Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Stabilization of polyiodide networks with Cu(II)-complexes of small methylated polyazacyclophanes: shifting directional control from H-bonds to I···I interactions

Álvaro Martínez-Camarena, Matteo Savastano, Carla Bazzicalupi, José M. Llinares, Begoña Verdejo, Antonio Bianchi, Enrique García-España

Content

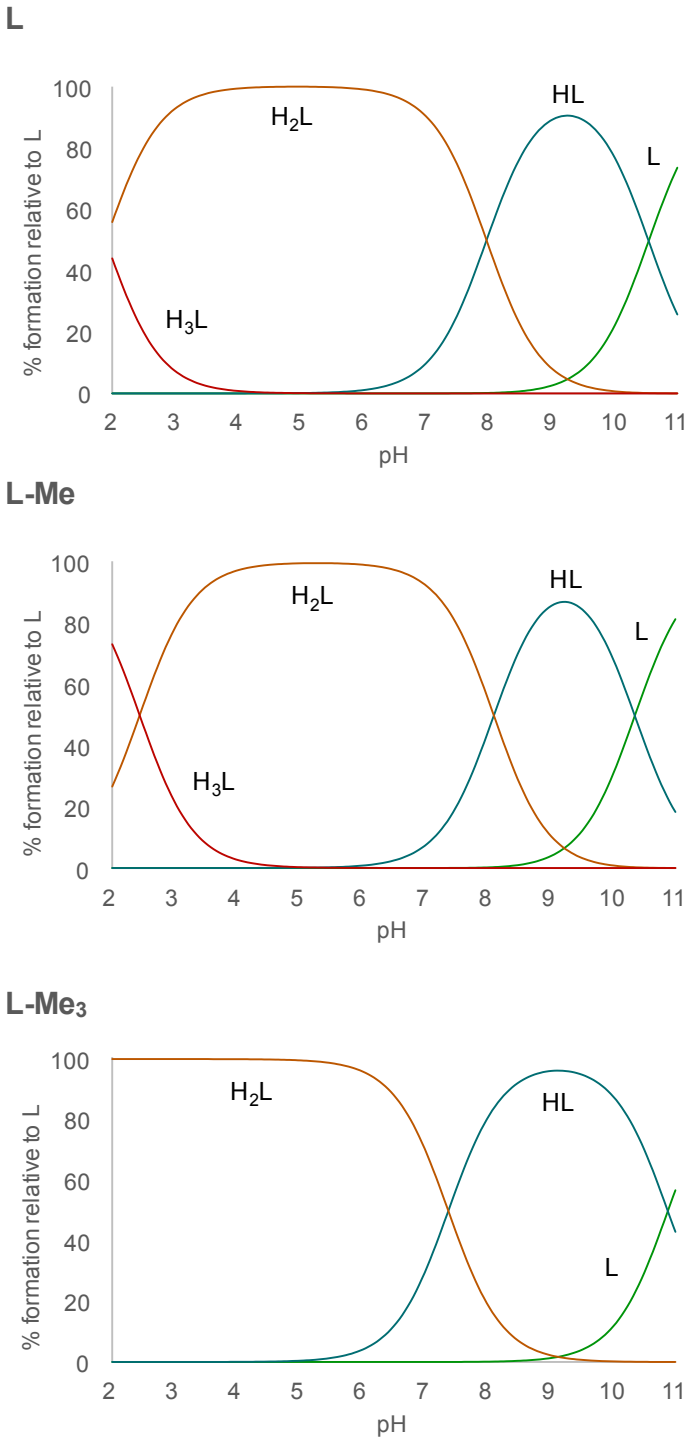

Fig. S1. Species distribution diagrams of the protonated species formed by **L**, **L-Me** and **L-Me$_3$**. [Ligand] = 1 mM.

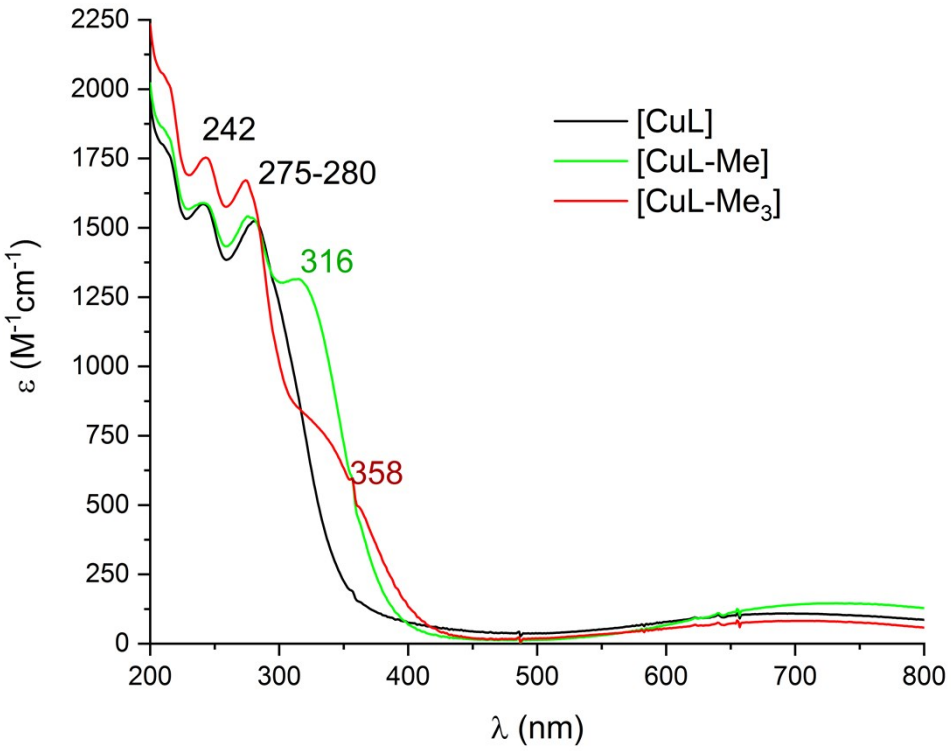

Fig. S2. UV-vis spectra of $[CuL]^{2+}$ complexes (L = **L**, **L-Me**, **L-Me$_3$**) in aqueous solution.

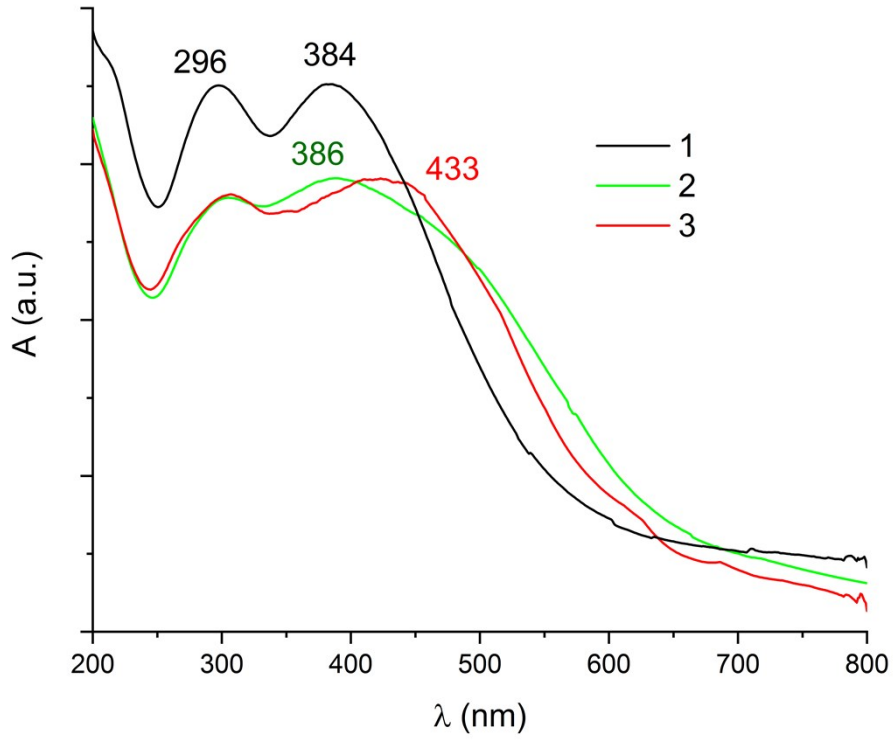

Fig. S3. UV-vis spectra of a thin film of (1) [(Cu**L**)I](I_3) and [(Cu**L**)I_3](I_5)·0.5I_2, (2) [Cu(**L-Me$_3$**)(I·I_2)](I_5) and (3) [Cu(**L-Me**)I](I_7).

Table S1. CH···I contacts (Å) in [Cu(**L-Me$_3$**)(I·I$_2$)](I$_5$).

I4···C12	-x+1,+y+1/2,-z+1/2	3.949(6)
I4···H12A	-x+1,+y+1/2,-z+1/2	3.133
I1···C8	x,+y-1,+z	4.127(8)
I1···H8A	x,+y-1,+z	3.171
I2···C9	-x+1,+y-1/2,-z+1/2	4.027(8)
I2···H9A	-x+1,+y-1/2,-z+1/2	3.167
I2···C12		4.006(6)
I2···H12B		3.061

Table S2. Breakdown of $[(CuL)I]^+$ (L = **L**, **L-Me**, **L-Me$_3$**) percent Hirshfeld surface composition in respective crystal structures ([(Cu**L**)I](I_3), [Cu(**L-Me**)I](I_7) and [Cu(**L-Me$_3$**)(I·I_2)](I_5)).

Inside Atom	Outside Atom				Total
			L		
	C	H	I	N	
C	-	3.7	2.8	-	6.5
Cu		0.0	0.1	-	0.2
H	1.8	39.3	35.7	-	76.8
I	0.4	13.8	0.9	-	15.1
N	-	0.1	1.3	-	1.4
Total	2.2	56.9	40.9	0.0	
			L-Me		
	C	H	I	N	
C	-	2.6	3.2	-	5.8
Cu	-	0.2	1.0	-	1.2
H	2.0	21.5	50.7	0.0	74.3
I	-	8.7	1.9	3.1	13.7
N	-	0.2	4.5	0.3	5.0
Total	2.0	33.1	61.4	3.4	
			L-Me$_3$		
	C	H	I	N	
C	-	2.4	3.5	-	5.9
Cu	-	-	0.2	-	0.2
H	1.8	28.0	53.6	-	83.3
I	-	5.4	4.0	-	9.4
N	-	0.0	1.1	-	1.1
Total	1.8	35.8	62.4	0.0	

Table S3. Crystal data and refinement parameters for [(Cu**L**)I](I_3), [Cu(**L-Me**)I](I_7) and [Cu(**L-Me$_3$**)(I·I_2)](I_5).

	[(Cu**L**)I](I_3)	[Cu(**L-Me**)I](I_7)	[Cu(**L-Me$_3$**)(I·I_2)](I_5)
Empirical formula	$C_{11}H_{18}CuI_4N_4$	$C_{12}H_{20}CuI_8N_4$	$C_{14}H_{24}CuI_8N_4$
Formula weight	777.43	1299.06	1327.11
Temperature (K)	100	100	100
space group	*P -1*	*C2/c*	*$P2_1/c$*
a (Å)	8.586(2)	33.318(6)	16.549(3)
b (Å)	9.296(2)	9.3647(18)	9.513(2)
c (Å)	12.161(3)	18.328(3)	18.843(3)
α (°)	93.253(11)	90	90
β (°)	94.373(10)	108.300(9)	103.482(6)
γ (°)	92.131(10)	90	90
Volume (Å^3)	965.5(4)	5429.5(17)	2884.7(8)
Z	2	8	4
Independent reflections / R(int)	3967/0.0780	4308/0.0430	8977/0.0892
μ (mm^{-1})	7.523(Mo-Kα)	9.909(Mo-Kα)	9.328(Mo-Kα)
R indices [I>2σ(I)]*	R1 = 0.0278 wR2 = 0.0595	R1 = 0.0329 wR2 = 0.0883	R1 = 0.0408 wR2 = 0.1052
R indices (all data)*	R1 = 0.0363 wR2 = 0.0643	R1 = 0.0337 wR2 = 0.0888	R1 = 0.0525 wR2 = 0.1148