Electronic Supplementary Material (ESI) for ChemComm.

Supramolecular Calix[4]pyrrole Polymers from a Complementary Pair of Homoditopic Host-Guest Molecules

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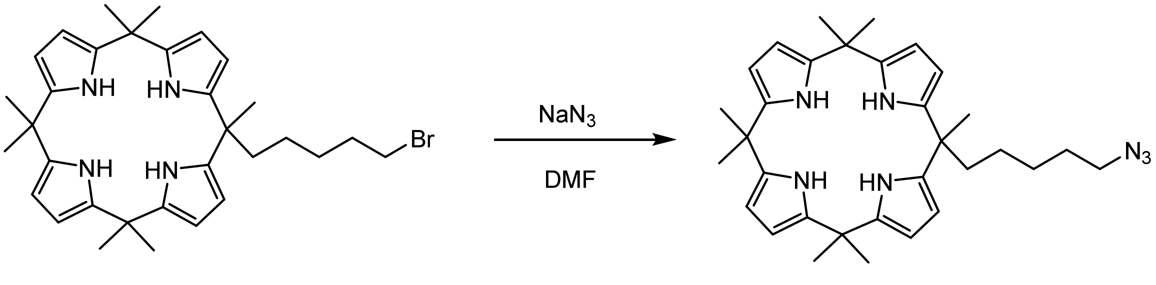
Contents

General Considerations

All solvents were dried before use according to standard procedures. Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were recorded on Agilent VNMRS 500 spectrometers using TMS as an internal reference. DOSY NMR spectra were recorded on a Bruker Ascend 500 MHz spectrometer. Mass spectra were measured on a Thermo Scientific Thermo Q Exactive HR mass spectrometer equipped with a LC unit. Viscosity measurements were carried out with an Ubbelohde micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 293 K in chloroform. Melting points were determined using a Gallenkamp instrument with 1 °C/min. temperature increment under ambient conditions. Compounds **6** was synthesized according to previously reported literature procedures.[1]

Synthesis and Characterization

Compound 5



4 **5**

To a solution of **4**[2] (1.15 g, 2.04 mmol) dissolved in 50 mL DMF, NaN_3 (605 mg, 10.2 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 24h while keeping from light. After the reaction was complete, DMF was removed under vacuum. The resulting crude material was dissolved in CH_2Cl_2 and washed with water three times. The organic layer was dried over Na_2SO_4 and the solvent was removed under vacuum, yielding the calix[4]pyrrole **5** as a light brown solid (960 mg, 98%). M.p.: decomposes over 208 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.10-1.13 (m, 2H, –C*H*$_2$–), 1.25-1.29 (m, 2H, –C*H*$_2$–), 1.41-1.53 (br m, 23H, *meso*–C*H*$_3$ and –C*H*$_2$–), 1.78-1.82 (m, 2H, –C*H*$_2$–), 3.17 (t, *J* = 8 Hz, 2H, –C*H*$_2$–), 5.88 (s, 8H, pyrrole–C*H*), 7.00 (br, 4H, NH). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.4, 137.3, 103.7, 102.8, 51.3, 40.4, 38.7, 35.2, 29.1, 27.0, 23.8. HRMS (ESI): m/z calcd for $C_{32}H_{44}N_7$ $[M+H]^+$: 526.36527; found: 526.36537.

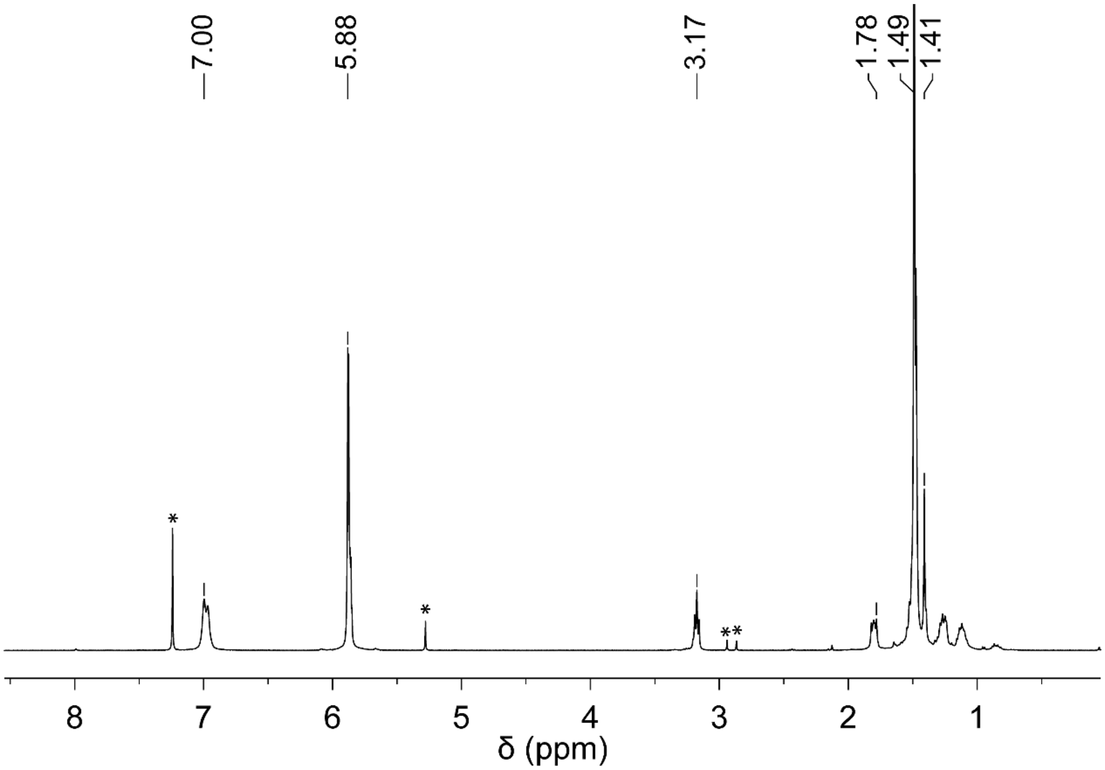


Figure S1. ^{1}H NMR spectrum of **4** recorded in $CDCl_3$ at 25 °C (* denotes solvent residual peaks).

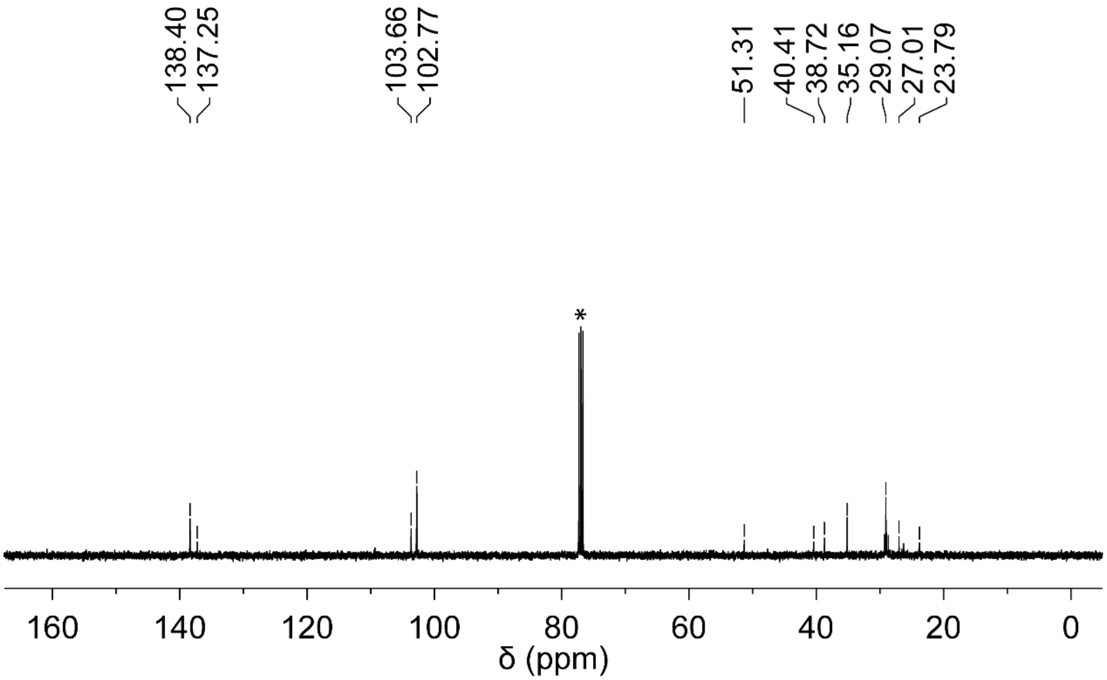


Figure S2. ^{13}C NMR spectrum of **4** recorded in $CDCl_3$ at 25 °C.

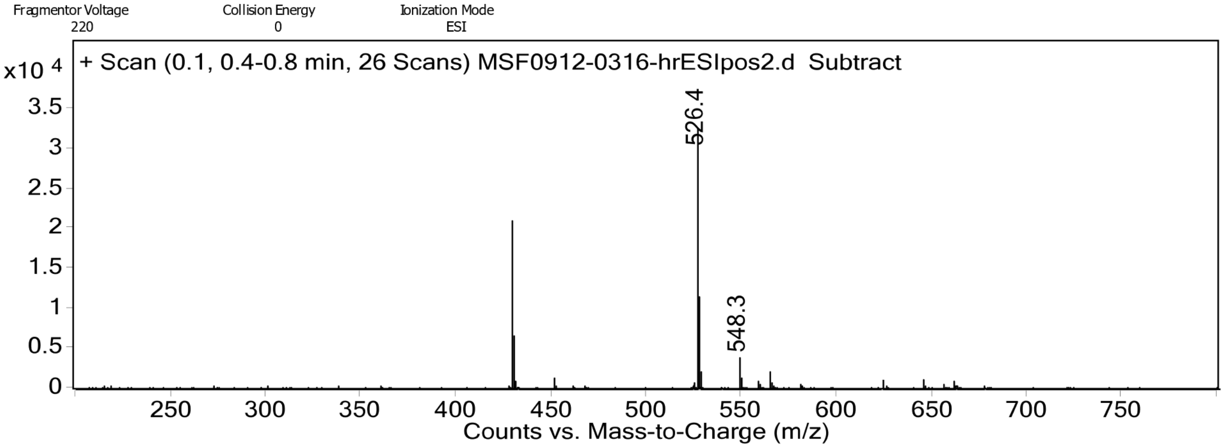
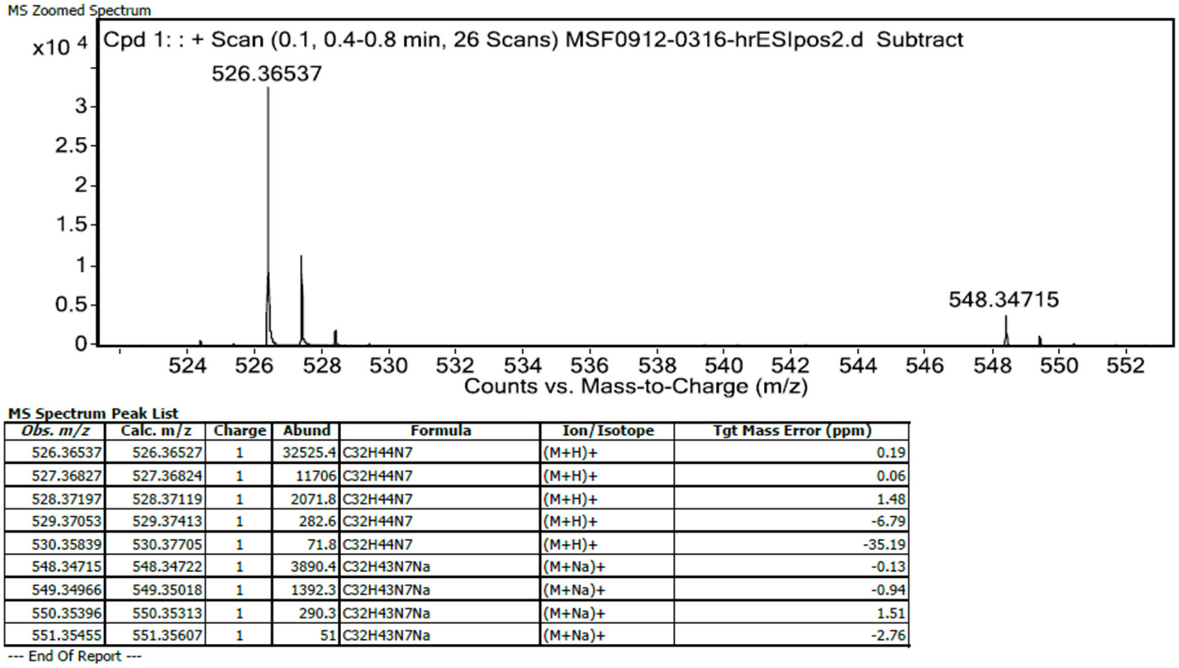


Figure S3. LRMS spectrum of **4**.



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
526.36537	526.36527	1	32525.4	C32H44N7	(M+H)+	0.19
527.36827	527.36824	1	11706	C32H44N7	(M+H)+	0.06
528.37197	528.37119	1	2071.8	C32H44N7	(M+H)+	1.48
529.37053	529.37413	1	282.6	C32H44N7	(M+H)+	-6.79
530.35839	530.37705	1	71.8	C32H44N7	(M+H)+	-35.19
548.34715	548.34722	1	3890.4	C32H43N7Na	(M+Na)+	-0.13
549.34966	549.35018	1	1392.3	C32H43N7Na	(M+Na)+	-0.94
550.35396	550.35313	1	290.3	C32H43N7Na	(M+Na)+	1.51
551.35455	551.35607	1	51	C32H43N7Na	(M+Na)+	-2.76

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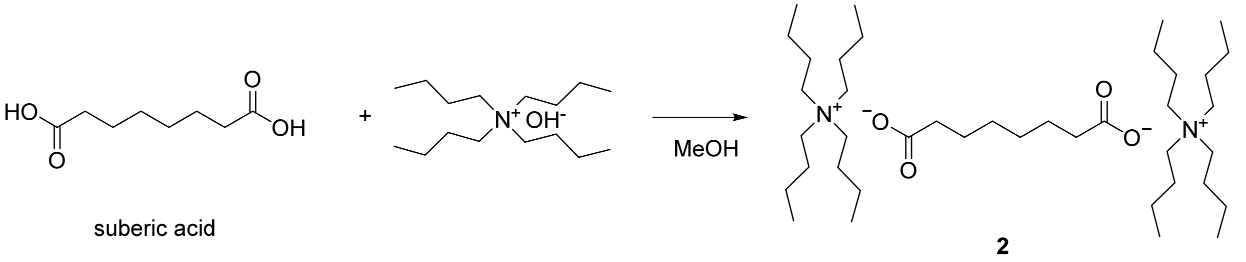
Figure S4. HRMS spectrum of **4**.

Compound 2[3]



To a methanol (2 mL) solution of suberic acid (535 mg, 3.07 mmol), methanol solution of tetrabutylammonium hydroxide (1 M, 6.14 mL) was added dropwise. The reaction mixture was stirred at room temperature for 3h. Removal of methanol followed by drying in vacuo afforded **2** quantitatively as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 0.98 (t, *J*=7 Hz, 24H, –C*H*$_3$), 1.29 (m, 4H, –C*H*$_2$–), 1.43 (m, 16H, –C*H*$_2$–), 1.61-1.67 (br m, 20H, –C*H*$_2$–), 2.14 (t, *J*=8 Hz, 4H, –C*H*$_2$–), 3.34 (q, 16H, –C*H*$_2$–). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 179.3, 58.8, 49.9, 39.7, 30.5, 27.7, 24.1, 19.8, 13.7. HRMS (ESI): m/z calcd for $C_{32}H_{72}N_2$ $[M]^{+2}$: 242.28423; found: 242.28421 (as tetrabutylammonium cation in positive ionization mode).

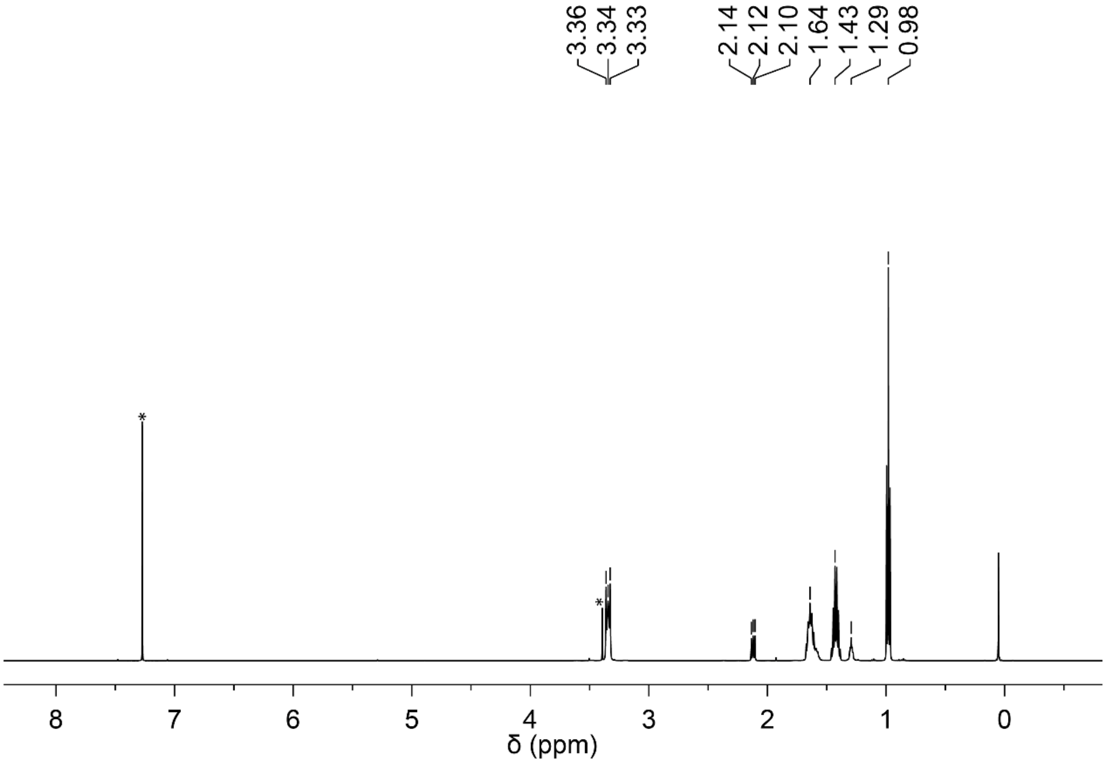


Figure S5. ^{1}H NMR spectrum of **2** recorded in CDCl$_3$.

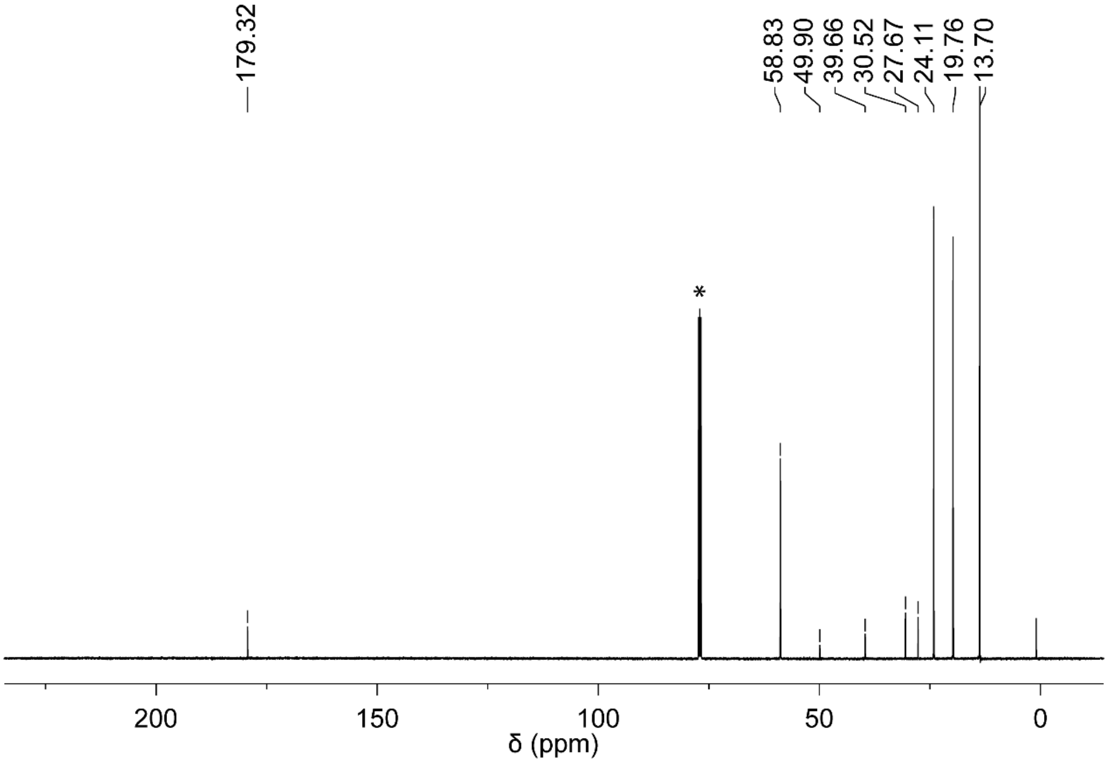


Figure S6. ^{13}C NMR spectrum of **2** recorded in $CDCl_3$.

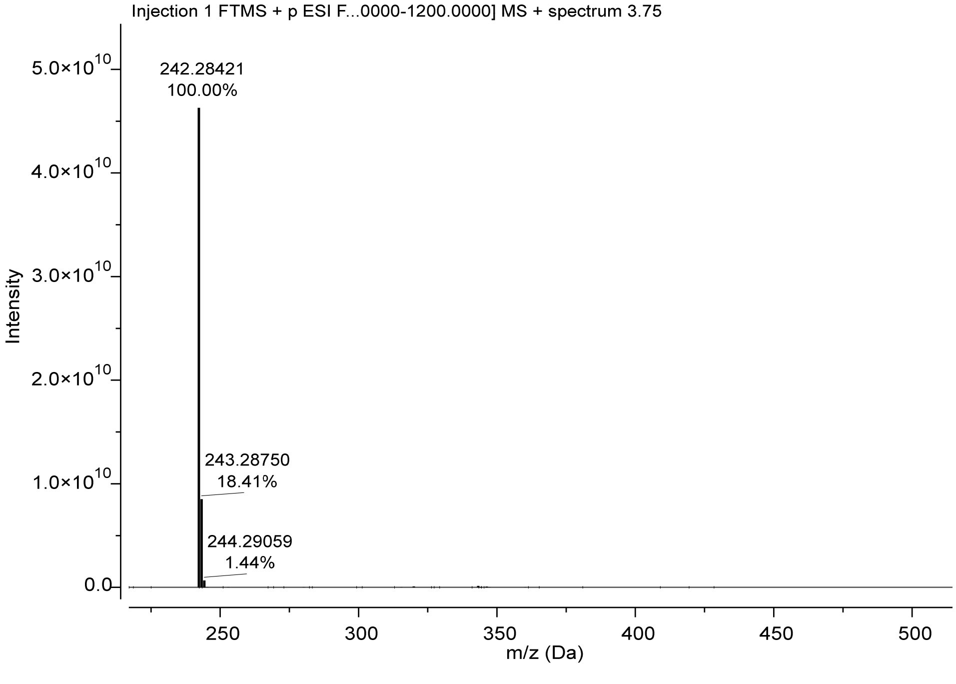
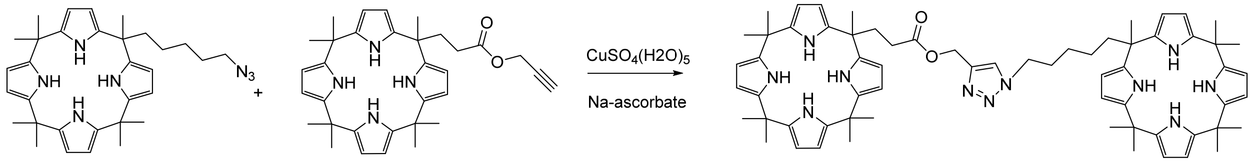


Figure S7. HRMS spectrum of **2** in positive ionization mode showing tetrabutylammonium ion.

Compound 1



5 **6** **1**

In a flask, **5** (272.6 mg, 0.52 mmol) and **6** (272.06 mg, 0.52 mmol) were dissolved in THF (50 mL). A freshly prepared aqueous solution of sodium ascorbate (226 mg, 1.14 mmol; 1 mL) was added, followed by an aqueous solution of copper(II) sulfate pentahydrate (272 mg, 0.57 mmol; 1 mL). The mixture was stirred for two days at ambient temperature. THF was removed under vacuum and the remaining crude mixture was dissolved in CH_2Cl_2 and washed with water three times. The organic layer was then dried over Na_2SO_4 and the excess of solvent was removed under vacuum. Tar material was removed by precipitation from diethyl ether. Supernatant was concentrated and precipitation from hexane afforded the compound **1** as a yellow solid (423 mg, 78%). M.p.: decomposes over 223 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.42-1.44 (br m, 4H, –C*H*$_2$–), 1.50-1.52 (br m, 44H, *meso*–C*H*$_3$ and –C*H*$_2$–), 1.79-1.87 (br m, 4H, –C*H*$_2$–), 2.19 (br m, 4H, –C*H*$_2$–), 4.27 (t, *J* = 7 Hz, 2H, –C*H*$_2$–), 5.87-5.90 (m, 16H, pyrrole C*H*), 7.01 (br m, 8H, N*H*), 7.50 (s, 1H, –CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 173.6, 138.4, 137.1, 136.1, 123.4, 102.9, 65.8, 57.6, 51.9, 50.3, 40.4, 38.7, 35.2, 29.1, 26.8, 25.8, 23.7, 15.3. HRMS (ESI): m/z calcd for $C_{65}H_{83}N_{11}O_2$ $[M]^{+\cdot}$: 1050.45400; found: 1050.68069.

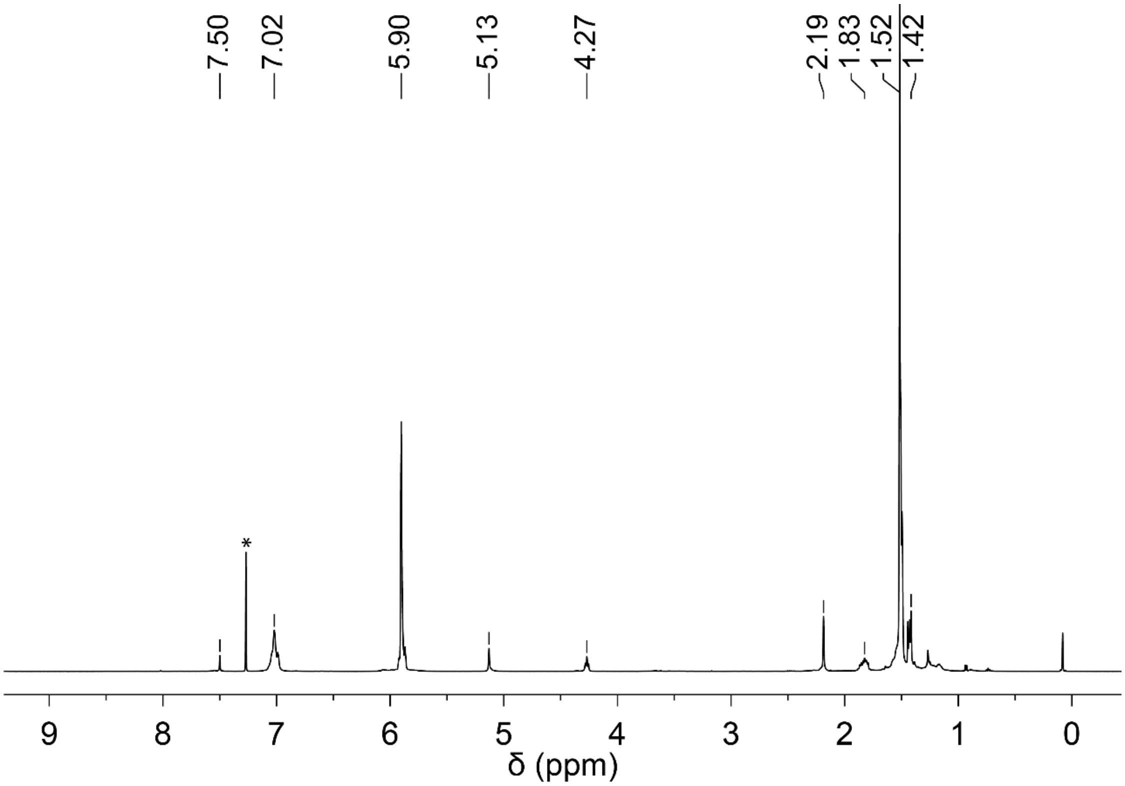


Figure S8. ^{1}H NMR spectrum of **2** recorded in $CDCl_3$.

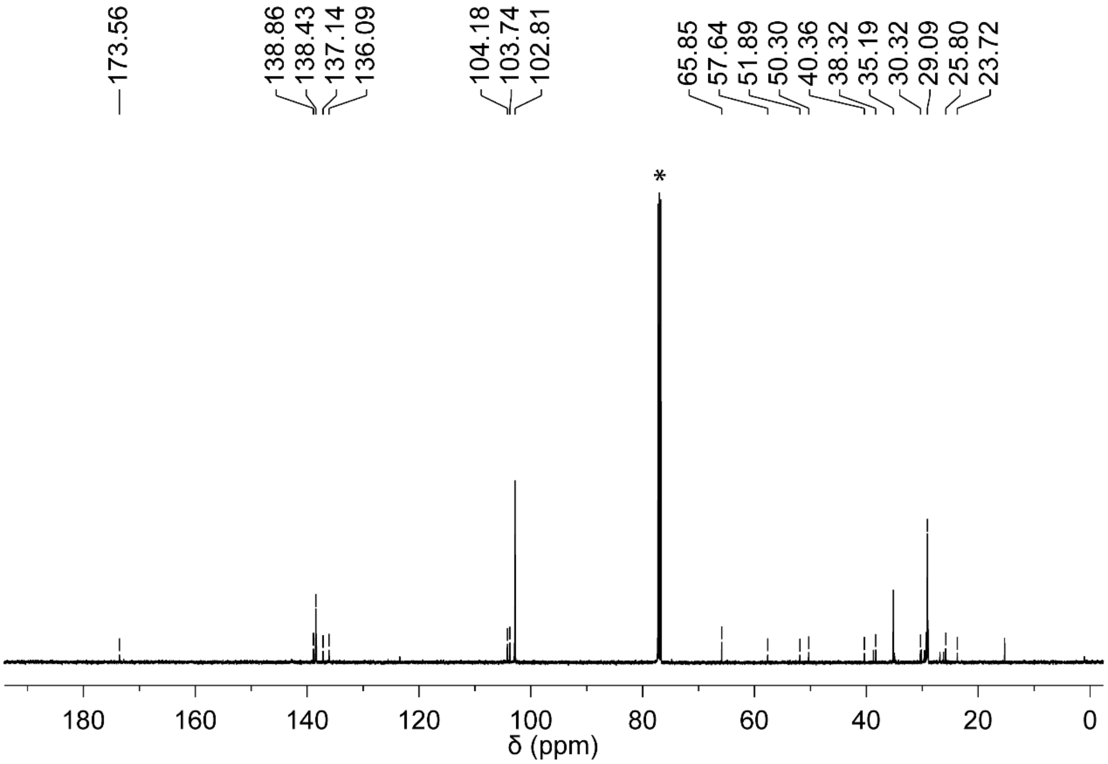


Figure S9. ^{13}C NMR spectrum of **2** recorded in $CDCl_3$

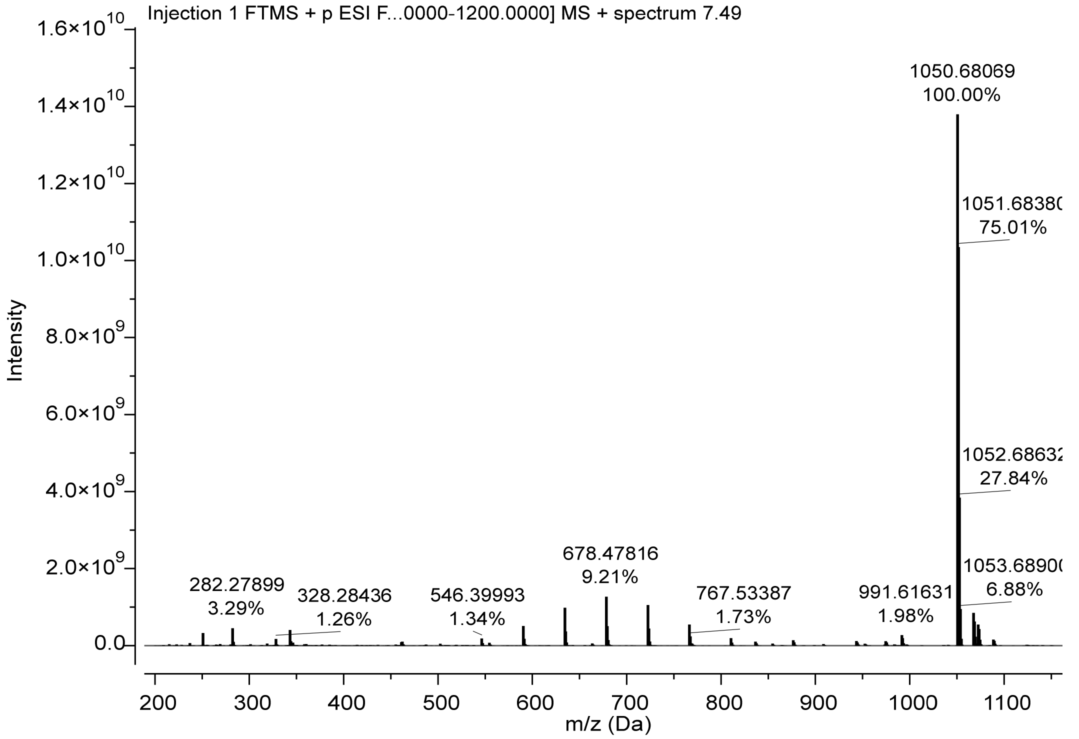


Figure S10. HRMS spectrum of **2**.

Stoichiometry and Association Constant Determination

To determine the stoichiometry and association constant between calix[4]pyrrole core of **1** and carboxylate units of **2**, octamethylcalix[4]pyrole (**3)** and tetrabutylammonium acetate (TBAOAc) were used as model compounds. ^{1}H NMR titrations were done with $CHCl_3$ solutions which had a constant concentration of **3** (4.87 mM) and varying concentrations of TBAOAc. By a non-linear curve-fitting method, the association constant between **3** and TBAOAc was determined to be $1.65\times10^3 \pm 54.3$ $M^{-1}$and the complexation stoichiometry between **3** and TBAOAc was found to be 1 as depicted in Figure S13.

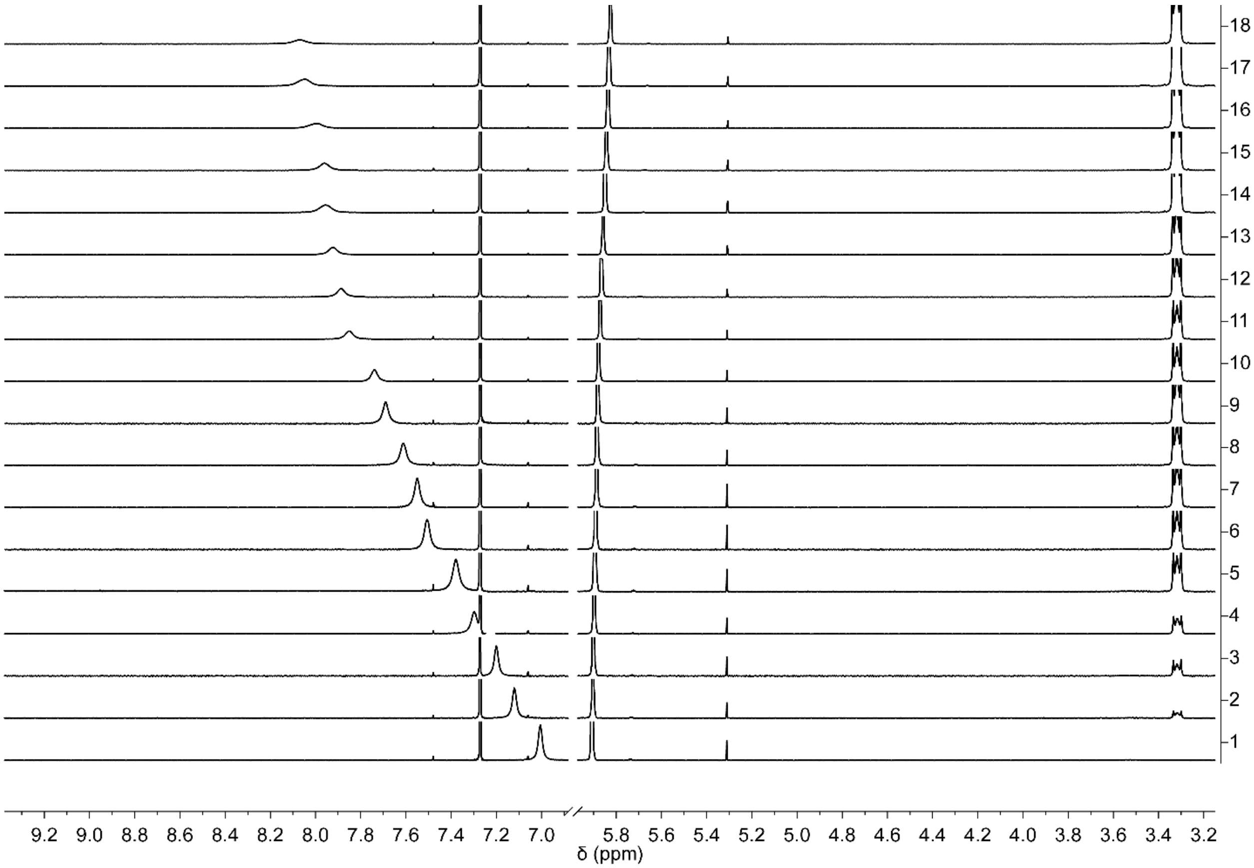
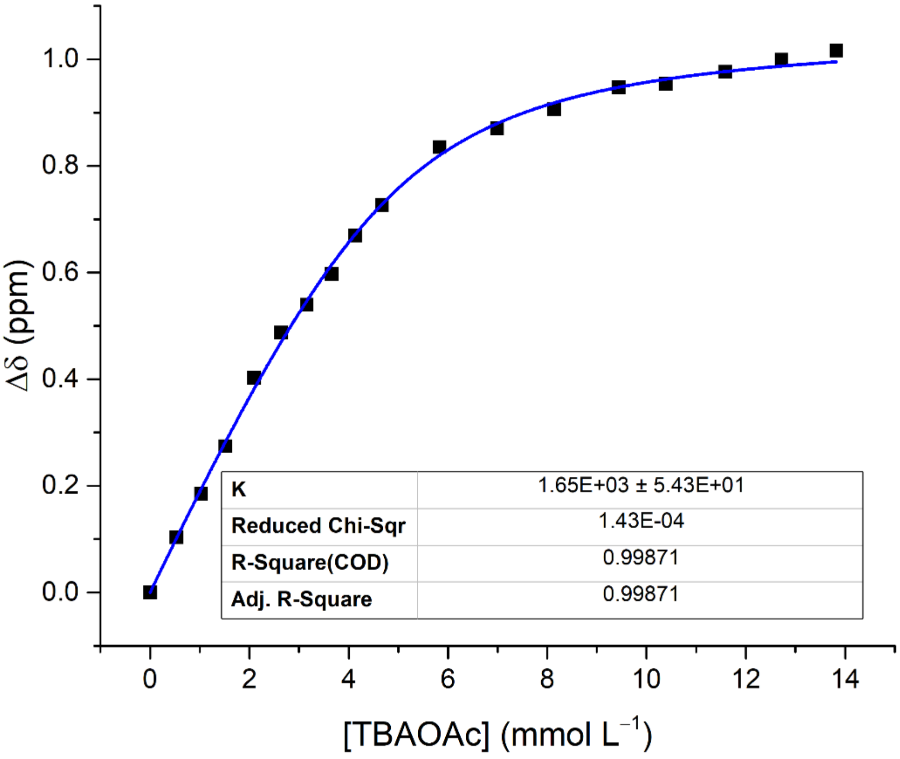


Figure S11. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of **3** at a constant concentration of 4.87 mM upon addition of TBAOAc at 0.00, 0.53, 1.03, 1.51, 2.09, 2.64, 3.16, 3.66, 4.13, 4.67, 5.83, 6.99, 8.14, 9.45, 10.38, 11.59, 12.72, 13.82 mM concentrations from bottom to top.



K	1.65E+03 ± 5.43E+01
Reduced Chi-Sqr	1.43E-04
R-Square(COD)	0.99871
Adj. R-Square	0.99871

Figure S12. Chemical shift changes of one of the pyrrole NH protons (initially at 7.01 ppm) belonging to **3** (4.87 mM) upon addition of TBAOAc. The blue solid line was obtained from a non-linear curve fitting using the equation provided within the table present as an inset to the figure.

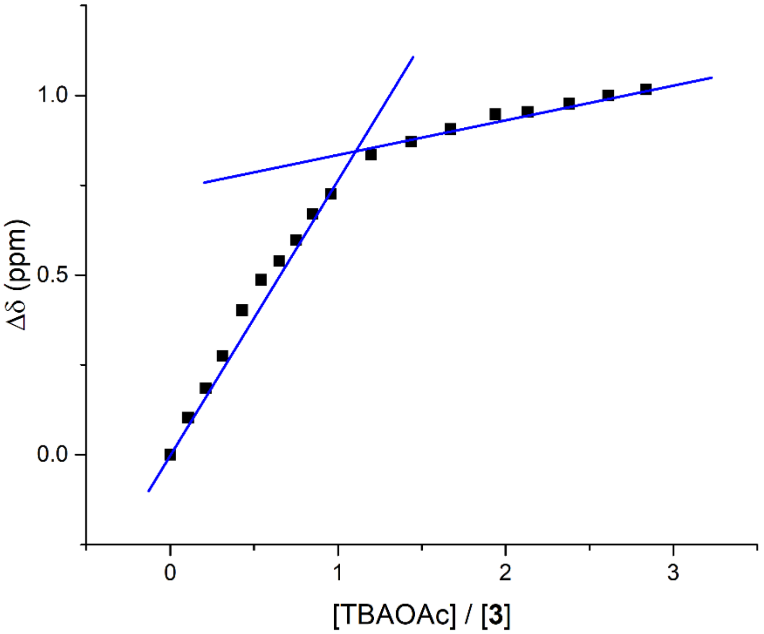


Figure S13. Molar ratio plot for the interaction of **3** with TBAOAc, indicating a 1:1 stoichiometry.

Estimated Values of Maximum Polymerization Degree (*DP*) at Different Concentrations

Using the Carothers equation and assuming that the same average association constant holds for each successive step (isodesmic model) and that cyclic species can either be ignored or considered, the average degree of polymerization, *DP*, may be derived from the equilibrium constant K_a and the initial monomer concentration as follows:

$$DP = \frac{1}{1-p} \tag{1}$$

If p is defined as the extend of complexation,

$$K_a = \frac{p[\mathbf{1}]}{(1-p)^2[\mathbf{1}]^2}$$

Solving this quadratic equation results in

$$1 - p = \frac{(1 + 4K_a[\mathbf{1}])^{1/2} - 1}{2K_a[\mathbf{1}]}$$

$$DP = \frac{1}{1-p} = \frac{2K_a[\mathbf{1}]}{(1 + 4K_a[\mathbf{1}])^{1/2} - 1} \tag{2}$$

If $4K_a[\mathbf{1}] \gg 1$,

$$DP = \frac{2K_a[\mathbf{2}]}{(4K_a[\mathbf{1}])^{1/2} - 1}$$

and if $\sqrt{4K_a[\mathbf{1}]} \gg 1$,

$$DP = \sqrt{K_a[\mathbf{1}]} \tag{3}$$

In this system the initial concentration of $[\mathbf{1}]_0 = 2[\mathbf{1}]_0$ and DP can be estimated as:

$$DP = \sqrt{K_a 2[\mathbf{1}]} \tag{4}$$[4]

In this system p is the extend of complexation of **1** and **2**. *DP* estimated in this way represents maximum values that in practice will be reduced by the presence of dimers, cyclic structures and reduction in the association constant (K_a) as the supramolecular polymer grows (the attenuation). Consequently, estimated size of supramolecular polymer converges to large values. Therefore, in addition to association constant ($K_a = 1.65 \times 10^3 \pm 54.3\ \mathrm{M}^{-1}$) between model compounds **3** and

TBAOAc maximum chemical shifts of 3+TBAOAc were also used to estimate *DP*. Table S1 shows the results of estimated *DP*s using Egs. 1 and 4.

Table S1. Estimated values of *p* and *DP* at different concentrations of equimolar mixtures of **1** and **2**.

	DP (Eq. 1)				***DP***$_{\text{max}}$ (Eq. 4)
[**1**] (mol L^{-1})	$\boldsymbol{\delta_{\text{max}}}$ (ppm)[a]	$\boldsymbol{\delta_{\text{obs}}}$ (ppm)[b]	***p***[c]	***DP***	
0.500	10.99	10.88	0.97 ± 0.002	36.18 ± 2.97	40.62 ± 0.19
0.250	10.22	10.09	0.96 ± 0.002	24.69 ± 1.14	28.72 ± 0.13
0.198	10.01	9.83	0.94 ± 0.002	16.67 ± 0.21	25.56 ± 0.10
0.125	9.74	9.53	0.92 ± 0.002	12.45 ± 0.11	20.31 ± 0.08
0.083	9.44	9.20	0.90 ± 0.002	9.92 ± 0.08	16.55 ± 0.05
0.031	8.47	8.23	0.84 ± 0.002	6.08 ± 0.05	10.16 ± 0.05
0.015	8.15	7.87	0.75 ± 0.001	4.07 ± 0.02	7.18 ± 0.03
0.0078	7.94	7.62	0.66 ± 0.001	2.91 ± 0.01	3.59 ± 0.01

[a] From Fig S14. [b] Observed chemical shifts. [c] Calculated from $p = (\delta_{obs} - \delta_u)/(\delta_{max} - \delta_u)$ where chemical shifts of pyrrole NH protons; δ_u: chemical shift of free host (7.01 ppm). Error bars reflects the potential error of 0.003 ppm in δ.

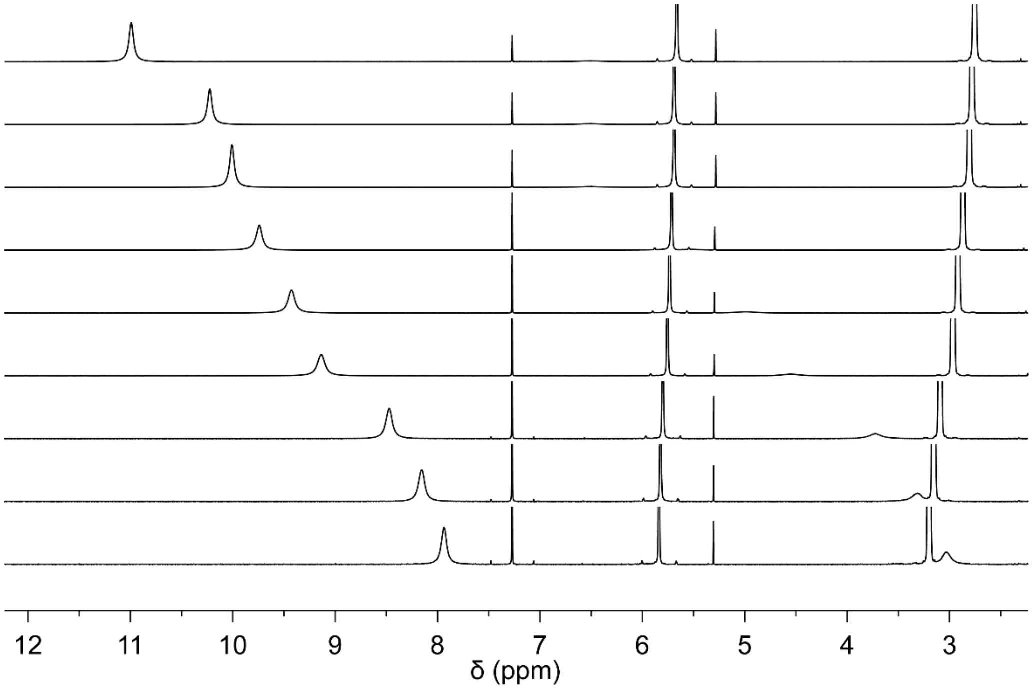


Figure S14. Partial ^{1}H NMR spectrum of **3** + excess TBAOAc recorded in $CDCl_3$ at 25 °C at different concentrations. The concentration of **3** from bottom to top 0.5, 0.25, 0.198, 0.083, 0.063, 0.031, 0.015, 0.0078 mol L^{-1}.

DOSY NMR Analyses

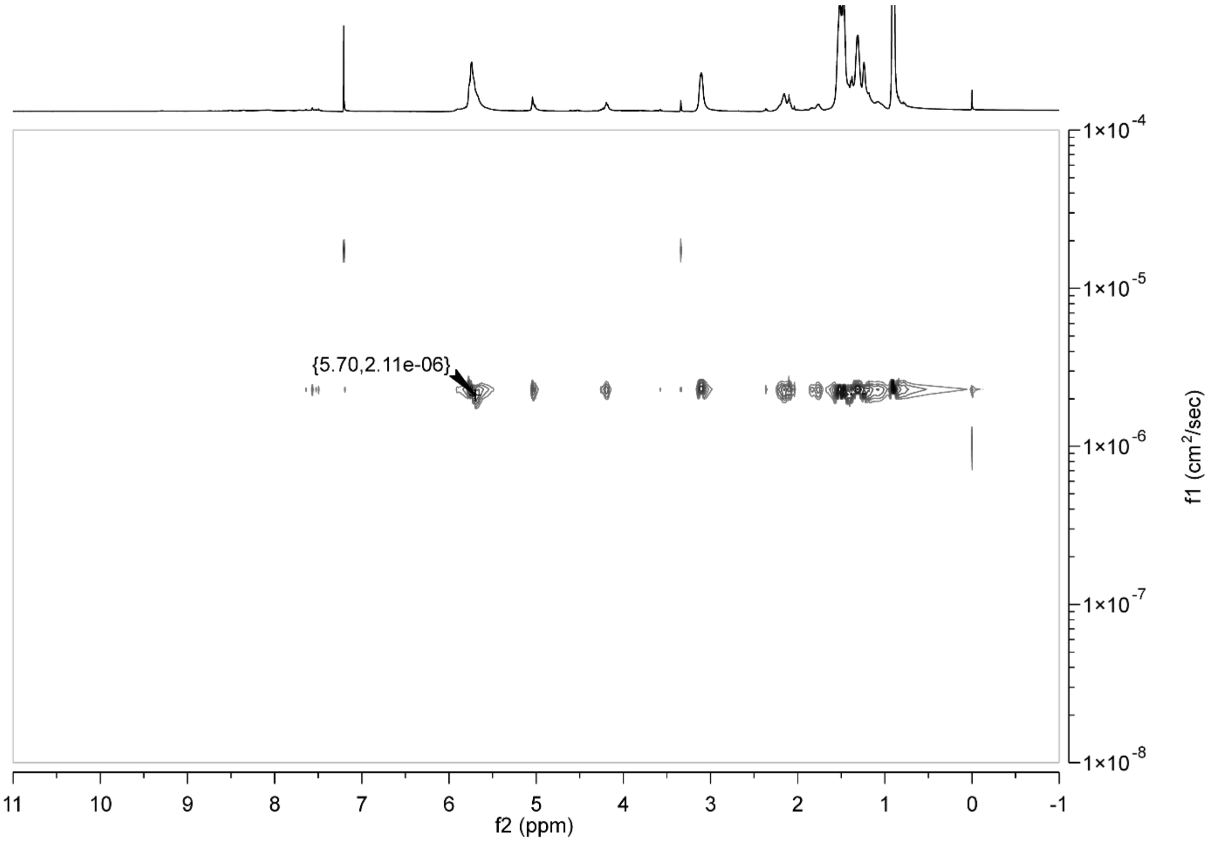


Figure S15. DOSY NMR spectrum of equimolar **1**+**2** (8 mM) recorded in $CDCl_3$ at 25 °C.

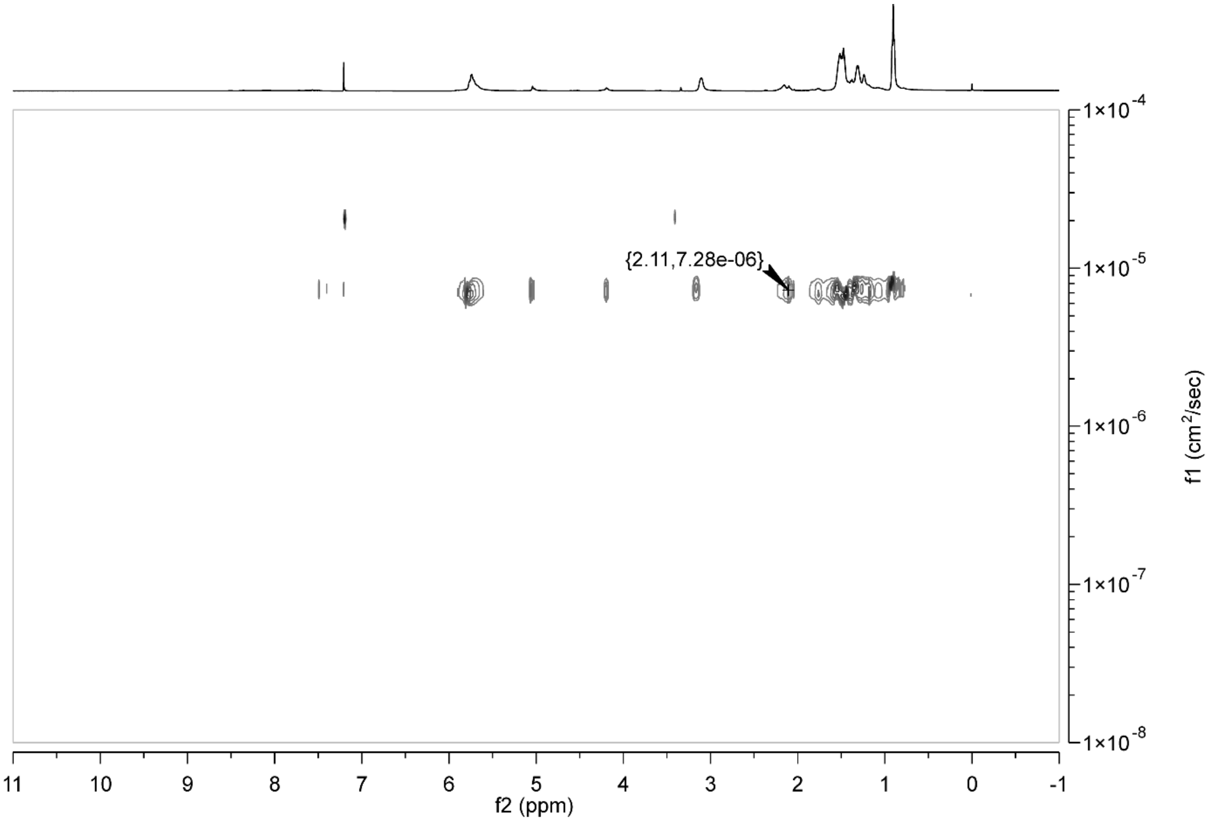


Figure S16. DOSY NMR spectrum of equimolar **1**+**2** (198 mM) recorded in $CDCl_3$ at 25 °C.

Supramolecular Polymerization in Other Solvents

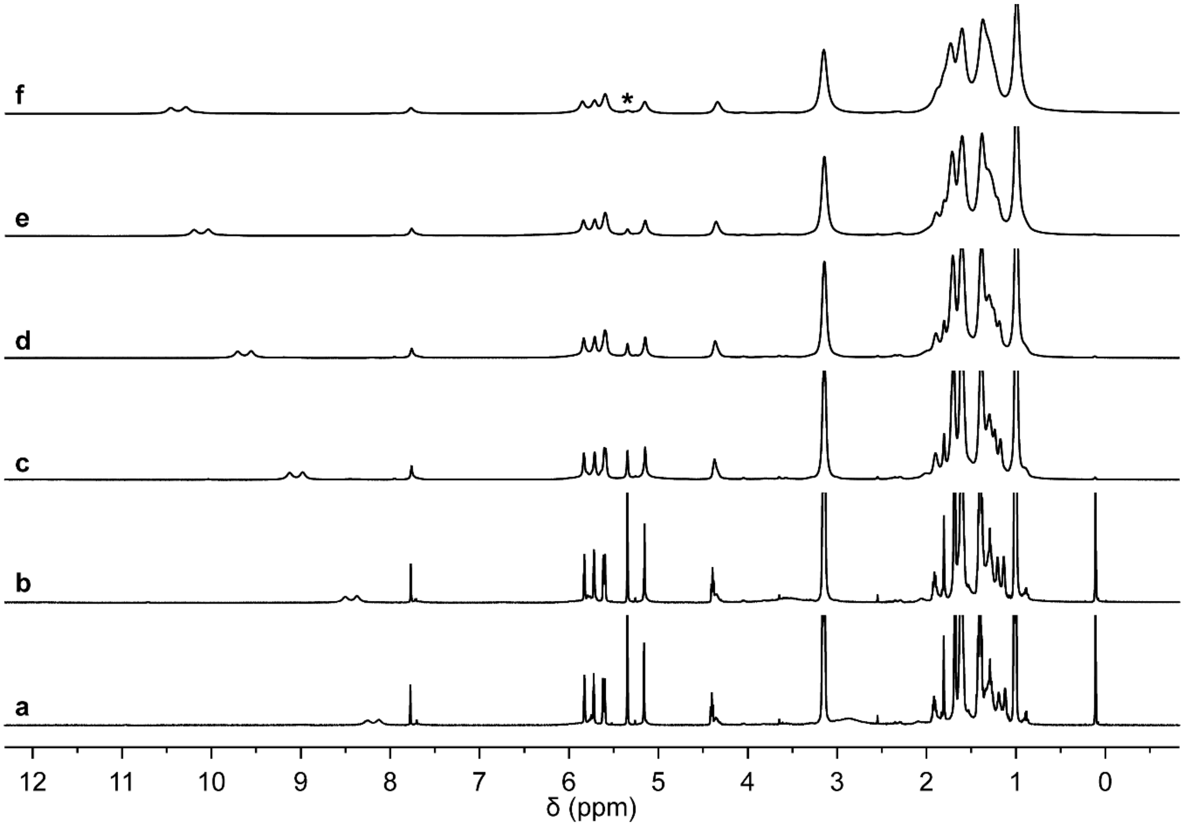


Figure S17. Variable concentration ^{1}H NMR spectrum of equimolar mixtures of 1+2 recorded in CD_2Cl_2 at 25 °C: a) 25, b) 52, c) 94, d) 136, e) 205, f) 224 mM. * denotes solvent residual peak.

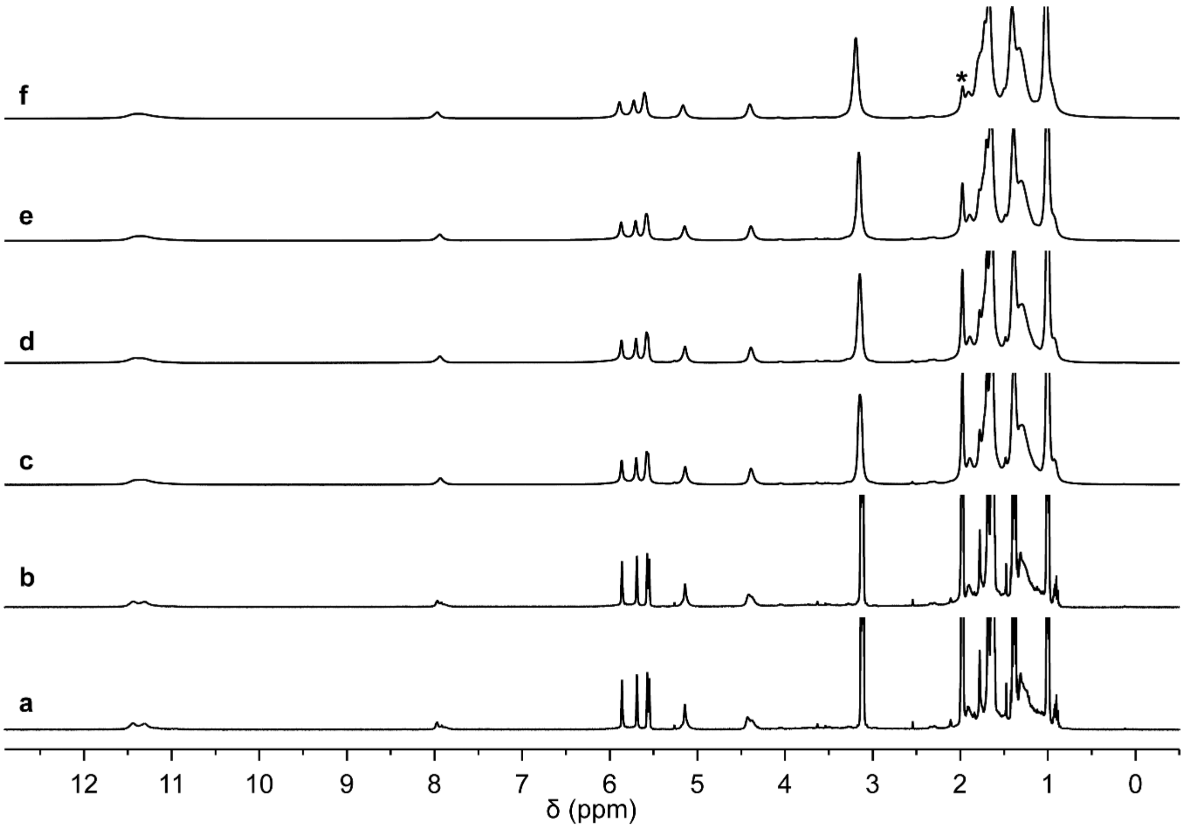


Figure S18. Variable concentration ^{1}H NMR spectrum of equimolar mixtures of **1**+**2** recorded in CD_3CN at 25 °C: a) 25, b) 52, c) 94, d) 136, e) 205, f) 224 mM. * denotes solvent residual peak.

References

1 A. Aydogan, A. Koca, M. K. Şener and J. L. Sessler, *Org. Lett.*, 2014, **16**, 3764-3767.
2 A. Aydogan, G. Lee, C.-H. Lee and J. L. Sessler, *Chem. Eur. J.*, 2015, **21**, 2368-2376.
3 N. Kiriyama, M. Ebihara, T. Udagawa and H. Miyaji, *RSC Adv.*, 2016, **6**, 19794-19796.
4 H. W. Gibson, N. Yamaguchi and J. W. Jones, *J. Am. Chem. Soc.*, 2003, **125**, 3522-3533.