Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

for:

Crystal structure, supramolecular assembly and preliminary reactivity behaviour of new heteropolytopic ligands based on oxalate/malonate skeleton and azolate moieties

by

Federica Garau,[a] Magda Monari,*[b] ‡ Luciano Pandolfo,*[a] Claudio Pettinari,*[c] Alfonso Venzo[d]

[a] *Dept. of Chemical Sciences, University of Padova, Via Marzolo, 1, I-35131 Padova, Italy.*
[b] *Dept. of Chemistry "G. Ciamician", University of Bologna, Via Selmi, 2, I-40126 Bologna, Italy*
[c] *Dept. of Chemical Sciences, Via S. Agostino, 1, University of Camerino, I-62032 Camerino (MC), Italy*
[d] *CNR – ISTM and INSTM, University of Padova, Via Marzolo, 1, I-35131 Padova, Italy.*

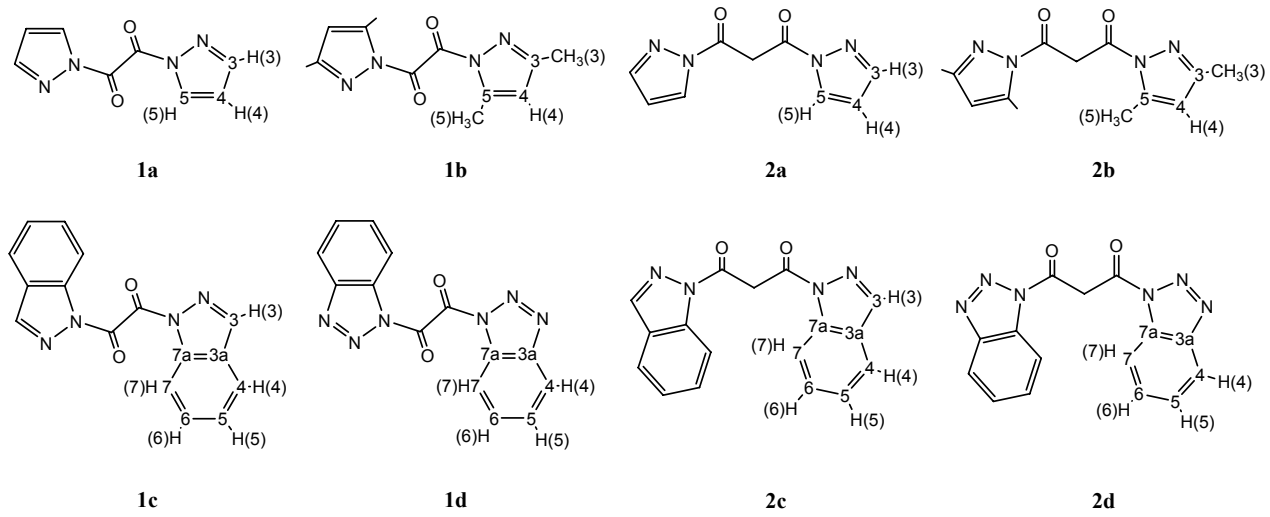


Chart S1 – Numbering scheme for ^{1}H and ^{13}C NMR signals assignments. NB The numbering doesn't correspond to the labels indicated in the crystal structure figures.

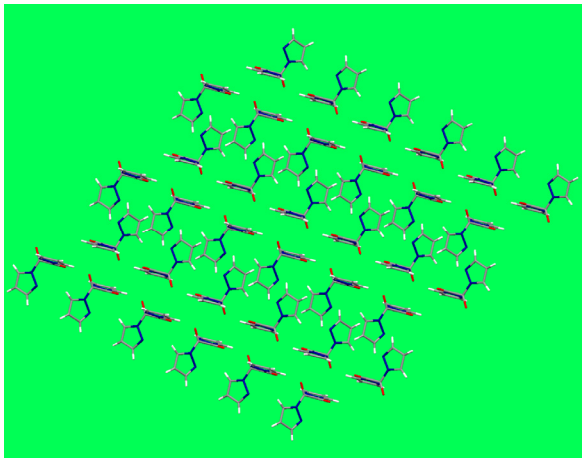
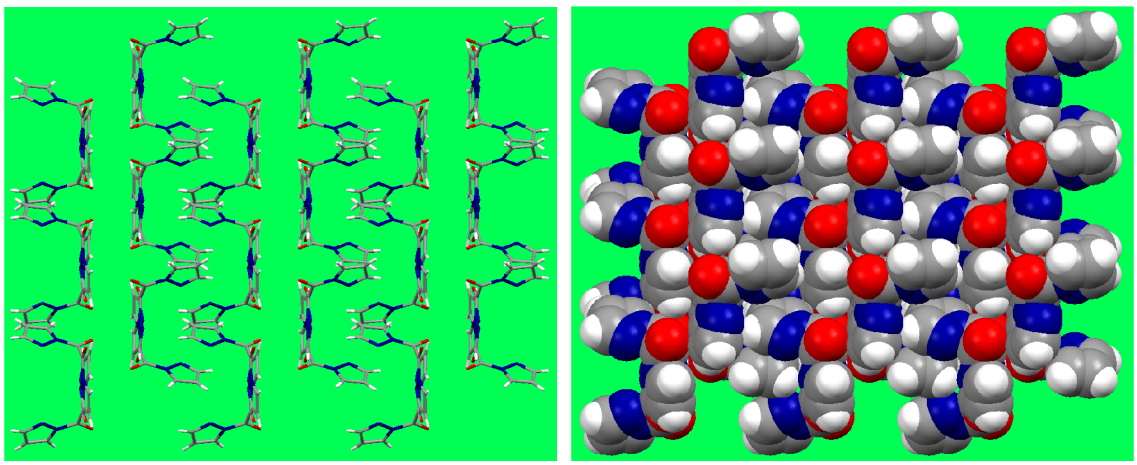


Figure S1 – Crystal packing of **1a** viewed down the crystallographic *b* axis.



a b

Figure S2 – Capped-stick (a) and space-filling (b) representation of the crystal packing of **1a** viewed down the crystallographic *c* axis.

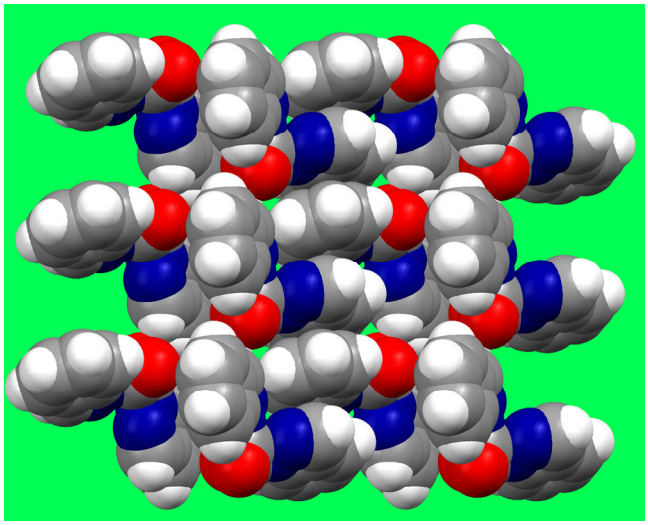
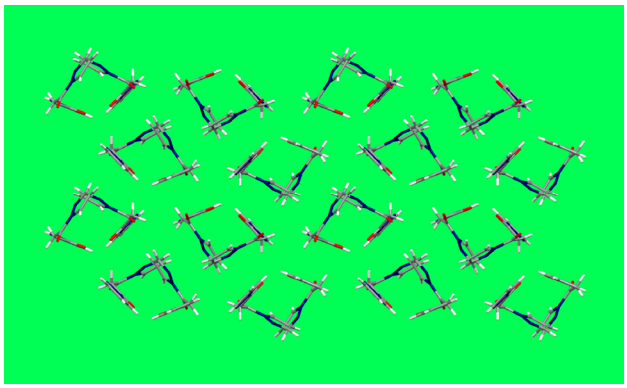
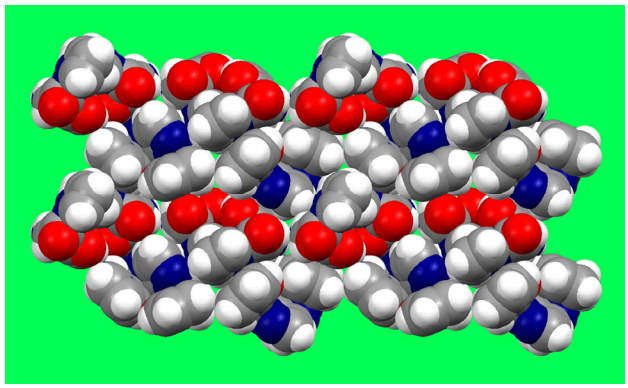


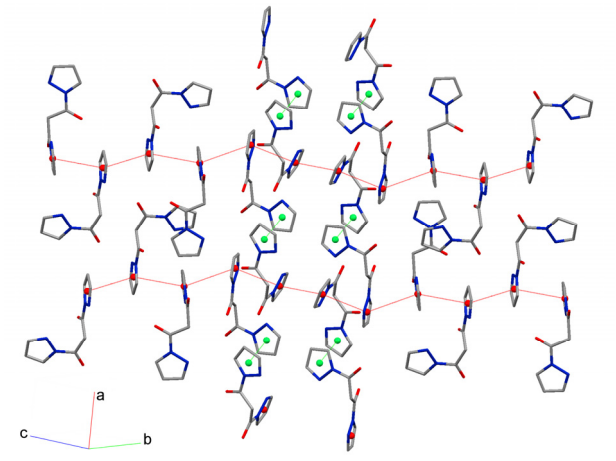
Figure S3 – Space-filling representation of the crystal packing of **1c** viewed down the crystallographic *b* axis, evidencing the presence of very narrow channels.



a



b



c

Figure S4 – Capped-stick (a) and space-filling (b) representation of the crystal packing of **2a** viewed down the crystallographic *a* axis and (c) an alternative view of **2a** highlighting the formation of a 3-D network through π-π interactions (hydrogen atoms omitted for clarity).

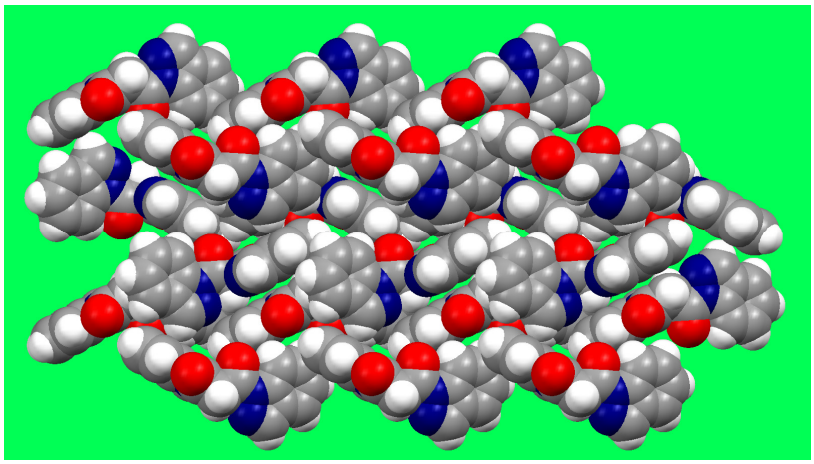


Figure S5 – View down the crystallographic *a* axis of crystal packing of **2c**, evidencing the presence of very narrow slits.

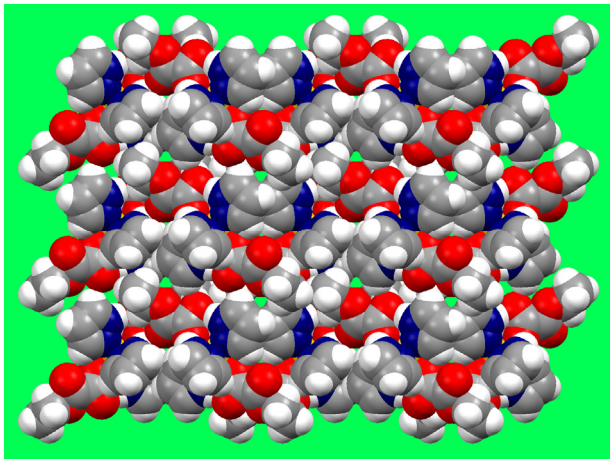


Figure S6 – Space-filling representation of **3** viewed down the crystallographic *c* axis, evidencing very narrow channels.

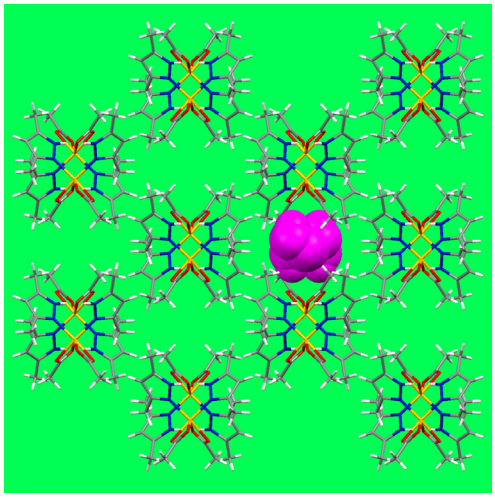


Figure S7 – Capped-stick representation of the crystal packing of **6** viewed down the crystallographic *c* axis. Disordered molecules of methanol (see text) occupying channels running parallel to the *c* axis, are evidenced in one channel with a space-filling pink representation while, in the other cases, the methanol has been fictionally removed showing the empty channels.

Table S1. Selected bond lengths (Å) and angles for **3.**

Cu-N(1)	2.003(2)	C(1)-C(2)	1.513(5)
Cu-N(3)	2.021(2)	C(2)-O(3)	1.194(4)
Cu-O(1)	2.359(2)	C(2)-O(4)	1.283(4)
C(1)-O(1)	1.244(3)	O(4)-C(3)	1.471(6)
C(1)-O(2)	1.243(4)		
N(1')-Cu-N(1) [a]	180.0(1)	N(3')-Cu-N(3) [a]	180.0(1)
N(1)-Cu-N(3') [a]	91.04(9)	N(1')-Cu-O(1) [a]	94.27(9)
N(1)-Cu-N(3)	88.96(9)	N(1)-Cu-O(1)	85.73(9)
N(3')-Cu-O(1) [a]	92.46(8)	N(3)-Cu-O(1)	87.54(8)
O(1)-Cu-O(1') [a]	180.0(1)	O(1)-C(1)-C(2)	115.4(3)
O(2)-C(1)-C(2)	116.5(3)	O(3)-C(2)-C(1)	122.5(3)
O(4)-C(2)-C(1)	113.8(3)		

[a] Symmetry transformations used to generate equivalent atoms: (I) -x+1,-y,-z+1.

Table S2. Selected bond lengths (Å) and angles for **6.**

Cu-N(1)	1.989(2)	Cu-O(2)	2.478(2)
Cu-O(1)	2.003(1)	O(2)-C(6)	1.242(3)
O(1)-C(6)	1.268(2)	C(6)-C(7)	1.503(3)
N(1')-Cu-N(1)[a]	92.4(1)	O(1')-Cu-O(1)[a]	88.20(9)
N(1)-Cu(1)-O(1)	166.59(6)	N(1')-Cu-O(1)[a]	91.20(7)
O(1)-Cu-O(2)	57.14(5)		

[a] Symmetry transformations used to generate equivalent atoms: (I) -x+1,y,-z+1/2.