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Arranging pseudorotaxanes octahedrally around [60]fullerene

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Supplementary Information

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S1. Synthesis

General Methods. Starting materials and reagents were purchased from Aldrich or Fisher and used as received. The bistriethyleneglycol-derivatised catechol[S1] **1** and the dibenzylammonium salt[S2] **5**·PF_6 were prepared following procedures reported in the literature. All reactions were performed under a nitrogen atmosphere and in dry solvents, unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel 60-F_{254} (Merck 5554). Flash column chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase. UV/Vis spectra were recorded at room temperature on a Varian 100 Bio-instrument. ^1H and ^{13}C NMR spectra were recorded on either a Bruker Avance 500 MHz or a Bruker Avance 600 MHz spectrometer at ambient temperature, unless otherwise noted. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ 7.26 ppm, CD_2Cl_2: δ 5.25 ppm. High resolution electrospray ionisation (HR–ESI) mass spectra were measured on a Micromass Q-TOF Ultima mass spectrometer.

Malonatobenzo[25]crown-8 (**2**). 1,2 Bis(2-(2-(2-ethoxy)ethoxy)ethanol) (**1**) (2.0 g, 5.35 mmol) in dry CH_2Cl_2 (50 mL) and malonyldichloride (0.6 mL) in dry CH_2Cl_2 (50 mL) was added over 6 h using syringe pump to a suspension of $NaHCO_3$ (1.0 g) in dry CH_2Cl_2 (350 mL). The resulting reaction mixture was stirred at room temperature for 12 h. The organic layer was washed with H_2O (2 x 100 mL), dried (Na_2SO_4) and evaporated under vacuum. The crude oil was purified by column chromatography (SiO_2) using 2% MeOH in CH_2Cl_2 as the eluent in order to obtain **2** (1.2 g, 52%) as yellow oil. ^1H NMR (125 MHz, CD_2Cl_2, 298 K) δ (in ppm): 6.89 (s, 4H), 4.25 (t, 4H), 4.11 (t, 4H), 3.83 (t, 4H), 3.70 (m, 8H), 3.63 (t, 4H), 3.38 (s, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ (in ppm): 166.86, 149.39, 121.84, 114.57, 71.32, 71.19, 70.27, 69.40, 69.35, 65.32 and 42.32. ESI-HRMS $[M+Na]^+$ *m/z* calculated 465.1737 found 465.1742.

Mono-adduct (3) of C_{60}. C_{60} (500 mg, 0.693 mmol, 1.5 equiv) was dissolved in dry PhMe (300 mL). After complete dissolution of the fullerene had occurred, CBr_4 (170 mg, 0.513 mmol, 1.1 equiv) and the malonate **2** (205 mg, 0.463 mmol, 1 equiv) were added to the PhMe solution.

Afterwards, a solution of DBU (80 μL, 0.513 mmol, 1.1 equiv) in PhMe (50 mL) was added dropwise during 4 h. After stirring overnight at ambient temperature, the reaction mixture was subjected directly to flash column chromatography (SiO_2) with PhMe as the eluent. After elution of traces of C_{60} with PhMe, the eluent was changed to PhMe/EtOAc (1:1) in order to isolate the product. Removal of the solvent gave **3** as a brown solid (312 mg, 0.269 mmol, 58 %). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ (in ppm): 6.89 (s, 4H), 4.61 (t, 4H), 4.14 (t, 4H), 3.89 (m, 8H), 3.78 (m, 4H), 3.73 (t, 4H). ^{13}C NMR (125 MHz, CD_2Cl_2, 298K) δ (in ppm): 163.90, 149.35, 145.86, 145.74, 145.68, 145.65, 145.37, 145.19, 145.16, 145.08, 144.38, 143.55, 143.48, 143.46, 142.70, 142.37, 141.43, 139.63, 121.81, 114.32, 72.12, 71.50, 71.20, 70.30, 69.35, 69.31, 67.06, 52.63. UV-Vis λ_{max} (in CH_2Cl_2): 258, 325, 425, 490 nm. ESI-HRMS $[M+H]^+$ *m/z* calculated 1161.1755 found 1161.1723.

Hexakis-adduct (4) of C_{60}. C_{60} (100 mg, 0.139 mmol, 1 equiv) was dissolved in dry PhMe (100 mL). After complete dissolution of the fullerene had occurred, CBr_4 (4.6 g, 13.9 mmol, 100 equiv) and the malonate **2** (614 mg, 1.39 mmol, 1 equiv) were added to the PhMe solution. Afterwards, a solution of DBU (420 μL, 2.80 mmol, 20 equiv) in PhMe (50 mL) was added dropwise over 4 h. After stirring for 48 h at ambient temperature, the reaction mixture was subjected directly to flash column chromatography (SiO_2) with PhMe as the eluent. After elution of traces of C_{60} with PhMe, the eluent was changed to CH_2Cl_2/MeOH (95:5) to isolate the crude product. A second column chromatographic separation (CH_2Cl_2/MeOH (96:4)) gave **4** as a orange solid (210 mg, 0.063 mmol, 45 %). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ (in ppm): 6.88 (s, 24H), 4.39 (t, 24H), 4.11 (m, 24H), 3.83 (m, 24H), 3.75 (m, 24H), 3.72 (m, 24H), 3.65 (m, 24H). ^{13}C NMR (125 MHz, CD_2Cl_2, 298K) δ (in ppm): 163.96, 149.38, 146.25, 141.54, 121.76, 114.35, 71.40, 71.06, 70.24, 69.60, 69.40, 69.15, 66.64, and 45.90. UV-Vis λ_{max} (in CH_2Cl_2): 270, 280, 315, 335 nm. ESI-HRMS $[M+Na]^+$ *m/z* calculated 3383.9993 found 3383.9868.

S2. NMR Spectroscopic Data

The [2]- and [7]pseudorotaxanes [$\mathbf{5}\cdot PF_6$ **3**] and [6.$\mathbf{5}\cdot PF_6$ **4**], respectively, were further characterised by ^{1}H-^{1}H correlation spectroscopy (COSY) (Figure S1 and S2). In order to obtain evidence for the formation of the inclusion complexes between the host **3** and **4** and guest $\mathbf{5}\cdot PF_6$

nuclear overhauser effect spectroscopy (NOESY) experiments (Figures S2 and S4) were performed on the [2]- and [7]pseudorotaxanes. The NH_2^+ protons on the $–CH_2NH_2^+CH_2–$ center can be correlated with the methylene protons (H_e and H_f) of the malonatobenzo[25]crown-8 host for both [2]- and [7]pseudorotaxanes (Figures S2 and S4). Additionally, in the case of the [2]pseudorotaxane, the methylene protons (H_e and H_f) of the host can be correlated with the benzylic protons (H_i) of the guest (Figure S2). These data support the proposal that the host **5**·PF_6 is threaded through the guests **3** and **4**, forming inclusion complexes.

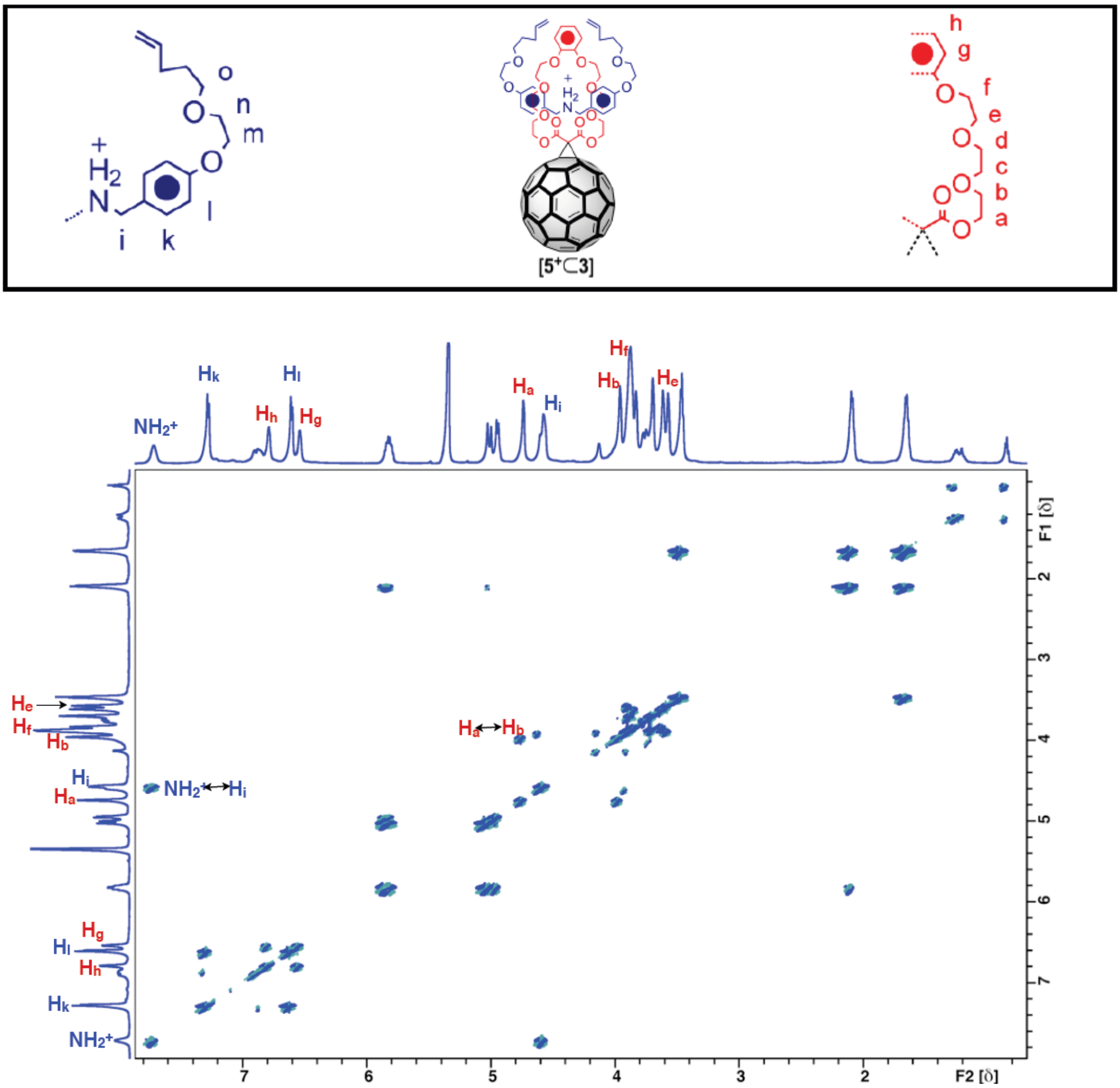

Figure S1. ^1H-^1H Correlation spectroscopy (COSY) of [$\mathbf{5}^+$ **3**] at 233 K in CD_2Cl_2.

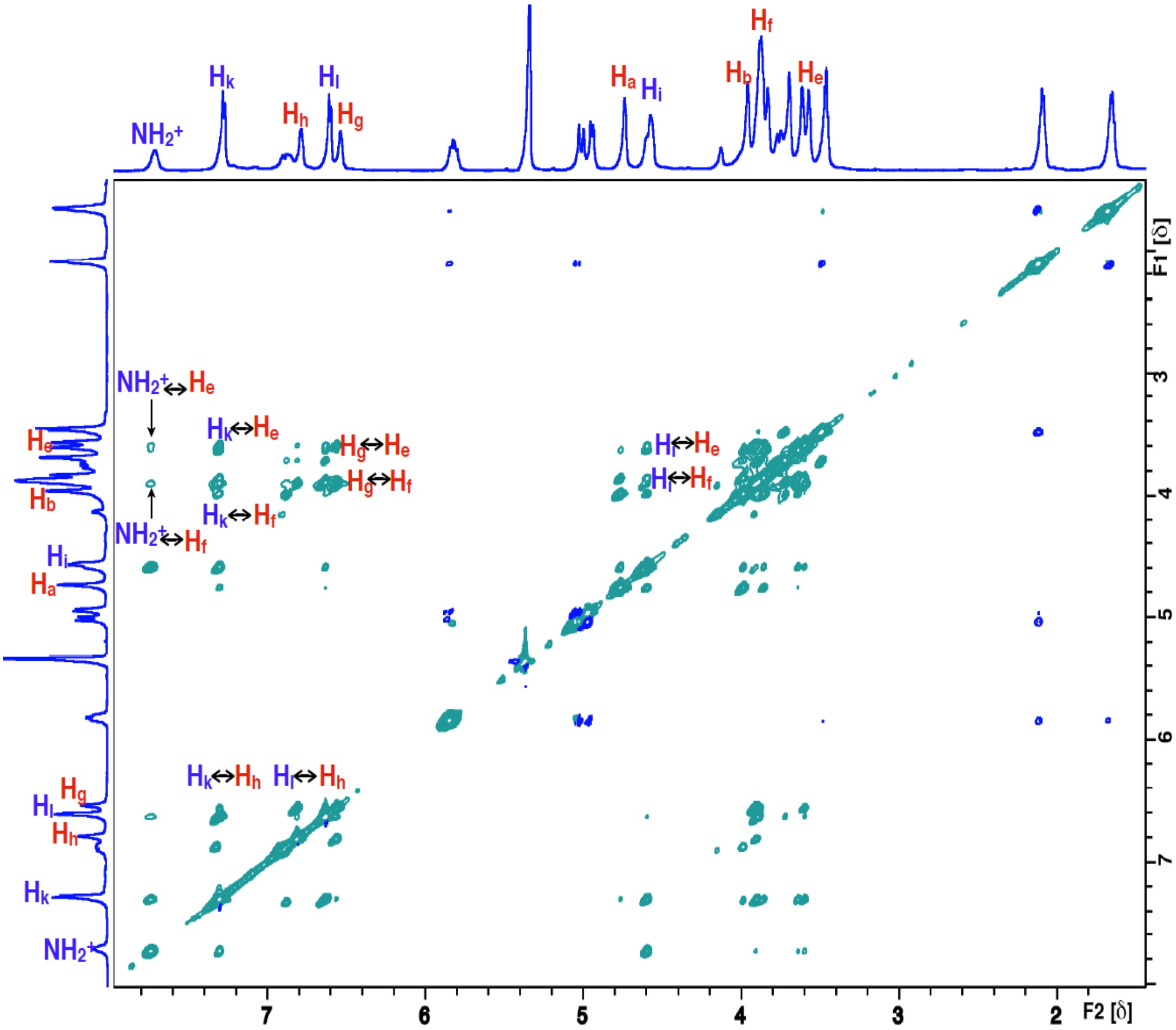

Figure S2. Nuclear Overhauser Effect Spectroscopy (NOESY) of $[\mathbf{5}^{+}\ \ \mathbf{3}]$ at 233 K in CD_2Cl_2.

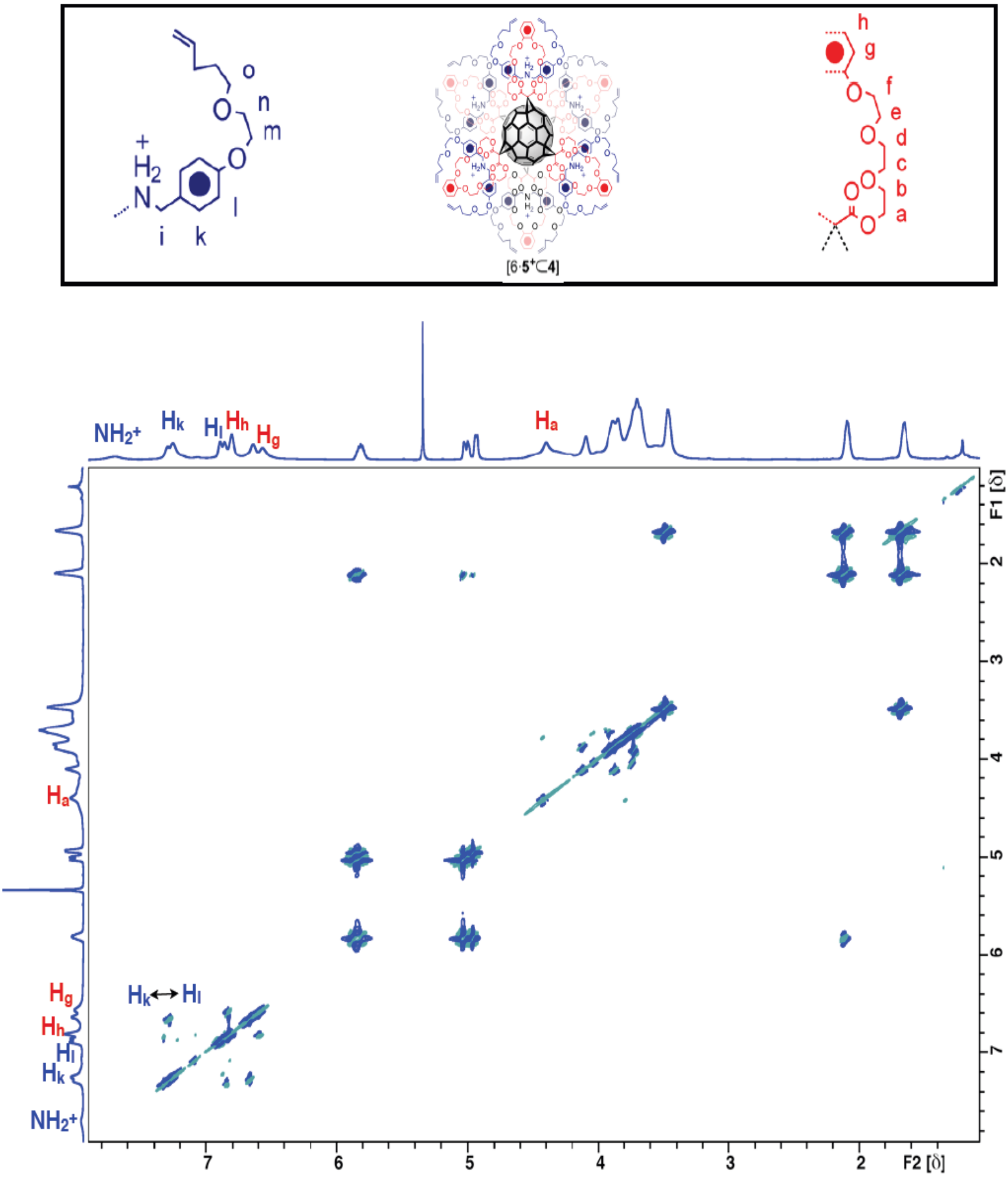

Figure S3. ^{1}H-^{1}H Correlation spectroscopy (COSY) of [6·**5**$^+$ **4**] at 233 K in CD_2Cl_2.

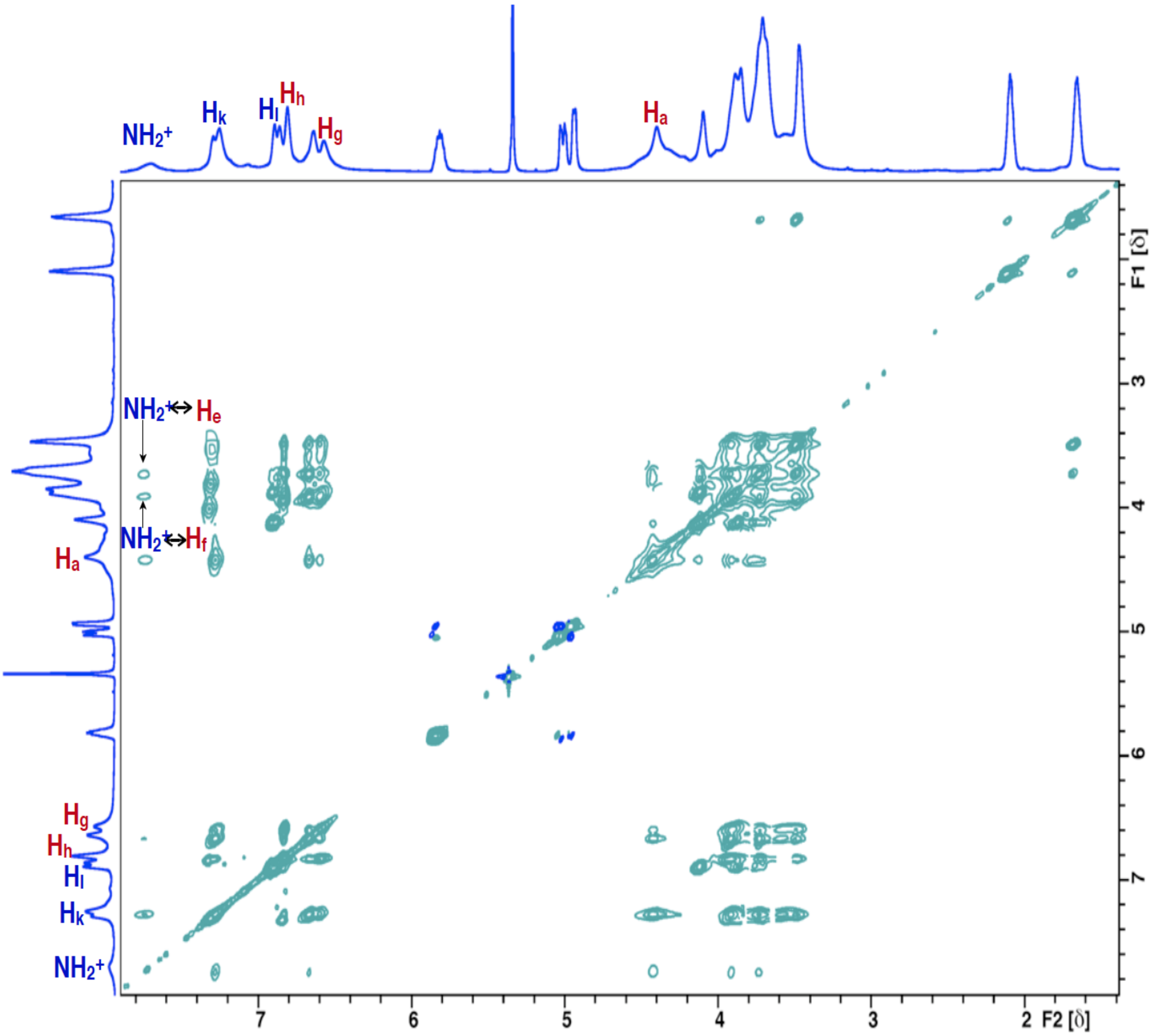

Figure S4. Nuclear Overhauser Effect Spectroscopy NOESY of [6·**5**$^+$ **4**] at 233 K in CD_2Cl_2.

In order to determine the association constant (K_a) between the hosts – the malonate **2** and mono- and hexakisadducts **3** and **4** of C_{60} – and the guest **5**·PF_6, ^{1}H NMR titrations (shown in Figures S5 to S7) were carried out at 298 K in CH_2Cl_2 with varying the molar ratios of host and guest, while keeping the total concentration constant. The K_a was determined by fitting the percentage of the complex formed at various concentrations to a host-guest binding model using the software program[S3] Dynafit.

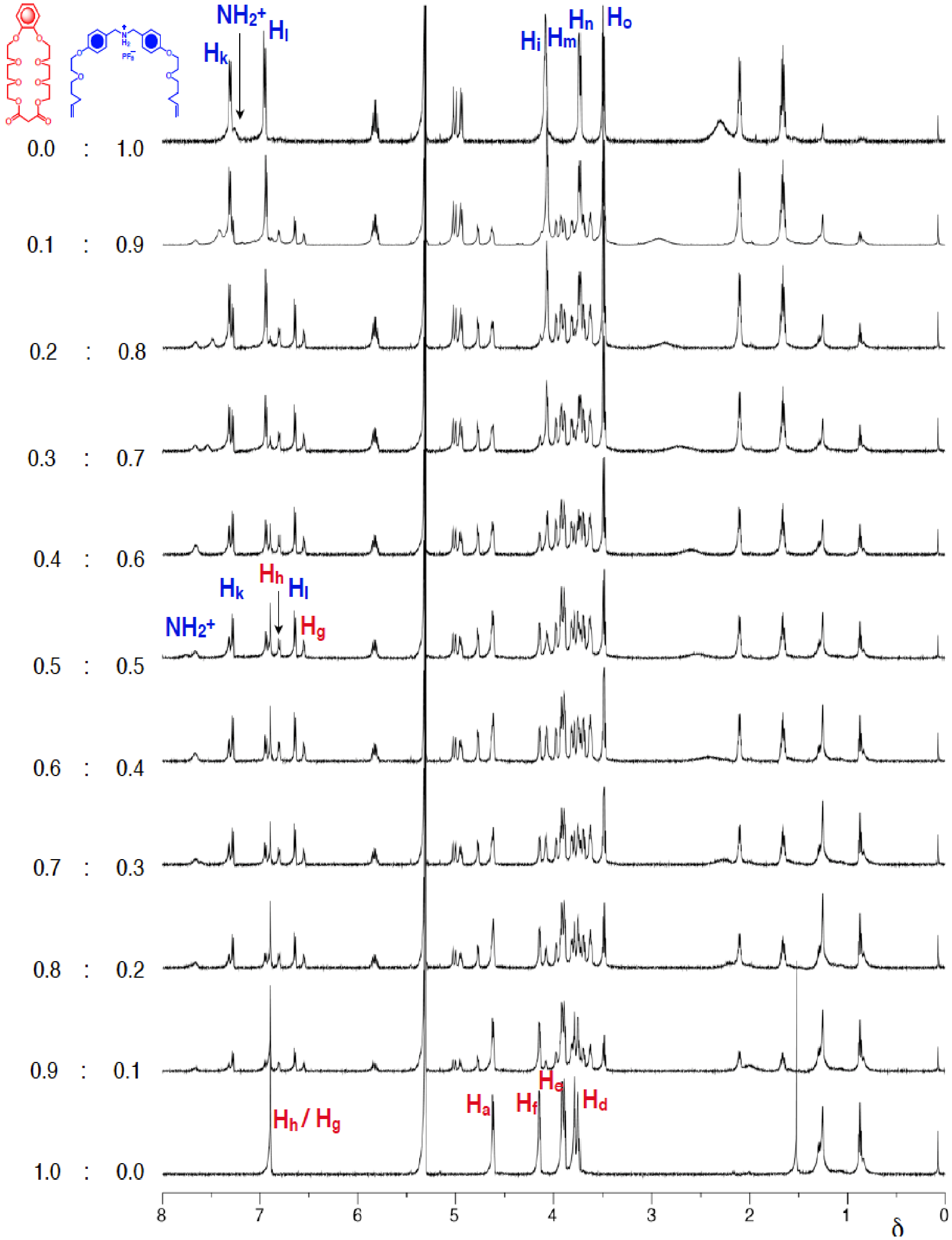

Figure S5. NMR Titration of **2** and **5**·PF_6 at 298 K in CD_2Cl_2.

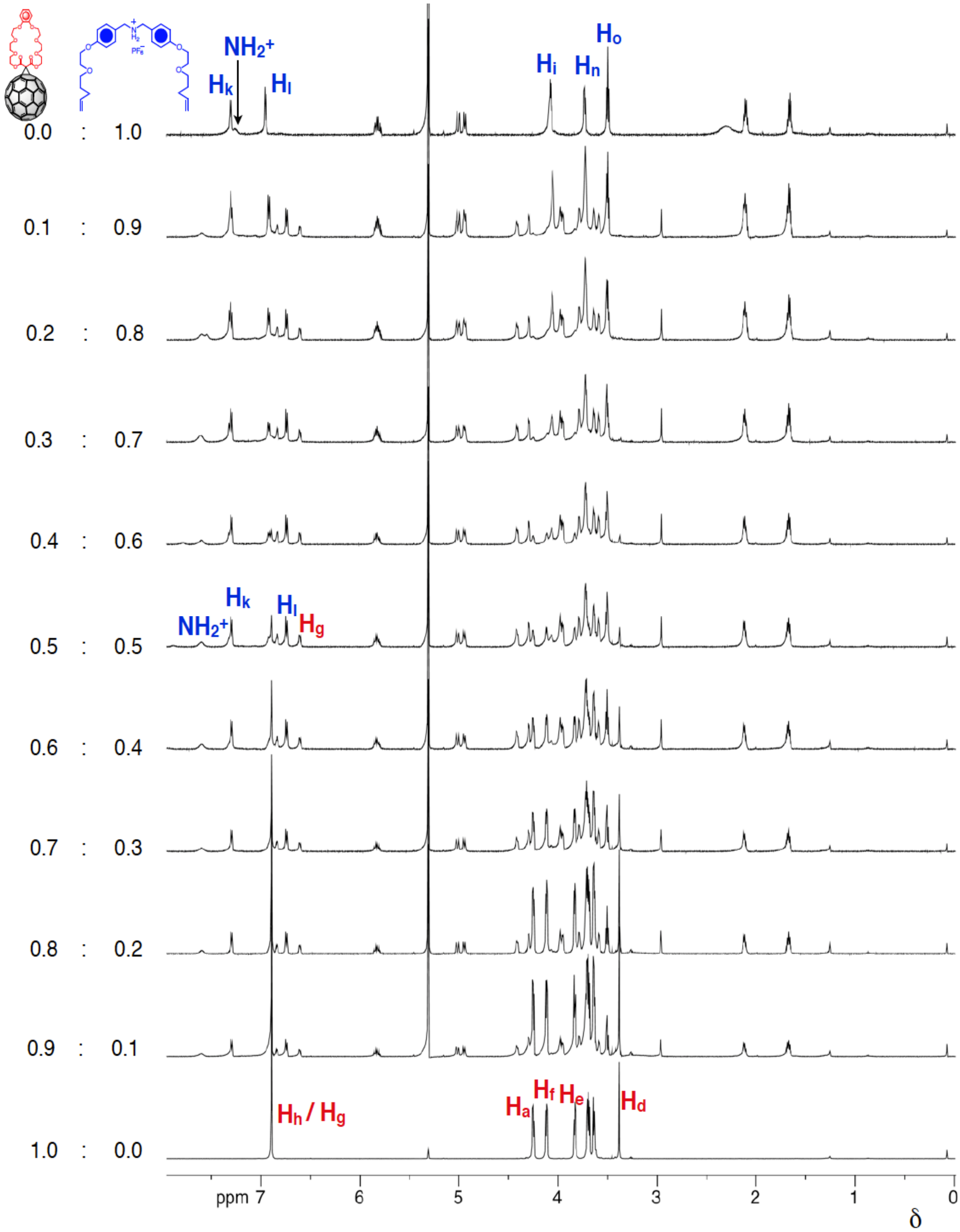

Figure S6. NMR Titration of **3** and **5**·$\mathbf{PF_6}$ at 298 K in CD_2Cl_2.

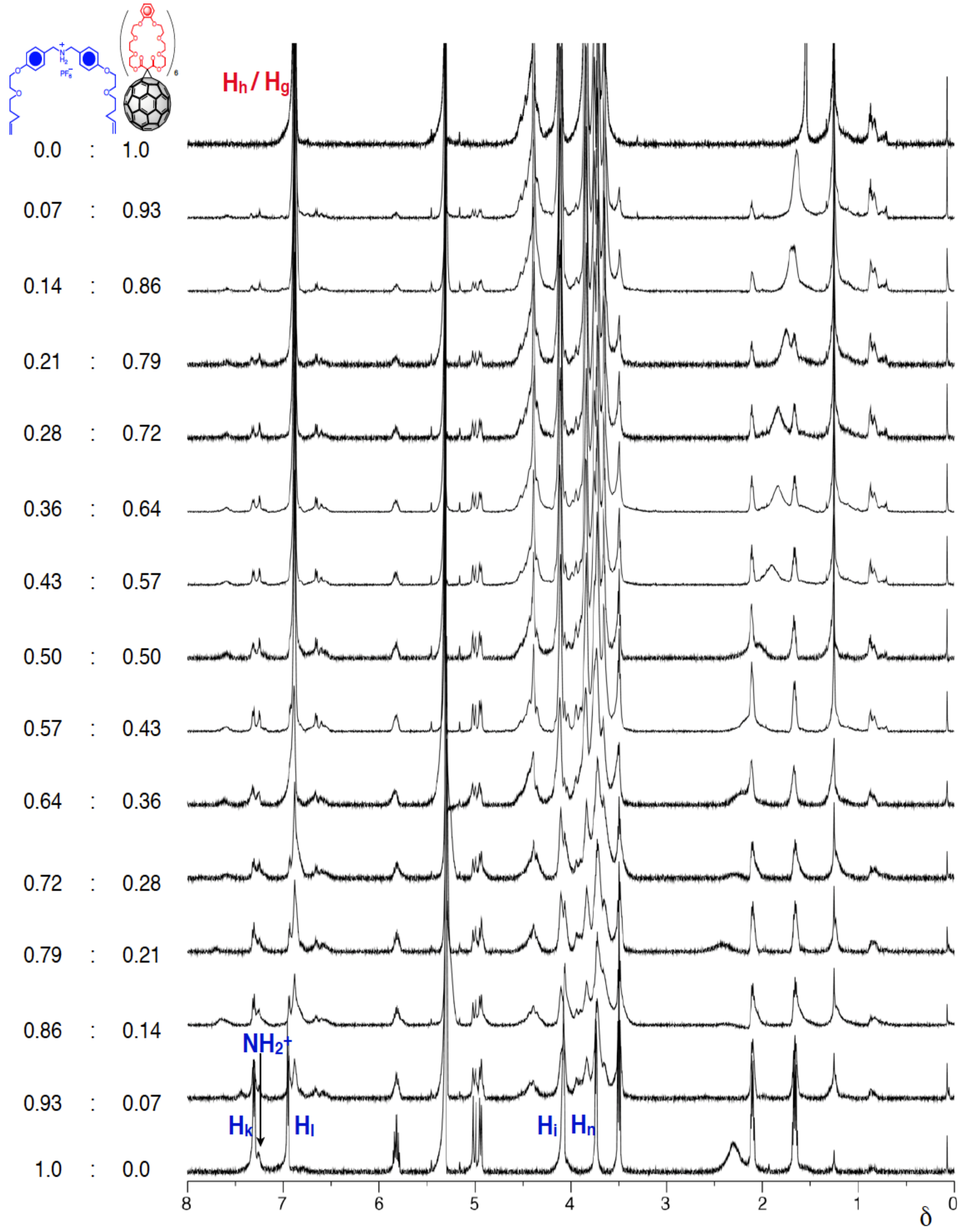

Figure S7. NMR Titration of **4** and **5**·PF_6 at 298 K in CD_2Cl_2.

S3. X-Ray Crystallography

Data Collection for [DBA$^+$ 2]: A colourless needle-like crystal of $C_{35}\ H_{46}\ F_6\ N\ O_{10}\ P$, with the approximate dimensions of 0.53 x 0.16 x 0.10 mm, was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a Bruker APEX-II C with graphite monochromated CuKα radiation. Cell constants and an orientation matrix for data collection corresponded to a monoclinic cell with dimensions:

$a =$ 15.7752(6) Å $\alpha =$ 90º
$b =$ 13.5842(5) Å $\beta =$ 102.141(3)º
$c =$ 17.3986(7) Å $\gamma =$ 90º
$V =$ 3645.0(2) Å3

For $Z = 4$ and FW = 785.70, the calculated density is 1.432 g·cm^{-3}. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: *P2(1)/c*. The data were collected at a temperature[S4] of 100 K with a θ range for data collection of 2.87 to 58.55º. Data were collected in 0.5º oscillations with 20 second exposures. The crystal-to-detector distance was 40.00 mm.

Data Reduction: Of the 18040 reflections which were collected, 5080 were unique (*R*int = 0.0388). Data were collected using Bruker APEX2 detector and processed using SAINTPLUS from Bruker. The linear absorption coefficient, μ, for CuKα radiation is 1.455 mm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement: The structure was solved by direct methods and expanded using Fourier techniques[S5]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[S6] on F2 was based on 5080 reflections and 486 variable parameters and converged (largest parameter shift was 0.000 times its esd) with unweighted and weighted agreement factors of:

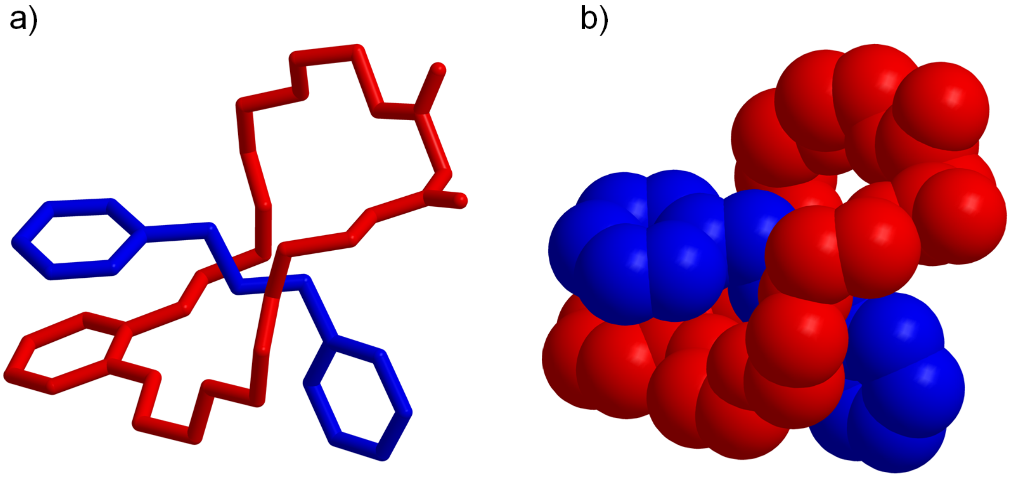

Figure S8. A stick (a) and space-filling (b) representation of the solid-state superstructure of **DBA**$^+$ **2**.

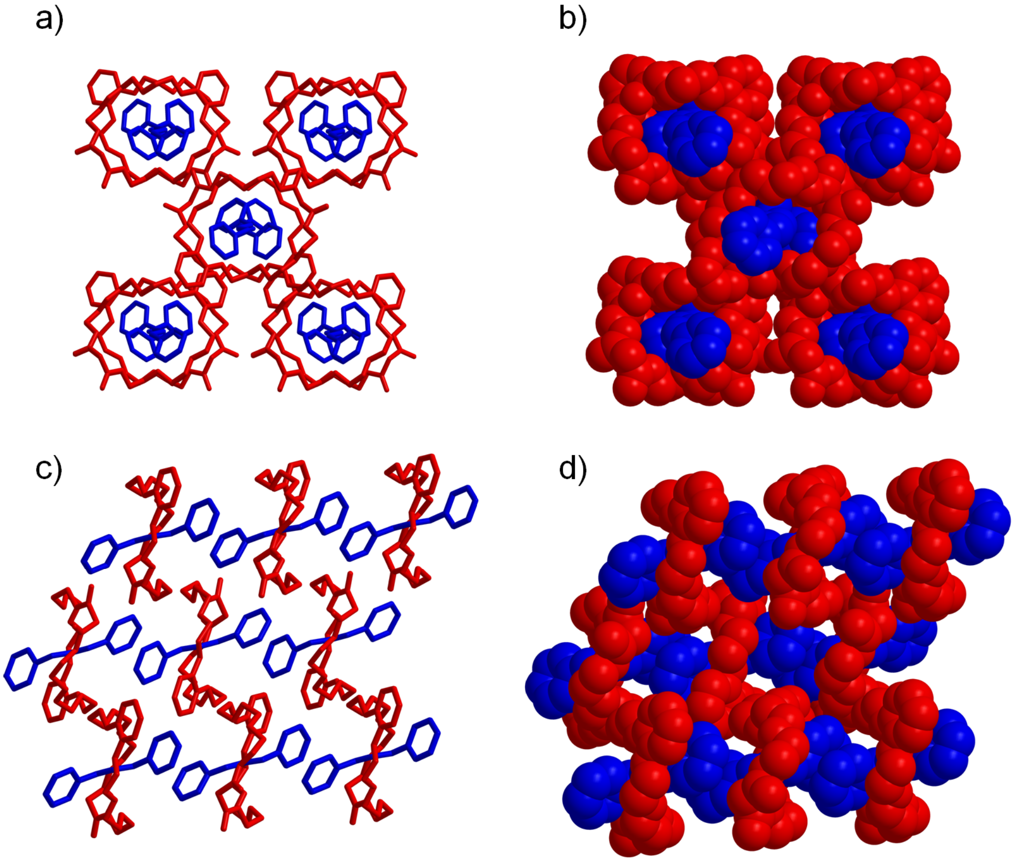

Figure S9. Two different views of the stick (a, c) and space-filling (b, d) representation of the packing of the solid-state superstructure **DBA**$^+$ **2**.

Table S1. Crystal Data and Structure Refinement for **DBA$^+$ 2**

Empiracal formula	$C_{35} H_{46} F_6 N O_{10} P$
Formula Weight	785.70
Temperature	100 K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, *P2(1)/c*
Unit cell dimensions	a = 15.7752(6)Å α = 90°
	b = 13.5842(5)Å β = 102.141(3)°
	c = 17.3986(7)Å γ = 90°
Volume, V	3645.0(2) Å^3
Z, Calculated density	4, 1.432 Mg/m^3
Absorption coefficient	1.455 mm^{-1}
F(000)	1648
Crystal size	0.53 x 0.16 x 0.10 mm
Theta range for data collection	2.87 to 58.55°
Limiting indices	-8<=h<=17, -14<=k<=14, -19<=l<=18
Reflections collected / unique	18040 / 5080 [R_{int} = 0.0388]
Completeness to theta = 58.55	98.2 %
Absorption correction	Numerical
Max. and min. transmission	0.8646 and 0.5110
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5080 / 0 / 486
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0378, wR_2 = 0.0948
R indices (all data)	R_1 = 0.0502, wR_2 = 0.1019
Largest diff. peak and hole	0.442 and -0.279 e·Å^{-3}

$$R_1 = \Sigma|\,|F_o|-|F_c|\,|/\Sigma|F_o| = 0.0378$$

$$wR^2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0948$$

The weighting scheme was $w = 1/[\sigma^2(F_o^2)+(0.0490P)^2 + 1.9825P]$ where $P=(F_o^2+2F_c^2)/3$

The standard deviation of an observation of unit weight[S7] was 1.034. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma\, w\, (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.442 and –0.279 e·Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S8]. Anomalous dispersion effects were included in F_{calc}[S9], the values for $D_{f'}$ and $D_{f''}$ were those of Creagh and McAuley[S10]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S11]. All calculations were performed using the Bruker SHELXTL[S5] crystallographic software package. The crystal data and refinement information is given in Table S1.

As might be anticipated from the NMR studies in solution, the dibenzyl ammonium salt threads through the macrocycle **2** in solid state as seen in the ball and stick (Figure S8 (a)) and the space filling model (Figure S8 (b)) representations of the crystal structure. The packing of the solid-state superstructure is shown in Figure S9. Crystallographic data (excluding structure factors) for the structures reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-776151.

S4. References

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S6. Full-Matrix Least-Squares refinement on F^2:
$wR^2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

S7. GooF = S = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ where n = number of reflections and p = total number of reflections refined.

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