Electronic Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

for

2,2'-bipyridine Zn(II) complexes: role of the 4,4' substituents on the crystalline solid state properties

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Figure S1. NMR spectra of the free ligand L1 (a) and the adduct **1a** $\{[(L1)_3Zn](PF_6)_2\}_2 \cdot L1 \cdot 2H_2O$ (b) with the proton of the coordinated bipyridines labeled as $_{Zn}H^3$, $_{Zn}H^5$ and $_{Zn}H^6$.

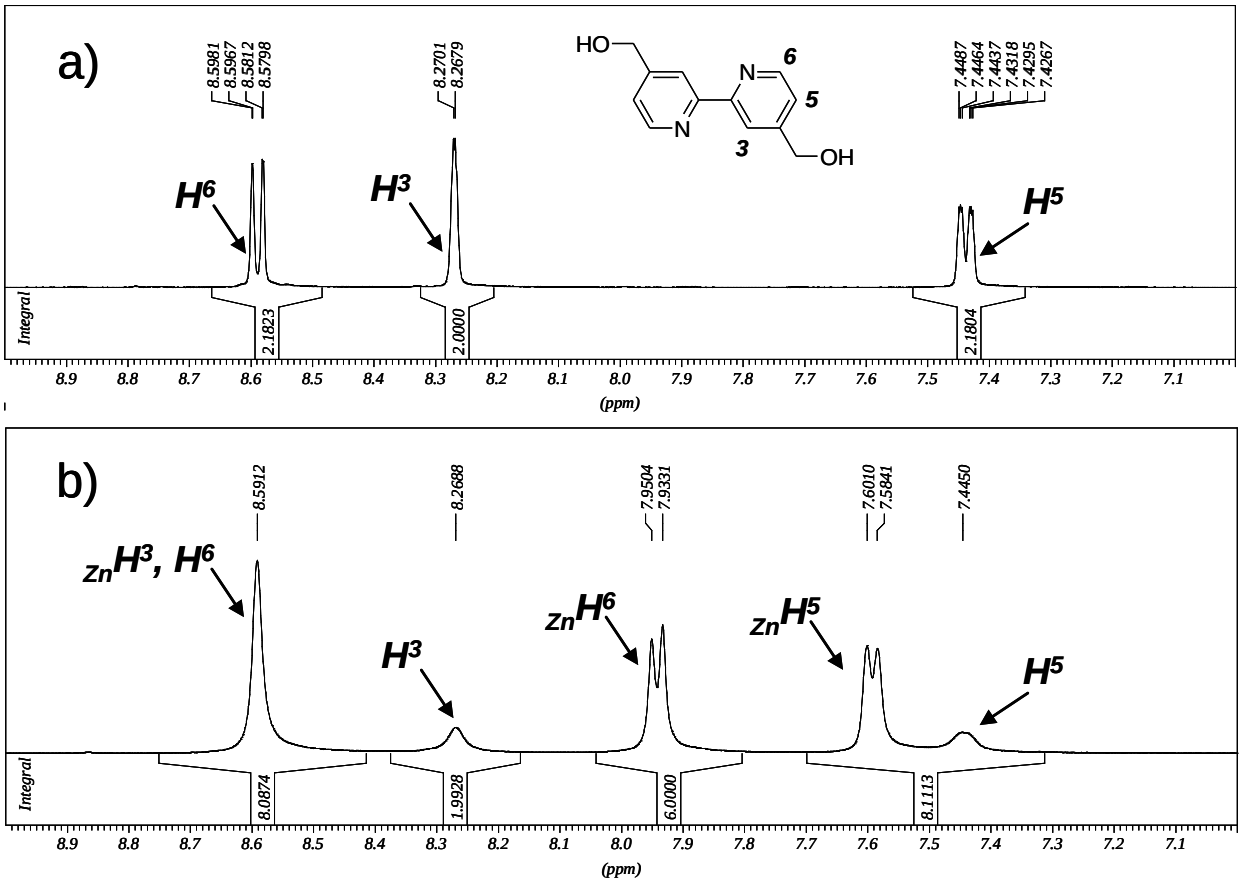


Figure S2. PXRD spectrum of the reaction product after grinding in the synthesis of **2a** (black line) superimposed to that of **2** (red line)

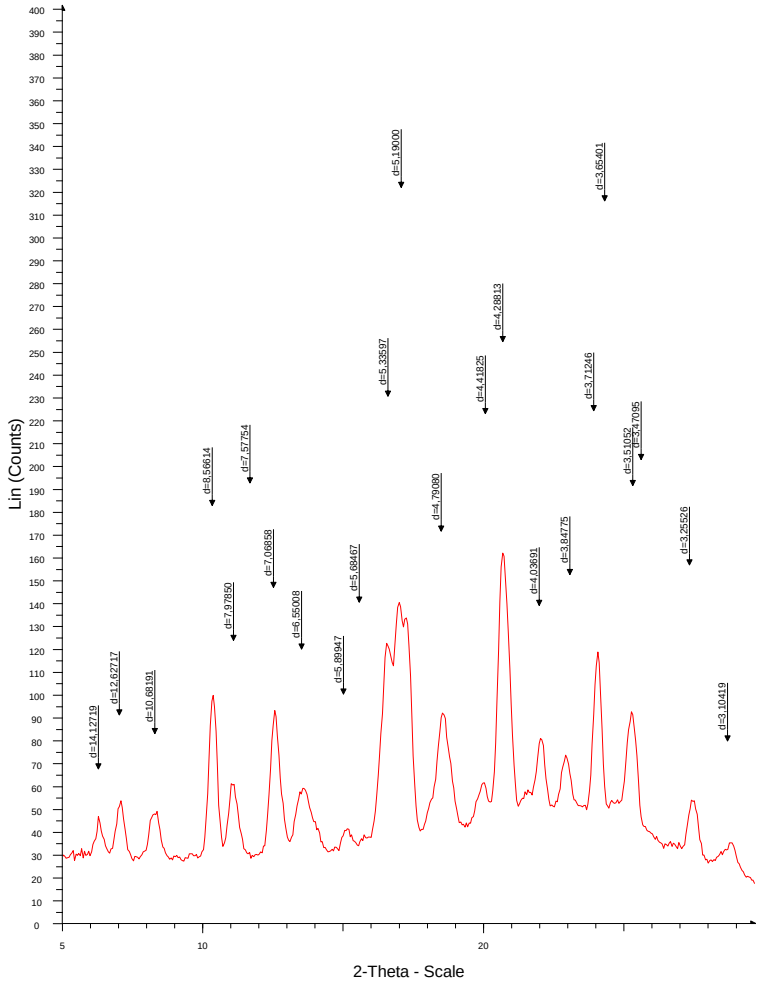


Figure S3. PXRD spectrum of the reaction product after grinding in the synthesis of **2b** (black line) superimposed to that of **2** (red line)

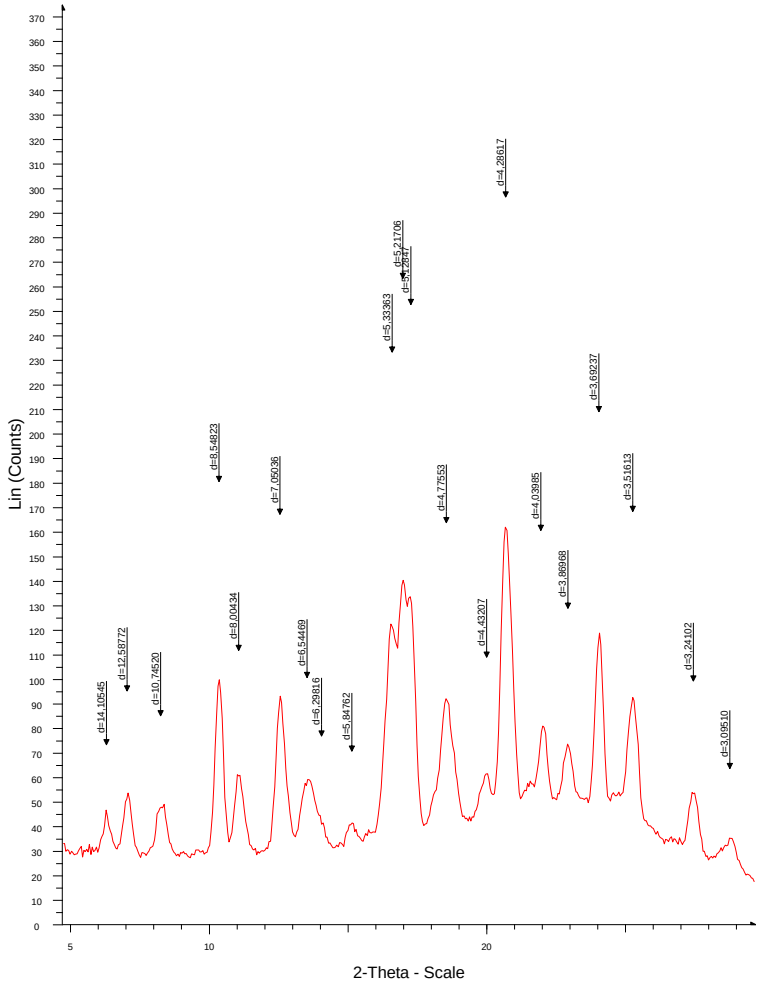


Figure S4. Crystals of the supramolecular adduct **2a** (a) and precursor **2 (**b).

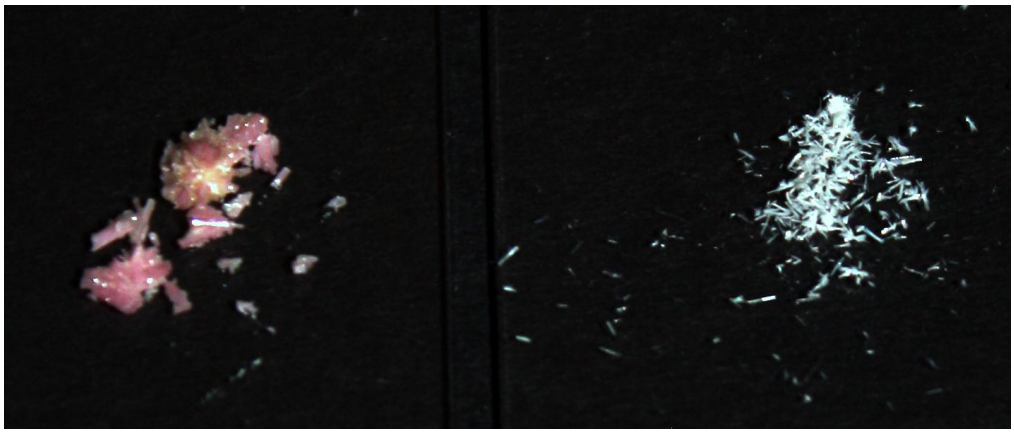
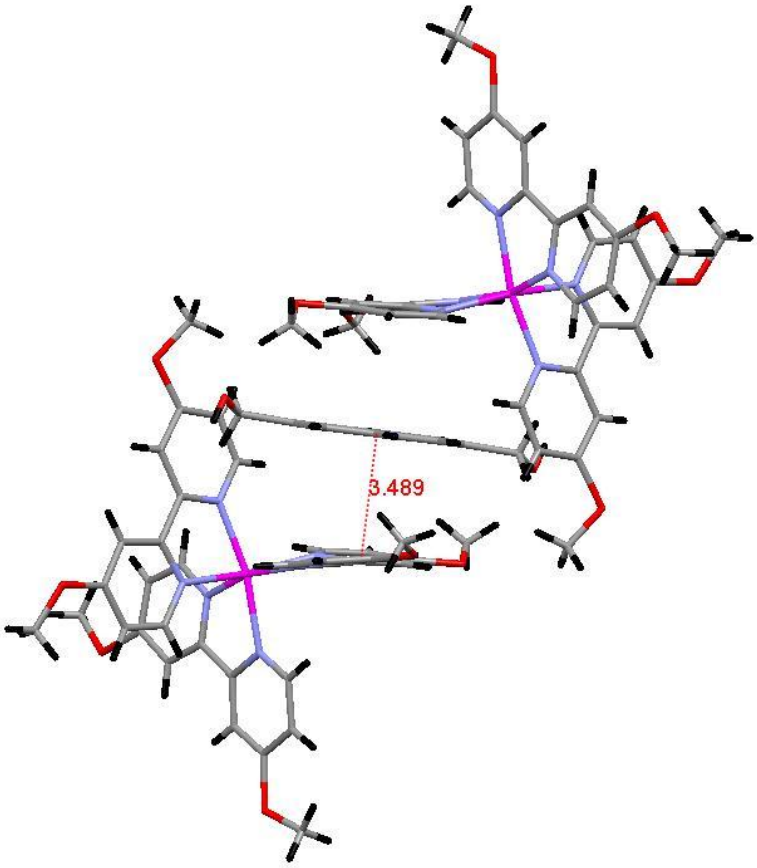


Table S1 Details of data collection and structure refinements for complexes **1a**, **2a** and **2**

	1a	**2a**	**2**	**L_1**
formula	$C_{84}H_{88}F_{24}N_{14}O_{16}P_4Zn_2$	$C_{84}H_{88}F_{24}N_{14}O_{16}P_4Zn_2$	$C_{36}H_{36}F_{12}N_6O_6P_2Zn$	$C_{12}H_{12}N_2O_2$
Mr	2260.30	2260.30	1004.02	216.24
crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
space group	*P-1*	*P-1*	*P-1*	*p(2)1/c*
a [Å]	12.0842(18)	12.1158(12)	11.354(3)	7.507(5)
b [Å]	14.630(2)	14.8243(18)	13.202(4)	12.063(8)
c [Å]	14.997(2)	15.0480(17)	15.056(5)	16.970(11)
α [°]	68.239(7)	67.610(5)	76.794(13)	90
β [°]	88.188(7)	87.958(5)	76.652(13)	96.79(2)
γ [°]	76.637(7)	76.494(5)	83.772(13)	90
V [$Å^3$]	2391.4(6)	2425.6(5)	2134.0(12)	1526.0(18)
Z	1	1	2	6
ρ cald [gcm^{-3}]	1.569		1.563	1.412
μ [cm^{-1}]	0.686		0.754	0.098
θ range [°]	1.46-26.33		1.42-26.15	2.08 to 25.02°
data collected	103631		69588	15114
unique data, R_{int}	9640, 0.0599		8353, 0.0414	2649, 0.0552
obs. data [$I > 2\sigma(I)$]	6787		6545	2649
no. parameters	647		568	220
R_1 [obs. data]	0.0873		0.0457	0.0485
wR_2 [all data]	0.2660		0.1394	0.1244
GOF	1.186		1.019	1.024

Figure S5 View of the supramolecular tetra-cationic complex supported by π-π stacking in **2a.**



Structural description of L1.

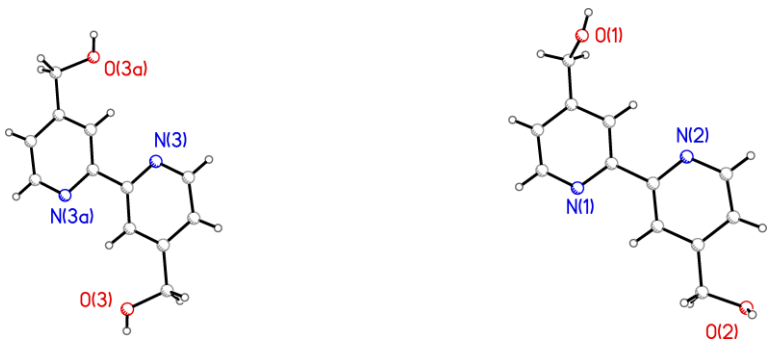


Figure S6 View of the $\mathbf{L_1}$ ligand showing the atomic labelling scheme; *a* = (*x*-1, 1-*y*, -*z*)

The crystal structure of the pure ligand **L1** is made up of two crystallographic non equivalent ligands, one of them lying on an inversion centre, both showing the usual NN *trans* conformation. The heteroaromatic rings of the ligands assemble into a columnar organization by means of π···π stacking interactions [shortest distances between pyridine planes in the range of 3.4-3.5 Å, as provided by PLATON analysis]. The shortest interplanar distances are observed between pairs of π···π stacked ligands for which the additional contribution of hydrogen bonding interactions, similar to those observed in **1a**, is present (Figure 3) [O(2)···O(1)^{i} 2.76(1); O(2)-H(2a)···O(1)^{i} distance and angle of 1.952 Å and 167.32° respectively; *i* = -*x*+1, -*y*, -*z*+2], proving the tendency of hydrogen bonds to support stacking interactions in these systems.

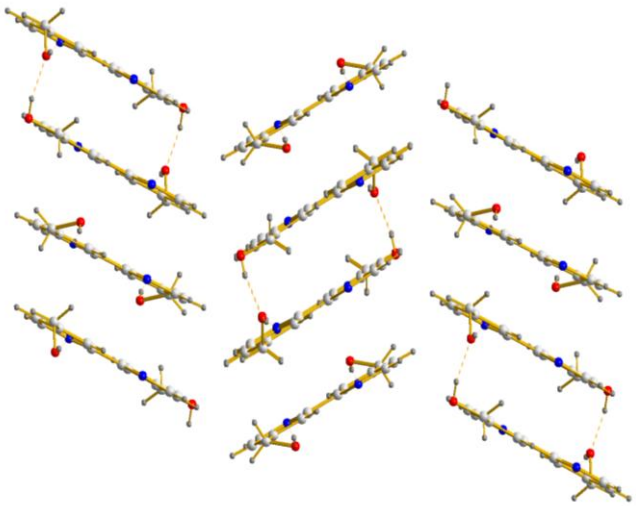


Figure S7 View of the supramolecular packing along the *a* crystallographic axis in $\mathbf{L_1}$.