



Volume 73 (2017)

Supporting information for article:

Crystallographic and computational study of a network composed of $[\text{ZnCl}_4]^{2-}$ anions and triply protonated 4'-functionalized terpyridine cations

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SUPPORTING INFORMATION SI1

Hirshfeld surface and Enrichment Ratio (ER) analysis

The three-dimensional Hirshfeld surfaces are used to visualize and analyze intermolecular interactions within the crystal structures, giving the possibility of obtaining quantitative information into the chemical nature of such intermolecular contacts (Spackman & Byrom, 1997). These interactions can be evaluated by using the recently introduced descriptor proposed in Jelsch *et al.*, 2014, the enrichment ratio (E_{xy}). The enrichment ratio of a pair of elements is defined as the ratio between the proportion of actual contacts in the crystal and the theoretical proportion of random contacts ($E_{xy} = C_{xy}/R_{xy}$). An E_{xy} value larger than unity, for a given pair of chemical species, indicates that these species have a higher propensity to form contacts in the crystal packing. Conversely, pairs with a low affinity to closeness should yield an E_{xy} value lower than unity.

In the present case Hirshfeld surfaces were computed around each of the independent groups (two ITPH_3^{3+} cations, three ZnCl_4^{2-} anions and one water solvate). In order to facilitate the generation of "individual" surfaces instead of a "single" one embracing the whole asymmetric unit and thus masking the details of interest, the groups involved were replaced by conveniently chosen symmetry equivalents, sufficiently far apart from each other as to avoid close inter-group contacts (Fig. SI1c).

With this artifact the Hirshfeld surfaces were generated and mapped with colors in accordance with the prevailing participation of the atoms involved in the contacts, differentiating the inner surface (Fig. SI1a) of the exterior (Fig. SI1b). So, each group constituent in this global arrangement presents a distinctive Hirshfeld surface, which allows us to make a comparison among the participants species in different environments.

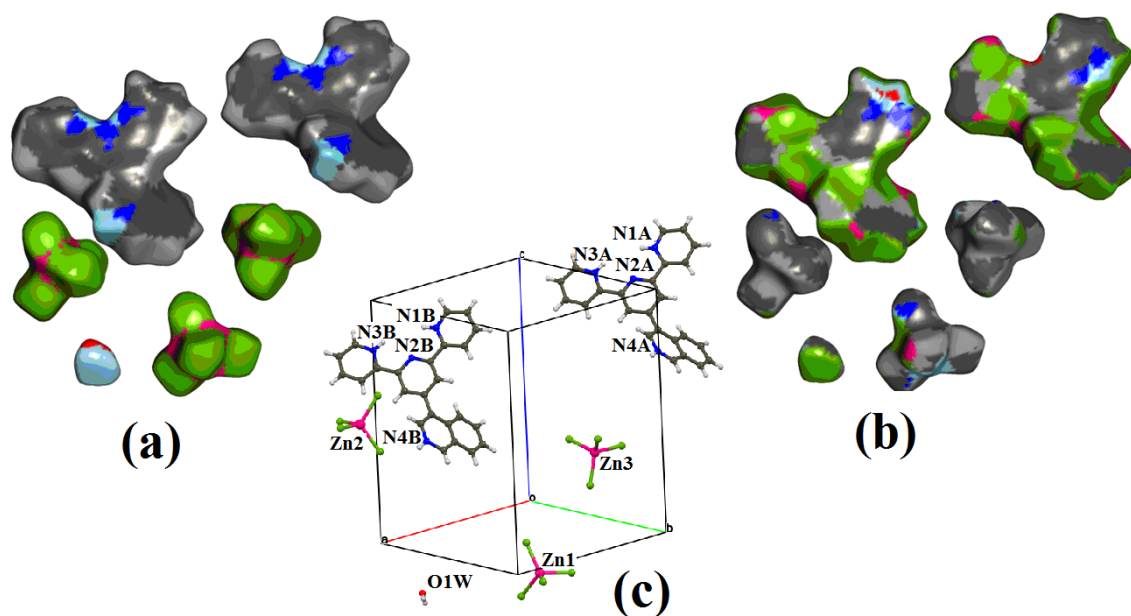


Figure S11. Right and left: Hirshfeld surfaces of the independent entities shown in (c) (conveniently set apart as to avoid overlapping). (a) With the surfaces coloured according to the interior atoms. (b) surfaces coloured according to the exterior atoms. (HC: grey, HN/O: light blue, C: dark-brown, N: blue, chloride: green, O: red, Zn: purple).

SUPPORTING INFORMATION SI2

Quantum-mechanical calculations and Atoms In Molecules (AIM) analysis

AIM (an acronym for the "Atoms In Molecules" theory; Bader, 1990, 2009) interprets chemical bonding in terms of shared or closed-shell interactions, characterized by the electron density [$\rho(\mathbf{r})$], its gradient vector [$\nabla\rho(\mathbf{r})$] and its Laplacian [$\nabla^2\rho(\mathbf{r})$] at particular points termed "Bond Critical Points", where the sign and magnitude of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ define the interaction type.

A note of caution.

In order to analyse the possible charge transfer in **II** we performed DFT calculations, in the light of recently published works in the literature where the technique has been applied to similar systems, viz., in Manna et al. (2014). In this latter work, a terpyridine perchlorate is analysed by means of a highly simplified system, representing the complex polyaromatic *tpy* by a single *py* ring, with the obvious aim of reducing computational time. Trying to explore the feasibility of such a simplifying approach in a complex system as ours, we indulged in a test case study of one of the multiple Zn-Cl...H-N(*X*) interactions present in **II** (See Fig. SI2 below. for the system investigated) varying the model for the (poly)aromatic ligand *X* in a sequential fashion of increasing complexity (*py* \rightarrow *isq* \rightarrow *tpy*). Our results (Table SI2) showed an impressive effect in the final calculated charge distribution, evidencing a significant charge transfer to the aromatic system which strongly depends on the aromatic substituent used. This fact convinced us that at least in the present case, the simplification was not an adequate short-cut for the costly (and finally disregarded) full calculation. In particular, our results show that the truncation on the atomic structure may lead to wrong conclusions on charge distributions (and presumably other related properties, as stabilization or interaction energies, etc.) and confirm what is already a truism: if computational efforts are to be reduced when performing DFT calculations, extreme care should be taken in the simplifying assumptions made, if meaningful results are to be expected.

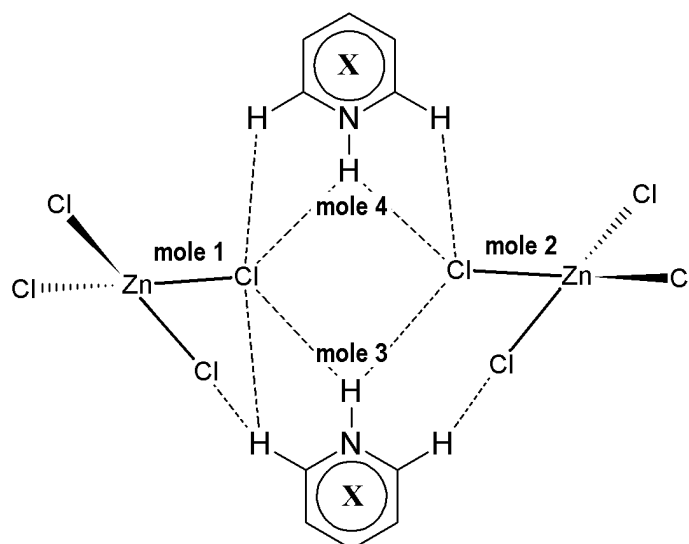


Figure SI2. Model used for DFT calculation, with ligands **X** of increasing complexity.

Table SI2. Partial atomic charge distribution derived from the Mulliken population analysis in the DFT calculations, as a function of the complexity of the model used for the (poly)aromatic ligand **X**.

	<i>X=py</i>	<i>X=isoq</i>	<i>X=tpy</i>
Zn(mole 1)	-0.18	-0.29	-0.76
Zn(mole 2)	-0.21	-0.31	-0.74
Cl(mole 1)	-0.16	-0.09	0.10
Cl(mole 2)	-0.03	0.02	0.30
H(mole 3)	0.16	0.16	0.08
H(mole 4)	0.22	0.22	0.17
N(mole 3)	0.38	0.41	0.53
N(mole 4)	0.36	0.37	0.42

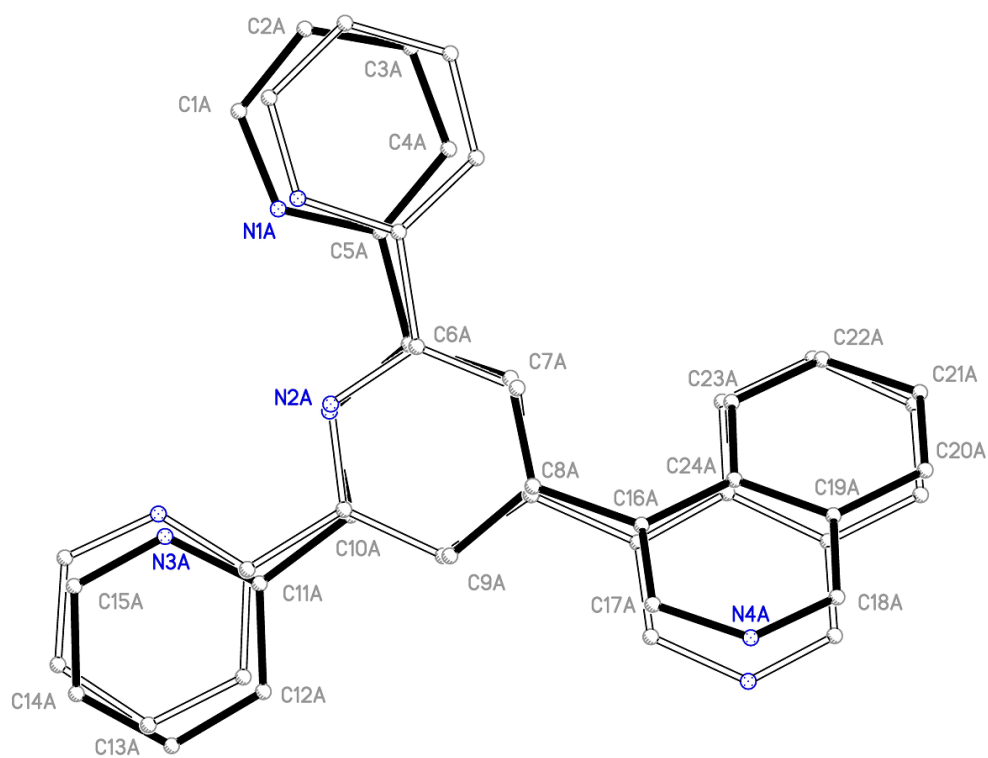
SUPPORTING INFORMATION SI3

Figure SI3. Molecular overlap in **II**, after a (0.22228, -0.31704, -0.15938) shift to molecule A, evidencing similarities in orientation and metrics.

SUPPORTING INFORMATION SI4

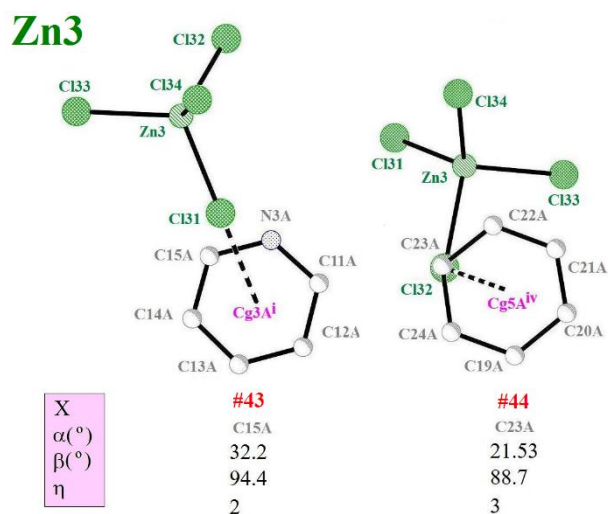
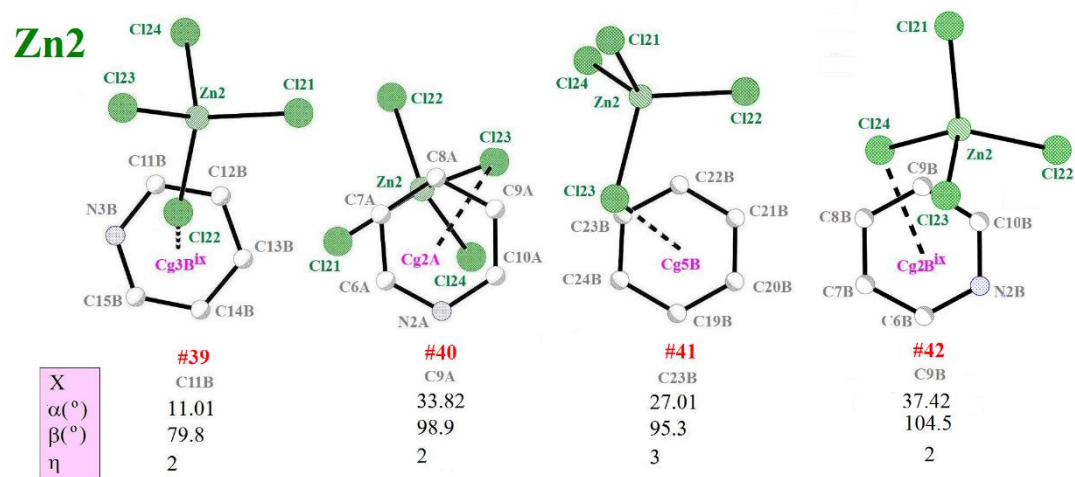
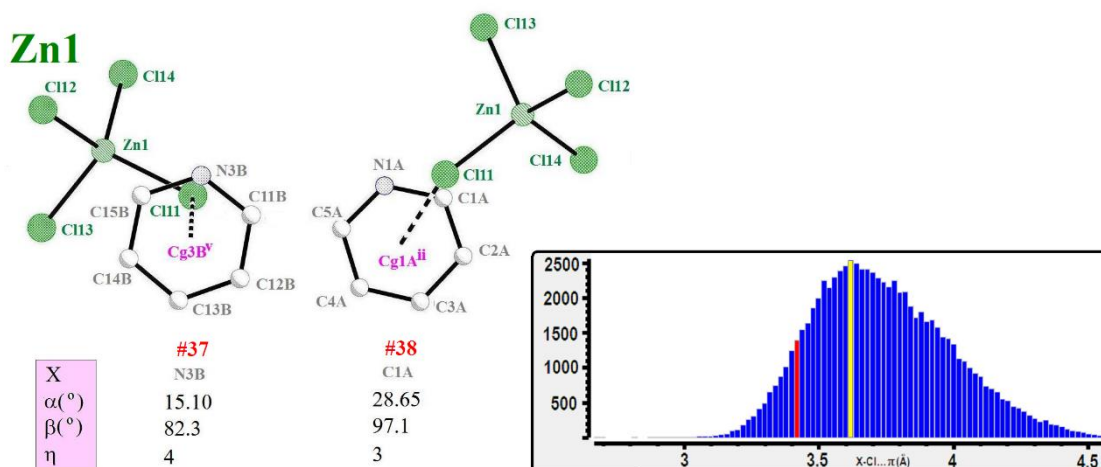


Figure SI4: Graphical view of the *anion*... π interactions in structure **II**. Each view is a projection along the ring normal, so as to assess the relative position of the anion with respect to the ring (inside, $\beta < 90^\circ$, outside $90^\circ < \beta < 100^\circ$). **Inset:** the distribution of the X-Cl...C distance (d) in *ca.* 80000 similar Cl... π contacts in the literature (CSD, v5.37, Groom *et al.*, 2016), showing a population maximum (mode) at ~ 3.62 Å (yellow bar). The mean value in the present structure is $3.41(14)$ Å (red bar).

SUPPORTING INFORMATION SI5**Table SI5a.** Hirshfeld contact surfaces and enrichment ratios for ITPH₃³⁺(A).

ITPH ₃ ³⁺ (A)								
Actual contacts % (merged)	Exterior							
Interior	C	N	O	Cl	Zn	H _C	H _N	H _{OH}
C	18.46							
N	5.09	0.04						
O	0.00	0.00	0.00					
Cl	13.69	1.25	0.00	0.00				
Zn	1.36	0.00	0.00	0.00	0.00			
H _C	11.48	0.42	0.37	29.23	4.29	4.00		
H _N	2.05	0.00	2.73	2.99	0.01	1.02	0.00	
H _{OH}	0.10	0.00	0.00	0.00	0.00	1.01	0.41	0.00
Surface interior %	42.32	4.08	0.00	0.00	0.00	46.13	7.47	0.00
Surface exterior %	28.37	2.76	3.11	47.16	5.66	9.68	1.75	1.52
Enrichment ratios (merged)								
C	1.54							
N	2.19	0.36						
O	0.00	0.00	nan					
Cl	0.69	0.65	nan	nan				
Zn	0.57	0.00	nan	nan	nan			
H _C	0.67	0.25	0.26	1.34	1.64	0.90		
H _N	0.72	0.00	11.78	0.85	0.03	0.67	0.00	
H _{OH}	0.16	0.00	nan	nan	nan	1.43	3.62	nan

Table SI5b. Hirshfeld contact surfaces and enrichment ratios for ITPH₃³⁺(B).

ITPH ₃ ³⁺ (B)								
Actual contacts % (merged)	Exterior							
Interior	C	N	O	Cl	Zn	H _C	H _N	H _{OH}
C	12.85							
N	4.06	0.04						
O	0.26	0.00	0.00					
Cl	17.47	1.12	0.00	0.00				
Zn	1.14	0.00	0.00	0.00	0.00			
H _C	14.88	1.76	0.00	27.56	3.36	5.36		
H _N	1.19	0.00	0.00	5.37	0.19	1.82	0.00	
H _{OH}	0.58	0.00	0.00	0.00	0.00	1.00	0.00	0.00
Surface interior %	43.24	4.14	0.00	0.00	0.00	45.40	7.22	0.00
Surface exterior %	22.04	2.88	0.26	51.52	4.69	15.69	1.35	1.57

Enrichment ratios (merged)								
C	1.35							
N	1.88	0.30						
O	2.31	0.00	nan					
Cl	0.78	0.53	nan	nan				
Zn	0.56	0.00	nan	nan	nan			
H _C	0.89	0.90	0.00	1.18	1.58	0.75		
H _N	0.55	0.00	0.00	1.44	0.57	1.04	0.00	
H _{OH}	0.85	0.00	nan	nan	nan	1.40	0.00	nan