SUPPLEMENTARY INFORMATION FOR

Progressive compression of 1,ω-diammonium-alkanes inside a rigid crystalline molecular cage

Dan Dumitrescu, Yves-Marie Legrand, Eddy Petit, Arie van der Lee, Mihail

Barboiu*

Institut Européen des Membranes – ENSCM-UMII-CNRS 5635, Place Eugène Bataillon, CC 047, F-34095 Montpellier, Cedex 5, France. E-mail:

mihail-dumitru.barboiu@univ-montp2.fr

Strategy: Our previous experience in the confinement of the unstable species inside a crystalline guanidinium-sulfonate, **GS** molecular flask led us to consider a similar approach for compressing alkanes. Alkanes, however, are not a preferred building block in crystal engineering, due to their very high number of possible conformations and general lack of affinity. In practice, it is very difficult to co-crystalize a long alkane, especially in a precise way. Furthermore, from the chemical point of view, alkanes are not very compatible with **GS** networks. To overcome this, we considered using relatively long $1,\omega$ -diammoniumalkanes instead of nalkanes. This 'functionalization' works twofold, the ammonium groups increasing the compatibility between the alkyl chain and the guanidiniumsulfonate network and providing tethering points for the otherwise too flexible alkane chain (Figure S1). In order to stabilize the supramolecular capsules, PTSG found it important to play the we on hydrophobic/hydrophilic balance. solvent, Using water as the

encapsulating component had to be hydrophobic, pyrene being a good candidate.



Figure S1. (a) flexible alkane with many free torsion angles; (b) diammonium alkane fixed at both ends with fewer degrees of freedom

Moreover, its tetrasulfonated form is commercially available, which reminds of tetrasulfonated calixarene, ideal to make ionic H-bonded complexes, but with a planar hydrophobic surface in the case of pyrene. Guanidinium cations were chosen as suitable counterions and hydrogen bond donors. Terminated ammonium alkyl chains were used as guest instead of the simple alkyl chains in order to provide an encoring point at both ends of the chains. A series of $1,\omega$ -diammoniumalkanes of varying length was chosen to screen the molecular compressibility of flexible entities inside a fairly robust cage with relatively fixed dimensions. It can be considered that a combinatorial approach was used to fabricate the confinement boxes, in the sense that several counter ions were placed in presence of the 1,3,5,8-pyrenetetrasulfonate polyanion, **PTS** and several pairing combinations can be generated. Guanidinium was used as counter ion and hydrogen bond donor. It is important to note that although other different supramolecular architectures were observed, these did not follow the same metrics as those presented herein.

Experimental: All the compounds were purchased from Sigma-Aldrich and were used without further purification. Suitable crystals for all the structures were readily obtained in large quantities by slow evaporation of aqueous solutions obtained by dissolving: 50 mg 1,3,5,8pyrenetetrasulfonate tetrasodium salt, 100 mg guanidinium hydrochloride, 30 mg alkane diamine and 50 μ L HCl 37% in 1 mL H₂O. After 1 week the crystals were filtered and dried under mild vacuum for 2 h.

NMR experiments: ¹H NMR experiments were performed on an ARX 300 MHz Bruker spectrometer in D_2O with the use of the residual solvent peak as reference. NMR titration experiments were performed by adding successive aliquots of 0.1 M D2O solutions of 1, ω -diammonium alkane dichloride and guanidinium to 0.4 ml 0.01M solution of sodium 1,3,5,8-pyrene tetrasulfonate. In the case of the 2D-NMR experiments 10 mg of the corresponding crystals obtained by the method described above were dissolved in 0.5 mL D₂O.

2D-DOSY (**D**iffusion-**O**rdered **S**pectroscop**Y**) NMR experiments were performed at 298 K with a Bruker Dual z-gradient probe head capable of producing gradients in the z direction with strength 55 G cm⁻¹. The DOSY spectra were acquired with the ledbpgp2s pulse program (2D sequence for diffusion measurement using echo and led with bipolar gradient pulse : D. Wu, A. Chen & C.S. Johnson Jr., J. Magn. Reson. A 115, 260-264 (1995)). All spectra were recorded with 8 K time domain data points in the F2 Frequency axis and 32 experiments (F1). The gradient strength was logarithmically incremented in 32 steps from 2% up to 95% of the maximum gradient strength. All measurements were performed with a diffusion delay D of 80 ms in order to keep the relaxation contribution to the signal attenuation constant for all samples. The gradient pulse length d was 5 ms in order to ensure full signal attenuation. The diffusion dimension of the 2D DOSY spectra was processed by means of the Bruker Topspin software (version 2.1).

2D-ROESY (**R**otating-frame **O**verhauser **E**ffect **S**pectroscop**Y**) NMR experiments were performed at 298 K applying the 180°–90° selective-spinlock—FID pulse sequence. The mixing time was recorded with 300 ms. A typical proton-proton COSY experiment was performed (cosygpqf). Spectra were acquired with 2 K data points in F2 Frequency axis and 128 experiments.

In all cases the prevalent interaction observed is the ion-pairing between **PTS** and the $1,\omega$ -diammonium alkane chain, even in the absence of

guanidinium, resulting in a shielding of the hydrogens in the middle of the chain by about 1 ppm. The signal corresponding to the hydrogens in the terminal 1 and ω positions of the alkane chain remains unchanged in the presence **PTS**. (Figures S2-S4). This is in good agreement with the crystal structures, where the middle of the chain is shielded by the pyrene rings and the terminal atoms are close to the edge of the box.

In general, higher concentrations of **G** resulted in a stronger shielding, with the exception of 1,10-diammonium decane mixtures where a dynamic process was observed (Figure S2). Although not clearly evident from the NMR titration experiments, it should be noted that crystals could only be obtained in 1:4:1 **PTS:G:1,\omega-diammonium alkane** ratios, with the exception of **PTS{1}**₂.

The stoichiometry of the complex present in solution was determined by titration experiments. A molar ratio of 1:2 pyrene:diammonium alkane was observed both in the case of C10 and that of C12. A contrained conformation of the alkane chain can be observed using ROESY experiments as an interaction 4 atoms away. No such interaction was observed in the case of **PTSG{1}**.(Figure S5) Progressively stronger signals were observed in the case of **PTSG{2}** and **PTSG{3}**. (Figures S6, 1)



Figure S2. NMR of **PTS:G:1,10-diammonium decane** in various molar ratios.



Figure S3. NMR of **PTS:Gua:1,11-diammonium undecane** in various ratios.



Figure S4. NMR of PTS:Gua:1,12-diammonium dodecane in various

ratios.



Figure S5. ROESY spectrum of PTS:1,10-diammonium decane 1:2. Close contacts can be observed 2 atoms away, indicating a normal zig-zag conformation of the alkyl chain.

The COSY-NOESY overlap of the C12 structure indicates a constrained conformation of the alkyl chain, with contacts as far between as H_a and $H_{e.}$



Figure S6. ROESY spectrum of **PTSG{2}**. Close contacts can be observed 3 atoms away, indicating a constrained conformation of the alkyl chain.

DOSY experiments showed the presence of a single entity in solution in three cases. (Figures S7-S9) The calculated diffusion coefficients get progressively larger from **PSTG{1}** to **PTSG{3}** (Table S1).



Figure S7. DOSY of $PTS{1}$ in D₂O. A single species is evident.



Figure S8. DOSY of $PTS{2}$ in D₂O. A single species is evident.



Figure S9. DOSY of PTS{1} in D₂O. A single species is evident.

Table S1. DOSY diffusion coefficients for **PTSG{1-3}**. For weighing, a constant diffusion coefficient of 2.00×10^{-9} m²/s was considered for HOD at 25 °C.

	PTSG{1}	PTSG{2}	PTSG{3}
Complex diffusion coeff. (m ² /s)	4.03x10 ⁻¹⁰	3.43x10 ⁻¹⁰	3.48x10 ⁻¹⁰
HOD diffusion coeff. (m ² /s)	2.04x10 ⁻⁹	2.00x10 ⁻⁹	2.06x10 ⁻⁹
Weighed complex diffusion coeff. (m ² /s)	3.95x10 ⁻¹⁰	3.43x10 ⁻¹⁰	3.38 x10 ⁻¹⁰

X-ray experiments: The presence of the guanidinium **G** as counter ion and hydrogen bond donor is crucial for the pyrene box formation. Although ion paring interactions between the pyrene rings and the diammonium alkane chains were observed in the absence of **G** in the NMR

experiments, only **PTS** $\{1_2\}$ could be obtained (Figure S10). No crystals were obtained for **2** or **3** in the absence of **G**.



Figure S10. Packing of PTS{1₂} along b.

Very few examples of *all-gauche* arrangements are present in the CCDC²⁹ while pyrene tetrasulfonate **PTS** was employed only recently in crystal engineering.³⁰

All the structures have been measured on an Agilent Technologies Gemini-S four circle diffractometer using Mo-*K*a radiation ($\lambda = 0.71073$ Å) and equipped with a Sapphire3 detector at 175 K at the joint X-ray scattering facility of the Pôle Balard at the University of Montpellier, France. The structures have been solved using the *ab-initio* charge flipping method as implemented in *SUPERFLIP* (Palatinus & Chapuis, 2007)

Hydrogen atom positions were determined using Fourier differential maps in the case of **PTSG{1}** and the structure of **PTSG{2a}**. Hydrogens in the case of **PTSG{2b}** and **PTSG{3}** were added geometrically. It should

be noted that in all cases the ammonium hydrogens were found using Fourrier maps. All structures were initially refined using non-linear leastsquares methods as implemented in *CRYSTALS* (Betteridge et al, 2003), in which the hydrogen atoms were treated as riding on their parent atoms and with $U_{iso}(H)$ constrained to in general 1.2-1.5 times $U_{eq}(H)$ that of the parent atom. The final difference Fourier maps showed in many cases residual peaks due to bonding effects (in the pyrene planes and on the sulfonate moieties), because of the in general very good resolution of the experimental data (mostly around 0.7 Å or better, where the experimental resolution is defined according to Dauter (1999)).



Figure S11. Structures of the low temperature PTSG{2a}, disordered room temperature PTSG{2b} and the 2 coexisting conformers PTSG{3a} and PTSG{3b}.

Table S3. Crystallographic information on data collection and structure

refinement

	PTS{1}2	PTSG{1}	PTSG{2a}	PTSG{2b}	PTSG{3}
	$C_{16}H_6O_{12}S_4,$	$C_{16}H_6O_{12}S_4,$	$C_{16}H_6O_{12}S_4,$	$C_{16}H_6O_{12}S_4,$	$C_{16}H_6O_{12}S_4,$
Formula	$2(C_{10}H_{26}N_2),$	$C_{10}H_{26}N_2$,	$C_{11}H_{28}N_2$,	$C_{11}H_{28}N_2$,	$C_{12}H_{30}N_{2}$,
	$4(H_2O)$	$2(CH_6N_3), 2(H_2O)$	$2(CH_6N_3), 2(H_2O)$	$2(CH_6N_3), 2(H_2O)$	$2(CH_6N_3), 2(H_2O)$
Crystal Class	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	P-1	P-1	P-1	P-1	P-1
<i>a</i> (Å)	7.8956(4)	9.7336(8)	9.8126(4)	9.8826(4)	9.7985(3)
<i>b</i> (Å)	9.6557(3)	9.7556(8)	10.2605(4)	10.2939(4)	9.8928(3)
<i>c</i> (Å)	14.9160(6)	10.1940(7)	19.4731(7)	9.8156(4)	10.2589(4)
α (°)	77.311(3)	95.207(6)	96.737(3)	96.289(3)	94.489(3)
β (°)	81.835(4)	95.926(6)	95.763(3)	95.622(3)	97.927(3)
γ (°)	86.214(3)	95.224(7)	94.085(3)	94.839(3)	95.090(3)
Volume (Å ³)	1097.43(8)	953.91(13)	1930.36(13)	983.19(7)	976.92(6)
Z	1	1	2	1	1
Radiation type	Μο-Κα	Μο-Κα	Μο-Κα	Μο-Κα	Μο-Κα
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ (gcm ⁻³)	1.421	1.478	1.485	1.458	1.490
Temperature (K)	175	175	125	293	175
Diffractometer type	Gemini	Gemini	Gemini	Gemini	Gemini
Scan type	ω	ω	ω	ω	ω
Reflections measured	15468	36619	15112	31497	35243
Independent reflec.	4495	5743	6676	5199	5973
R _{int}	0.032	0.038	0.022	0.038	0.038
Average size (mm)	0.25x0.35x0 .50	0.30x0.40x0.60	0.30x0.50x0.70	0.40x0.45x0.50	0.30x0.50x0.70
Refinement on	F	F	F	F	F
<i>R</i> -factor	0.0437	0.0353	0.0418	0.0479	0.0404
wR	0.0483	0.0299	0.0489	0.0539	0.0494
$<\sigma(I)/I>$	0.0422	0.0408	0.0368	0.0473	0.0433
Number of parameters	289	244	496	298	299
Goodness of fit	1.0944	0.9998	0.9891	1.02233	1.0533

Disorder models and temperature dependence : In the case of 1,10diammonium decane and 1,12-diammonium dodecane the asymmetric unit contains $\frac{1}{2}$ of a pyrene and $\frac{1}{2}$ of a chain. This is due to a local inversion center at the middle of the alkandyil chain. At 175 K, in the case of 1,11-diammonium undecane, this inversion center disappears and the

unit cell is doubled over the *c* axis. However, at room temperature (298) K), the unit cell is again halved (i.e. the same as for **1** and **3**). The structure of 2 below room temperature can thus be considered as a commensurate superstructure of the room temperature structure with wave vector $q = 0.5c^*_{RT}$ where c^*_{RT} is the room-temperature reciprocal cvector. Reflections *hkl*: l=2n+1 are in the low-temperature phase in general much weaker than reflections hkI: I=2n. The superstructure is only due to the disorder in the alkandyl chains, the **PTS** and **G** moieties remaining exactly in place in neighboring unit cells. The disappearance of the low-temperature superstructure with rising temperature was monitored by plotting the ratio of the mean $< I/(I) >_{I=odd}$ over $< I/(I) >_{I=even}$ (Fig. xx). Structurally this means that the low-temperature superstructure has a pseudo inversion center at the middle of the undecane chain, which becomes a real inversion center, *i.e.* belonging to the space group symmetry, only at room temperature where the rapid movement of the gauche conformation from one end of the chain to the other makes that the two confirmations are even likely. Fig. xxxx shows the site occupancy factor of one of the two conformers at intermediate temperatures between the lowest recorded (125 K) and room temperature, the site occupancy factor of the two conformers summing up to 1.0. This process was found to be completely reversible. The room temperature structure of **PTSG{2}** can be alternatively refined in the doubled unit cell as well as in the small unit cell (the same as for **PTSG{1**}, since the disorder is nearly complete, but because of the very

faint intensity of the commensurate super reflections, the refinement is not very stable in the doubled unit cell. In the small unit cell the site occupancy factors of the two disordered parts is necessarily 0.5, because of the presence of the space group inversion center at the middle of the odd-numbered chain. The site occupancy factors of the two disordered conformers of **3** were also refined as a function of temperature, but no significant temperature dependence was observed, showing that the movement of 3 is most possibly impossible due to a too high confinement in the pyrene box.

Table S4. Dimensions of the pyrene box in all the three cases. Length was defined as the distance between the 1 and ω - nitrogen atoms, width as the distance between the opposing guanidinium planes and height as the distance between the opposing pyrene rings. The theoretical elongated length was calculated using the Gaussian09 computation packadge at the B3-LYP level of theory.

	1,10-	1,11-	1,12-
Pyrene box	diammonium	diammonium	diammonium
	decane (1)	undecane (2)	dodecane (3)
Length (Å)	13.807	14.239	14.465
Theoretical N-N elongated length	13.810	15.036	16.534
Compression rate (%)	0	5	13
Width (Å)	7.386	7.952	7.949
Height (Å)	8.137	8.161	8.508







Figure S12. Overlay between the PTSG{1} (blue) and PTSG{2} (orange) (A.), PTSG{1} (blue) and PSTG{3} (red) (B.) and PTSG{2} (orange) and PSTG{3} (red), respectively (C.). Hydrogen atoms were omitted for clarity.



Figure S13. ORTEP diagrams of structures. Thermal elipsoids are drawn at 50% probability.

NCI plots: In order to visualize the non-covalent interactions, the structures were analyzed using the NCI script. The NCI plots were performed at the promolecular level and all representations correspond to an isovalue of 0.4. Hydrogen bonds were normalized beforehand to standard crystallographic values C-H = 1.089, N-H = 1.015 and O-H = 0.993. When considering only the alkyl chain sampling was performed at 0.1 Bohr units, and in the case of the alkyl chain inside the pyrene box at 0.2 Bohr units. In standard NCI plots (reference) strong attractive interactions are shown in blue, weak interactions such as van der Waals forces in green and repulsive interactions in red. It should be noted that ring strains appear as red interactions.