*Electronic Supplementary Information*

# Self-assembly of a supramolecular network with pseudo-rotaxane cross-linking nodes and its transformation into a mechanically locked structure by rotaxane formation

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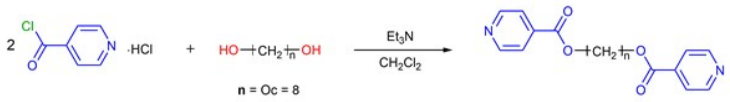
## 1. General

Chemicals were purchased from Aldrich and used without further purification. Nuclear magnetic resonance (NMR) experiments were acquired on Jeol 500 MHz, Bruker 400 MHz and Jeol 270 MHz. $^{1}H$ and $^{13}C$ NMR chemical shifts are given in parts per million (ppm) considering $Me_4Si$ as an external reference; *J* values are reported in Hz and multiplicity is denoted as s (singlet), d (doublet), t (triplet) or br (broad signal). High-resolution mass spectra (HR-MS) were recorded on an Agilent G1969A ESI-TOF mass spectrometer. FT-IR experiments were obtained using a Perkin Elmer Spectrum GX. Polymer molecular weight distribution was determined by a gel permeation system (Waters 1525) coupled to a diode array detector (Waters 2998). Chromatographer was equipped with a Waters Styragel HR4 column ($M_w$: 5 – 600 kDa); measurements were performed at 35 °C using tetrahydrofuran as eluent with a rate flow of 0.5 mL/min. System was calibrated with polystyrene standards, $M_w$: 400 – 2.5 × $10^3$ Da (Waters ReadyCal-kit). Differential scanning calorimetry (DSC) experiments were performed on a TA instruments Q2000 calorimeter. Thermal response was analysed in a Reichert thermovar microscope.

## 2. Synthesis and characterisation

### *2.1 Synthesis of pyridine-containing spacer **1,8-bis(pyridyl)octylene***




**Scheme S1.** Synthesis of precursor **1,8-bis(pyridyl)octylene**.

To a solution of isonicotinoyl chloride (1.0 g, 5.34 mmol) and 1,8-octanediol (380.2 mg, 2.6 mmol), in $CH_2Cl_2$ (10 mL), triethylamine (3 mL, 21.3 mmol) was slowly added; the mixture was heated to reflux for 18 h, which resulted in a suspension. It was then separated by filtration and the filtrate washed with $H_2O$ (3 × 15 mL) and dried ($Na_2SO_4$). The solvent was removed under vacuum to obtain a yellow solid residue (655.0 mg, 71%) identified as the expected compound **1,8-bis(pyridyl)octylene**. $^1$H NMR (270 MHz, $CDCl_3$), $\delta_H$ 1.38 (br, 8 H, $H_e$ and $H_f$), 1.75 (m, 4 H, $H_d$), 4.32 (t, $^3J_{c\text{-}d}$ = 6.6 Hz, 4 H, $H_c$), 7.81 (d, $^3J_{b\text{-}a}$ = 6.0 Hz, 4 H, $H_b$), 8.75 (d, $^3J_{a\text{-}b}$ = 6.0 Hz, 4 H, $H_a$): $^{13}$C RMN {$^1$H} (68 MHz, $CDCl_3$), $\delta_C$ 25.9 ($C_e$), 28.6 ($C_d$), 29.2 ($C_f$), 65.9 ($C_c$), 122.9 ($C_b$), 137.7 ($C_{ipso}$), 150.7 ($C_a$), 165.2 ($C_{C=O}$): ESI-HRMS, *m/z* found for [(**1,8-bis(pyridyl)octylene**) + **H**]$^+$ 357.181151, calculated 357.180883, error 0.7 ppm.

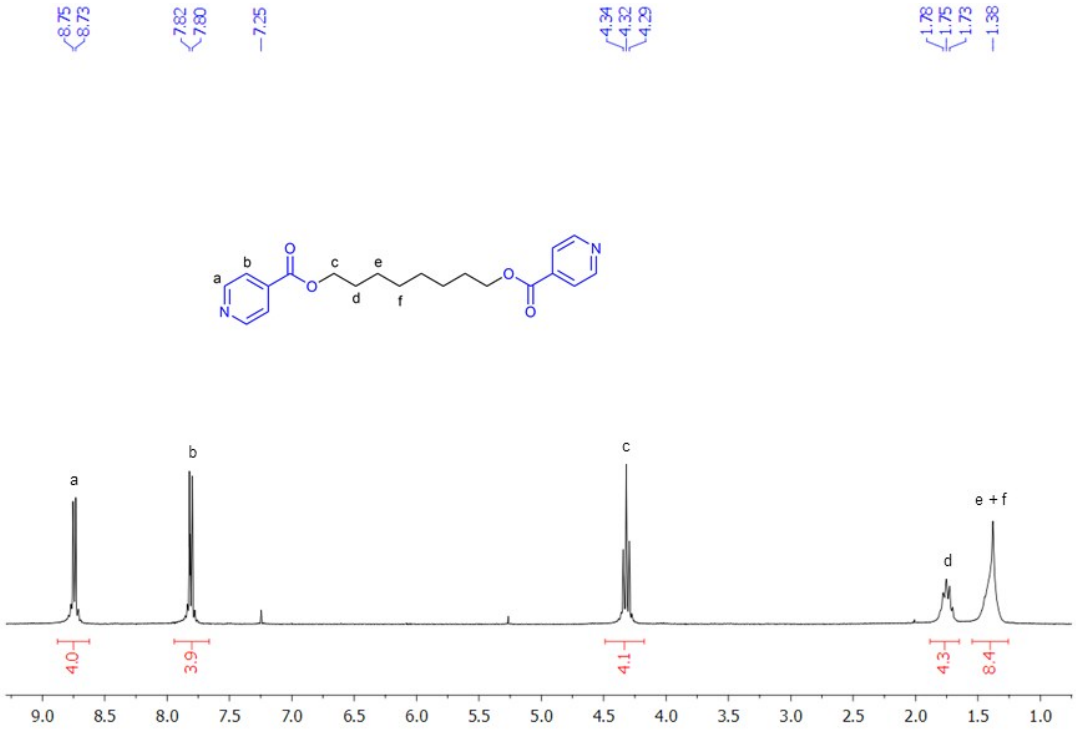



**Figure S1.** $^1$H NMR spectrum (270 MHz, $CDCl_3$) of precursor **1,8-bis(pyridyl)octylene** at 298 K.

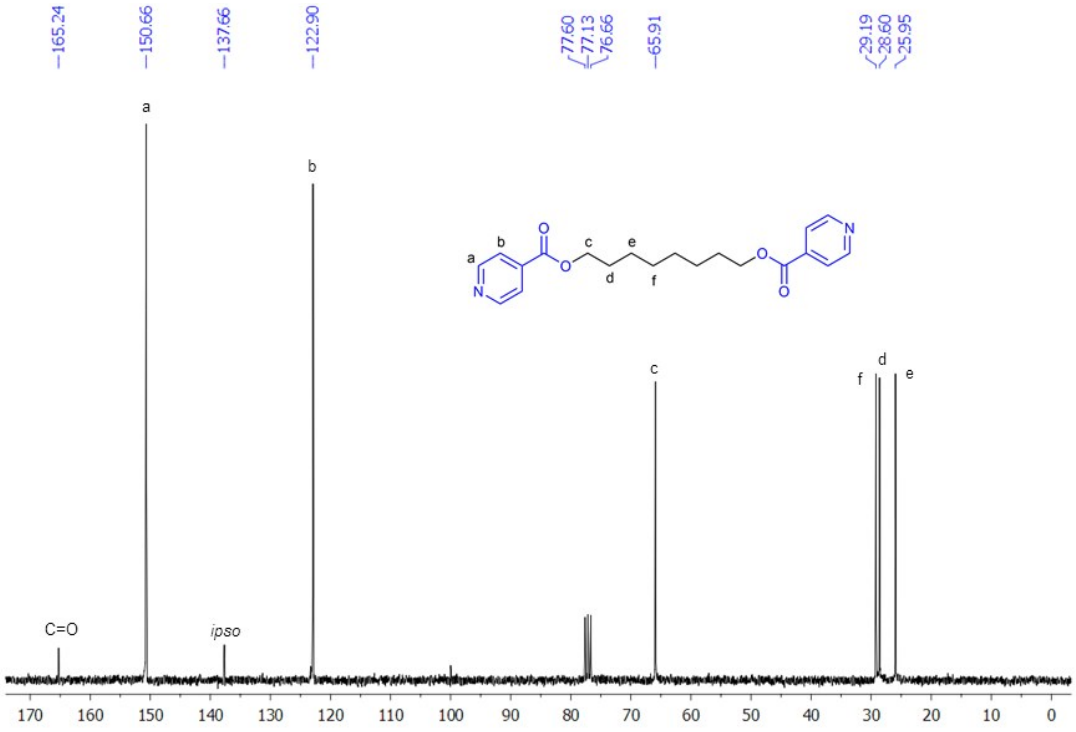



**Figure S2.** $^{13}C$ {$^{1}H$} NMR spectrum (68 MHz, $CDCl_3$) of compound **1,8-bis(pyridyl)octylene** at 298 K.

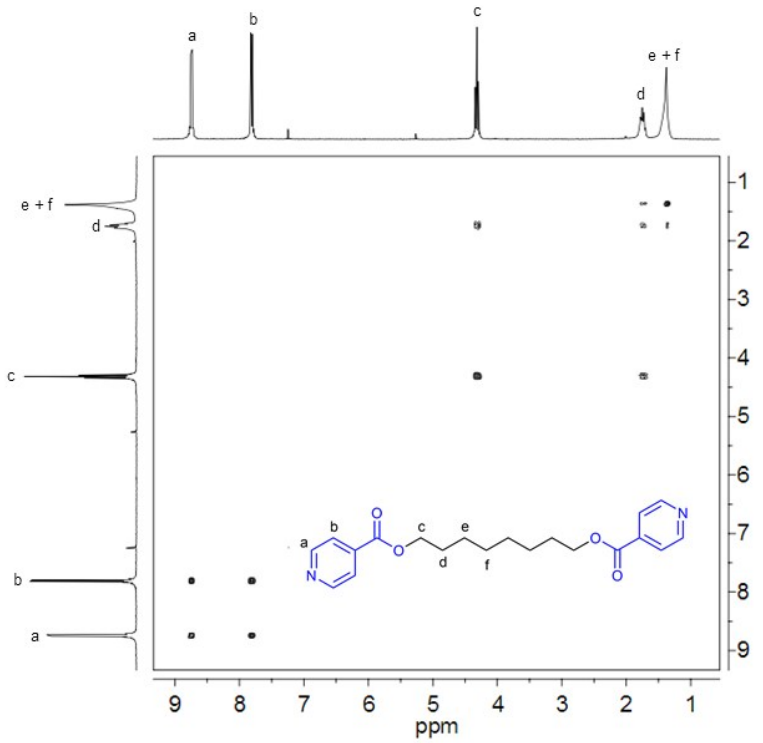



**Figure S3.** 2D COSY-NMR spectrum (270 MHz, $CDCl_3$) of precursor **1,8-bis(pyridyl)octylene**.

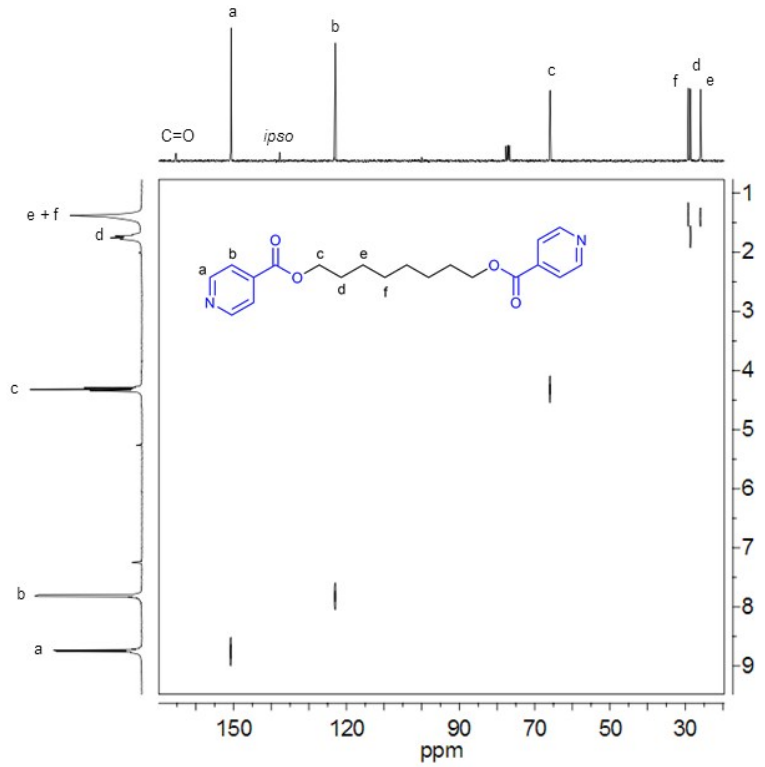



**Figure S4.** 2D HETCOR-NMR spectrum (270 MHz, $CDCl_3$) of compound **1,8-bis(pyridyl)octylene**.

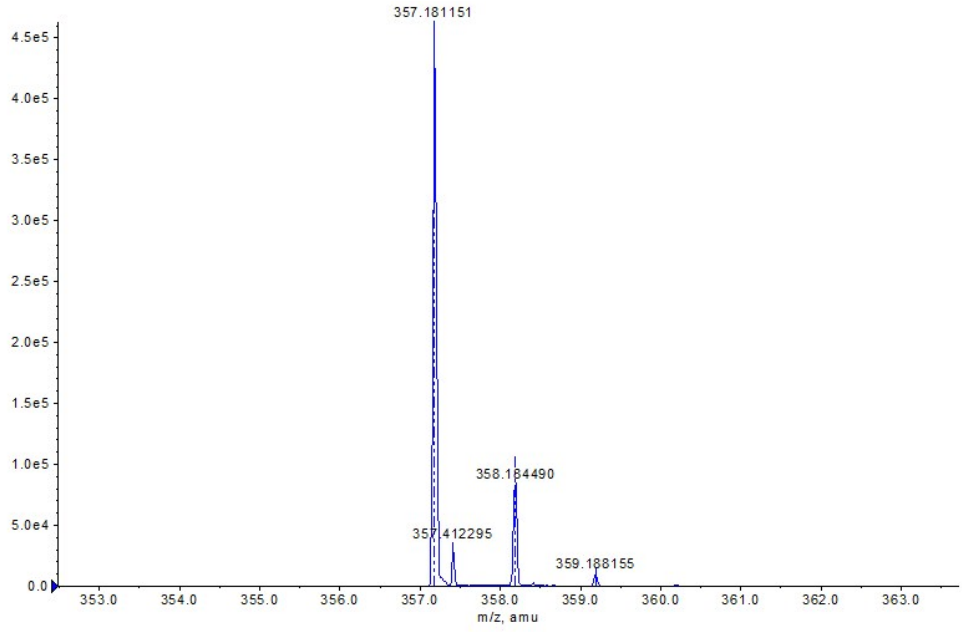
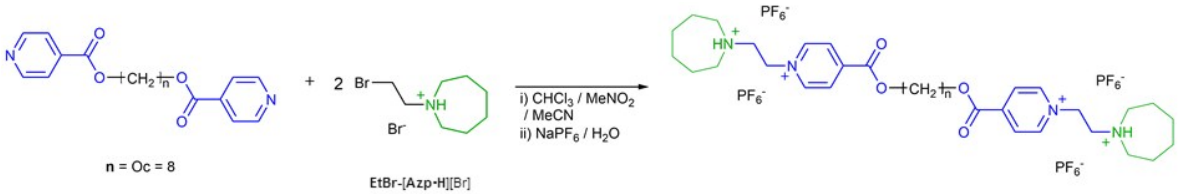



**Figure S5.** HR mass spectrum for the molecular ion [(**1,8-bis(pyridyl)octylene)** + H]$^+$.

*2.2 Guest [**1·H$_2$**][PF$_6$]$_4$*




**Scheme S2.** Synthesis of guest [**1·H$_2$**][PF$_6$]$_4$.

A solution of **EtBr**-[**Azp·H**][Br][1] (1.0 g, 3.57 mmol) and **1,8-bis(pyridyl)octylene** (318.3 mg, 0.89 mmol) in 10 mL of a 6:3:1 mixture of MeCN, $CHCl_3$ and $MeNO_2$ was heated to reflux for 10 days. After cooling to RT, $CHCl_3$ (30 mL) was added; the formed solid was separated by filtration, washed with MeCN (20 mL) and $CHCl_3$ (20 mL) and allowed to air-dry. The isolated white powder was identified as compound [**1·H$_2$**][Br]$_4$ (650 mg, 80%); all material was then solved in $H_2O$ and ion exchanged using $NaPF_6$ to quantitatively yield guest [**1·H$_2$**][PF$_6$]$_4$ as a white solid. $^1$H NMR (270 MHz, $CD_3NO_2$), $\delta_H$ 1.45 (br, 8 H, $H_j$ and $H_k$), 1.79 (br, 8 H, $H_a$), 1.85 (br, 4 H, $H_i$), 2.05 (br, 8 H, $H_b$), 3.50 (br, 4 H, $H_c$), 3.76 (br, 4 H, $H_{c'}$), 4.00 (t, $^3J_{d\text{-}e}$ = 7.5 Hz, 4 H, $H_d$), 4.48 (t, $^3J_{h\text{-}i}$ = 6.6 Hz, 4 H, $H_h$), 5.29 (t, $^3J_{e\text{-}d}$ = 7.5 Hz, 4 H, $H_e$), 7.86 (br, 2 H, $H_{NH}$), 8.64 (d, $^3J_{g\text{-}f}$ = 6.6 Hz, 4 H, $H_g$), 9.08 (d, $^3J_{f\text{-}g}$ = 6.6 Hz, 4 H, $H_f$): $^{13}$C RMN {$^1$H} (68 MHz, $CD_3NO_2$), $\delta_C$ 23.6 ($C_b$), 25.5 ($C_j$), 25.9 ($C_a$), 28.1 ($C_i$), 28.8 ($C_k$), 55.7 ($C_d$), 55.9 ($C_e$), 57.0 ($C_c$), 67.8 ($C_h$), 128.5 ($C_g$), 146.5 ($C_f$), 146.8 ($C_{ipso}$), 161.9 ($C_{C=O}$): ESI-HRMS, *m/z* found for [**1** + 2H]$^{4+}$ 152.610511, calculated 152.610903, error -1.0 ppm.

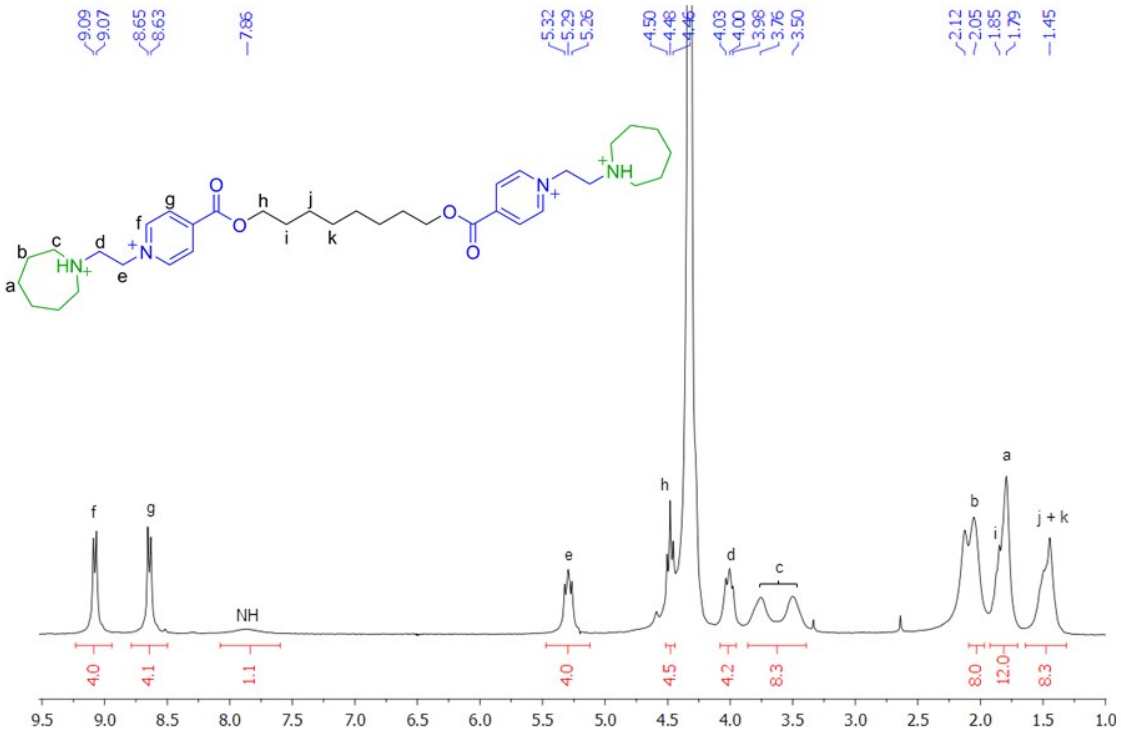



**Figure S6.** $^1$H NMR spectrum (270 MHz, $CD_3NO_2$) of guest [**1·H$_2$**][PF$_6$]$_4$ at 298 K.

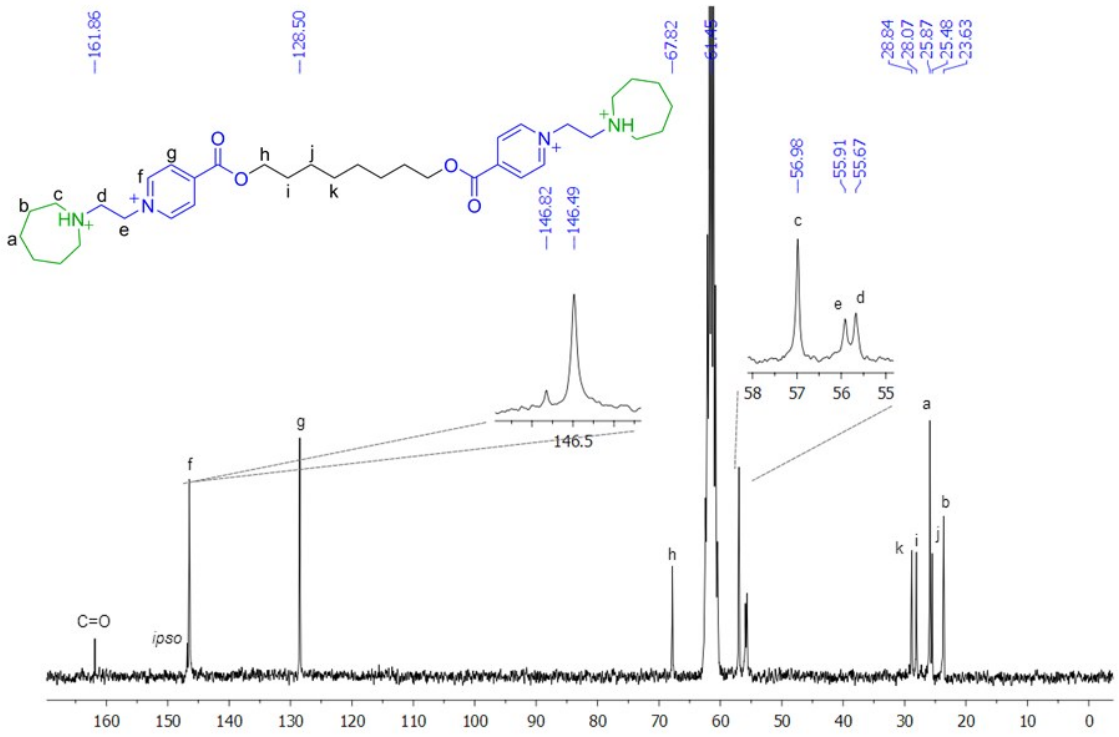



**Figure S7.** $^{13}C$ {$^{1}H$} NMR spectrum (68 MHz, $CD_3NO_2$) of compound [**1·H$_2$**][$PF_6$]$_4$ at 298 K.

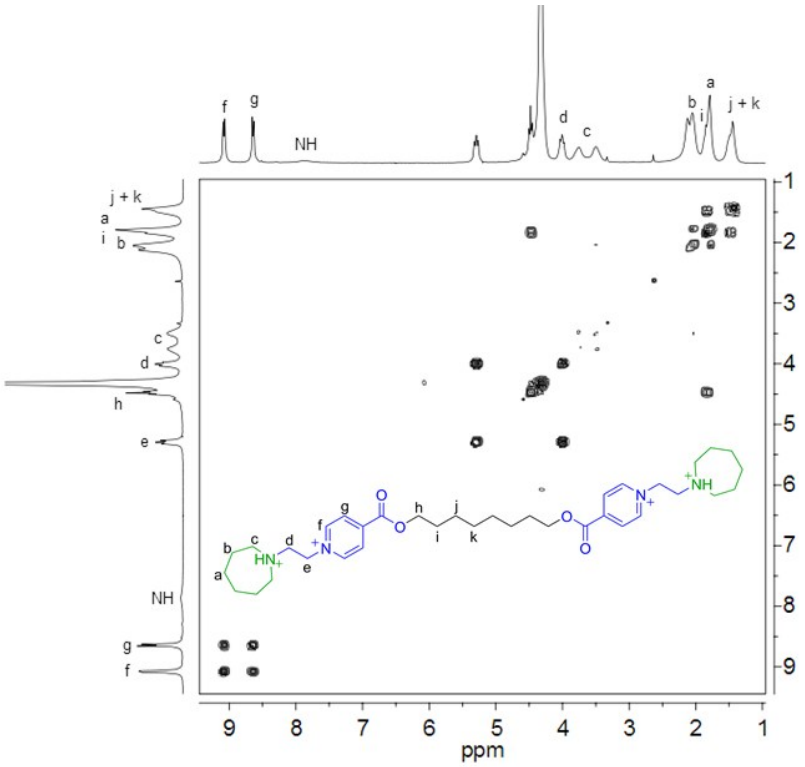



**Figure S8.** 2D COSY-NMR spectrum (270 MHz, $CD_3NO_2$) of guest [**1·H$_2$**][$PF_6$]$_4$.

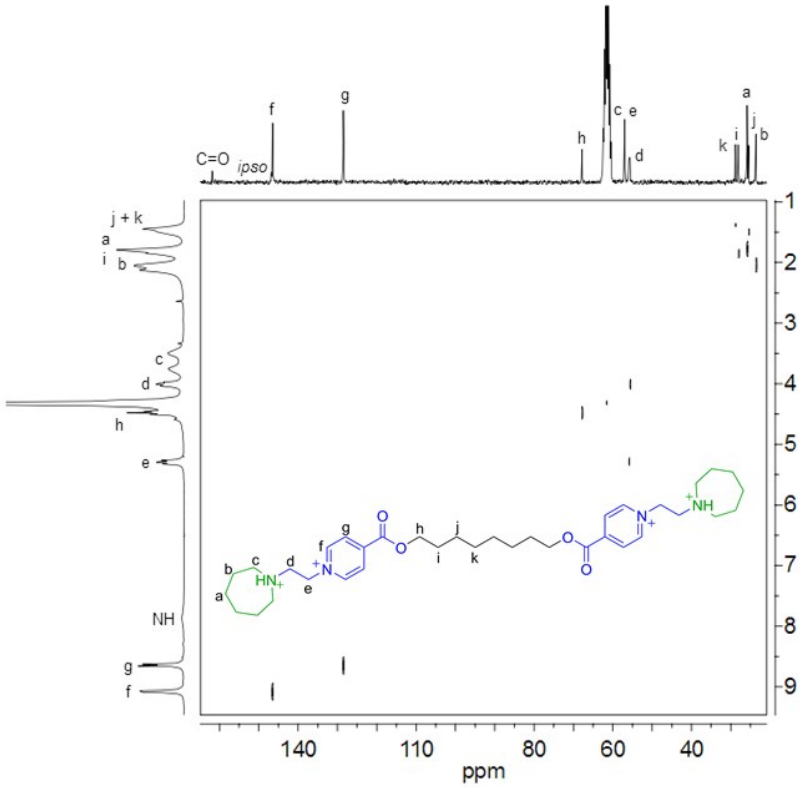



**Figure S9.** 2D HETCOR-NMR spectrum (270 MHz, $CD_3NO_2$) of compound [**1**·$H_2$][$PF_6$]$_4$.

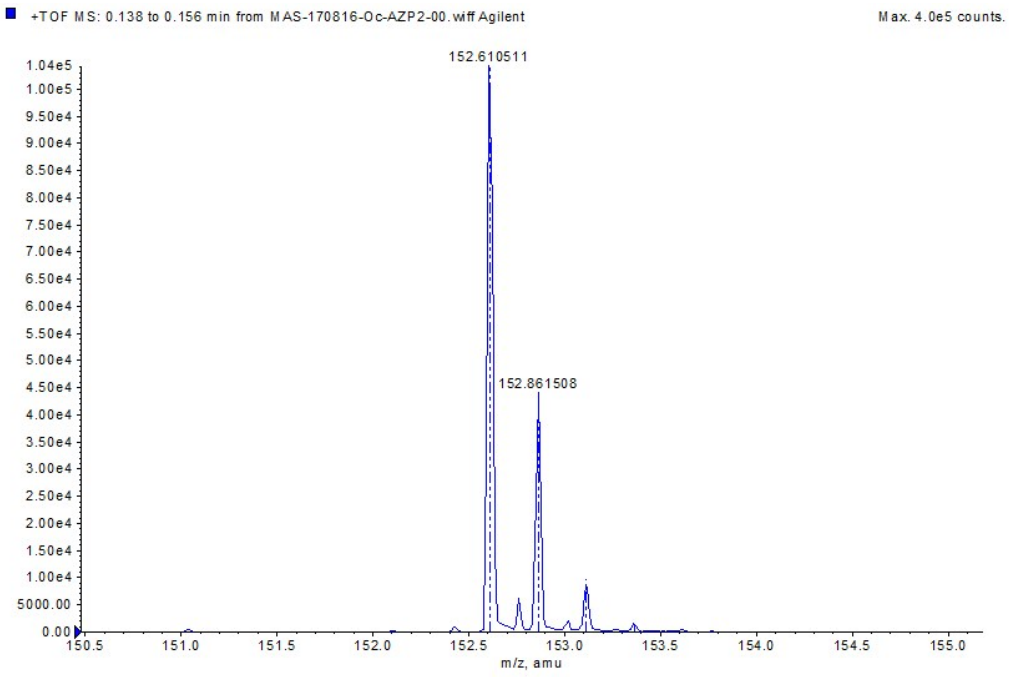
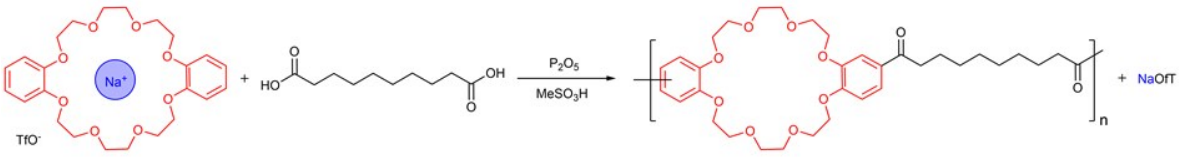



**Figure S10.** HR mass spectrum for the molecular ion [**1** + 2H]$^{4+}$.

*2.3 Precursor poly[ketone]*




**Scheme S3.** Synthesis of poly[ketone].

Polymeric precursor was synthesized by a procedure modified from the literature.[2] Complex [**DB24C8·Na**][TfO] was prepared by combination of NaTfO (1.1 g, 6.25 mmol) and **DB24C8** (572.1 mg, 1.25 mmol) in MeCN (9 mL), once the components were solvated, MeCN was removed by rotatory evaporation at 20 °C to obtain a solid residue, just after drying, all material was poured into 4 mL of Eaton's reagent (7.7 %, w/w) at 35 °C and combined with grounded sebacic acid (252.8 mg, 1.25 mmol), this mixture was stirred for 5.5 h at 35 °C. The resulting purple mixture was poured in cold $H_2O$ (100 mL) to generate a white sticky solid; it was stirred overnight in $H_2O$ and then separated by filtration and thoroughly washed with $H_2O$ to remove any residual sodium salt. After air-dying the solid was solved in $CHCl_3$ (50 mL) and poured into diethyl ether (250 mL) to re-precipitate the material which was filtered and washed with $H_2O$ (100 mL), hot MeOH (100 mL) and hot acetone (100 mL). The white solid residue (653.2 mg, 85%) was identified as the expected poly[ketone]. $^1$H NMR (500 MHz, $CDCl_3$), $\delta_H$ 1.33 (br, 8 H, $H_i$ and $H_j$), 1.69 (br, 4 H, $H_h$), 2.87 (t, $^3J_{g\text{-}h}$ = 7.2 Hz, 4 H, $H_g$), 3.83 (t, $^3J_{c\text{-}b}$ = 5.3 Hz, 8 H, $H_c$), 3.93 (br, 8 H, $H_b$), 4.19 (br, 8 H, $H_a$), 6.81 (d, $^3J_{f\text{-}e}$ = 8.3 Hz, 2 H, $H_f$), 7.48 (s, 2 H, $H_d$), 7.53 (d, $^3J_{e\text{-}f}$ = 8.3, 2 H, $H_e$): $^{13}$C RMN {$^1$H} (125 MHz, $CDCl_3$) $\delta_C$ 24.7 ($C_h$), 29.4 ($C_i$ and $C_j$), 38.2 ($C_g$), 69.2-69.4 ($C_c$), 69.6-69.8 ($C_b$), 71.3-71.4 ($C_a$), 111.7 ($C_f$), 112.5 ($C_d$), 123.1 ($C_e$), 130.6 ($C_{ipso}$), 148.5 ($C_{ipso}$), 153.0 ($C_{ipso}$), 199.3 ($C_{C=O}$): $\nu_{max}$/cm$^{-1}$ 1675 ($C_{C=O}$): mp 112 °C: $M_w$ = 8.1 kDa, $Đ$ = 1.3.

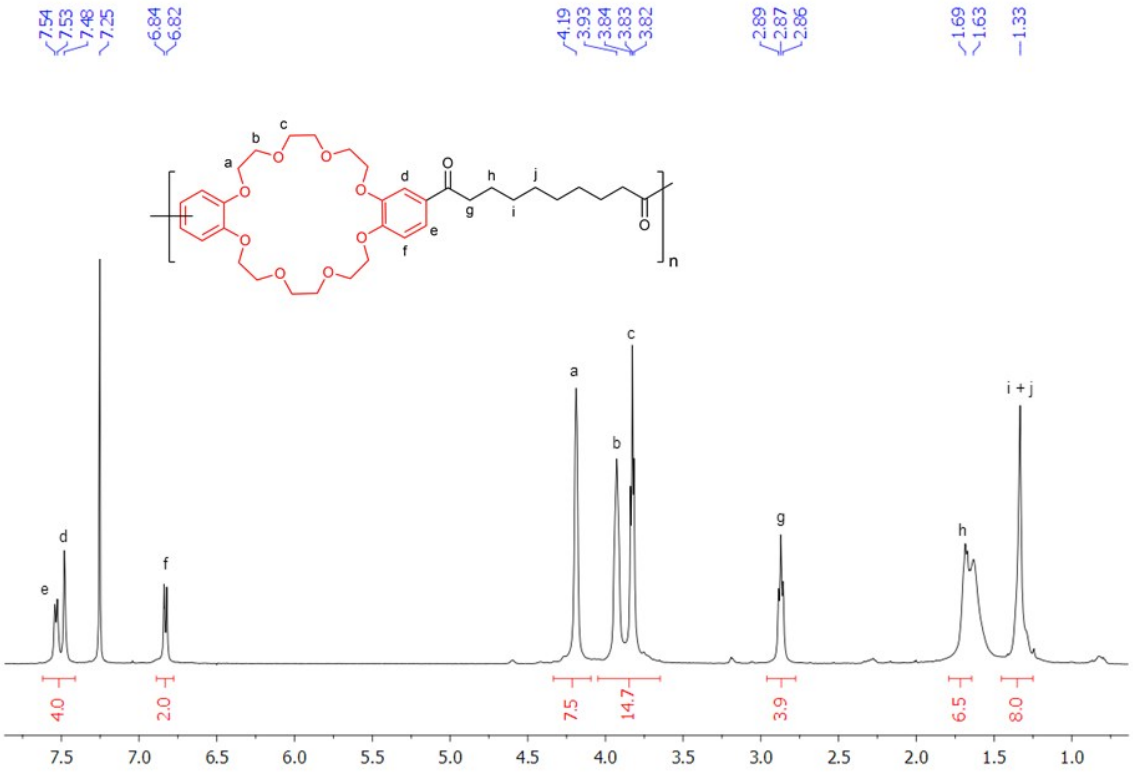



**Figure S11.** $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of poly[ketone] at 298 K.

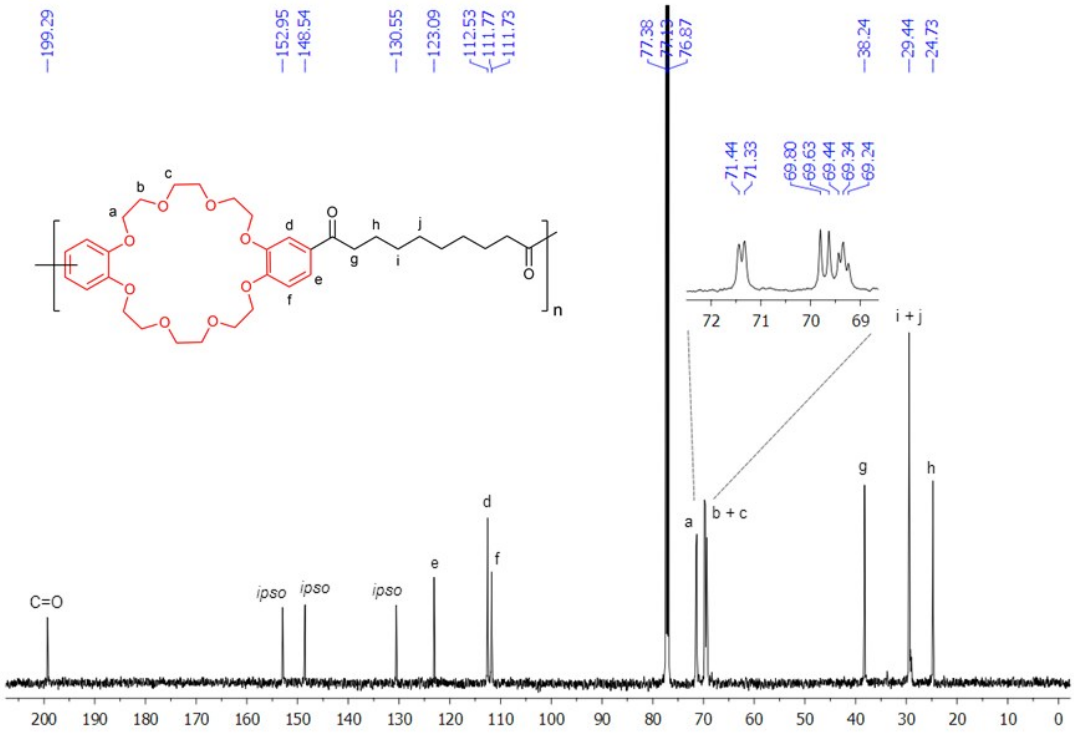



**Figure S12.** $^{13}C$ {$^{1}H$} NMR spectrum (125 MHz, $CDCl_3$) of poly[ketone] at 298 K.

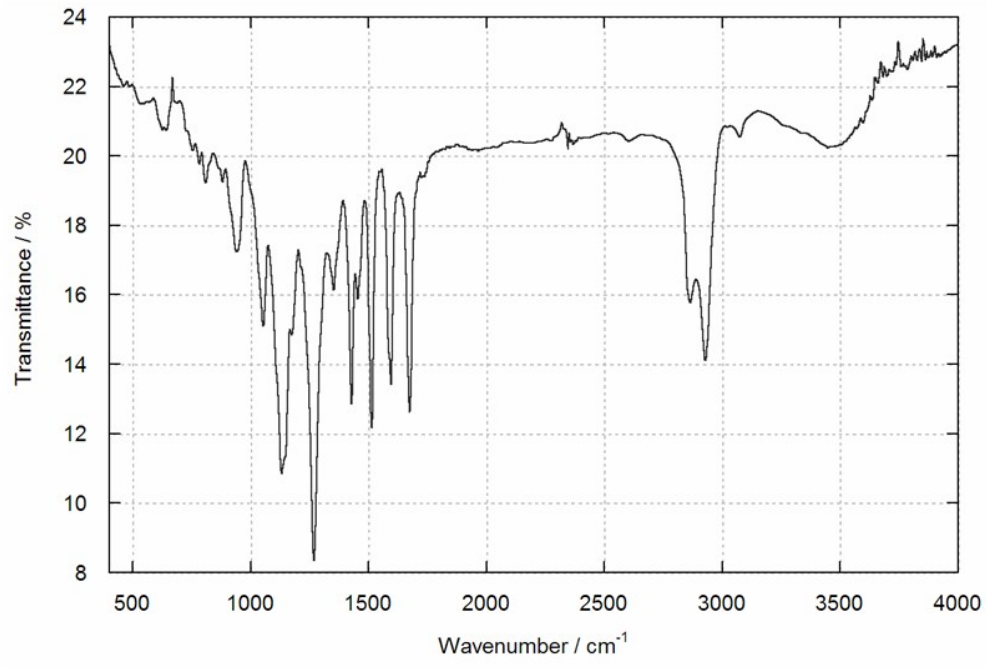



**Figure S13.** FT-IR spectrum of precursor poly[ketone].

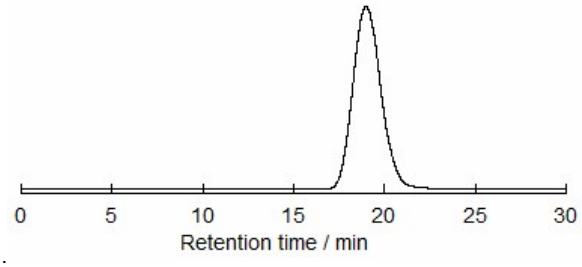
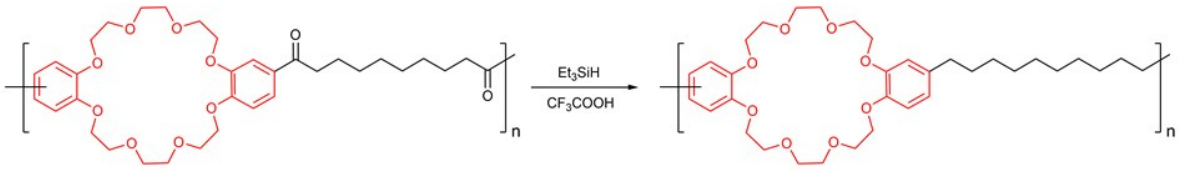



**Figure S14.** GPC traces for the obtained poly[ketone].

## *2.4 Poly[**DB24C8**]*




**Scheme S4.** Synthesis of poly[**DB24C8**].

Poly[**DB24C8**] was prepared following a previously reported method.[2] To a solution of poly[ketone] (400 mg, 0.65 mmol) and $CF_3COOH$ (2.8 mL) in $CH_2Cl_2$ (3.3 mL), $Et_3SiH$ (1.5 mL, 8.99 mmol) was slowly added under $N_2$ atmosphere; the mixture was stirred at RT for 18 h. The solution was then poured into EtOH (100 mL) to obtain a yellowish solid, it was separated by filtration and washed with hot MeOH (100 mL) and acetone (100 mL); the pale yellow powder was determined to be poly[**DB24C8**] (343.3 mg, 90%). $^1$H NMR (500 MHz, $CDCl_3$), $\delta_H$ 1.27 (br, 12 H, $H_i$, $H_j$ and $H_k$), 1.54 (br, 4 H, $H_h$), 2.49 (t, $^3J_{g\text{-}h}$ = 7.5 Hz, 4 H, $H_g$), 3.81 (br, 8 H, $H_c$), 3.89 (br, 8 H, $H_b$), 4.13 (br, 8 H, $H_a$), 6.68 (br, 4 H, $H_d$ and $H_f$), 7.76 (d, $^3J_{e\text{-}f}$ = 8.0 Hz, 2 H, $H_e$): $^{13}$C RMN {$^1$H} (125 MHz, $CDCl_3$), $\delta_C$ 29.4 ($C_h$), 29.6 ($C_i$), 29.7 ($C_j$), 31.8 ($C_k$), 35.6 ($C_g$), 69.5-69.7 ($C_c$), 70.1 ($C_b$), 71.3 ($C_a$), 114.3 ($C_f$), 114.6 ($C_d$), 121.0 ($C_e$), 136.5 ($C_{ipso}$), 146.9 ($C_{ipso}$), 148.8 ($C_{ipso}$): mp 80 °C: $M_w$ = 24.5 kDa, $Đ$ = 1.3.

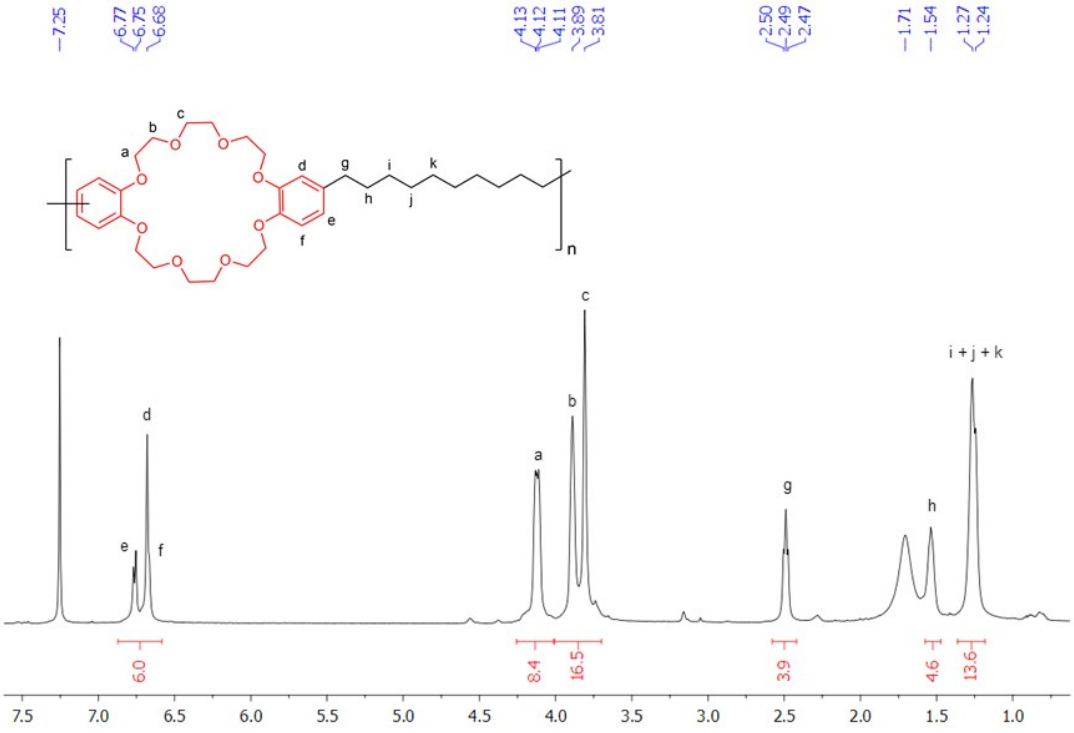



**Figure S15.** $^1$H NMR spectrum (500 MHz, $CDCl_3$) of poly[**DB24C8**] at 298 K.

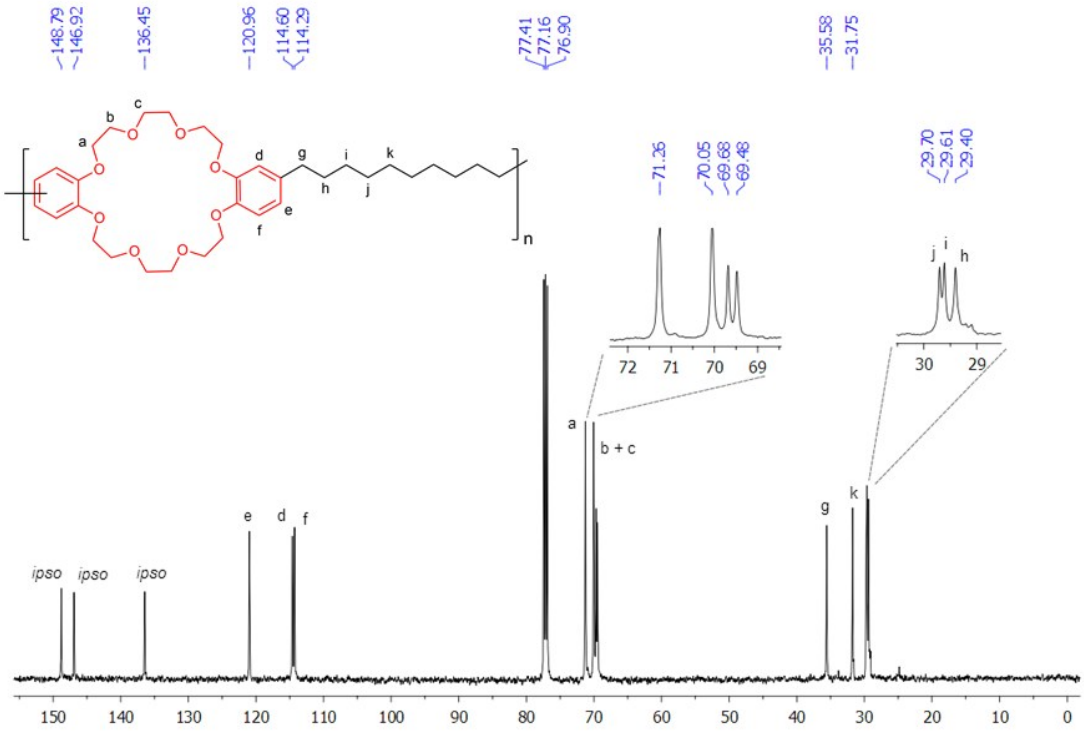



**Figure S16.** $^{13}C$ {$^{1}H$} NMR spectrum (125 MHz, $CDCl_3$) of poly[**DB24C8**] at 298 K.

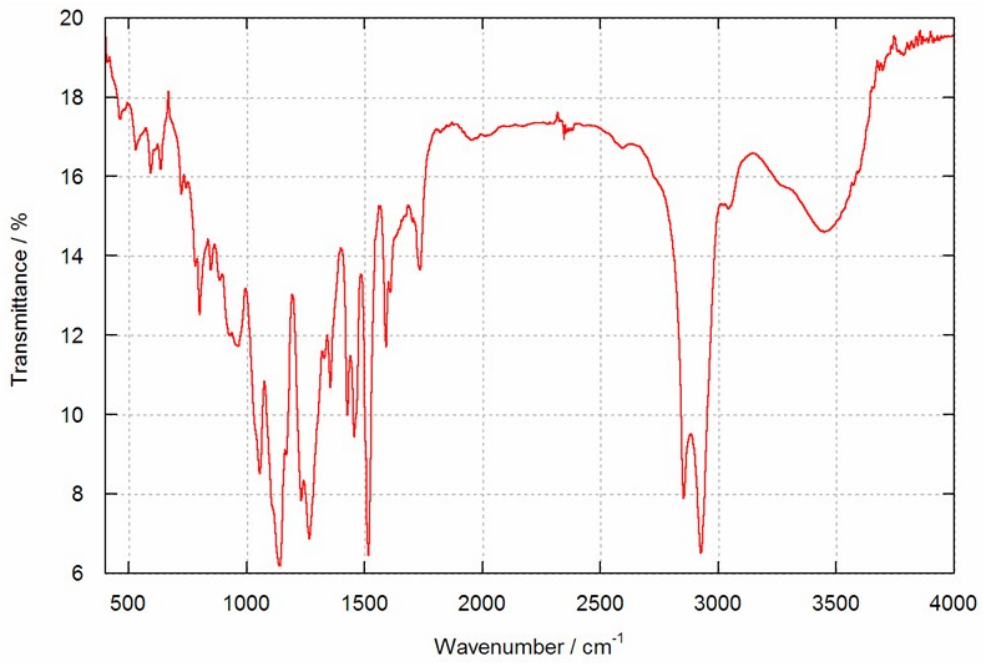



**Figure S17.** FT-IR spectrum of poly[**DB24C8**].

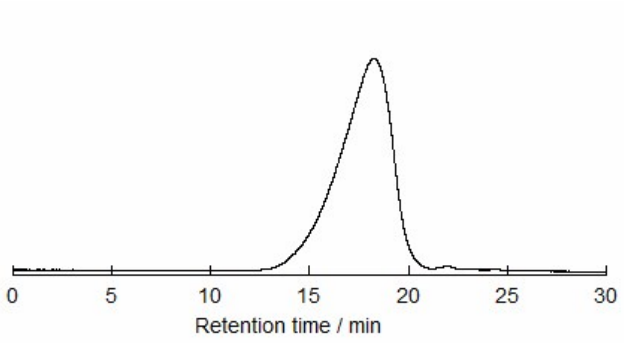
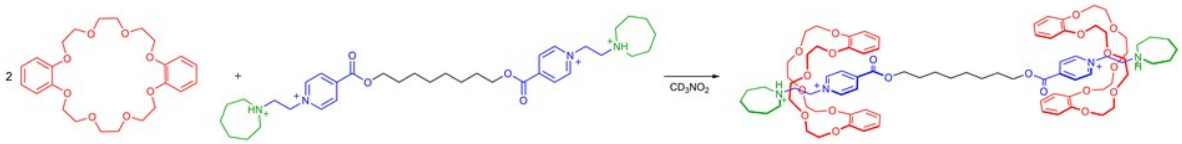



**Figure S18.** GPC traces for the synthesized poly[**DB24C8**].

## 3. Molecular and macromolecular complexes

### *3.1 [3]Pseudo-rotaxane [**1**·$H_2$⊂(**DB24C8**)$_2$][$PF_6$]$_4$*




**Scheme S5.** Formation of complex [**1**·$H_2$⊂(**DB24C8**)$_2$][$PF_6$]$_4$.

To form complex [**1**·$H_2$⊂(**DB24C8**)$_2$][$PF_6$]$_4$, **DB24C8** ether was mixed with guest [**1**·$H_2$][$PF_6$]$_4$ in nitromethane-$d_3$, [guest] = 3 x $10^{-3}$ M; [host] = 2[guest]. Solution was maintained at 20 °C for 20 days and periodically monitored by $^1$H NMR spectroscopy (see Fig. S19). Complex formation was evidenced by a colour change in solution, from colourless to yellow.

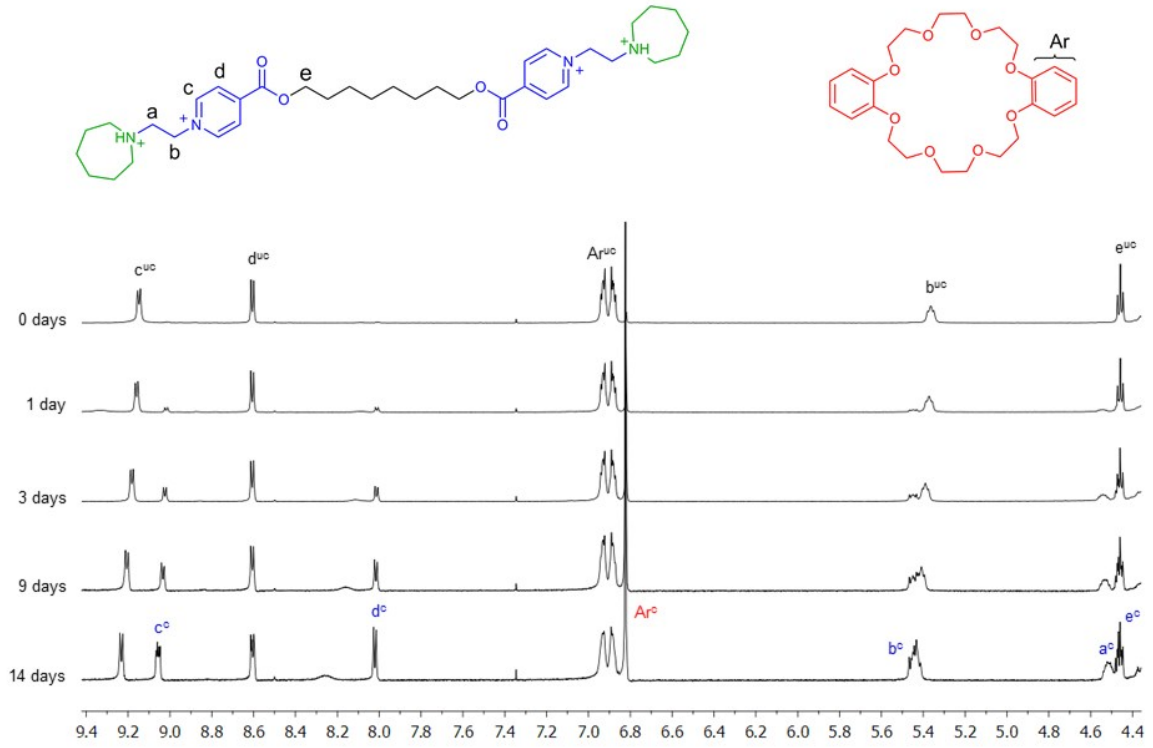



**Figure S19.** Partial $^1$H NMR spectra (500 MHz, $CD_3NO_2$) for the formation of [**1**·$H_2$⊂(**DB24C8**)$_2$][$PF_6$]$_4$ at 293 K. Superscripts denote complex (c) and un-complex (uc) species.

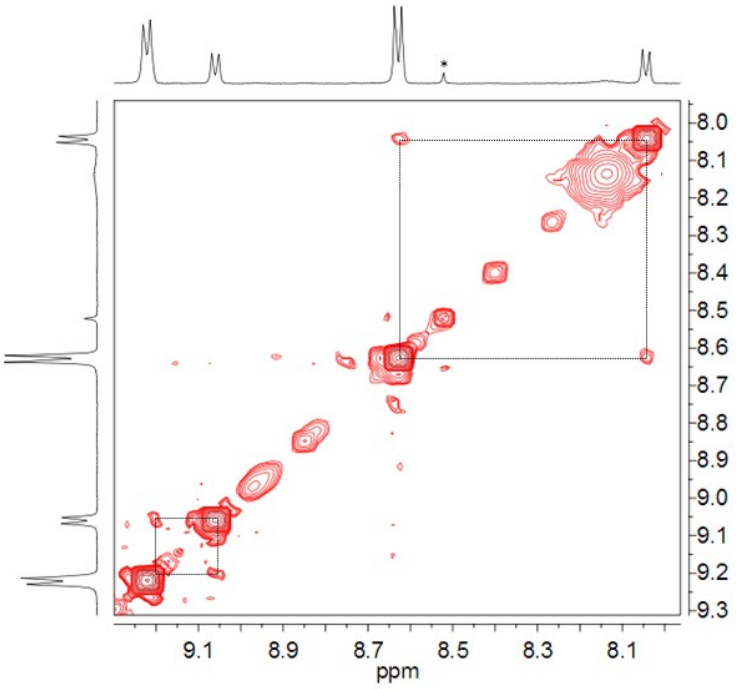



**Figure S20.** Partial 2D ROESY-NMR spectrum (400 MHz, $CD_3NO_2$) of complex [**1**·$H_2$⊂(**DB24C8**)$_2$][$PF_6$]$_4$. Crossed peaks represent chemical exchange on aromatic region. *Solvent impurity.

[3]Pseudo-rotaxane was additionally characterised by HR-MS, the recorded spectrum is shown in Fig. S21. ESI-HRMS, *m/z* found for [**1** + H + 2(**DB24C8**)]$^{3+}$ 501.951518, calculated 501.951924, error -0.8 ppm.

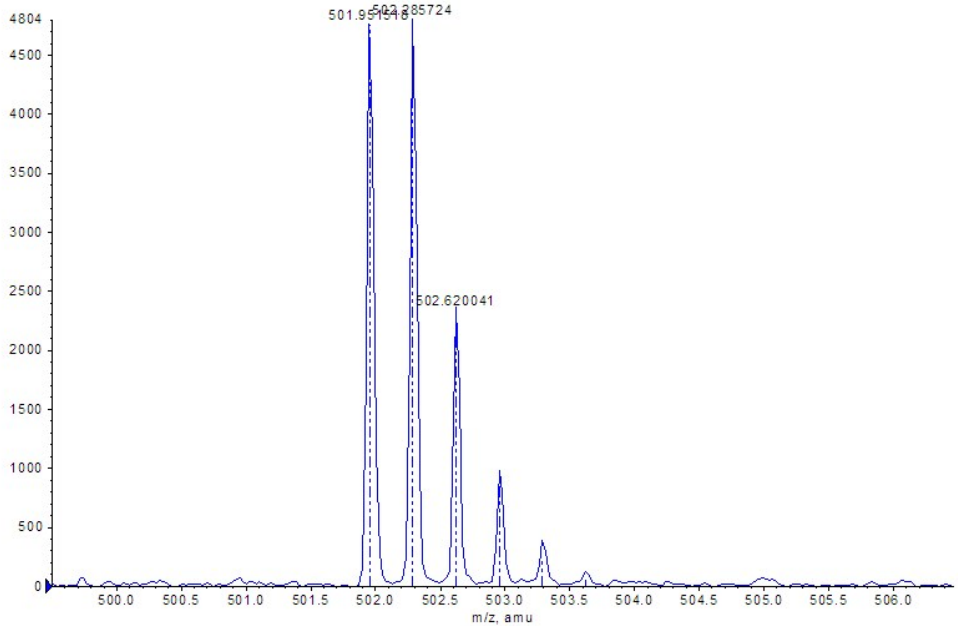



**Figure S21.** HR mass spectrum for the molecular ion [**1** + H +2(**DB24C8**)]$^{3+}$.

Global association constant $\beta$ (Eq. 1) for [3]pseudo-rotaxane formation was calculated using the equilibrium concentrations, which were estimated by signal integration on the system shown in Fig. S19. Guest signal $H_d$ was considered to obtain the proper data.

$$\beta = \frac{[Complex]}{[Guest][Host]^2} \quad \text{..... (Eq. 1)}$$

$H_d$ integral; 0.91 (complexed), 1.00 (un-complexed)

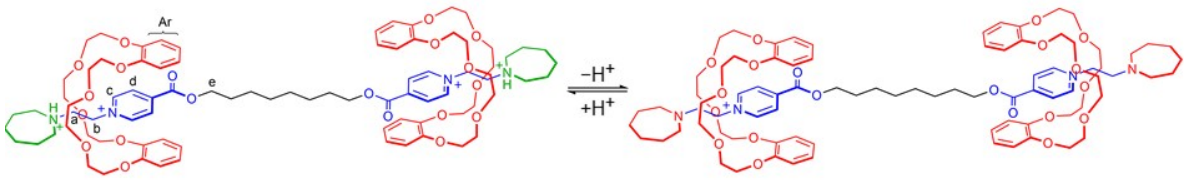
Initial concentration; [Guest] = $3 \times 10^{-3}$ M; [Host] = $6 \times 10^{-3}$ M

Equilibrium concentration; [Complex] = $1.44 \times 10^{-3}$; [Guest] = $1.56 \times 10^{-3}$ M; [Host] = $3.12 \times 10^{-3}$ M

Then, considering the obtained data;

$$\beta = \frac{1.4 \times 10^{-3} M}{(1.6 \times 10^{-3} M)(3.1 \times 10^{-3} M)^2} = 9.47 \times 10^4\ M^{-2}$$

*3.2 [3]Rotaxane [**1**⊂(**DB24C8**)$_2$][PF$_6$]$_2$*




**Scheme S6.** Transformation of [**1**·**H$_2$**⊂(**DB24C8**)$_2$]$^{4+}$ into [**1**⊂(**DB24C8**)$_2$]$^{2+}$.

[3]Pseudo-rotaxane complex [**1**·**H$_2$**⊂(**DB24C8**)$_2$]$^{4+}$ was transformed into its permanently interlocked analogue, [3]rotaxane [**1**⊂(**DB24C8**)$_2$]$^{2+}$, by a proton transfer reaction. To a solution of [**1**·**H$_2$**⊂(**DB24C8**)$_2$][PF$_6$]$_4$, obtained with guest [**1**·**H$_2$**][PF$_6$]$_4$ ($1 \times 10^{-2}$ M) and host **DB24C8** ($2 \times 10^{-2}$ M) in nitromethane-$d_3$ at 50 °C for 12 h, $^t$BuOK (2.0 equivalents) was added from a 1.0 M solution in $^t$BuOH. Deprotonation was confirmed by significant changes observed in the $^1$H NMR resonances of product respect to those for the precursor (see Fig. S22); relative integrals also demonstrated no dissociation of **DB24C8** macrocycles after removing the ammonium site.

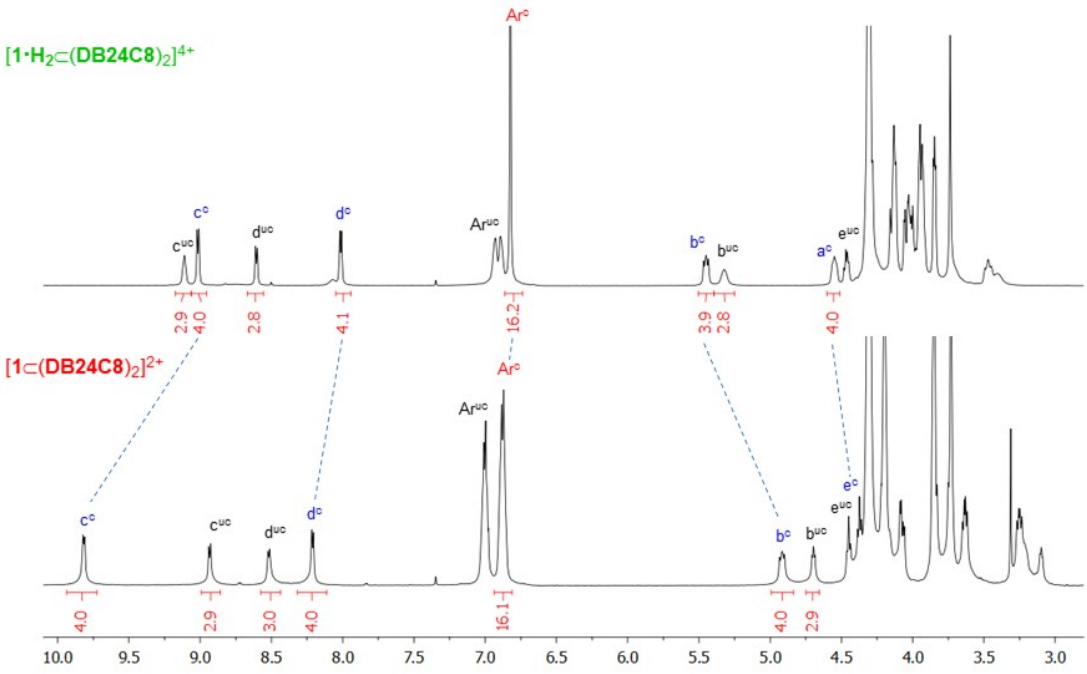
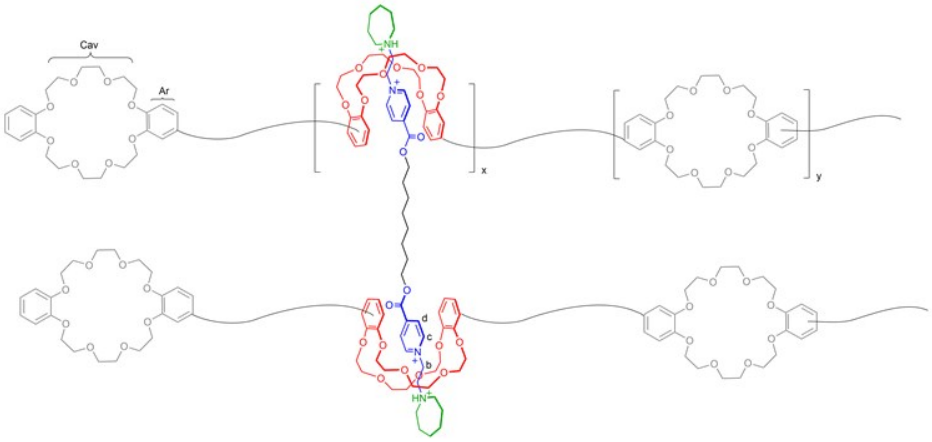



**Figure S22.** Partial $^1$H NMR spectra (500 MHz, $CD_3NO_2$) for [**1·H$_2$⊂(DB24C8)$_2$**]$^{4+}$ and its deprotonation to generate [**1⊂(DB24C8)$_2$**]$^{2+}$. Superscripts represent complex (c) and un-complex (uc) components.

### *3.3 Unlocked system **u-SPN***




**Scheme S7.** Generalized chemical structure for ***u*-SPN**.

Unlocked network based on pseudo-rotaxane units, ***u*-SPN**, was prepared by mixing a 1 × $10^{-2}$ M $CDCl_3$ solution of poly[**DB24C8**] and 5 × $10^{-3}$ M $CD_3NO_2$ solution of cross-linking molecule

[**1·H$_2$**][PF$_6$]$_4$; the resulting mixture was maintained at 20 °C and periodically monitored by $^1$H NMR (see Fig. S23). After 16 days, solvents were removed by rotatory evaporation at 30 °C and the residue was re-dissolved in $CD_3NO_2$ and preserved at 20 °C for 14 extra days to yield a deep yellow solution, containing ***u*-SPN**.

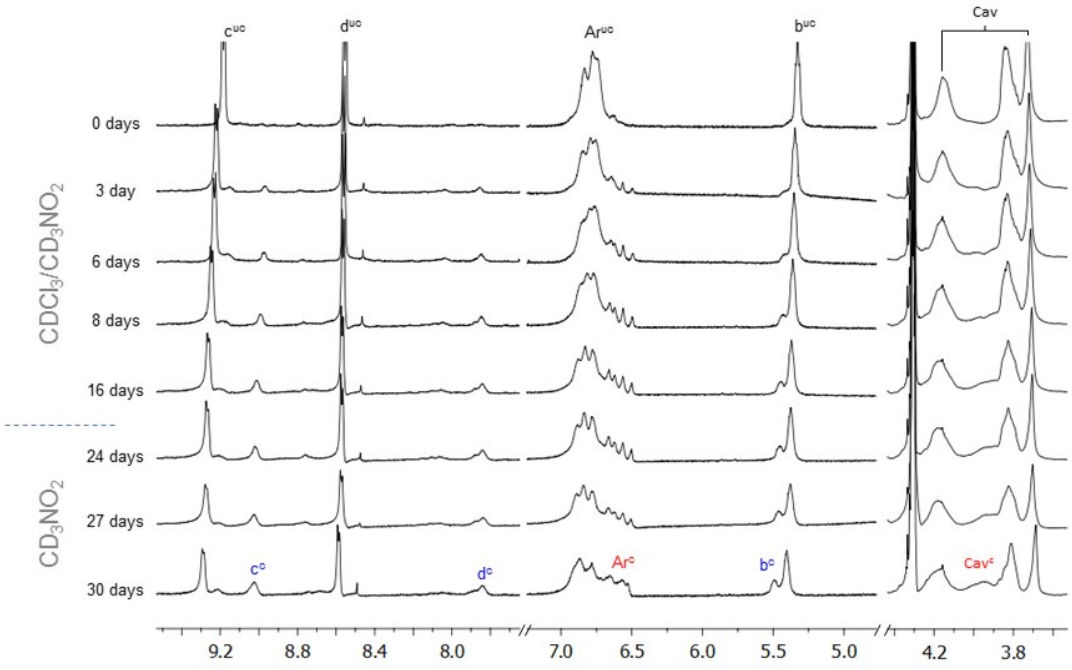
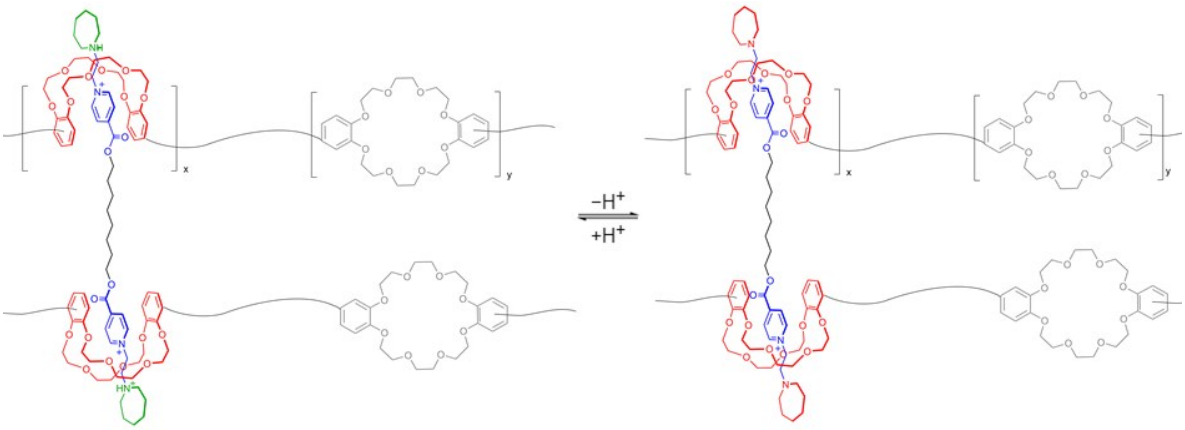



**Figure S23.** Partial $^1$H NMR spectra (500 MHz, 293 K) for the formation of ***u*-SPN**. Superscripts denote complex (c) and un-complex (uc) species.

Supramolecular gels were prepared under same conditions (time and solvents) but at higher concentrations; 1 × 10$^{-1}$ M and 5 × 10$^{-2}$ M for poly[**DB24C8**] and [**1·H$_2$**][PF$_6$]$_4$, respectively. Time for self-assembly can be reduced by increasing reagents concentration or by heating at 40 °C. Polymeric films were casted from ***u*-SPN** solutions in $MeNO_2$ or MeCN.

*3.4 Locked system **l-SPN***




**Scheme S8.** Transformation of ***u*-SPN** into ***l*-SPN**.

Unlocked network, ***u*-SPN**, was transformed into a rotaxane-based locked material, ***l*-SPN**, by a proton transfer reaction. A portion of ***l*-SPN**, in a film form, was poured in a DIEA solution (1.0 M in MeCN), the suspension was maintained at RT for 2 hours and then solvent was removed under vacuum; all residue was copiously washed with DMSO to eliminate any traces of DIEA and non-associated [**1**][$PF_6$]$_2$, rinsed with MeCN and acetone and dried under vacuum to obtain the corresponding rotaxane network as yellow films.

Deprotonation reaction was further confirmed in a diluted system, 2 × $10^{-2}$ M of poly[**DB24C8**] and 1 × $10^{-2}$ M of guest [**1**·$\mathbf{H_2}$][$PF_6$]$_4$; $^1$H NMR experiments were recorded before and after adding DIEA, see Figure S24.

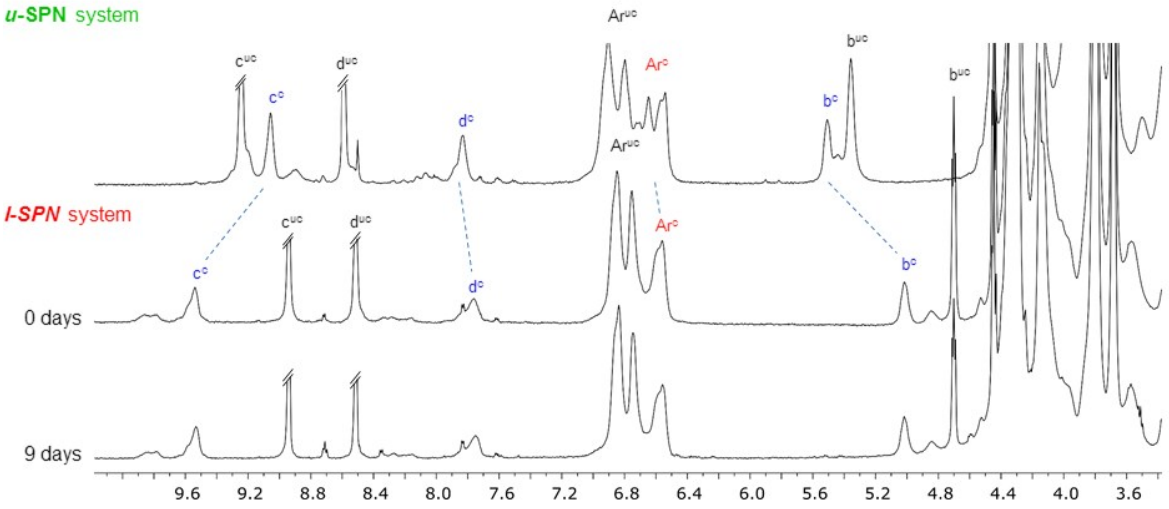



**Figure S24.** Partial $^1$H NMR spectra (500 MHz, $CD_3NO_2$) for the ***u*-SPN** and its transformation into ***l*-SPN** by base addition. Superscripts represent complex (c) and un-complex (uc) species.

## 4. Supramolecular networks

*4.1 Solvent polarity effect*

To analyse the dissociation process of the prepared supramolecular networks, ***u*-SPN** and ***l*-SPN**, 5 mg of both materials were treated separately with 0.6 mL of DMSO-$d_6$. Each system was maintained at RT and studied by $^1$H NMR spectroscopy.

Just after recording the first NMR experiment for the pseudo-rotaxane network (~5 min) all expected signals for guest molecule [**1**·$\mathbf{H_2}$]$^{4+}$ were observed. Using an external reference it was determined that compound concentration reached a maximum in about 0.5 h. In the NMR tube a white solid residue was generated; it was filtered and washed with MeCN and acetone and then solved in $CDCl_3$ to be analysed in a $^1$H NMR experiment, where the polymeric precursor poly[**DB24C8**] was exclusively identified (Figure S25).

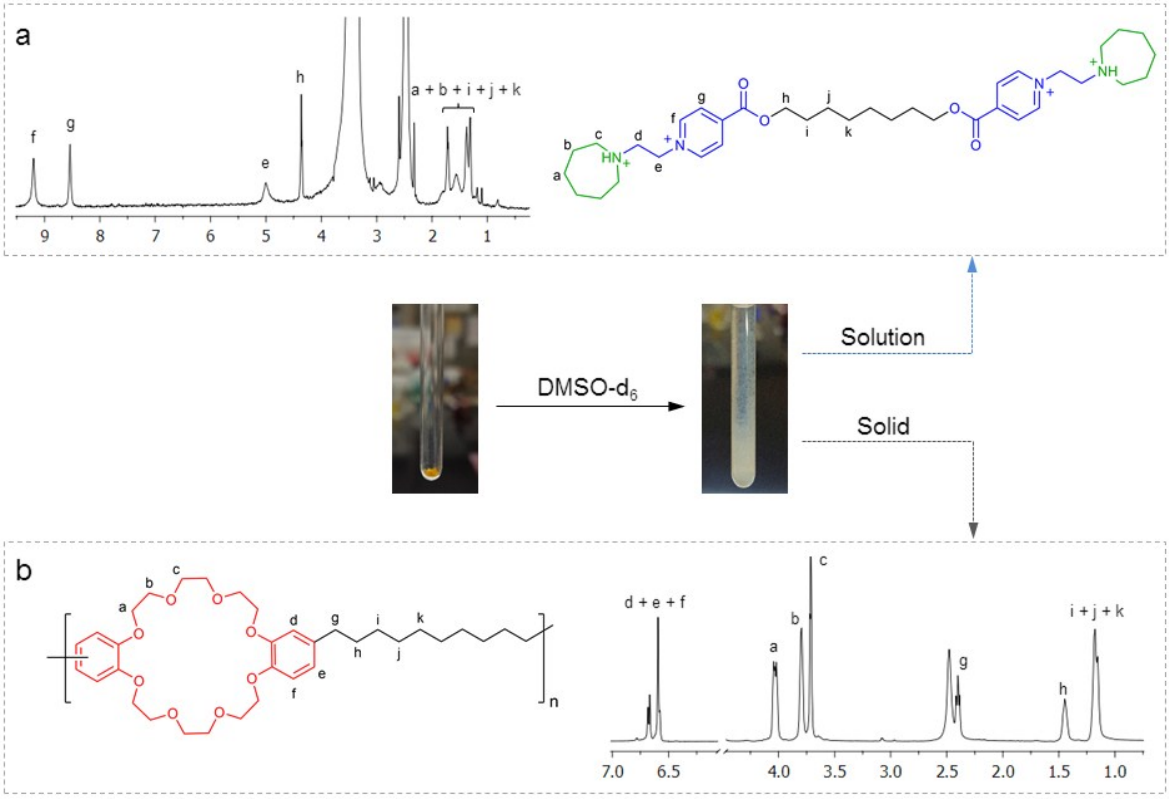



**Figure S25.** Behaviour of ***u*-SPN** material to solvent polarity. Partial $^1$H NMR spectra (500 MHz) for the dissociated components; (a) guest [**1**·$\mathbf{H_2}$][$PF_6$]$_4$ in DMSO-$d_6$ and (b) poly[**DB24C8**] solved in $CDCl_3$.

On the other hand, a contrasting behaviour was established for ***l*-SPN**, even after 3 days in DMSO-$d_6$ dissociation was not observed on the NMR experiments; this system was heated up to 60 °C during 2 hours and a new $^1$H NMR experiment was recorded, however, no signs of dissociation were detected (see Figure S26).

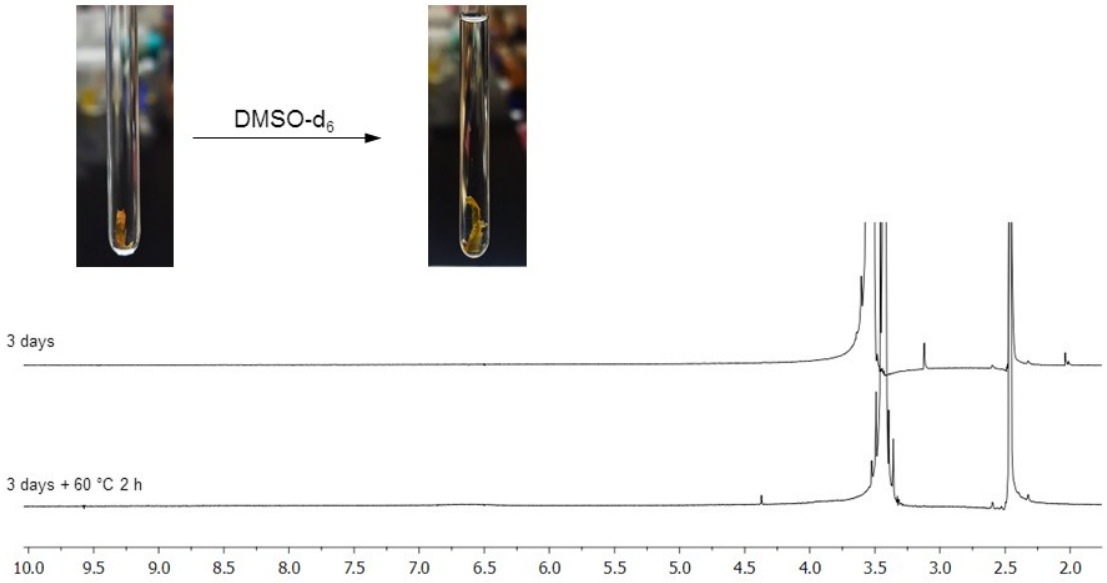



**Figure S26.** Solvent polarity effect over ***l*-SPN**. $^{1}$H NMR spectra (500 MHz) for the rotaxane material submerged in DMSO-$d_6$.

*4.2 Temperature effect*

Macroscopic response of the supramolecular networks to temperature was analysed with a microscope equipped with a heating plate; both materials in film forms were heated from room temperature to ~150 °C. Dissociation of the yellow ***u*-SPN** film generated a pale yellow opaque material containing polymer poly[**DB24C8**] and crystallised guest [**1·H$_2$**][PF$_6$]$_4$ (Figure S27a). On the other hand, the experiment with rotaxane material did not show any significant change over this temperature range; only softening and a slight colour change were confirmed (see Figure S27b).

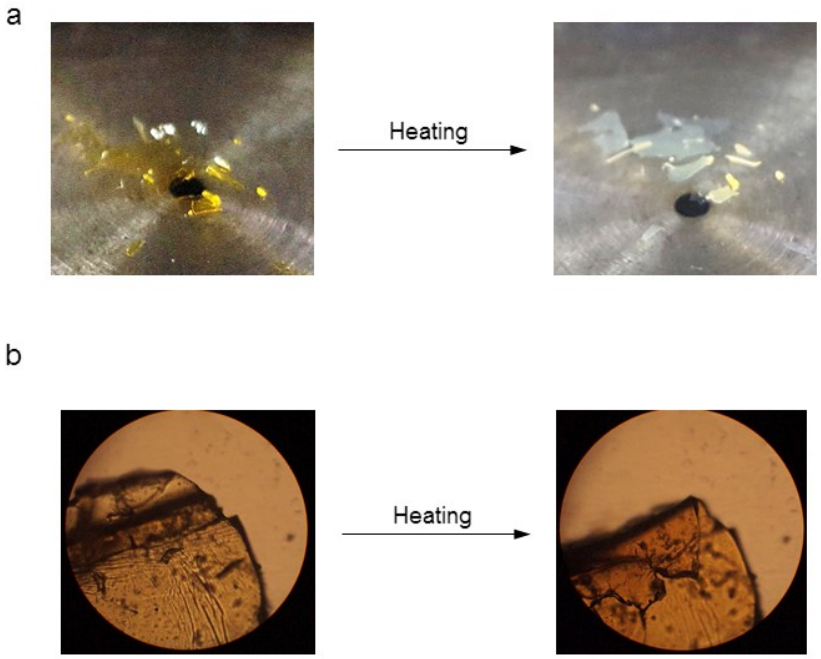



**Figure S27.** Macroscopic effect to temperature of (a) ***u*-SPN** and (b) ***l*-SPN**.

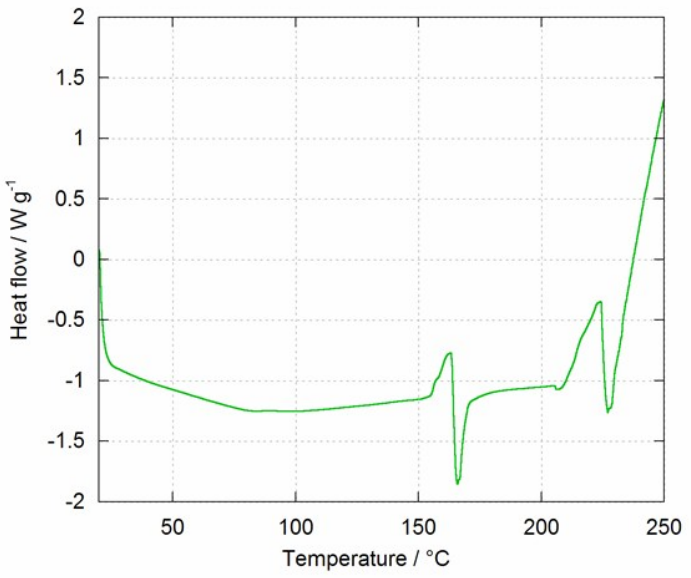



**Figure S28.** DSC traces for the dissociated ***u*-SPN**. Poly[**DB24C8**] $T_f$ = 80 °C; [**1**·$H_2$][$PF_6$]$_4$ $T_f$ = 170 °C; $T_{decomp}$ = 230 °C.

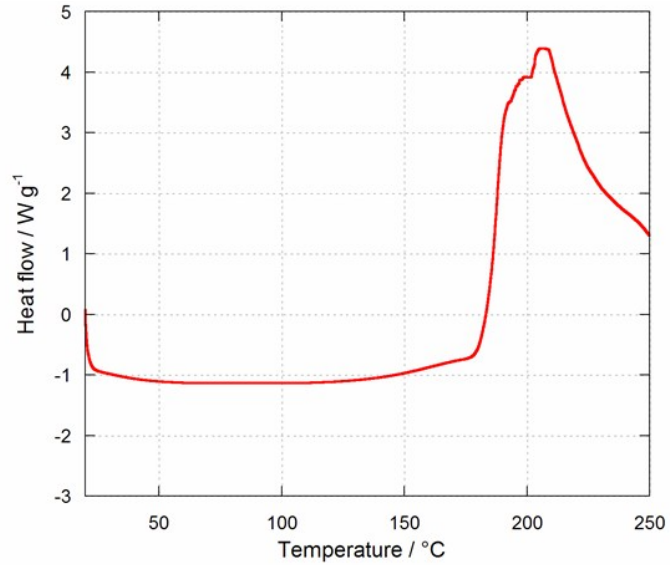



**Figure S29.** DSC traces of ***I*-SPN** material.

*4.3 Acid effect*

To convert the rotaxane network in a dissociable one, macromolecular complex was protonated to reactivate the ammonium group. Rotaxane material (5 mg) was poured in TfOH (0.05 mL) and maintained at ambient conditions for 1 hour; then 0.5 mL of $CD_3NO_2$ were added and all material became soluble. A $^1H$ NMR experiment was recorded (see Fig. S30) where the corresponding resonances for poly[**DB24C8**] and compound [**1**·$\mathbf{H_2}$][TfO]$_4$ were detected.

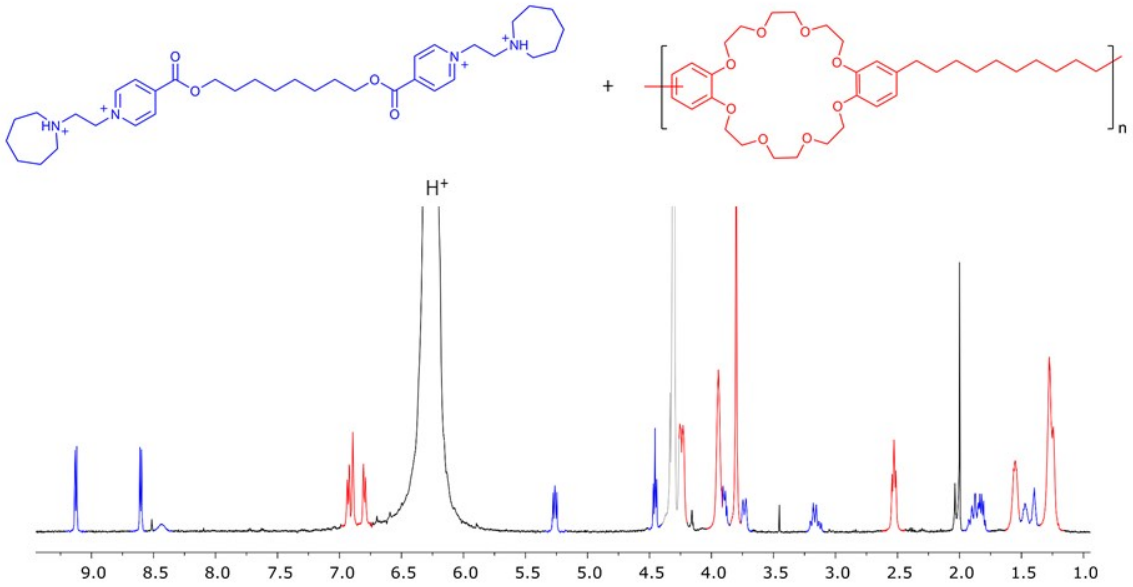



**Figure S30.** ***I*-SPN** dissociation driven by re-protonation. $^1H$ NMR spectrum (500 MHz, $CD_3NO_2$). Colour code: guest (blue) and polymer (red).

## 6. References

[1] M. G. Zolotukhin, M. C. Hernández, A. M. Lopez, *et al.*, *Macromolecules*, 2006, **39**, 4696–4703.

[2] A. C. Catalan and J. Tiburcio, *Chem. Commun.*, 2016, **52**, 9526–9529.