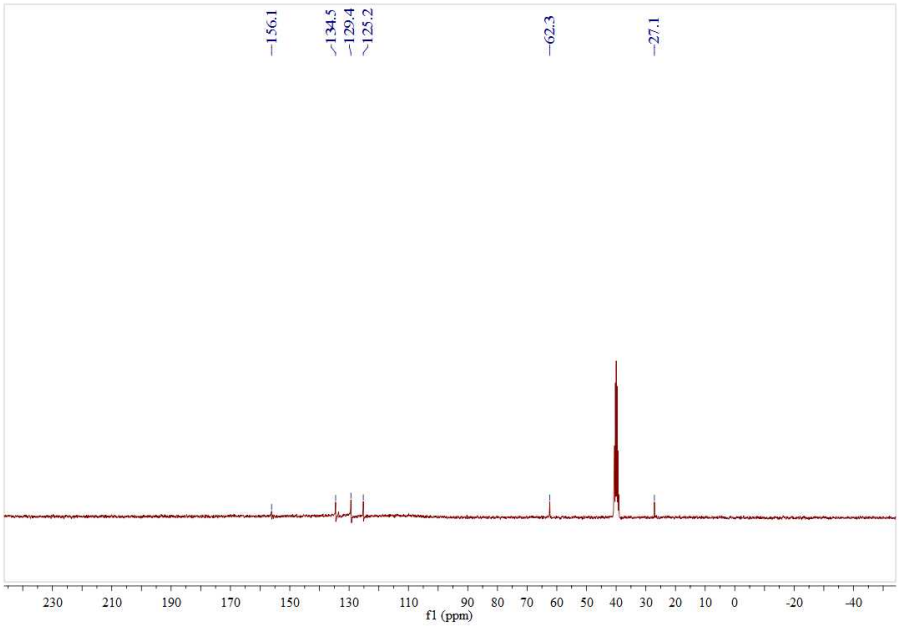
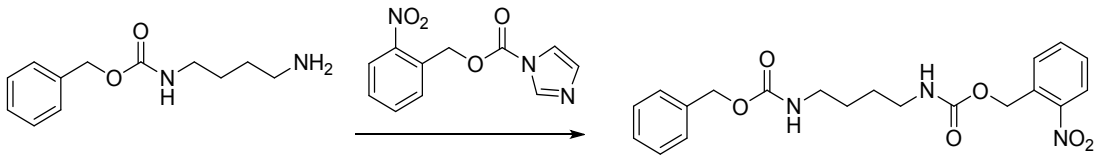


Fig. S13 ^{13}C NMR spectrum (75 MHz, DMSO-d_6, 298 K) of **G6**



Scheme S9. Synthetic route to **G7**

Synthesis of **G7**: **G7$_p$** (0.20g, 0.89 mmol) and **Gs** (0.22 g, 0.89 mmol) were added in DMSO (20 mL). The mixture was stirred at room temperature for 12 hours. The reaction mixture was washed by brine and extracted by ethyl acetate. The organic layer was dried by Na_2SO_4 and evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 40/1, *v/v*) to afford **G7** (0.20 g, 55.9 %). m.p. 117−119 °C. ^{1}H NMR (300 MHz, chloroform-*d*, 298 K) δ (ppm): 8.09 (d, J =8.06 Hz, 1H, ArH), 7.67−7.57 (m, 2H, ArH), 7.47 (t, J =7.56 Hz, 1H, ArH), 7.36−7.31 (m, 5H, ArH), 5.51 (s, 2H, CH_2), 5.10 (s, 2H, CH_2), 3.22 (s, 4H, CH_2), 1.56 (s, 4H, CH_2, overlapped with the solvent peak of water). ^{13}C NMR (75 MHz, chloroform-*d*, 298 K) δ (ppm): 156.5, 155.9, 133.7, 128.5, 128.1, 125.0, 667, 63.2, 40.7, 40.6, 27.2. LR-ESI-MS is: *m/z* calcd for $[M + H]^+$, 402.16, found 402.10; calcd for $[M + Na]^+$,

424.14, found 424.05. HR-ESI-MS is: *m/z* calcd for $[M + Na]^+$, $C_{20}H_{22}N_3O_6Na^+$, 424.1479, found 424.1479.

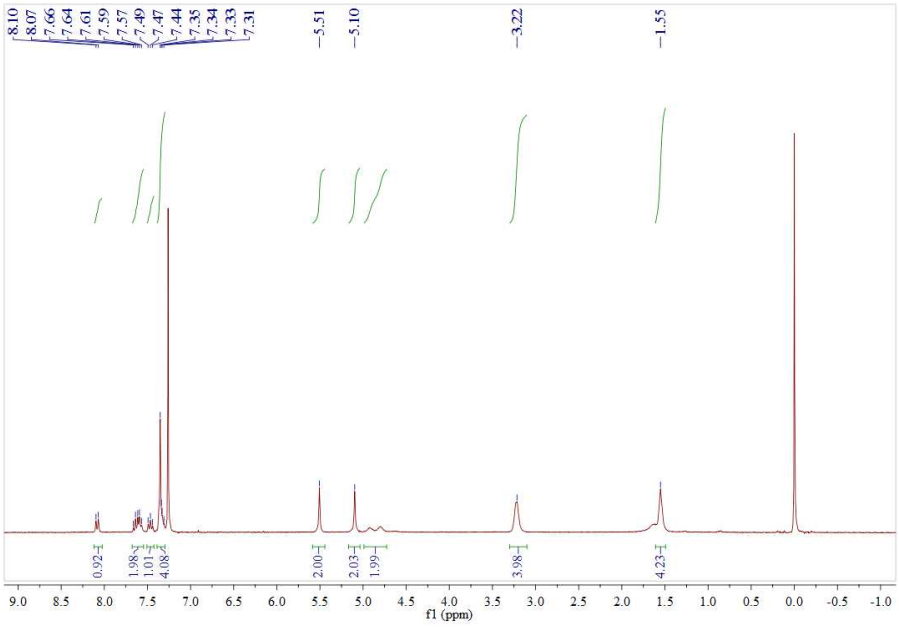


Fig. S14 ^{1}H NMR spectrum (300 MHz, chloroform-*d*, 298 K) of **G7**

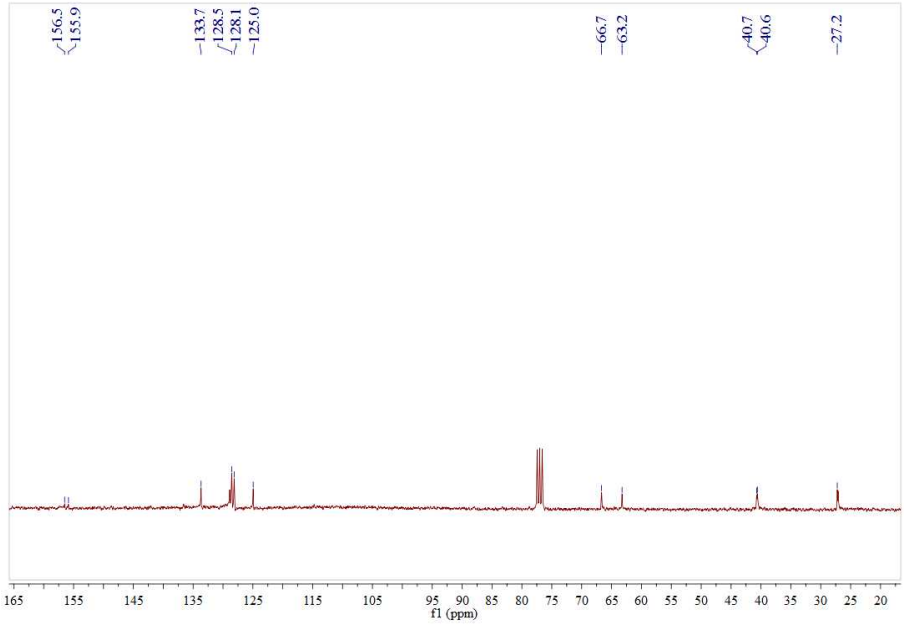


Fig. S15 ^{13}C NMR spectrum (75 MHz, chloroform-*d*, 298 K) of **G7**

3. *Investigation of the interactions between **EtP[5]**A and **Guest** by ^1H NMR*

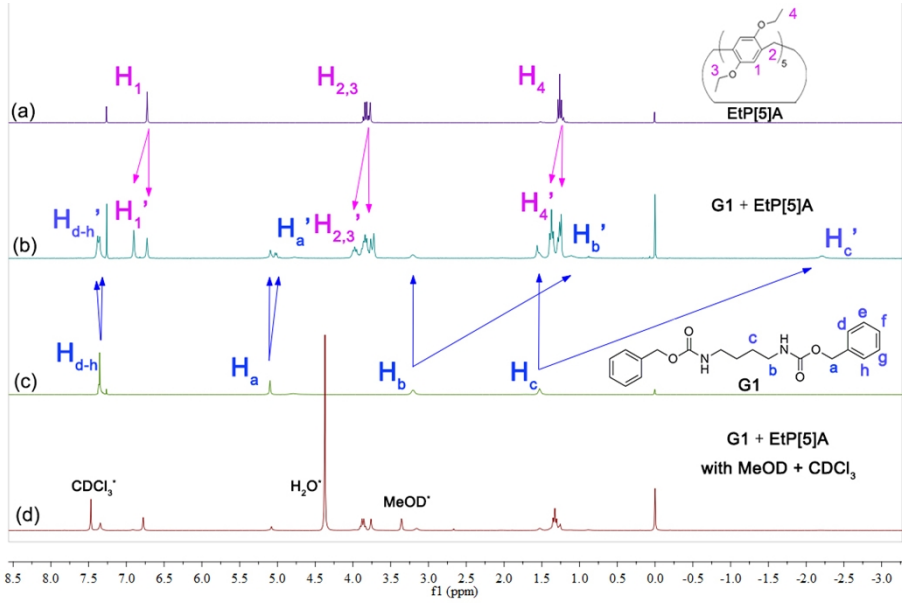


Fig. S16 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K): (a) **EtP[5]A** (2.5 mM); (b) equimolar mixture of **G1**(2.5 mM) and **EtP[5]A** (2.5 mM); (c) **G1** (2.5 mM) ; (d) 0.2 mL methanol-d_4 was added into the NMR tube with the mixture of **G1** (2.5 mM) and **EtP[5]A** (2.5 mM) in 0.5 mL chloroform-*d*. The association constant $K_{a,\mathbf{G1}\bullet\mathbf{EtP[5]A}}$ value calculated from integrations of complexed and uncomplexed peaks of H_1 of **EtP[5]A** is $[(2.09/3.63) \times 1.00 \times 10^{-3}]/[(1 - 2.09/3.63) \times 1.00 \times 10^{-3}]^2 = 1279\ M^{-1}$. The association constant $K_{a,G1\bullet EtP[5]A}$ value calculated from integrations of complexed and uncomplexed peaks of H_b of **G1** is $[(1.35/2.35) \times 2.50 \times 10^{-3}]/[(1 - 1.35/2.35) \times 2.50 \times 10^{-3}]^2 = 1269\ M^{-1}$. Therefore, $K_{a,\mathbf{G1}\bullet\mathbf{EtP[5]A}} = (1279 + 1269)/2 = (1274 \pm 5)\ M^{-1}$

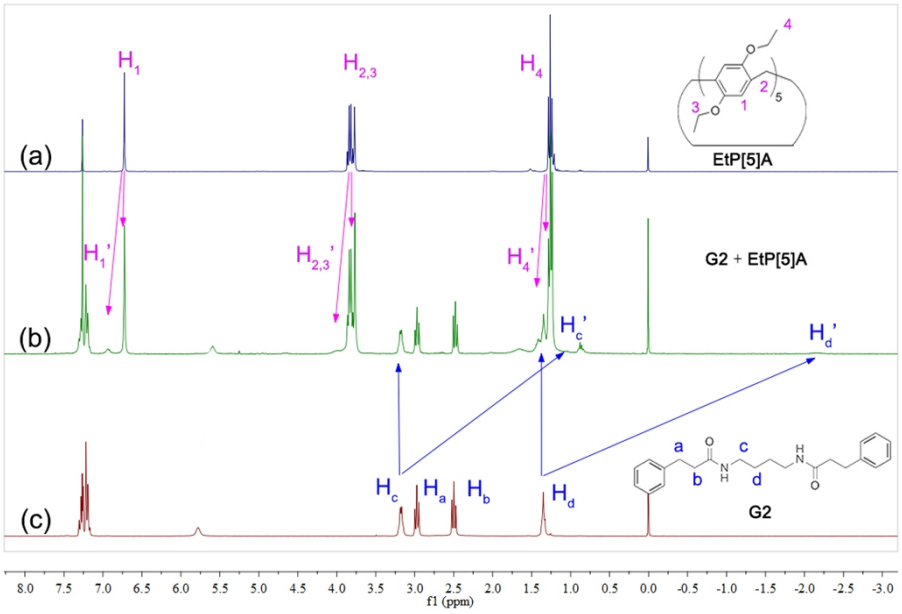


Fig. S17 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K): (a) **EtP[5]A** (2.5 mM); (b) equimolar mixture of **G2**(2.5 mM) and **EtP[5]A** (2.5 mM); (c) **G2** (2.5 mM) The association constant $K_{a,\mathbf{G2}\bullet\mathbf{EtP[5]A}}$ value calculated from integrations of complexed and uncomplexed peaks of H_1 of **EtP[5]A** is $[(0.16/1.16) \times 2.50 \times 10^{-3}]/[(1 - 0.16/1.16) \times 2.50 \times 10^{-3}]^2 = 74\ M^{-1}$. The association constant $K_{a,\mathbf{G2}\bullet\mathbf{EtP[5]A}}$ value calculated from integrations of complexed and uncomplexed peaks of H_c of **G2** is $[(0.08/0.61) \times 2.50 \times 10^{-3}]/[(1 - 0.08/0.61) \times 2.50 \times 10^{-3}]^2 = 69\ M^{-1}$. Therefore, $K_{a,\mathbf{G2}\bullet\mathbf{EtP[5]A}} = (74 + 69)/2 = (71.5 \pm 2.5)\ M^{-1}$

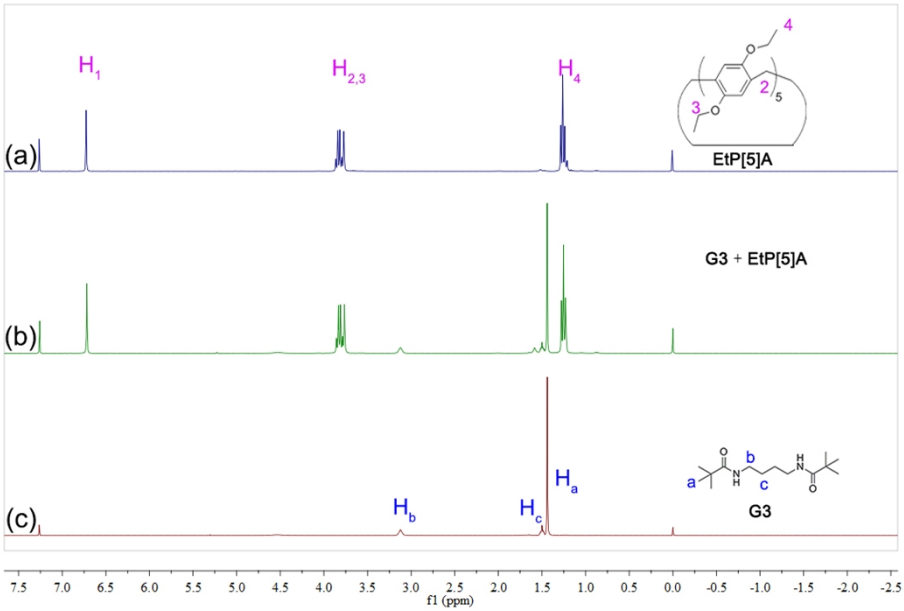


Fig. S18 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K): (a) **EtP[5]A** (2.5 mM); (b) equimolar mixture of **G3**(2.5 mM) and **EtP[5]A** (2.5 mM); (c) **G3** (2.5 mM)

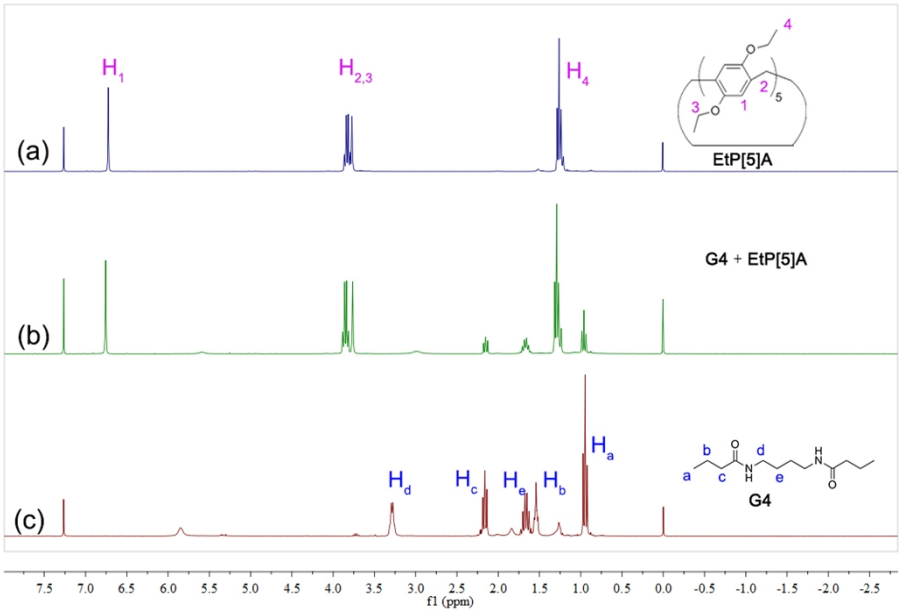


Fig. S19 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K): (a) **EtP[5]A** (2.5 mM); (b) equimolar mixture of **G4**(2.5 mM) and **EtP[5]A** (2.5 mM); (c) **G4** (2.5 mM)

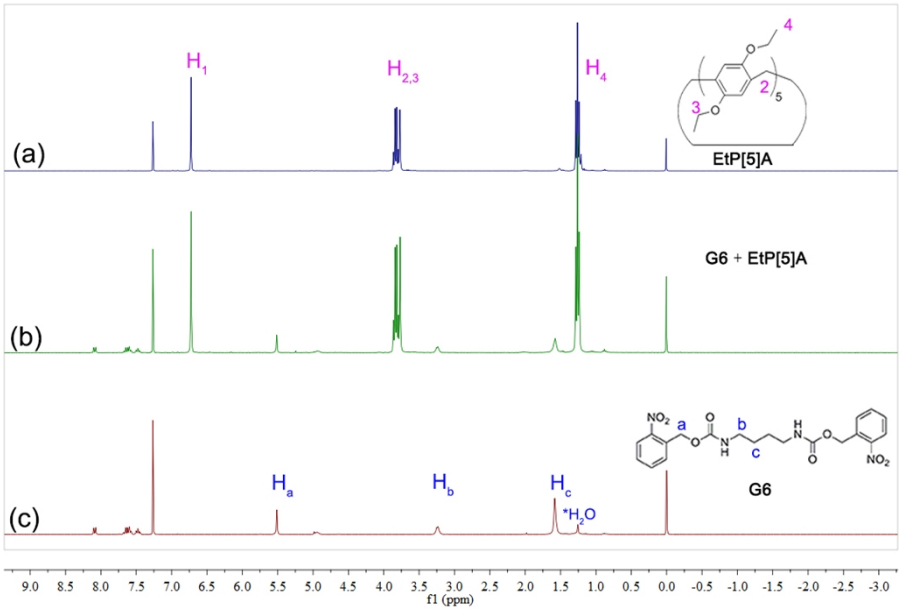


Fig. S20 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K): (a) **EtP[5]A** (2.5 mM); (b) equimolar mixture of **G6**(2.5 mM) and **EtP[5]A** (2.5 mM); (c) **G6** (2.5 mM)

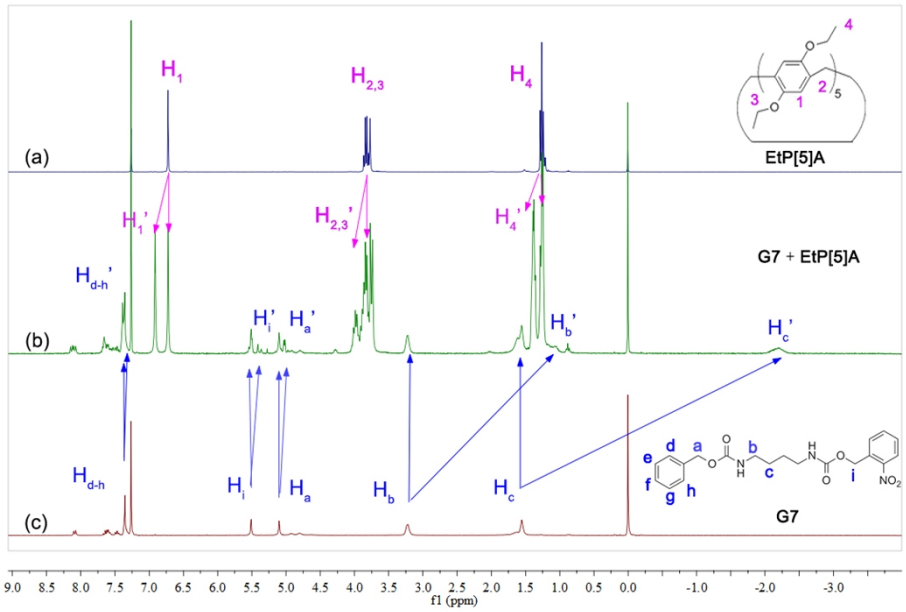


Fig. S21 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of (a) **EtP[5]A** (2.5 mM) ; (b) equimolar mixture of **G7**(2.5 mM) and **EtP[5]A** (2.5 mM); (c) **G7** (2.5 mM). The association constant $K_{a,\mathbf{G7}\bullet\mathbf{EtP[5]A}}$ value calculated from integrations of complexed and uncomplexed peaks of H_1 of **EtP[5]A** is $[(1.05/2.05) \times 2.50 \times 10^{-3}]/[(1 - 1.05/2.05) \times 2.50 \times 10^{-3}]^2 = 861\ M^{-1}$. The association constant $K_{a,\mathbf{G7}\bullet\mathbf{EtP[5]A}}$ value calculated from integrations of complexed and uncomplexed peaks of H_b of **G7** is $[(0.49/0.96) \times 2.50 \times 10^{-3}]/[(1 - 0.49/0.96) \times 2.50 \times 10^{-3}]^2 = 851\ M^{-1}$. Therefore, $K_{a,\mathbf{G7}\bullet\mathbf{EtP[5]A}} = (861 + 851)/2 = (856 \pm 5)\ M^{-1}$

4. *Partial 2D NOSEY NMR spectra of **G1⊂EtP[5]A***

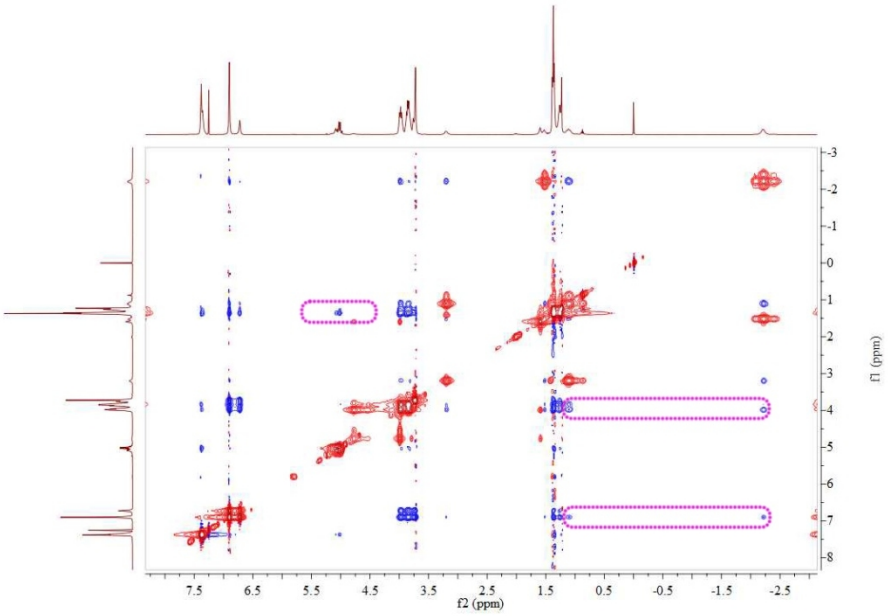


Fig. S22 2D NOSEY analysis of equimolar mixture **G1⊂EtP[5]A** in $CDCl_3$ (20 mM, 400 MHz, 298 K)

5. *Study of the photocleavage **G7⊂EtP[5]A** via UV 365nm by ^{1}H NMR*

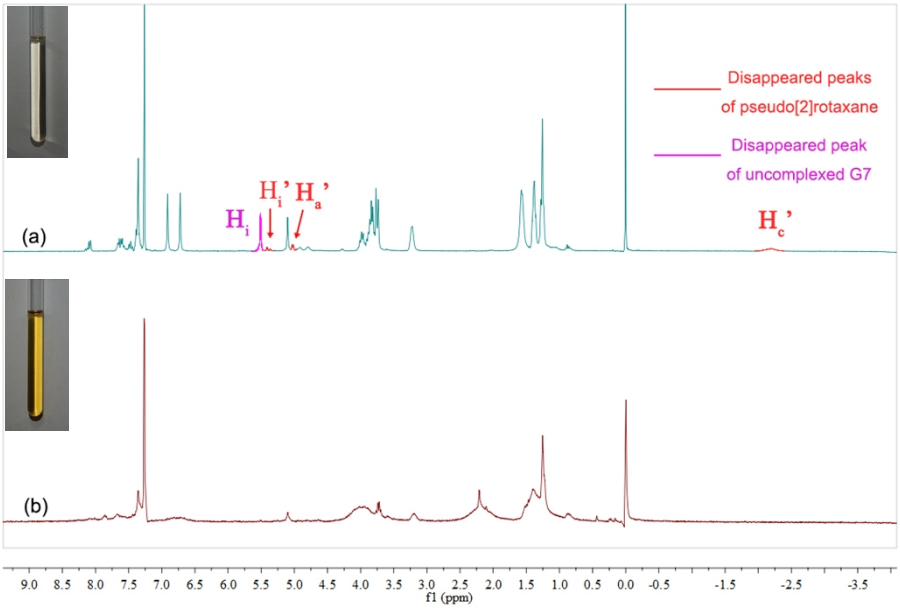


Fig. S23 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of (a) **G7⊂ EtP[5]A** (1 : 1, 2.5mM) in the absence (b) **G7⊂ EtP[5]A** (1 : 1, 2.5mM)after UV 365 nm .

6. *Reference*

S1. D. R. Cao, Y. H. Kou, J. Q. Liang, Z. Z. Chen, L. Y. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721.