

Hydrogen bond-assisted solid-state formation of a salt-bridged calix[5]arene pseudo-dimer

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Electronic Supplementary Information

Table S1 Crystal data and structure refinement for (*n*-BuNH₃⁺C1a⁻·1a·H₂O·CH₃CN).

2 (<i>n</i> -BuNH ₃ ⁺ C1a ⁻ ·1a·H ₂ O·CH ₃ CN)	
Empirical formula	2(C ₈₁ H ₁₁₉ O ₇), 2(C ₄ H ₁₂ N ₁), 2(C ₈₁ H ₁₂₀ O ₇), 2(C ₂ H ₃ N ₁)
Formula weight	5051.46
Temperature (K)	100(2)
Wavelength (Å)	0.77491
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)	a = 21.54(2), α = 90.92(4) b = 25.71(2), β = 88.87(2) c = 31.95(1), γ = 74.53(2)
Volume (Å ³)	17045(19)
<i>Z</i>	2
ρ_{calcd} (g/cm ³)	0.984
μ (mm ⁻¹)	0.049
Reflections collected	39242
Data / restraints / parameters	38444 / 102 / 3422
Goof	1.047
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1276, <i>wR</i> ₂ = 0.3302
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1352, <i>wR</i> ₂ = 0.3342

Table S2. H-bond and CH— π interactions detected in the crystal structure of pseudo-dimers **I** and **II** ($n\text{-BuNH}_3^+\text{C1a}^- \cdot \mathbf{1a} \cdot \text{H}\text{C}\text{H}_3\text{CN}$) [\AA , $^\circ$].

D–H\cdotsA	<i>d</i>(D–H)	<i>d</i>(H\cdotsA)	<i>d</i>(D\cdotsA)	(DHA)
<i>n</i>-BuNH$_3^+$C1a$^-$ (I)				
N(1)–H(1b) \cdots O(1l)	0.89	2.00	2.767(7)	143.4
N(1)–H(1b) \cdots O(1g)	0.89	2.12	2.820(7)	134.8
N(1)–H(1a) \cdots O(4g)	0.89	2.01	2.815(7)	149.4
N(1)–H(1c) \cdots O(5g)	0.89	2.00	2.857(7)	162.2
C(2)–H(2b) \cdots Cg(B) ^a	0.97	2.98	3.850(7)	149.3
C(2)–H(2a) \cdots Cg(B') ^a	0.97	2.85	3.711(7)	148.0
C(3)–H(3b) \cdots Cg(C) ^a	0.97	2.86	3.800(8)	162.3
C(3)–H(3a) \cdots Cg(C') ^a	0.97	2.97	3.889(9)	159.2
CH$_3$CNC1a·H (I)				
C(8)–H(8a) \cdots Cg(A) ^a	0.96	2.64	3.561(8)	162.1
C(8)–H(8c) \cdots Cg(C') ^a	0.96	2.65	3.582(8)	163.3
O(6l)–H(6l) \cdots O(1m)	0.82	1.67	2.445(8)	158.0
<i>n</i>-BuNH$_3^+$C1a$^-$ (II)				
N(9)–H(9b) \cdots O(11l)	0.89	2.04	2.772(7)	138.7
N(9)–H(9b) \cdots O(11g)	0.89	2.04	2.791(7)	140.7
N(9)–H(9c) \cdots O(13g)	0.89	1.90	2.783(6)	172.9
N(9)–H(9a) \cdots O(14g)	0.89	2.13	2.828(7)	134.5
C(10)–H(10b) \cdots Cg(B) ^a	0.97	2.70	3.636(7)	161.8
C(10)–H(10a) \cdots Cg(B') ^a	0.97	2.95	3.702(7)	135.6
C(11)–H(11b) \cdots Cg(C) ^a	0.97	3.20	4.161(7)	170.9
C(11)–H(11a) \cdots Cg(C') ^a	0.97	2.83	3.690(8)	147.9
CH$_3$CNC1a·H (II)				
C(16)–H(16a) \cdots Cg(A) ^a	0.96	2.63	3.547(7)	160.4
C(16)–H(16c) \cdots Cg(C') ^a	0.96	2.59	3.529(8)	167.5
O(16l)–H(16l) \cdots O(11m)	0.82	1.77	2.462(7)	141.4

^aC_g (A), (B), (B'), (C), (C'): gravity centres of the A, B, B', C and C' aryl rings, respectively.

Table S3. Comparison of the relevant conformational parameters of the two calix[5]arene units present in the crystal structure of pseudo-dimers **I** and **II** ($n\text{-BuNH}_3^+\text{C1a}^- \cdot \mathbf{1a} \cdot \text{H}\text{C}\text{H}_3\text{CN}$).

Pseudo-dimer	$\theta_A(^\circ)^a$	$\theta_B(^\circ)^a$	$\theta_{B'}(^\circ)^a$	$\theta_C(^\circ)^a$	$\theta_{C'}(^\circ)^a$	
(I)	$n\text{-BuNH}_3^+\text{C1a}^-$	130.1(2)	105.4(2)	99.4(1)	118.3(2)	120.6(1)
	CH $_3$ CNC1a·H	89.8(2)	126.1(2)	142.9(1)	124.9(1)	82.4(1)
(II)	$n\text{-BuNH}_3^+\text{C1a}^-$	129.9(1)	96.1(1)	130.5(1)	115.9(2)	104.9(1)
	CH $_3$ CNC1a·H	86.5(2)	132.1(2)	150.9(1)	123.4(1)	80.6(2)

^aDihedral angles calculated between the least-square mean planes of rings A, B, B', C and C' and the macrocycle reference plane defined by the five bridging methylene carbon atoms.

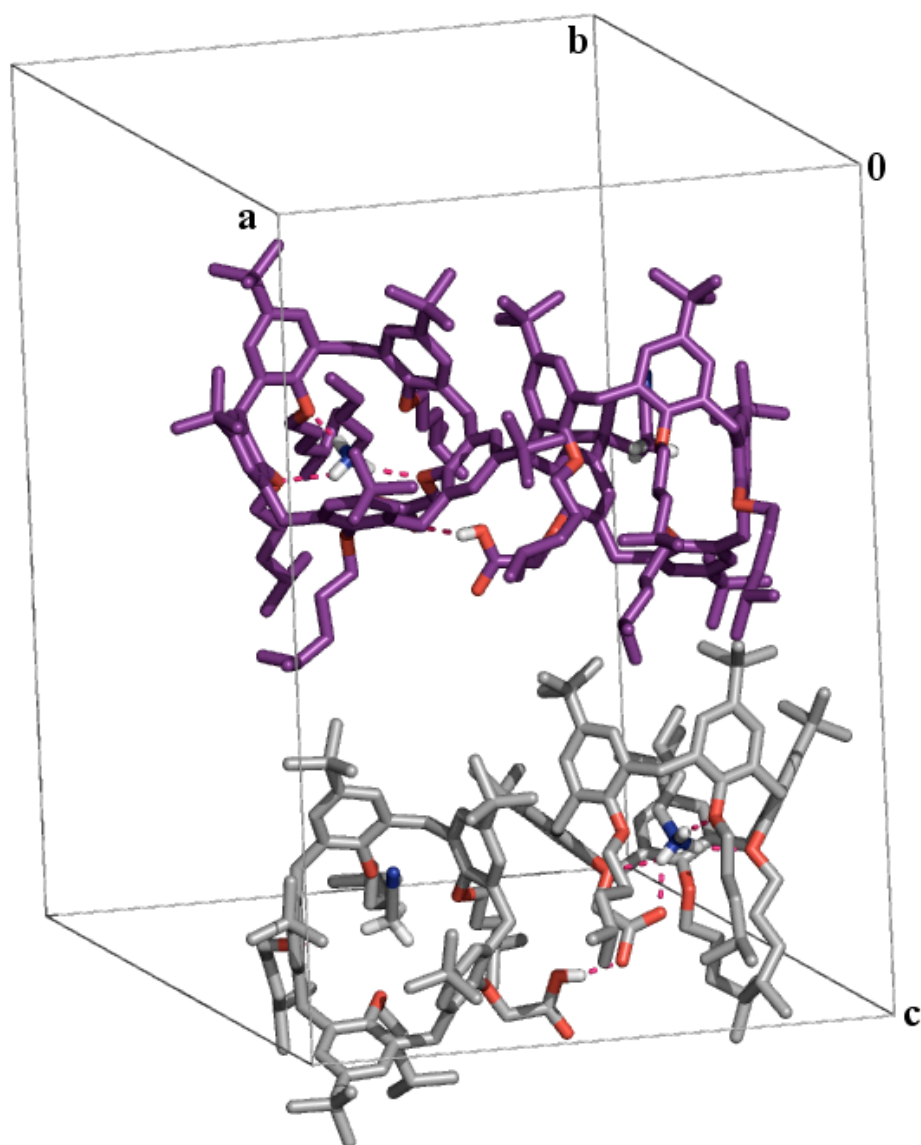


Fig. S1 The symmetric unit of the supramolecular aggregates ($n\text{-BuNH}_3^+\text{C1a}^- \cdot \mathbf{1a} \cdot \text{H}\text{OCH}_3\text{CN}$). The two pseudo-dimers **I** and **II** are depicted in grey and violet, respectively.

General Experimental. Calix[5]arene **1a**·H was prepared according to a literature procedure.¹ *n*-Butylamine and CD₂Cl₂ were freshly distilled over CaH₂ prior to use. ¹H NMR spectra (500 MHz) were recorded at 273±0.1 K in CD₂Cl₂. Sample solutions of **1a**·H (1.0 mM) and a 2:1 mixture of **1a**·H and *n*-BuNH₂ (1.0 and 0.5 mM, respectively), used for ¹H NMR and Diffusion-Ordered Spectroscopy (DOSY) analysis, were directly prepared in the NMR tube from CD₂Cl₂ stock solutions of the calixarene and the amine (10.0 and 100.0 mM, respectively).

¹H NMR Studies.

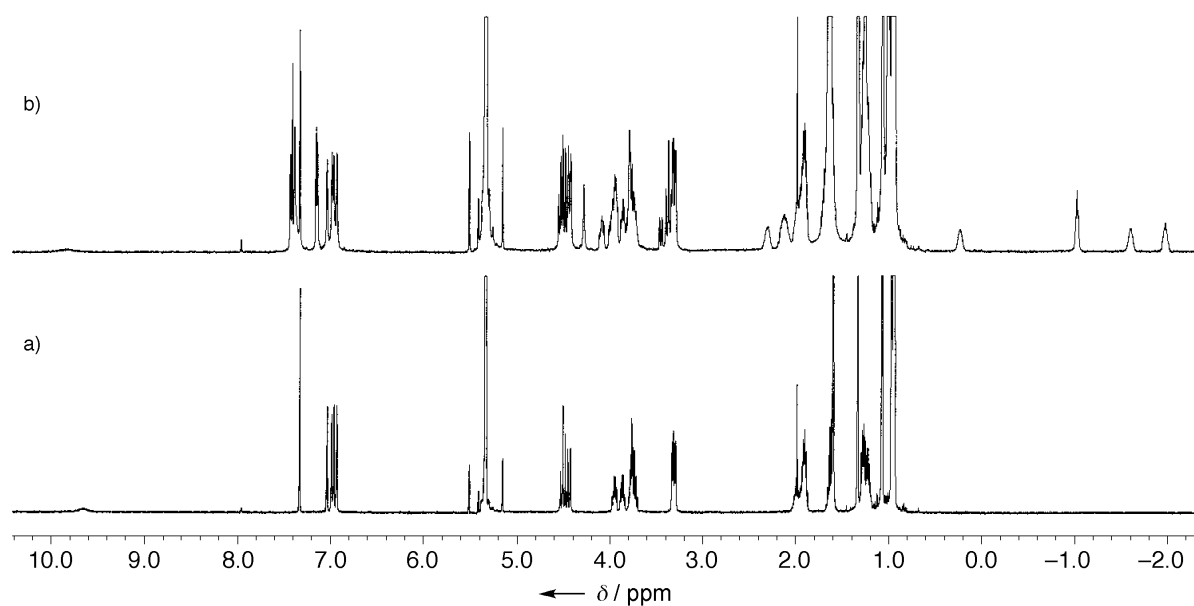


Fig. S2 ¹H NMR spectra (500 MHz, CD₂Cl₂, 273 K) of: a) [**1a**·H] = 1.0 mM and b) [**1a**·H] = 1.0 mM and [*n*-BuNH₂] = 0.5 mM.

1. C. Capici, G. Gattuso, A. Notti, M. F. Parisi, S. Pappalardo, G. Brancatelli and S. Geremia, *J. Org. Chem.*, 2012, **77**, 9668–9675.

Diffusion-Ordered Spectroscopy. 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 CD₂Cl₂ at 273±0.1 K, using a gradient stimulated echo with spin-lock and convection compensation pulse sequence.²

Diffusion coefficient (*D*) values, reported in Table S4, were calculated from DOSY experiments carried out on a 2:1 mixture of **1a**·H and *n*-BuNH₂ (1.0 and 0.5 mM, respectively), **1a**·H (1.0 mM) as well as the ‘model’ bis-calix[5]arene **2** (1.0 mM). The latter was chosen as a model compound for a species with a molecular weight roughly similar to the supramolecular pseudo-dimer (*n*-BuNH₃⁺Cl⁻·**1a**·H)·CH₃CN formed in the solid state.

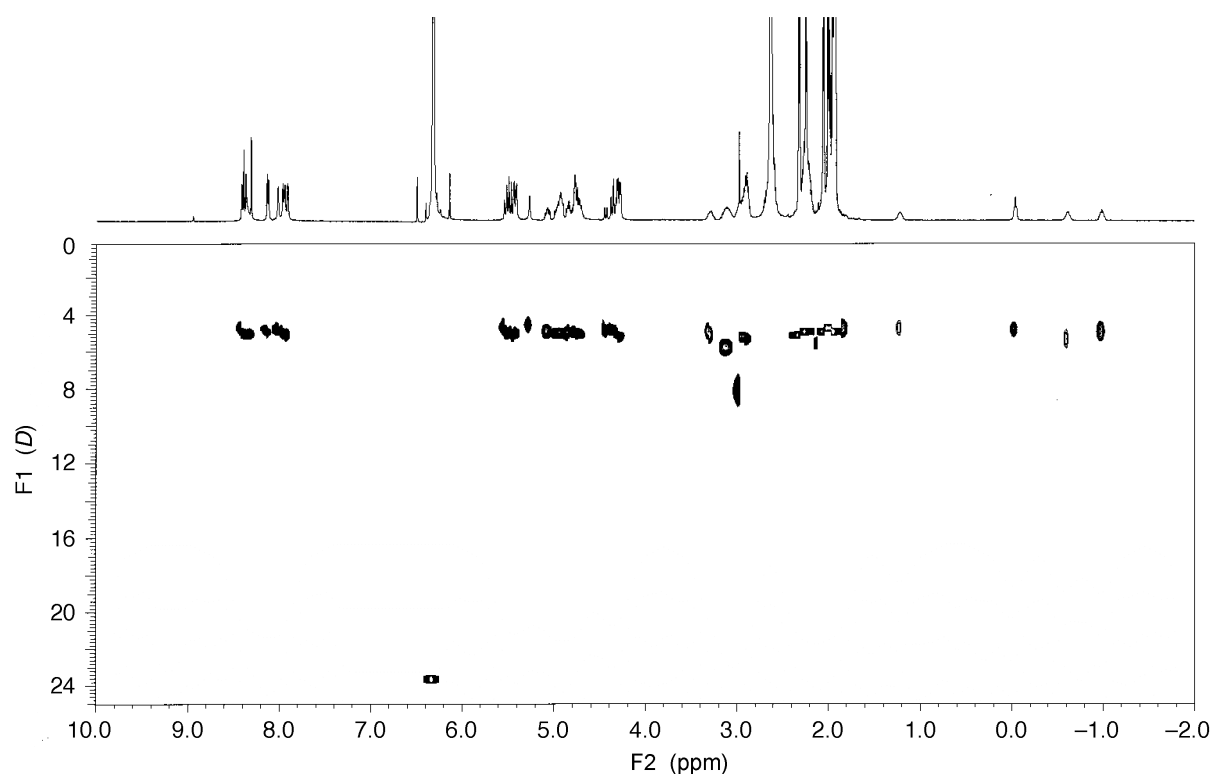


Fig. S3 DOSY plot (500 MHz, CD₂Cl₂, 273 K) of a 2:1 mixture of **1a**·H and *n*-BuNH₂ (1.0 and 0.5 mM, respectively).

2. A. Jerchow and N. Müller, *J. Magn. Reson.*, 1997, **125**, 372–375.

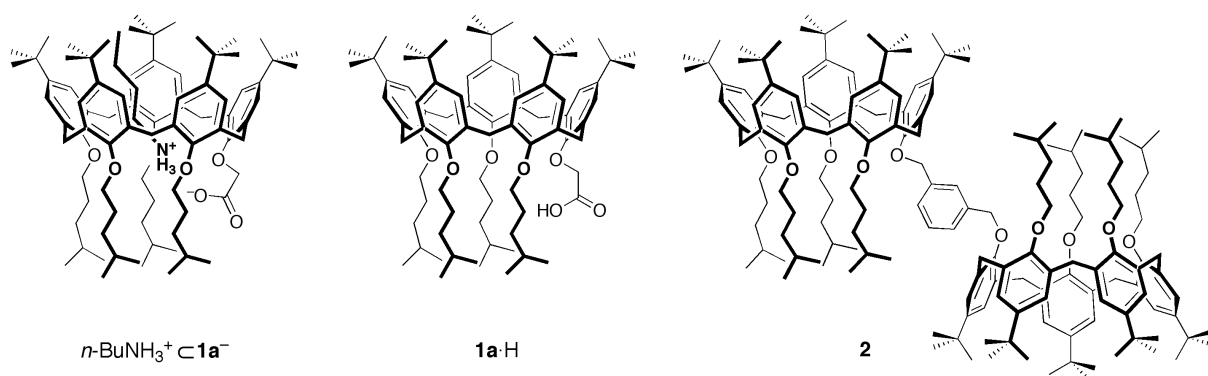


Table S4. Diffusion coefficients (D) for $n\text{-BuNH}_3^+ \cdot \mathbf{1a}^-$, $\mathbf{1a} \cdot \text{H}$ and $\mathbf{2}$.^a

Peak	D [$\times 10^{-10} \cdot \text{m}^2 \cdot \text{s}^{-1}$]		
	$(\delta$ [ppm])		
	$n\text{-BuNH}_3^+ \cdot \mathbf{1a}^-$	$\mathbf{1a} \cdot \text{H}$	$\mathbf{2}$
$\gamma\text{-CH}_2$	4.70±0.30 (-1.99)	—	—
$\delta\text{-CH}_3$	4.78±0.16 (-1.04)	—	—
OCH ₂	4.79±0.20 (4.07)	4.90±0.09 (3.93)	3.88±0.03 (3.40)
Ar-H	4.84±0.08 (7.13)	4.93±0.04 (6.93)	3.75±0.01 (7.13)
Ar-H	4.75±0.07 (7.14)	4.94±0.03 (6.96)	3.76±0.01 (7.20)
CHDCl ₂ (residual)	23.85±0.03 (5.32)	23.90±0.03 (5.32)	23.84±0.02 (5.32)

^aDiffusion experiments were recorded at 273 K on 1.0 mM CD₂Cl₂ solutions. In the case of the $n\text{-BuNH}_3^+ \cdot \mathbf{1a}^-$ complex, a CD₂Cl₂ solution of $\mathbf{1a} \cdot \text{H}$ and $n\text{-BuNH}_2$ (1.0 and 0.5 mM, respectively) solution was used.