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Electronic Supplementary Information

Self-sorting assembly of a calixarene/crown ether polypseudorotaxane gated by ion-pairing

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Experimental section

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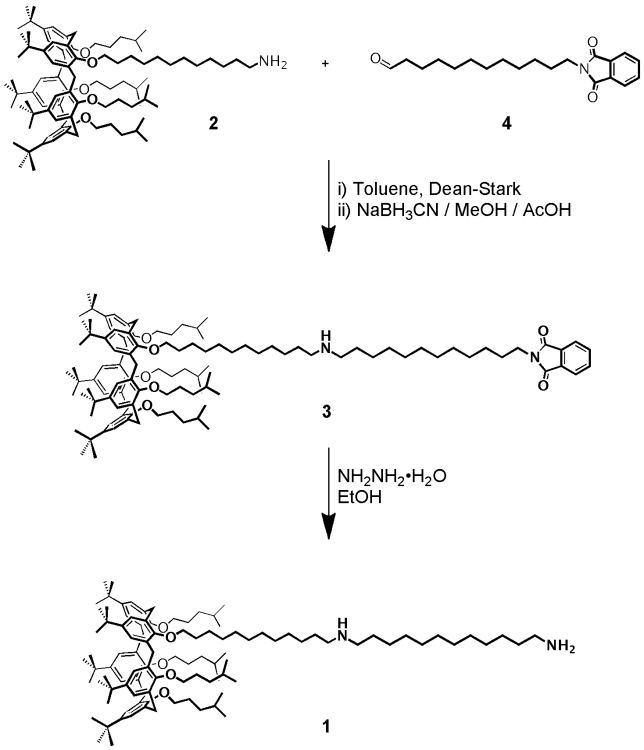
General

^{1}H NMR spectra (500 MHz) were recorded at 298 K in either in $CDCl_3$ or CD_2Cl_2. Chemical shifts are reported in ppm and are referenced to the residual solvent (7.26 and 5.32 ppm, respectively). ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$, at 125 MHz. Chemical shifts are reported in ppm and are referenced to the residual solvent (77.0 ppm). Where present, ^{1}H NMR peak assignments follow from COSY experiments. Mass spectra were measured on an ion trap electrospray instrument. ESI(+)-MS measurements were performed on a triple-quadrupole mass spectrometer equipped with an electrospray ion source, using $CHCl_3$ as the solvent. Anhydrous solvents were either obtained commercially or dried by standard methods prior to use, while other chemicals were reagent grade, routinely used without any further purification. Column chromatography was performed on silica gel (Merck, 230–400 mesh).



Scheme S1. Synthesis of 12-((12-aminododecyl)amino)dodecyloxy-calix[5]arene **1**

Synthesis of 31-[12-((12-phthalimidododecyl)amino)dodecyloxy]-32,33,34,35-tetra-(4-methylpentyloxy)-5,11,17,23,29-penta-*tert*-butylcalix[5]arene (3)

A solution of 12-aminododecyloxy-calix[5]arene[S1] **2** (250 mg, 0.188 mmol) and 12-(*N*-phthalimido)-dodecanal[S2] **4** (62 mg, 0.188 mmol) in toluene (50 mL) was heated under reflux with stirring in a Dean-Stark apparatus for 18 h. The reaction mixture was cooled down to room temperature and treated with a solution of $NaCNBH_3$ (35 mg, 0.564 mmol) in anhydrous MeOH (10 mL) and glacial AcOH (25 mL). The resulting mixture was stirred at room temperature under

S1 S. Pappalardo, V. Villari, S. Slovak, Y. Cohen, G. Gattuso, A. Notti, A. Pappalardo, I. Pisagatti and M. F. Parisi, *Chem. Eur. J.*, 2007, **13**, 8164–8173.

S2 I. Sprung , A. Ziegler and S. L. Flitsch, *Chem. Commun.*, 2002, 2676–2677.

N_2 for a further 24 h. Water (15 mL) was then added and the reaction mixture was stirred at room temperature for 1 h. The solvents were evaporated under reduced pressure and the residue was partitioned between water (30 mL) and CH_2Cl_2 (30 mL). The aqueous layer was extracted with CH_2Cl_2 (2x30 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. Column chromatography (SiO_2, AcOEt/*n*-hexane 6:1, v/v) afforded **3** as an amorphous solid (110 mg, 35%).

^{1}H NMR ($CDCl_3$) δ 7.87–7.80 and 7.75–7.67 (2×m, Phth*H*, 4 H), 6.94, 6.92 and 6.90 (3×s, 1:2:2 ratio, Ar*H*, 10 H); 4.54 and 3.24 (AX system, *J* = 13.9 Hz, ArC*H*$_2$Ar, 10 H), 3.70–3.55 (m, C*H*$_2$O and C*H*$_2$NPhth, 12 H), 2.97–2.85 (m, C*H*$_2$NHC*H*$_2$, 4 H), 2.10–2.00, 1.94–1.84, 1.72–1.58 and 1.40–1.20 (4×m, 60 H), 1.06, 1.04, 1.02 (3×s, 2:2:1, C(C*H*$_3$)$_3$, 45 H), 0.94 (d, *J* = 6.2 Hz, CH(C*H*$_3$)$_2$, 24 H) ppm; ^{13}C NMR ($CDCl_3$) δ 168.5, 152.8, 152.7, 144.5(×2), 133.9, 133.8(×2), 132.2, 125.5, 125.4, 125.3, 125.2, 123.1(×2), 74.3, 38.1, 35.20, 35.15, 34.0, 33.9, 31.42(×2), 31.37(×2), 30.6, 30.2, 30.1, 29.44, 20.36, 29.2, 28.6, 28.4(×2), 28.3(×2), 26.9, 26.3, 22.8(×2). ESI MS *m/z* 1663 ([M+NH$_4$]$^+$, 100% rel. int.). Anal. Calcd for $C_{111}H_{170}N_2O_7$: C, 81.07; H, 10.42; N, 1.70. Found: C, 80.94; H, 10.44, N, 1.68.

Synthesis of 31-[12-((12-aminododecyl)amino)dodecyloxy]-32,33,34,35-tetra-(4-methylpentyloxy)-5,11,17,23,29-penta-*tert*-butylcalix[5]arene (1)

A stirred mixture of calix[5]arene **2** (100 mg, 0.060 mmol) and hydrazine monohydrate (30 μL, 0.6 mmol) in EtOH (10 mL) was refluxed for 3 h. The solvent was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$, washed with aqueous NaOH (5% w/w), dried (Na_2SO_4), and the solution was evaporated to dryness. Precipitation of the residue from $CH_3CN/CHCl_3$ afforded **1** as an amorphous solid (47 mg, 52%).

^{1}H NMR ($CDCl_3$) δ 7.03, 7.01 and 6.95 (3×s, 1:2:2 ratio, Ar*H*, 10 H); 4.54 and 3.25 (AX system, *J* = 13.4 Hz, ArC*H*$_2$Ar, 10 H), 3.73–3.60 (m, C*H*$_2$O, 10 H), 2.67 (t, *J* = 7.0 Hz, C*H*$_2$NH$_2$, 2 H), 2.58 (t, *J* = 7.2 Hz, C*H*$_2$NHC*H*$_2$, 4 H), 1.93–1.82 (m, 10 H), 1.66–1.53 (m, 8 H), 1.40–1.20 (3×m, 42 H), 1.12, 1.10, 1.04 (3×s, 2:2:1, C(C*H*$_3$)$_3$, 45 H), 0.94 (d, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$, 24 H) ppm; ^{13}C NMR ($CDCl_3$) δ 152.8, 152.7, 144.5(×2), 133.92, 133.88(×2), 133.76, 133.74, 125.5, 125.42, 125.36, 125.2, 74.3, 35.2, 35.1, 33.94, 33.93, 31.44, 31.41(×2), 31.36(×2), 29.70, 29.68, 29.5, 29.4, 29.3, 28.4, 28.3, 22.8(×2). ESI MS *m/z* 1516 ([M+H]$^+$, 100% rel. int.). Anal. Calcd for $C_{103}H_{168}N_2O_5$: C, 81.69; H, 11.18; N, 1.85. Found: C, 81.33; H, 11.29, N, 1.78.

General procedure for the formation of $(\mathbf{1}\cdot 2H^+\cdot 2Cl^-)_n$ and $(\mathbf{1}\cdot 2H^+\cdot 2OPic^-)_n$

A solution of the diamino precursor **1** (50 mg in 5 mL of CH_2Cl_2) was shaken with 5 mL of the pertinent acid solution (1 M HCl/H_2O for $(\mathbf{1}\cdot 2H^+\cdot 2Cl^-)_n$, and 1% picric acid in H_2O for $(\mathbf{1}\cdot 2H^+\cdot 2OPic^-)_n$). The organic layer was separated from the aqueous one, washed twice with 5 mL of H_2O, dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The solid residue obtained was kept under high vacuum (2 h, rt) and each sample used as such to prepare the relevant stock solutions. CH_2Cl_2 was passed through neutral alumina prior to use.

$TFPB^-/Cl^-$ anion exchange

A solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (44 mg, 50 μmol) in dry methanol (2 mL) was added to a solution of $(\mathbf{1}\cdot 2H^+\cdot 2Cl^-)_n$ (31 mg, 20 μmol) in dry CH_2Cl_2 (3 mL). The resulting solution was stirred overnight

at room temperature under an Ar atmosphere. After removing the solvents by evaporation, the solid residue was taken up in CH_2Cl_2, filtered and the resulting solution was evaporated to dryness.[S3]

^{1}H NMR Titrations and diffusion-ordered spectroscopy studies

Prior to use, solvents were filtered through neutral aluminium oxide to remove any traces of acid. Sample stock solutions (1 or 5 mM) of (**1**·2H$^+$·2Cl$^-$)$_n$ and (**1**·2H$^+$·2OPic$^-$)$_n$ were prepared by dissolving the solid in CD_2Cl_2. The stock solution of DB24C8 (25 mM) used for the ^{1}H NMR titrations was prepared by using the above-mentioned 1 or 5 mM solutions as the solvent, so as to keep a constant polymer concentration during crown ether addition.

DOSY experiments were carried out on a 500 MHz NMR spectrometer equipped with a z-gradient system capable of producing pulse gradients up to 50 gauss·cm^{-1}. All spectra were recorded in CD_2Cl_2 at 298 K, using a gradient stimulated echo with spin-lock and a convection compensation pulse sequence.

S3. Adapted from: C. Gaeta, F. Troisi and P. Neri, *Org. Lett.*, 2010, **12**, 2092–2095.

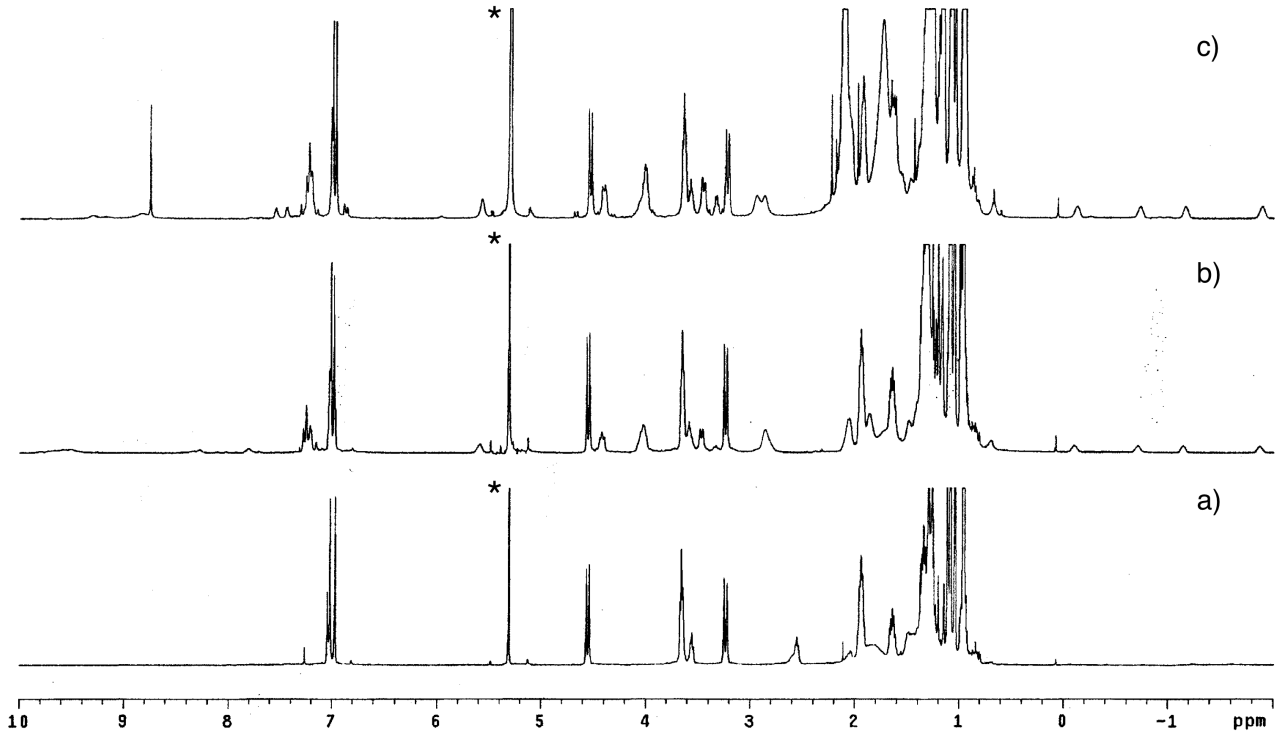


Fig. S1 ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of: a) [**1**] = 5 mM; b) [(**1**·2H^{+}·2Cl^{-})$_n$] = 5 mM and c) [(**1**·2H^{+}·2OPic^{-})$_n$] = 5 mM. Asterisks designate the residual solvent peak.

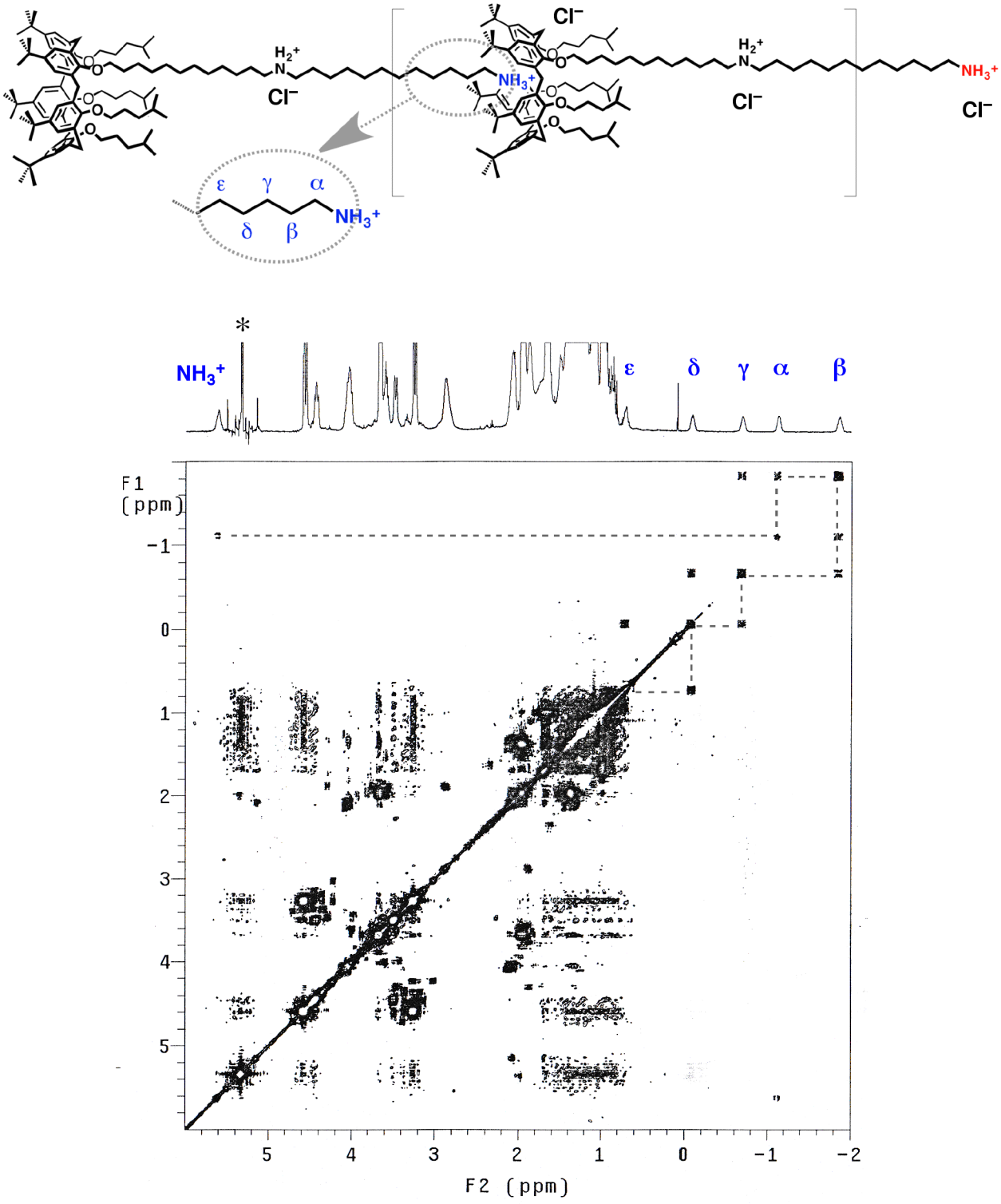


Fig. S2 COSY NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of $[(\mathbf{1}\cdot 2H^+\cdot 2Cl^-)_n]$ = 5 mM. The asterisk designates the residual solvent peak.

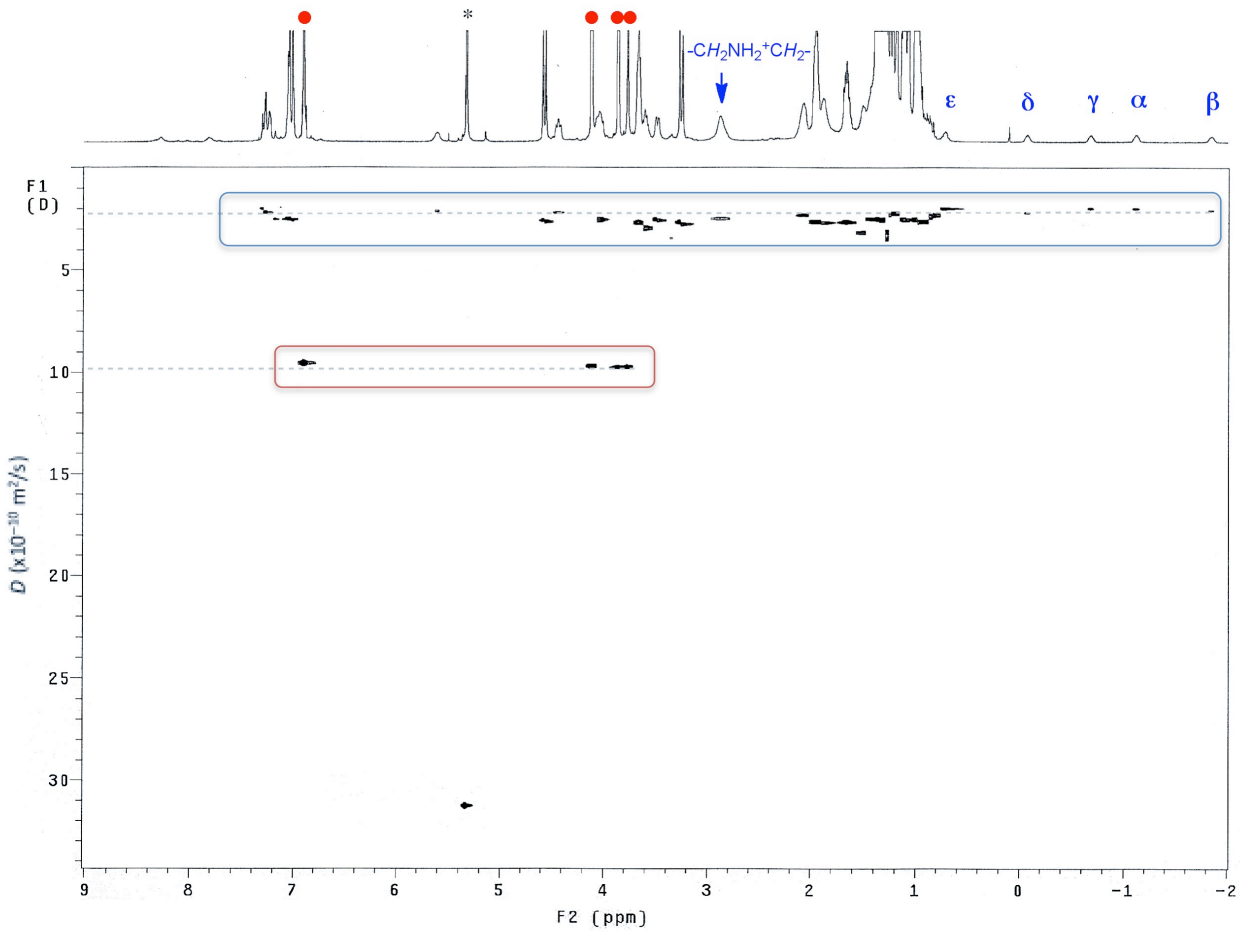


Fig. S3 DOSY plot (500 MHz, CD_2Cl_2, 298 K) of $[(\mathbf{1}\cdot 2H^+\cdot 2Cl^-)_n]$ = [DB24C8] = 5 mM. Red dots indicate DB24C8 resonances. The asterisk designates the residual solvent peak.

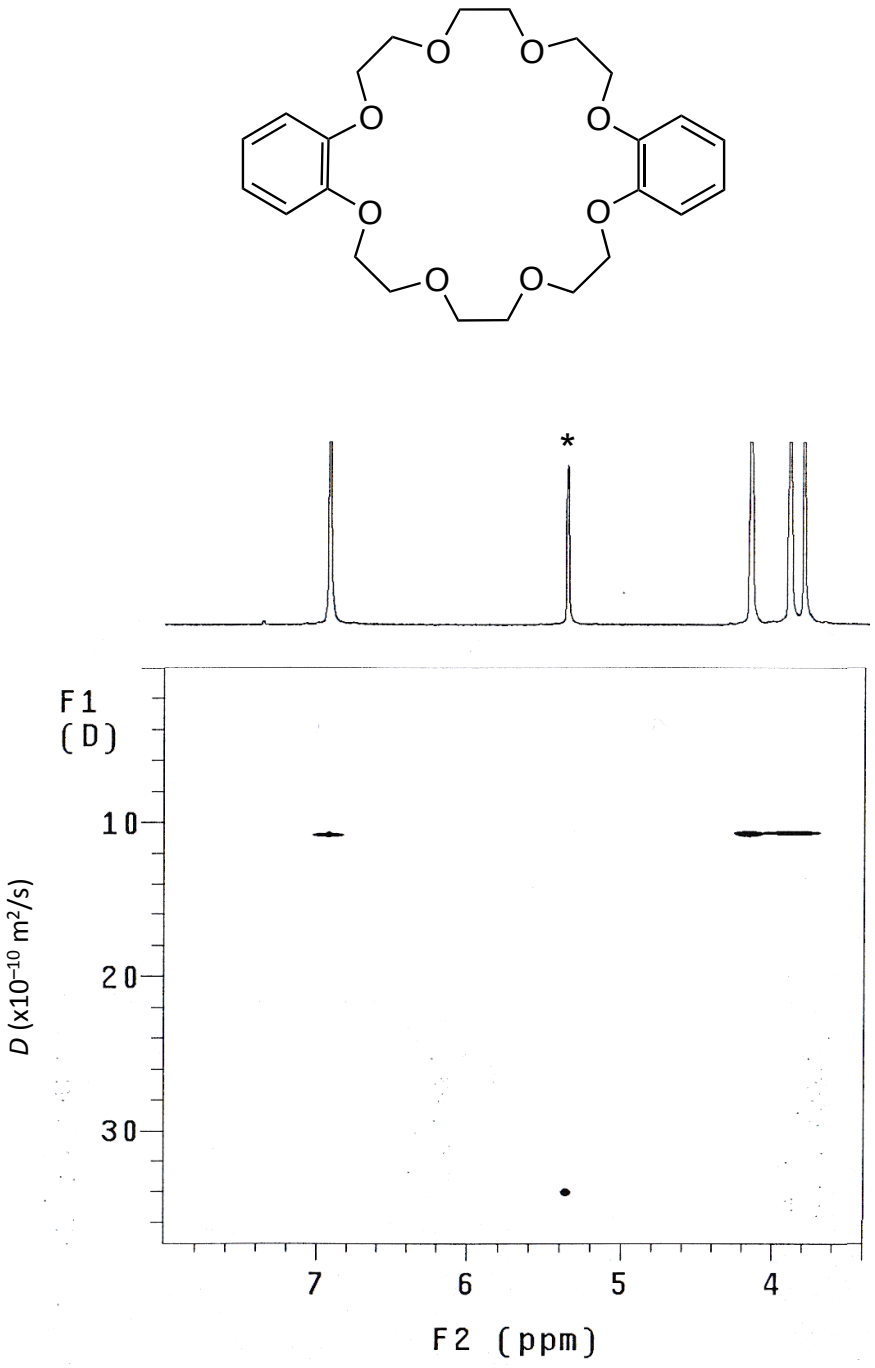


Fig. S4 DOSY plot (500 MHz, CD_2Cl_2, 298 K) of [DB24C8] = 5 mM. The asterisk designates the residual solvent peak.

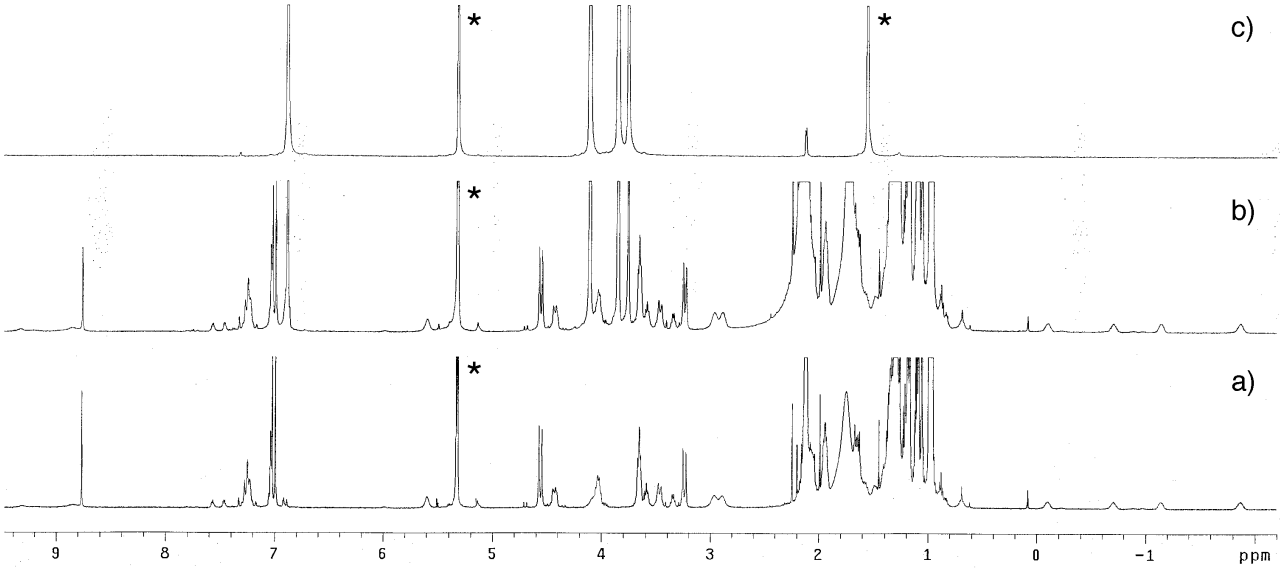
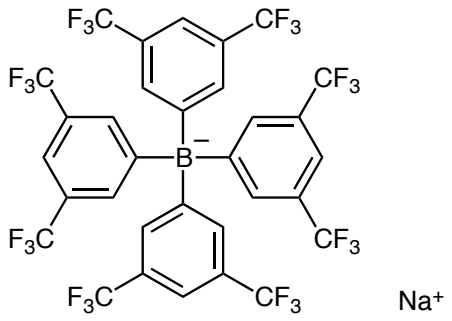


Fig. S5 ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of: a) [(**1**·2H^{+}·2OPic^{-})$_n$] = 1 mM ; b) [(**1**·2H^{+}·2OPic^{-})$_n$] = [DB24C8] = 1 mM; c) [DB24C8]= 1 mM. Asterisks designate residual solvent peaks.



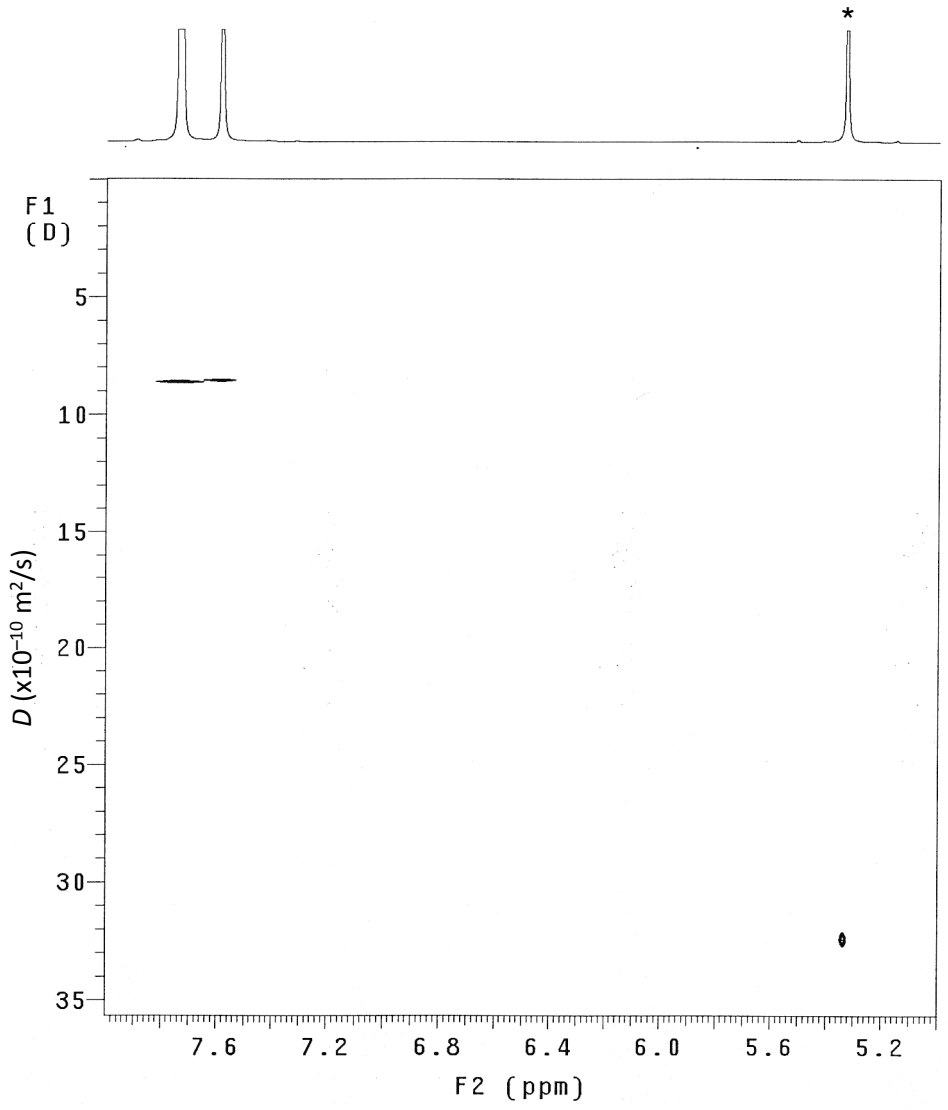


Fig. S6 DOSY plot (500 MHz, CD_2Cl_2, 298 K) of [Na^+TFPB^-] = 5 mM. The asterisk designates the residual solvent peak.

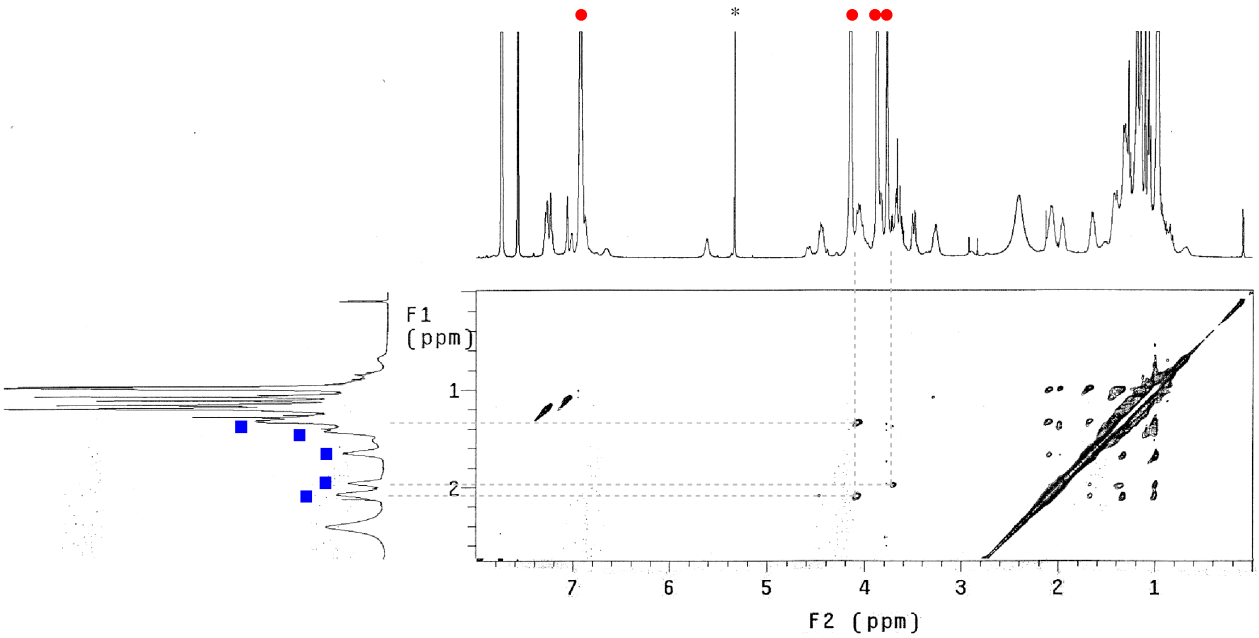


Fig. S7 ROESY NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of $[(\mathbf{1}\cdot 2H^{+}\cdot 2TFPB^{-})_n]$ = [DB24C8] = 1 mM. Red dots indicate DB24C8 resonances, blue squares indicate some resonances belonging to the dodecylaminododecyl moiety. The asterisk designates the residual solvent peak.

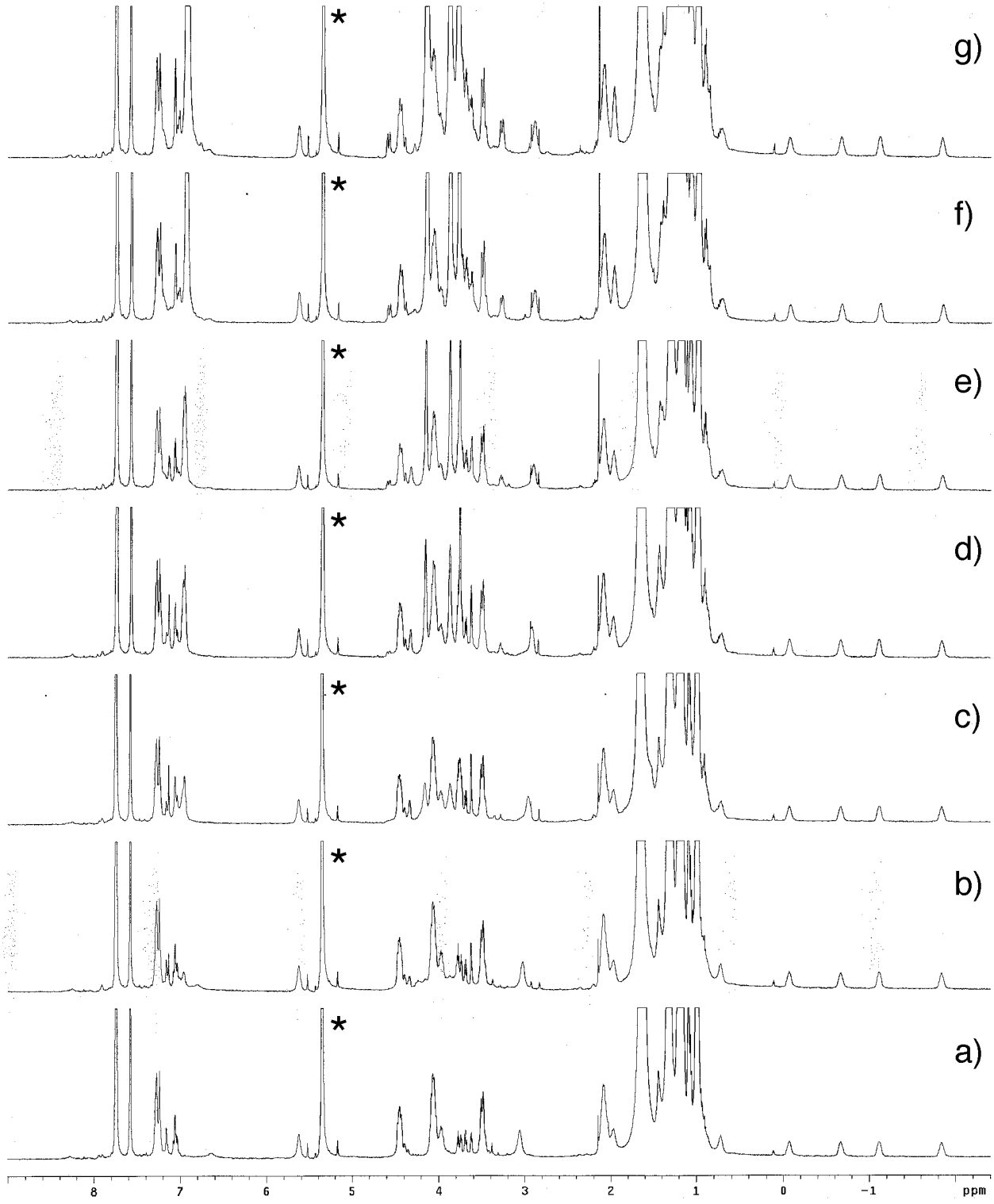


Figure S8. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of the titration of [(**1**·2H^{+}·2TFPB^{-})$_n$] = 1 mM (a) with DB24C8 ((b–g) = 0.25, 0.5, 0.75, 1, 2, 5 equiv., respectively). Asterisks designate the residual solvent peak.

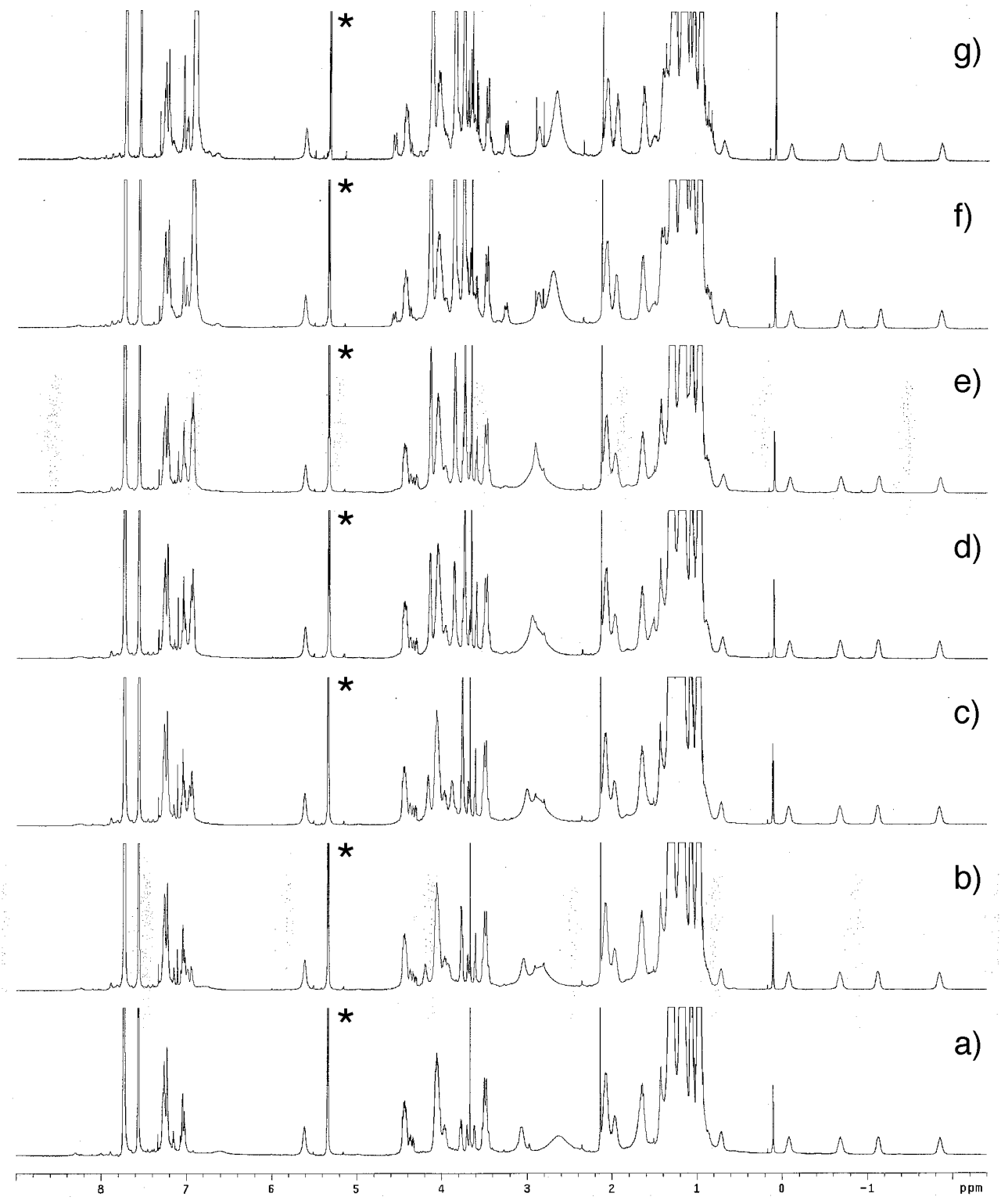


Figure S9. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of the titration of [(**1**·2H^{+}·2TFPB^{-})$_n$] = 5 mM (a) with DB24C8 ((b–g) = 0.25, 0.5, 0.75, 1, 2, 5 equiv., respectively). Asterisks designate the residual solvent peak.

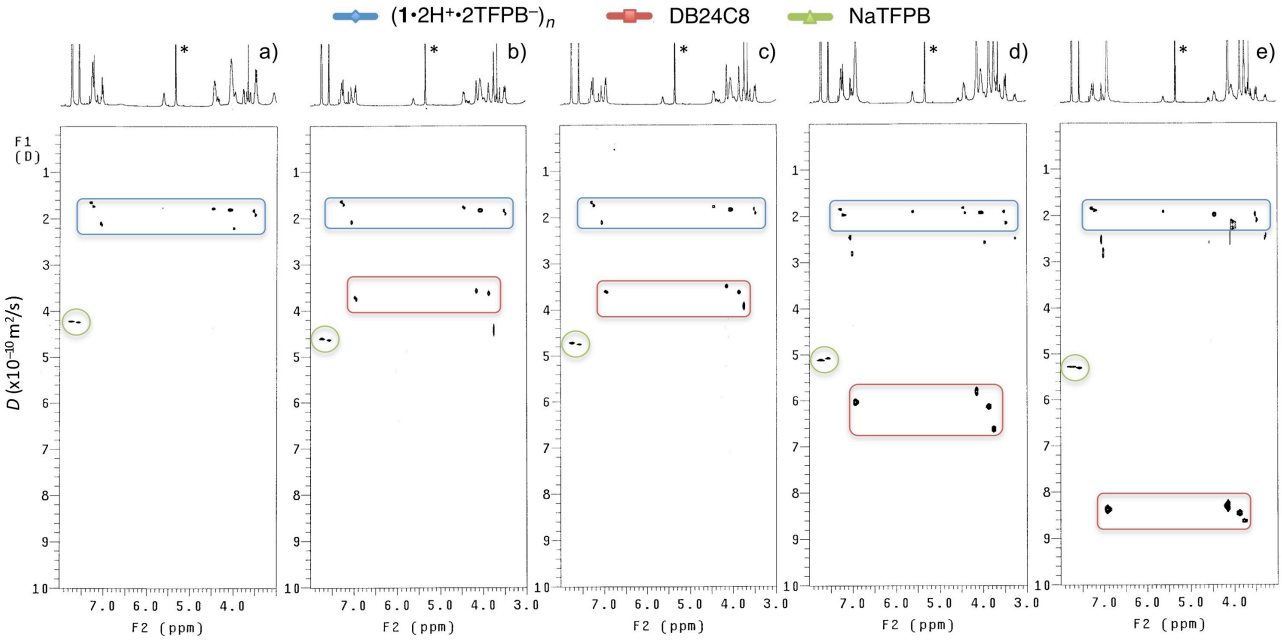


Figure S10. DOSY plots (500 MHz, CD_2Cl_2, 298 K) of the titration of [(**1**·$2H^+$·$2TFPB^-$)$_n$] = 5 mM (a) with DB24C8 ((b–e) = 0.75, 1, 2, 5 equiv., respectively). Asterisks designate the residual solvent peak.