Formation of a discrete helical assembly and packing pattern through charged hydrogen bonds and van der Waals interactions

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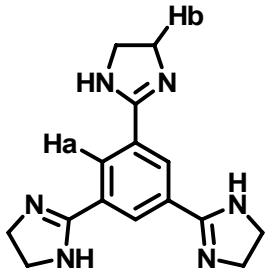
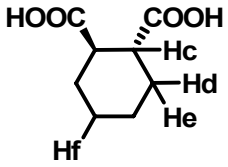
Supplementary Information



1



2

^{1}H NMR and ^{13}C NMR of $\mathbf{1}_2\cdot\mathbf{2}_3$

^{1}H NMR (300 MHz in D_2O): 8.60 (s, 6H, H_a of **1**), 4.23 (s, 24H, H_b of **1**), 2.37 (broad m, 6H, H_c of **2**), 1.99 (broad m, 6H, H_d of **2**), 1.97 (broad m, 6H, H_e of **2**), 1.34 (broad m, 12H, H_f of **2**).

^{13}C NMR (60 MHz in D_2O): 185.6 (carbonyl), 164.6 ($(NH)_2C$-Ar of **1**), 132.2 (aromatic), 126.3 (aromatic), 104.9 (aliphatic), 49.8 (aliphatic), 45.9 (aliphatic), 30.0 (aliphatic), 25.8 (aliphatic).

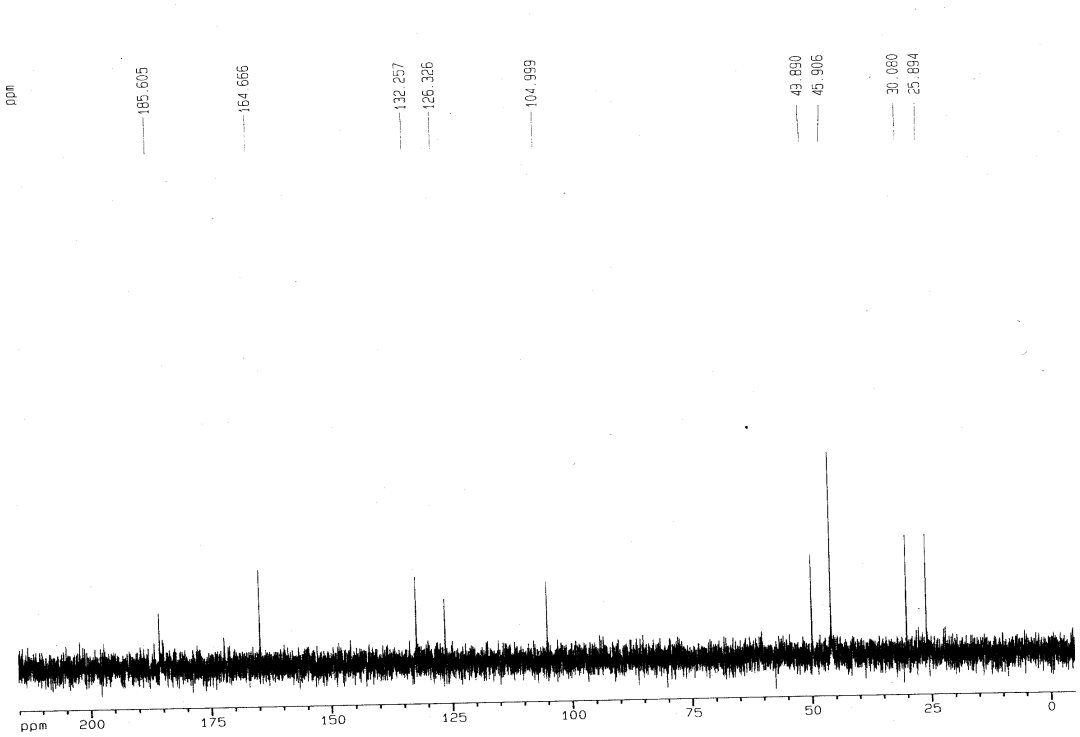


Figure S1. ^{13}C NMR of $\mathbf{1}_2\cdot\mathbf{2}_3$ in D_2O at 298 K.

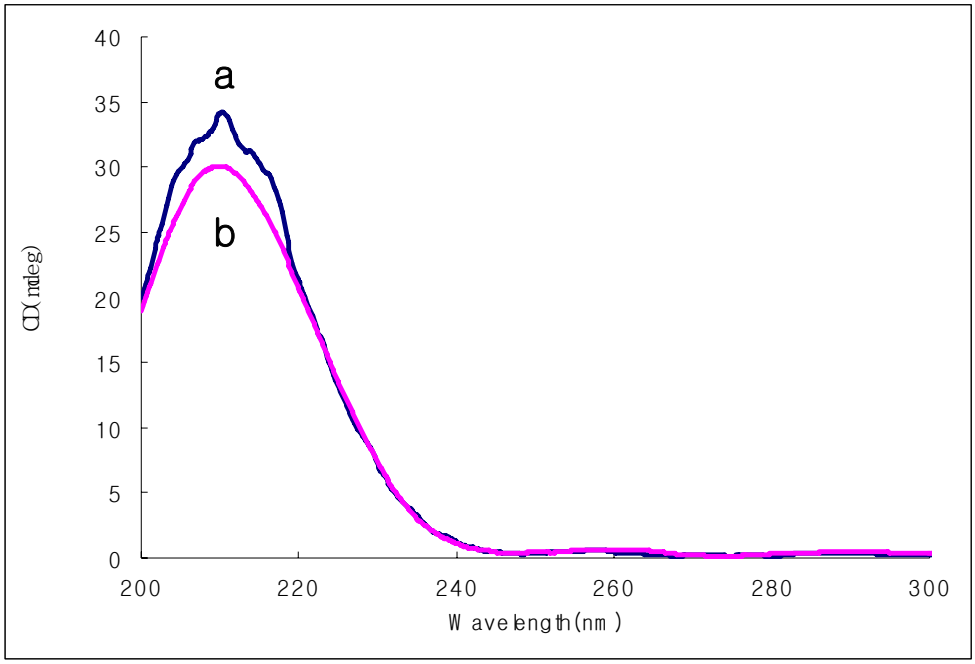


Figure S2. CD spectra in H_2O at 298 K (1mm cell): (a) **1** [0.5 mM] + $\mathbf{2}^{RR}$ [4 mM], (b) $\mathbf{2}^{RR}$ [4 mM] + **KOH** [1.5 mM].

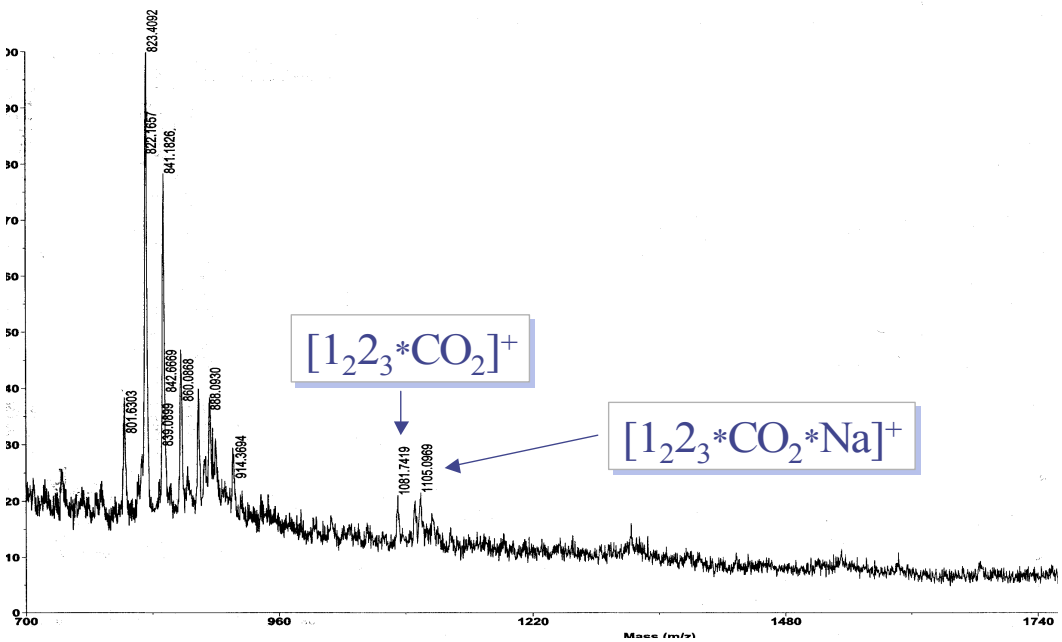


Figure S3. MALDI-TOF mass spectra of $\mathbf{1}_2$·$\mathbf{2}_3$.

Crystal data

Structure solution and refinement of the structure were carried out using the SHELXTL-PLUS (5.03) software package (Sheldrick, G. M., Brukers Analytical X-Ray Division, Madison, WI, 1997). The structure was solved by direct method and refined successfully in the space group R-3c. Full matrix least-squares refinement was carried out by minimizing $(Fo^2-Fc^2)^2$. All non-hydrogen atoms were refined anisotropically. The two hydrogen atoms of the imidazolinium group involved in hydrogen bonding were located and refined isotropically, and the remaining hydrogen atoms were also located but assigned with isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U (Cmethyl). A disordered solvent methanol site was treated with statistical disorder model and the hydrogen atoms were treated using appropriate riding model. The final refinement converged with R1 = 0.0729, wR2 = 0.2045 (I>2s(I)); R1 = 0.1472, wR2 = 0.2573 (all data).

Table S1. Crystal data and structure refinement for $\mathbf{1}_2\cdot\mathbf{2}_3$.

Identification code	o3_128tg	
Empirical formula	C60 H96 N12 O18	
Formula weight	1273.49	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R-3*c*	
Unit cell dimensions	a = 27.5164(19) Å	α= 90°.
	b = 27.5164(19) Å	β= 90°.
	c = 14.685(2) Å	γ = 120°.
Volume	9629.2(17) Å^3	
Z	6	
Density (calculated)	1.318 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	4104	
Crystal size	0.40 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.48 to 28.30°.	
Index ranges	-35<=h<=28, -36<=k<=36, -19<=l<=19	
Reflections collected	18655	
Independent reflections	2641 [R(int) = 0.0546]	
Completeness to theta = 28.30°	98.8 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9807 and 0.9619
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2641 / 2 / 188
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0729, wR2 = 0.2045
R indices (all data)	R1 = 0.1472, wR2 = 0.2573
Largest diff. peak and hole	0.347 and -0.297 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $\mathbf{1}_2 \cdot \mathbf{2}_3$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3181(1)	4923(1)	10525(2)	70(1)
O(2)	2423(1)	4639(1)	9688(2)	89(1)
C(6)	3029(2)	4286(1)	9300(3)	65(1)
C(7)	2872(2)	3746(2)	9827(3)	83(1)
C(8)	3029(3)	3371(2)	9296(4)	108(2)
C(9)	2868(2)	4648(1)	9876(2)	61(1)
N(1)	3214(1)	7973(1)	448(2)	65(1)
N(2)	4085(1)	8229(1)	758(2)	64(1)
C(1)	2901(1)	6790(1)	453(2)	54(1)
C(2)	3461(1)	7225(1)	451(2)	53(1)
C(3)	3590(1)	7814(1)	536(2)	56(1)
C(4)	3474(2)	8580(2)	607(3)	70(1)
C(5)	4083(2)	8759(2)	815(3)	70(1)
O(1S)	1504(4)	3556(4)	9077(6)	132(4)
C(1S)	1154(4)	3289(3)	9653(6)	158(3)
O(2S)	1314(4)	3831(4)	9638(8)	138(4)
C(2S)	1154(4)	3289(3)	9653(6)	158(3)

Table S3. Bond lengths [Å] and angles [°] for $\mathbf{1}_2 \cdot \mathbf{2}_3$.

O(1)-C(9)	1.253(4)
O(2)-C(9)	1.243(4)
C(6)-C(6)#1	1.504(7)
C(6)-C(9)	1.530(5)
C(6)-C(7)	1.535(5)
C(7)-C(8)	1.518(7)
C(8)-C(8)#1	1.501(12)
N(1)-C(3)	1.314(4)
N(1)-C(4)	1.470(5)
N(2)-C(3)	1.307(4)
N(2)-C(5)	1.462(4)
C(1)-C(2)#2	1.385(4)
C(1)-C(2)	1.400(4)
C(2)-C(1)#3	1.385(4)
C(2)-C(3)	1.483(4)
C(4)-C(5)	1.523(6)
O(1S)-C(1S)	1.215(9)

C(6)#1-C(6)-C(9)	112.7(3)
C(6)#1-C(6)-C(7)	111.5(3)
C(9)-C(6)-C(7)	108.7(3)
C(8)-C(7)-C(6)	111.2(4)
C(8)#1-C(8)-C(7)	111.6(4)
O(2)-C(9)-O(1)	123.6(3)
O(2)-C(9)-C(6)	117.8(3)
O(1)-C(9)-C(6)	118.6(3)
C(3)-N(1)-C(4)	110.2(3)
C(3)-N(2)-C(5)	111.3(3)
C(2)#2-C(1)-C(2)	120.2(3)
C(1)#3-C(2)-C(1)	119.8(3)
C(1)#3-C(2)-C(3)	120.4(3)
C(1)-C(2)-C(3)	119.6(3)
N(2)-C(3)-N(1)	112.6(3)
N(2)-C(3)-C(2)	123.4(3)

N(1)-C(3)-C(2)	123.9(3)
N(1)-C(4)-C(5)	103.4(3)
N(2)-C(5)-C(4)	102.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2/3,-x+y+1/3,-z+11/6 #2 -y+1,x-y+1,z #3 -x+y,-x+1,z

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\mathbf{1}_2 \cdot \mathbf{2}_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	60(2)	53(1)	92(2)	1(1)	6(1)	25(1)
O(2)	74(2)	99(2)	105(2)	-21(2)	-7(2)	53(2)
C(6)	75(2)	44(2)	78(2)	2(2)	0(2)	32(2)
C(7)	97(3)	48(2)	105(3)	15(2)	7(3)	37(2)
C(8)	161(5)	52(2)	120(4)	4(3)	-11(4)	58(3)
C(9)	54(2)	45(2)	73(2)	4(2)	8(2)	17(2)
N(1)	56(2)	52(2)	88(2)	-1(2)	2(2)	28(2)
N(2)	53(2)	50(2)	87(2)	-4(1)	5(2)	24(2)
C(1)	51(2)	55(2)	58(2)	3(1)	1(1)	28(2)
C(2)	54(2)	50(2)	53(2)	-1(1)	-1(1)	25(2)
C(3)	55(2)	53(2)	61(2)	2(1)	6(1)	28(2)
C(4)	72(2)	50(2)	89(3)	0(2)	6(2)	31(2)
C(5)	63(2)	48(2)	96(3)	-2(2)	13(2)	25(2)
O(1S)	107(6)	125(8)	125(7)	-19(6)	12(5)	29(6)
C(1S)	161(7)	120(6)	187(8)	-19(5)	4(6)	66(5)
O(2S)	133(7)	99(6)	183(9)	-14(6)	-7(7)	60(5)
C(2S)	161(7)	120(6)	187(8)	-19(5)	4(6)	66(5)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $\mathbf{1}_2 \cdot \mathbf{2}_3$.

	x	y	z	U(eq)
H(6)	2843(15)	4214(15)	8630(30)	78
H(7A)	3127(19)	3895(19)	10360(30)	99
H(7B)	2480(20)	3552(18)	10120(30)	99
H(8A)	2918(15)	3006(16)	9690(30)	73
H(8B)	2840(16)	3274(16)	8680(30)	73
H(1N)	2859(17)	7761(17)	230(30)	73(11)
H(2N)	4377(18)	8207(16)	750(30)	72(12)
H(1)	2601(14)	6850(14)	460(20)	65
H(4A)	3267(16)	8647(15)	1120(30)	84
H(4B)	3411(17)	8750(17)	170(30)	84
H(5A)	4379(17)	9041(17)	360(30)	84
H(5B)	4200(17)	8921(17)	1460(30)	84
H(1S)	1822	3729	9321	198
H(1S1)	864	3397	9651	237
H(1S2)	1333	3366	10253	237
H(1S3)	982	2887	9519	237
H(2S)	1667	4022	9649	206
H(2S1)	852	3096	10099	237
H(2S2)	1473	3243	9822	237
H(2S3)	1018	3127	9048	237

Table S6. Hydrogen bonds for $\mathbf{1}_2 \cdot \mathbf{2}_3$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(2)#4	0.91(4)	1.77(4)	2.642(4)	161(4)
N(2)-H(2N)...O(1)#5	0.84(4)	1.89(4)	2.714(4)	169(4)
O(1S)-H(1S)...O(2)	0.84	2.27	2.923(10)	134.8
O(2S)-H(2S)...O(2)	0.84	1.92	2.733(10)	162.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+2/3,-x+y+1/3,-z+11/6 #2 -y+1,x-y+1,z #3 -x+y,-x+1,z

#4 -x+y,-x+1,z-1 #5 -y+1,x-y+1,z-1