A pillar[5]arene/imidazolium [2]rotaxane: solvent- and thermo-driven molecular motions and supramolecular gel formation

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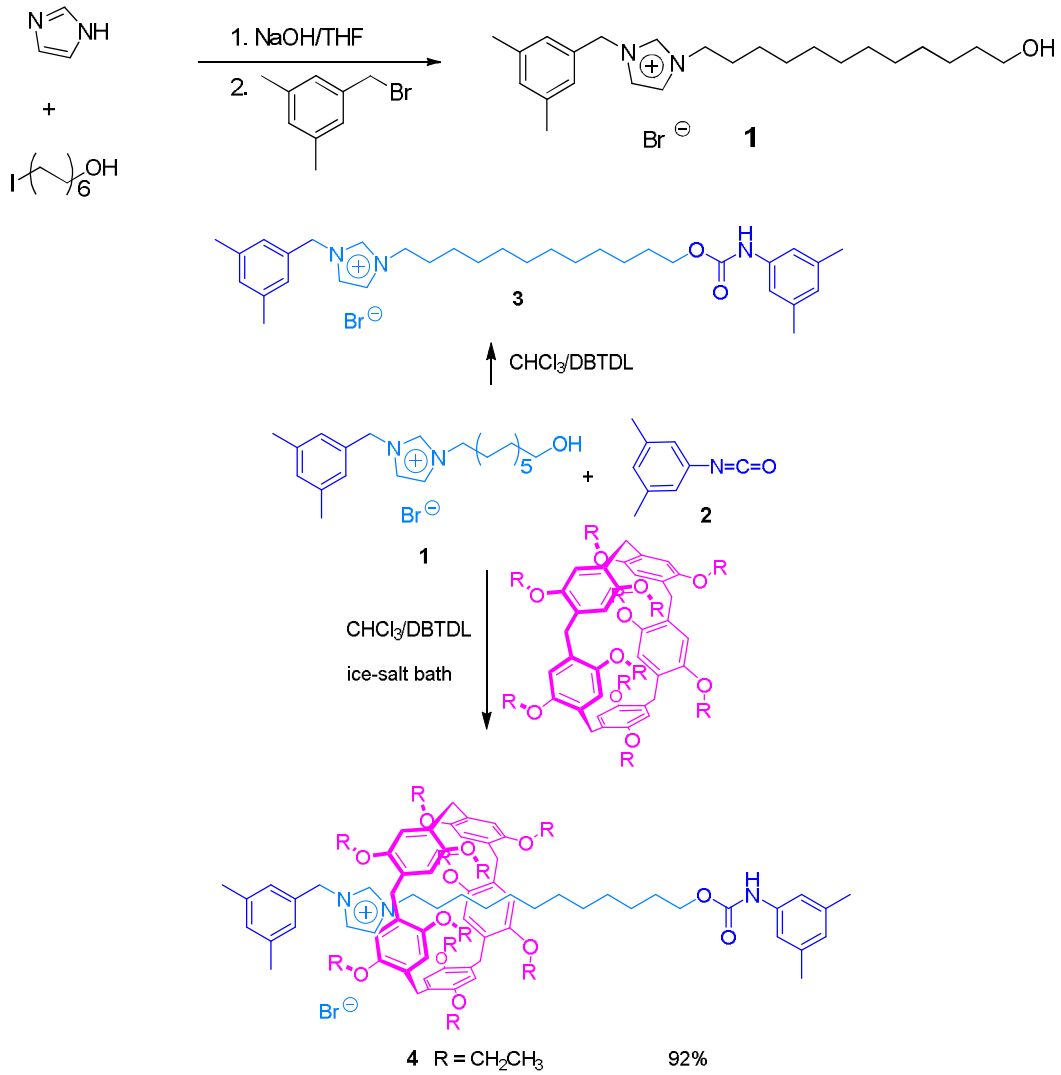
Electronic Supplementary Information

1. Materials and methods

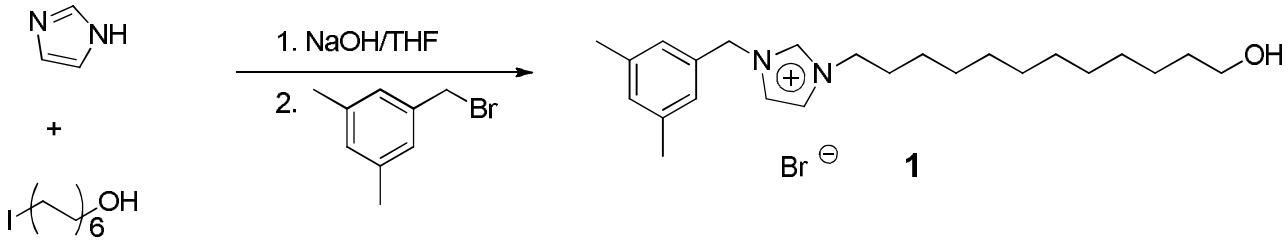
All reagents were commercially available and used as supplied without further purification. 1,4-Diethoxypillar[5]arene (**DEP5**) was prepared according to the published procedures.[S1,S2] ^{1}H NMR spectra were collected on a temperature-controlled 400 or 600 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument operating at an energy of 15 Kev or 20 Kev.

2. Synthesis of [2]rotaxanes

Scheme S1. Synthesis of [2]rotaxane **4** and the corresponding dumbbell-shaped component **3**



*2.1. Synthesis of compound **1***



1*H*-imidazole (0.680 g, 10.0 mmol)，NaOH (0.400 g, 10.0 mmol) and 12-iodododecan-1-ol (3.12 g, 10.0 mmol) in THF (125 mL) were refluxed for 24 hours. After filtration, the solvent was removed to yield a white solid. This white solid and 1-(bromomethyl)-3,5-dimethylbenzene (1.98 g, 10.0 mmol) were refluxed in CH_3CN (100 mL) for 24 hours. After filtration, the residue was dried by air to afford **1** as a white solid (3.02 g, 67% for two steps), mp 86.1–88.0 °C. The ^{1}H NMR spectrum of compound **1** is shown in Figure S1. ^{1}H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 10.87 (s, 1H), 7.17 (s, 1H), 7.12 (s, 1H), 7.03 (s, 3H), 5.50 (s, 2H), 4.33 (d, J = 8.0 Hz, 2H), 3.65 (d, J = 8.0 Hz, 2H), 2.32 (s, 6H),1.57 (m, 2H), 1.34–1.26 (m, 16H). The ^{13}C NMR spectrum of **1** is shown in Figure S2. ^{13}C NMR (125 MHz, DMSO-d_6, room temperature) δ (ppm): 139.26, 139.21, 137.31, 132.61, 131.19, 131.14, 126.71, 126.65, 122.26, 121.65, 121.54, 62.88, 53.51, 53.43, 50.25, 32.75, 30.22, 30.07, 29.39, 29.30, 29.28, 29.27, 29.22, 28.86, 28.47, 26.22, 25.93, 25.68, 21.20. LRESIMS is shown in Figure S3: *m*/*z* 371.4 $[M - Br]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M - Br]^+$ $C_{24}H_{39}N_2O_1^+$, 371.3057, found 371.3074, error –5 ppm.

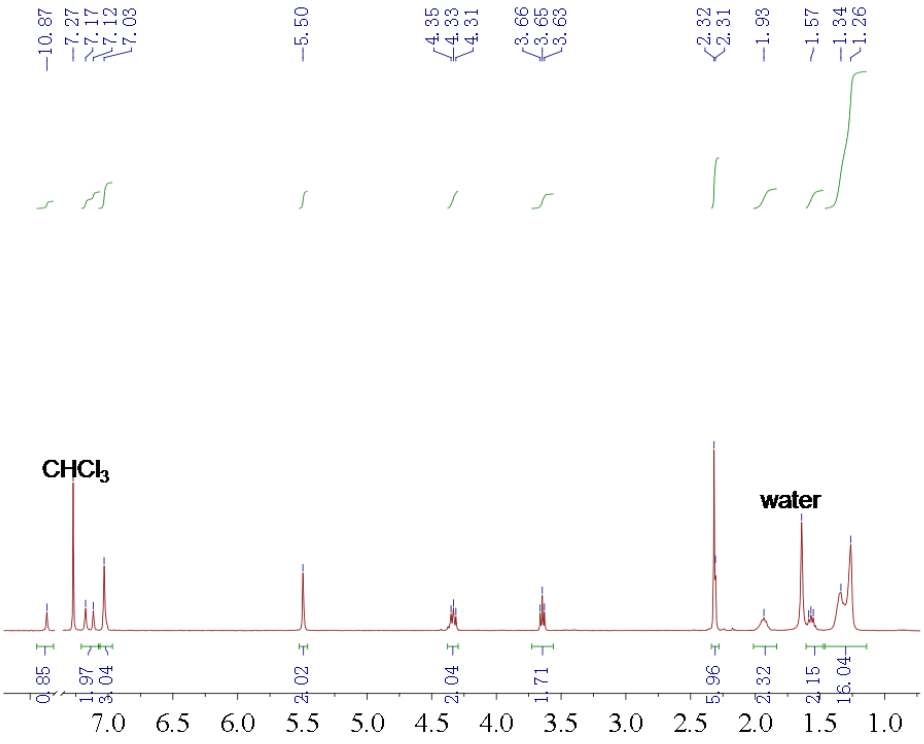


Figure S1. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **1**.

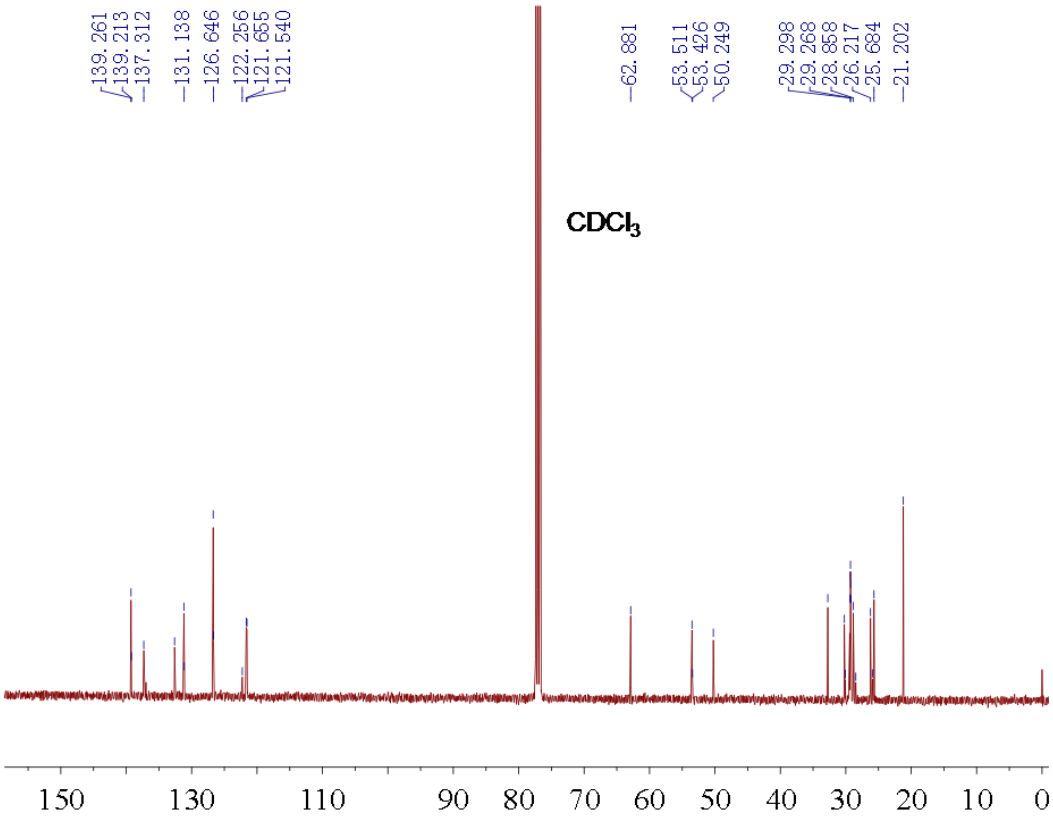


Figure S2. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, room temperature) of **1**.

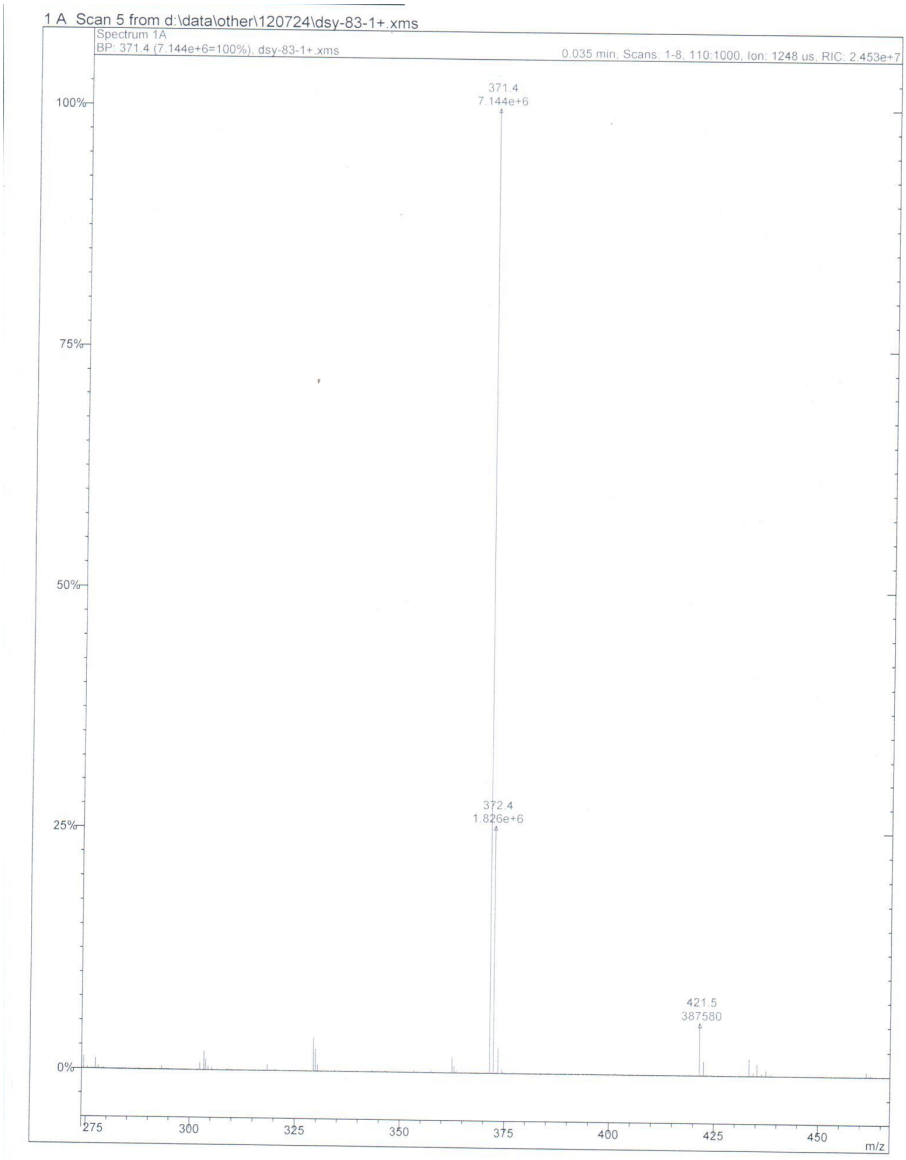
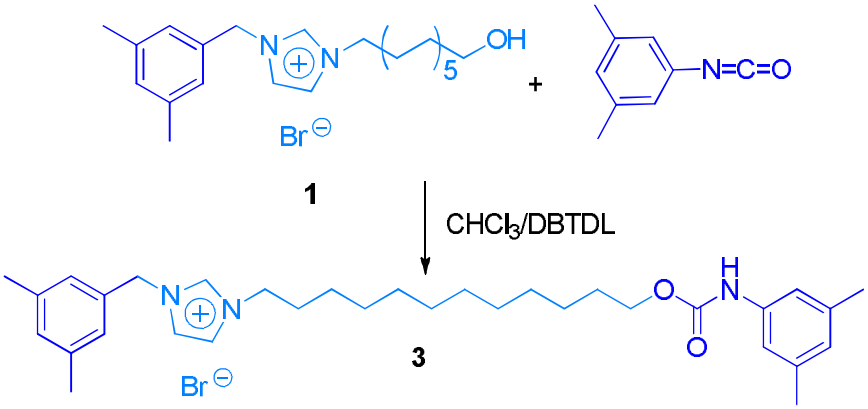


Figure S3. Electrospray ionization mass spectrum of **1**.

2.2. Synthesis of compound ***3***



A mixture of **1** (2.25 g, 5.00 mmol), DBTDL (dibutyltindilaurate, one drop) and 1-isocyanato-3,5-dimethylbenzene (1.47 g, 10.0 mmol) in $CHCl_3$ (0.5 mL) was stirred for 48 hours at room temperature. After filtration and solvent evaporation, the crude product was purified by flash column chromatography (CH_2Cl_2/MeOH, 10:1, *v/v*) to yield compound **3** as a white solid (2.45 g, 82%), mp: 117.2–119.1ºC. The ^{1}H NMR spectrum of compound **3** is shown in Figure S4. ^{1}H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 10.78 (s, 1H), 7.20 (s, 1H), 7.14 (s, 1H), 7.03 (s, 4H), 6.70 (s, 1H), 6.58 (s, 1H), 5.49 (s, 2H), 4.32 (d, J = 8.0 Hz, 2H), 4.14 (d, J = 8.0 Hz, 2H), 2.32 (s, 6H), 2.29 (s, 6H), 1.92 (m, 2H), 1.63 (m, 2H), 1.33–1.26 (m, 16H). The ^{13}C NMR spectrum of **3** is shown in Figure S5. ^{13}C NMR (125 MHz, CD_3SOCD_3, room temperature) δ (ppm): 153.98, 139.37, 138.55, 138.00, 136.35, 135.04, 130.45, 126.25, 124.25, 123.08, 122.94, 116.29, 64.34, 52.27, 49.31, 29.55, 29.28, 29.21, 29.02, 28.88, 28.67, 25.83, 25.69, 21.47, 21.16. LRESIMS is shown in Figure S6: *m/z* 518.5 $[M - Br]^+$ (100%). HRESIMS: *m/z* calcd for $[M - Br]^+$ $C_{33}H_{48}N3O_2^+$, 518.3741, found 518.3752, error –2 ppm.

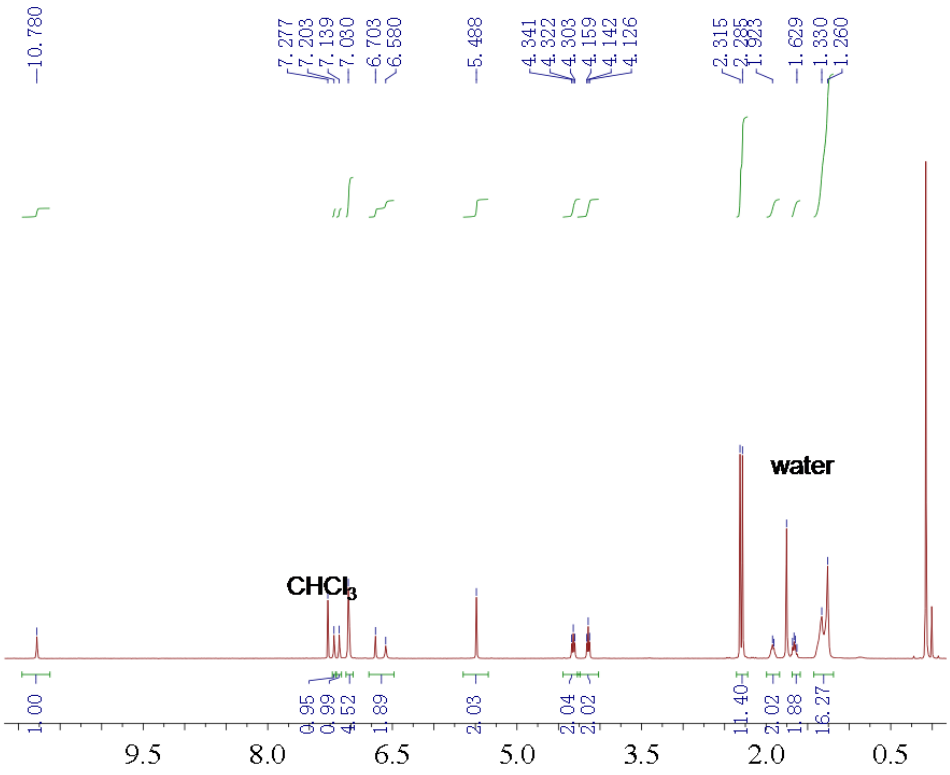


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **3**.

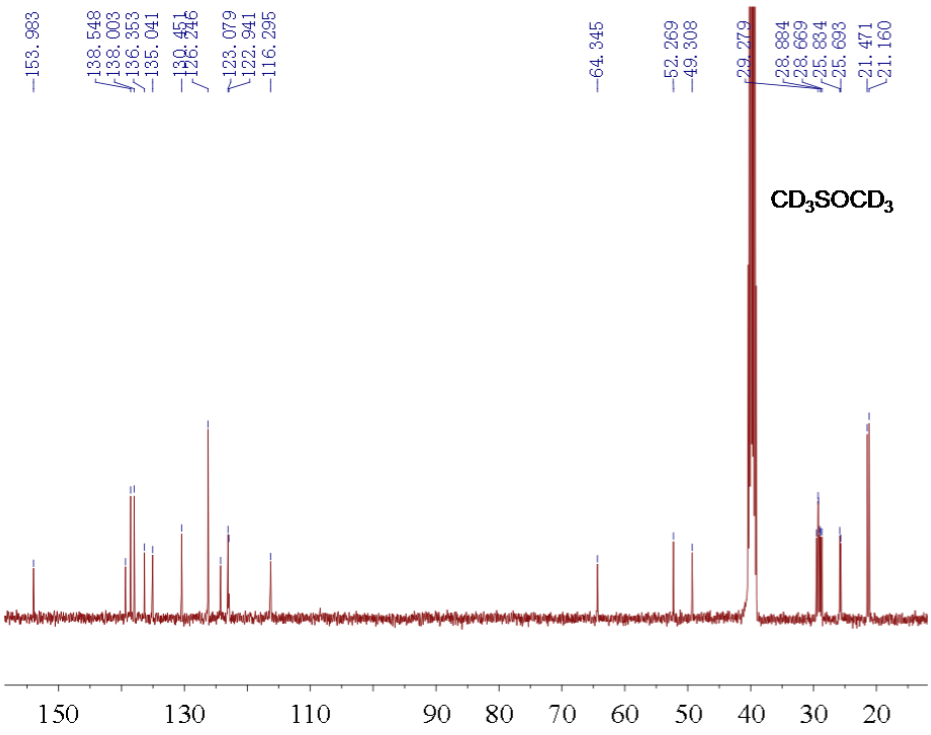


Figure S5. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, room temperature) of **3**.

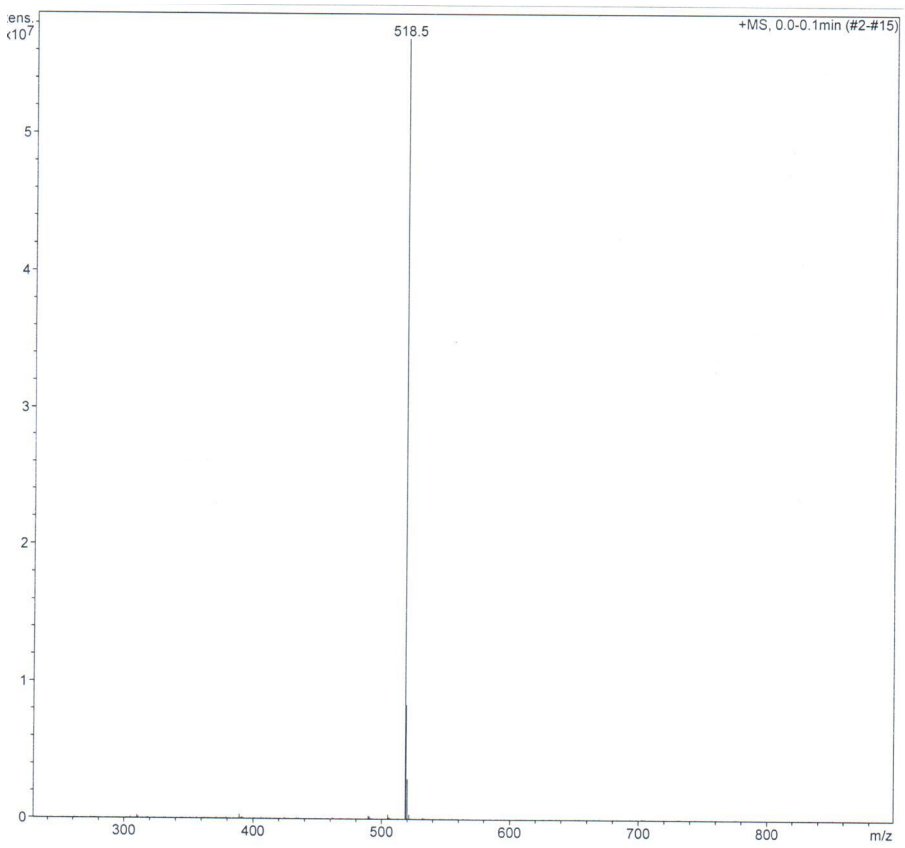
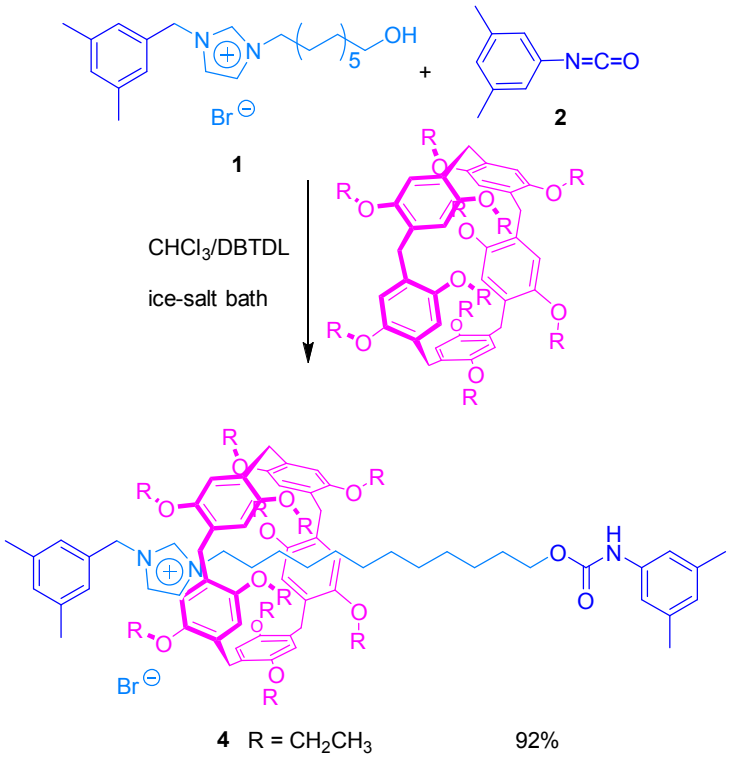


Figure S6. Electrospray ionization mass spectrum of **3**.

*2.3. Synthesis of [2]rotaxanes **4***



4 R = CH_2CH_3 92%

A mixture of **1** (0.100 g, 0.220 mmol) and **DEP5** (0.500 g, 0.480 mmol) was stirred in $CHCl_3$ (0.3 mL) in an ice-salt bath for 2 h. Then DBTDL (one drop) and **2** (0.500 g, 2.00 mmol) were added. The mixture was further stirred for 3 hours. The solvent was removed and the residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 100/1, *v*/*v*) to afford **4** as a white solid (0.300 g, 92%), mp: 132.7–135.1 ºC. The ^{1}H NMR spectrum of compound **4** is shown in Figure S7. ^{1}H NMR (400 MHz, chloroform-*d*, 298 K) δ (ppm): 8.04 (s, 1H), 7.43(s, 2H), 7.36 (s, 1H), 7.08 (s, 3H), 6.96 (s, 5H), 6.79 (s, 5H), 6.74 (s, 1H), 6.59 (s, 1H), 6.04 (s, 1H), 5.77 (d, J = 12.0 Hz, 1H), 5.41 (d, J = 12.0 Hz, 1H), 4.06 (m, 7H), 3.92 (m, 6H), 3.81 (m, 16H), 3.73 (s, 3H), 3.70 (s, 2H), 2.43 (s, 6H), 2.32 (s, 6H), 1.50 (t, J = 8.0 Hz, 15H), 1.36 (t, J = 8.0 Hz, 15H), 1.29 (m, 10H), 0.99 (m, 2H), 0.89 (m, 2H), 0.45 (m, 2H), –0.40 (m, 2H), –1.23 (m, 2H). The ^{13}C NMR spectrum of **4** is shown in Figure S8. ^{13}C NMR (125 MHz, chloroform-*d*, 298 K) δ (ppm): 153.72, 150.35, 149.68, 149.59, 149.33, 139.15, 138.67, 138.03, 133.12, 132.87, 131.22, 129.93, 128.97, 126.97, 124.96, 121.68, 121.51, 116.33, 114.76, 65.68, 65.12, 63.84, 52.97, 47.97, 31.92, 31.07, 30.54, 30.27, 29.86, 29.69, 29.51, 29.22, 28.84, 28.63, 27.01, 26.59, 25.47, 22.68, 21.39, 21.33, 15.53, 15.44, 14.11. LRESIMS of **4** is shown in Figure S9: *m*/*z* 1409.0 $[M-Br]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M-Br]^+$ $C_{88}H_{118}N_3O_{12}^+$, 1408.8691; found 1408.8710, error 1 ppm.

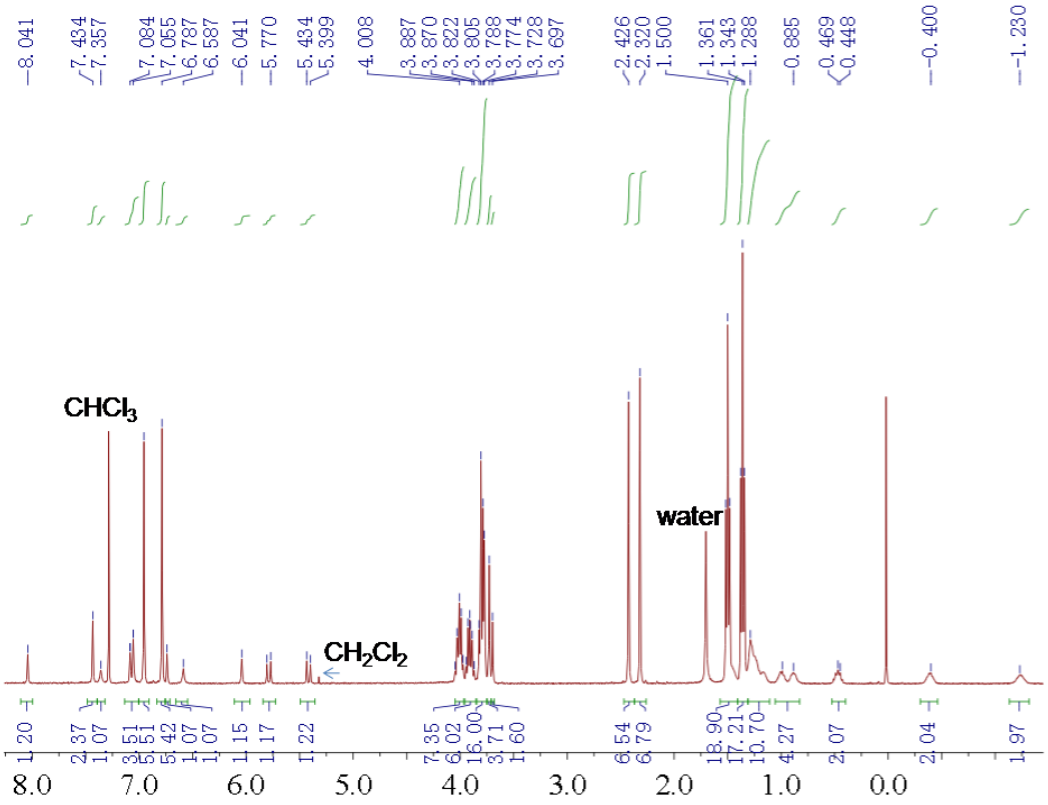


Figure S7. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, room temperature) of **4**.

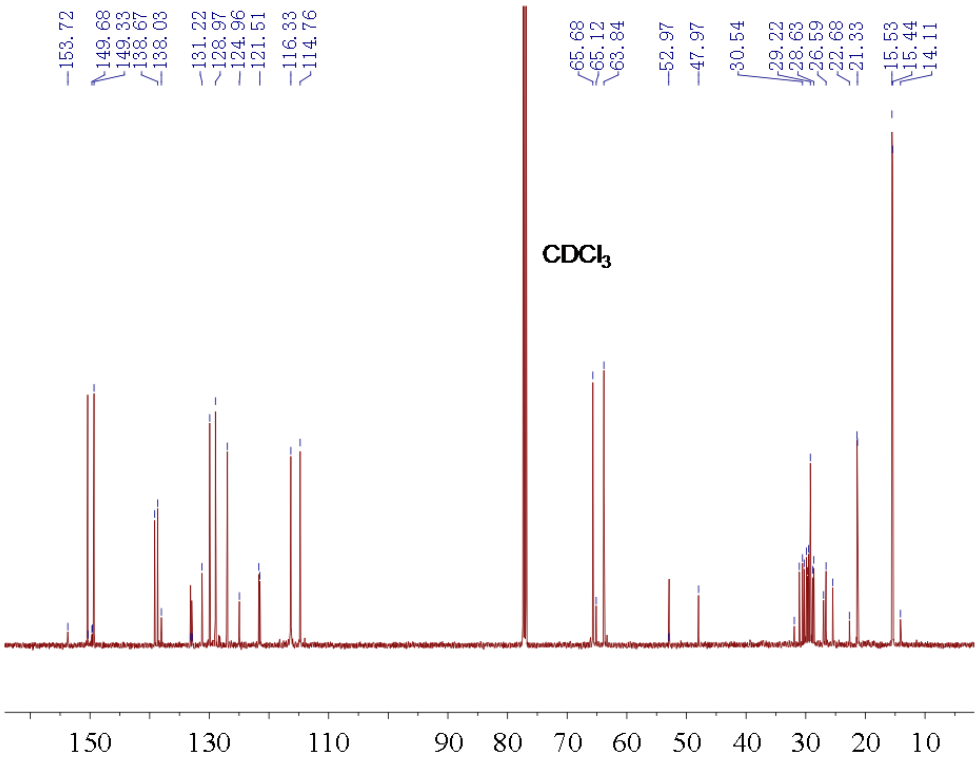


Figure S8. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, room temperature) of **4**.

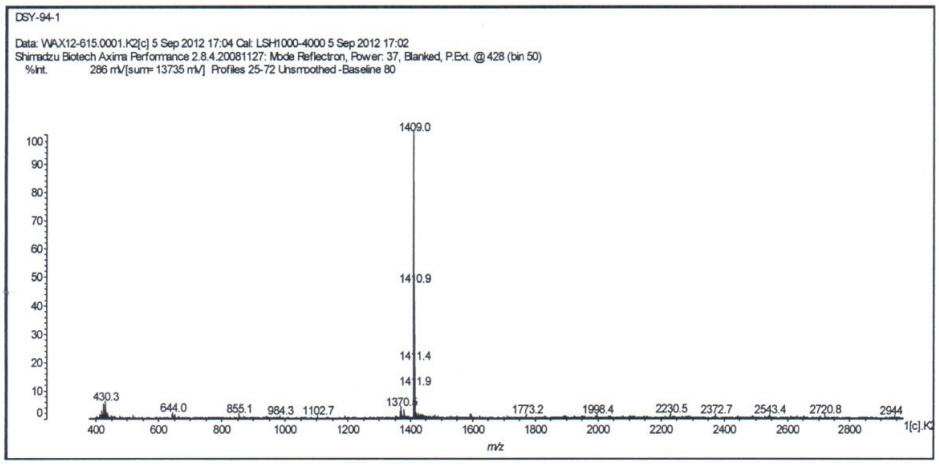


Figure S9. Electrospray ionization mass spectrum of **4**.

*3. Partial COSY NMR spectrum of [2]rotaxane **4***

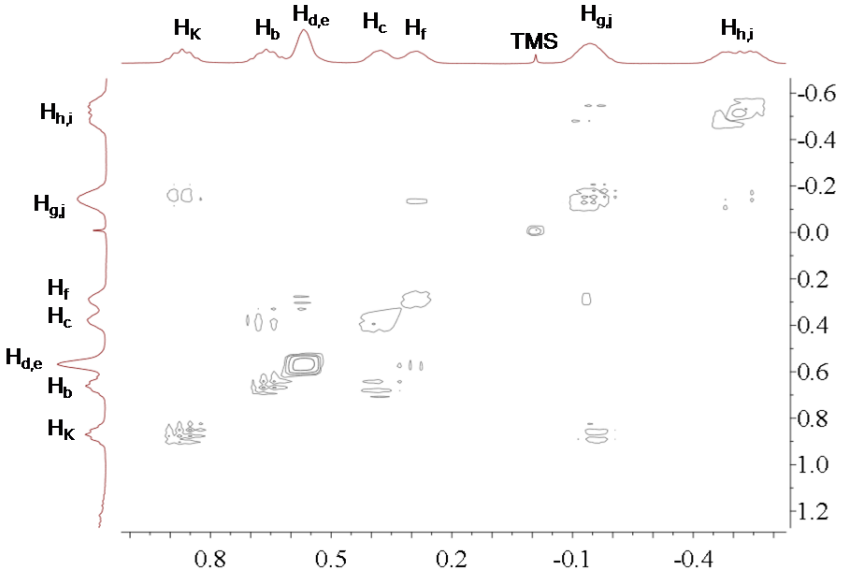


Figure S10. Partial COSY NMR spectrum (400 MHz, DMSO-d_6, 25 mM) of [2]rotaxane **4**.

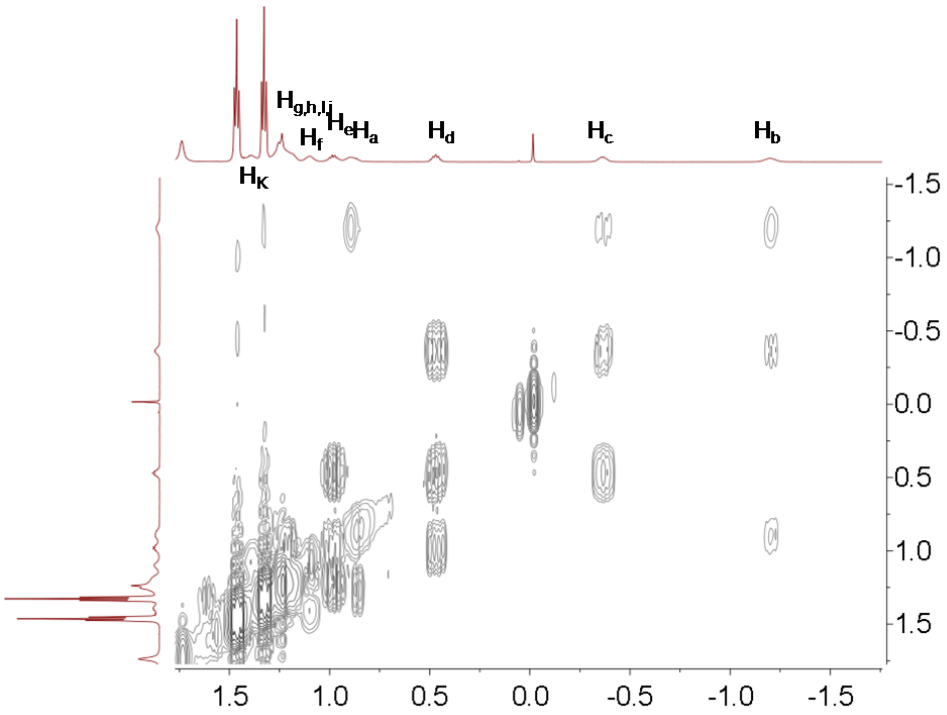


Figure S11. Partial COSY NMR spectrum (400 MHz, chloroform-*d*, 25 mM) of [2]rotaxane **4**.

*4. Partial NOESY spectrum of [2]rotaxane **4***

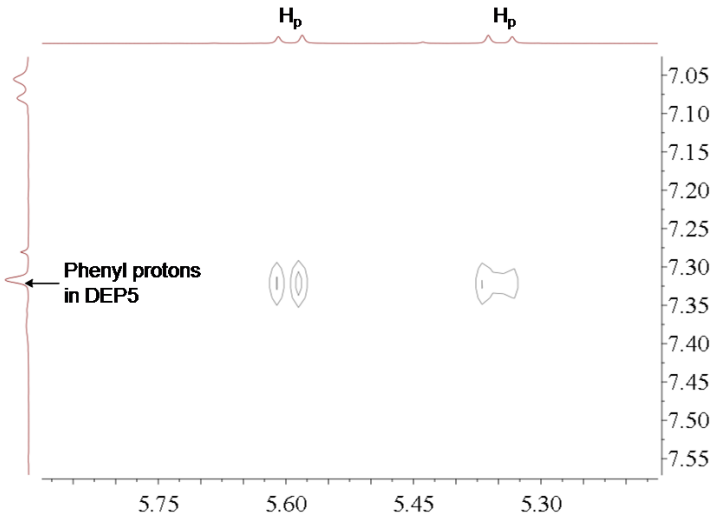


Figure S12. Partial NOESY spectrum (600 MHz, chloroform-*d*, 25 mM) of [2]rotaxane **4**. Due to the shielding effect of the pillar[5]arene ring, the signal of protons H_p split into two peaks. However, in DMSO-d_6, the pillararene ring was far away from the imidazolium part so the signal of H_p showed only one peak.[S2]

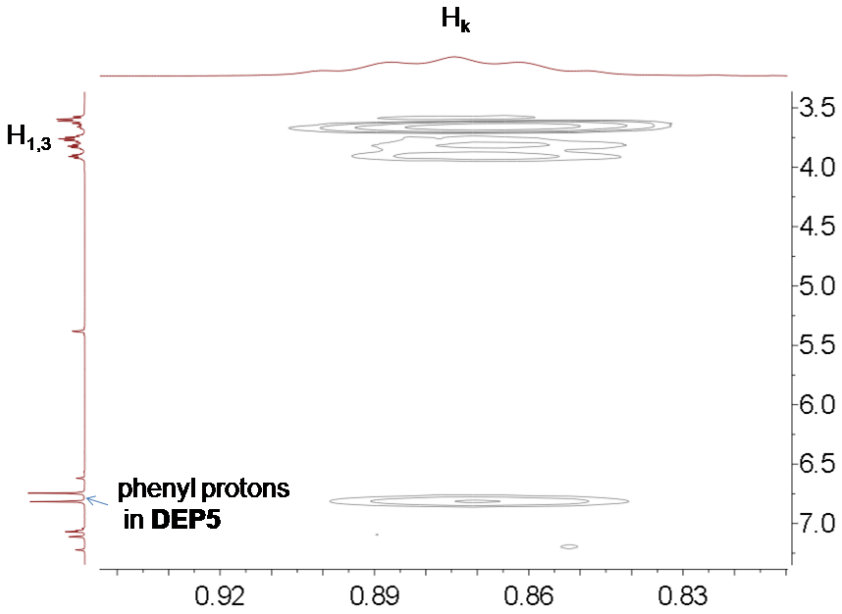


Figure 13. Partial NOESY spectrum (600 MHz, DMSO-d_6, 25 mM) of [2]rotaxane **4**. In DMSO-d_6, the pillar[5]arene ring was located on the methylene groups of the alkyl chain which were far away from the imidazolium part. Due to the asymmetric structure of the dumbbell-shaped component, the signal of phenyl protons of the pillar[5]arene ring split into two peaks, which was consistent with the ^{1}H NMR and NOESY spectra of a [2]rotaxane constructed by pillar[5]arene/alkyl chain molecular recognition.[S2]

5. Solvent-dependent chemical shifts of H^a and H^k

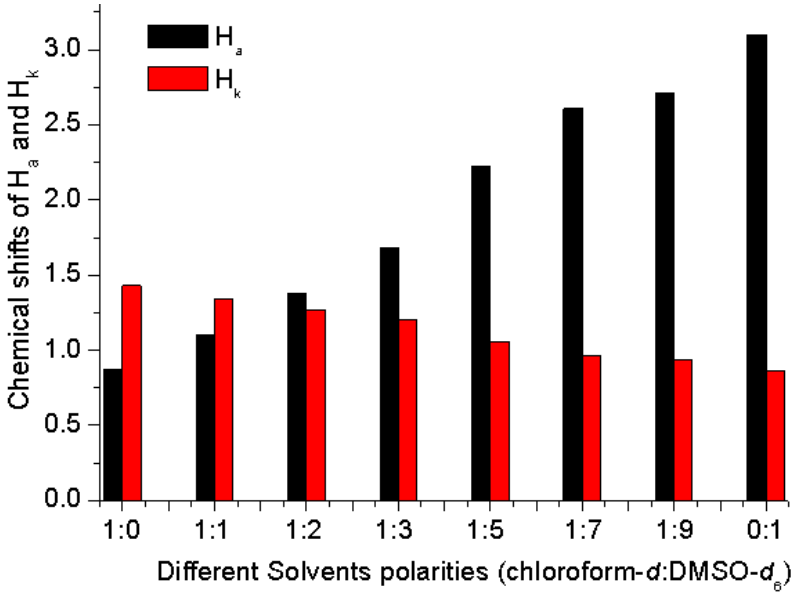


Figure 14. Solvent-dependent chemical shifts of H_a and H_k on [2]rotaxane **4**.

6. Gel properties and a possible gelation mechanism

[2]Rotaxane **4** formed transparent supramolecular gels in DMSO or DMSO/water (about 5:1 in *v: v*) while dumbbell-shaped component **3** itself could not form supramolecular gels under same conditions. These supramolecular gels (in DMSO) were quite stable. The critical gelation concentration for **4**/DMSO at room temperature was about 9.5 wt%. In DMSO, for gelator **4**, its imidazolium unit is solvophilic while the rest is solvophobic. Furthermore, in DMSO, the pillar[5]arene ring was far away from the imidazolium unit. Therefore, gelator **4** is an amphiphilic molecule in DMSO. Due to the electrostatic interactions between organic salts, the π-π stacking interactions among the phenylene rings of the pillar[5]arene rings, and van der Waals forces between long alkyl chains, gelator **4** formed one dimensional supramolecular arrays. These one-dimensional arrays subsequently self-organized to form a physically cross-linked network which acted as the matrix for the supramolecular gel. By entrapping the solvent molecules into this network, the supramolecular gel finally formed. Considering the difference of gelation properties between [2]rotaxane **4** and dumbbell-shaped component **3**, it was reasonable that the pillar[5]arene ring played a crucial role in the formation of gels. The introduction of the pillar[5]arene ring made the alkyl chain more rigid, which was helpful for the formation of the framework for gels. Another possible reason was that there would be additional interactions between the aromatic rings of different pillar[5]arene units.[S3]

References:

S1. T. Ogoshi, K. Kitajima, T. Aoki, S. Fujinami, T-a, Yamagishi and Y. Nakamoto, *J. Org. Chem*. 2010, **75**, 3268–3273.

S2. S. Dong, C. Han, B. Zheng, M. Zhang and F. Huang, *Tetrahedron Lett.* 2012, **53**, 3668–3671

S3. S. Dong, B. Zheng, D. Xu, X. Yan, M. Zhang and F. Huang, *Adv. Mater.* 2012, **24**, 3191–3195.