Hybrid organic-inorganic chlorozincate and molecular zinc complex involving *in situ* formed imidazo[1,5-a]pyridinium cation: serendipitous oxidative cyclization, structures and photophysical properties

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Supplementary data

Table S1 Selected bond distances (Å) for the pendant pyridyl moieties of L in **1**, **2** and **3**

	1	**2**	**3**
C131–N132	1.344(3)	1.3473(9)	1.348(2)
C131–C136	1.390(3)	1.3872(11)	1.389(2)
N132–C133	1.340(3)	1.3442(9)	1.336(2)
C133–C134	1.388(3)	1.3885(11)	1.391(3)
C134–C135	1.375(3)	1.3813(13)	1.381(3)
C135–C136	1.383(3)	1.3941(13)	1.389(3)
C231–N232	1.348(3)		1.341(2)
C231–C236	1.391(3)		1.390(2)
N232–C233	1.331(3)		1.333(2)
C233–C234	1.382(3)		1.389(3)
C234–C235	1.383(3)		1.377(3)
C235–C236	1.386(3)		1.383(3)

Table S2 Selected bond angles (°) for the imidazo[1,5-*a*]pyridine moieties of L in **1**, **2** and **3**

	1	**2**	**3**
L1			
C13–N12–C11	110.80(19)	110.56(6)	110.63(15)
C13–N12–C12	126.94(19)	124.56(6)	126.17(15)
C11–N12–C12	122.20(19)	124.34(7)	123.11(15)
C13–N13A–C14	130.05(19)	128.99(6)	129.05(16)
C13–N13A–C17A	109.25(18)	109.07(6)	109.31(15)
C14–N13A–C17A	120.69(18)	121.94(6)	121.56(15)
L2			
C23–N22–C21	110.93(17)		110.45(15)
C23–N22–C22	126.45(19)		126.43(16)

C21–N22–C22	122.52(17)	123.05(16)
C23–N23A–C24	129.60(18)	129.53(15)
C23–N23A–C27A	109.19(17)	108.95(15)
C24–N23A–C27A	121.21(17)	121.47(15)

Table S3 Bond distances (Å) and angles (°) for the $ZnCl_4^{2-}$ anion in **1** and $ZnCl_3N$ moiety in **2**

	1	**2**
Zn1–Cl1	2.2771(5)	2.2540(2)
Zn1–Cl2	2.2734(6)	2.22759(19)
Zn1–Cl3	2.3185(6)	2.2440(2)
Zn1–Cl4	2.2359(6)	
Zn1–N32		2.1160(6)
Cl1–Zn1–Cl3	106.72(2)	117.20(2)
Cl2–Zn1–Cl1	110.39(2)	113.56(3)
Cl2–Zn1–Cl3	103.11(2)	111.23(2)
Cl4–Zn1–Cl1	113.49(2)	
Cl4–Zn1–Cl2	109.74(2)	
Cl4–Zn1–Cl3	112.87(2)	
N32–Zn1–Cl1		99.843(18)
N32–Zn1–Cl2		113.484(17)
N32–Zn1–Cl3		100.209(18)

Table S4 C–H···Cl distances (Å) and angles (°) in **1**–**3**

N	Atom1*	Atom2	Symm. op. 2	Length	Angle
	1				
1	Cl1	H27–C27	1-x,1-y,2-z	2.881	141.92
2	Cl1	H16–C16	1/2-x,y-1/2,z	2.853	140.63
3	Cl2	H134–C134	x,y,z	2.736	141.93
4	Cl2	H11–C11	1-x,y-1/2,3/2-z	2.871	125.19
5	Cl2	H17–C17	1-x,y-1/2,3/2-z	2.805	129.66
6	Cl2	H12A–C12	x-1/2,y,3/2-z	2.782	173.50
7	Cl2	H235–C235	x-1,y,z	2.745	164.83

8	Cl3	H21–C21	1-x,1-y,2-z	2.804	147.04
9	Cl3	H22B–C22	1-x,1-y,2-z	2.821	151.83
10	Cl3	H26–C26	2-x,1-y,2-z	2.913	167.16
11	Cl3	H233–C233	3/2-x,y-1/2,z	2.896	141.26
12	Cl4	H24–C24	x,y,z	2.847	129.37
	2				
1	Cl1	H12A–C12	x,y-1,z	2.836	122.57
2	Cl1	H133–C133	1-x,y,3/2-z	2.949	131.83
3	Cl1	H14–C14	x,1-y,z-1/2	2.855	137.62
4	Cl2	H15–C15	x,1-y,z-1/2	2.763	153.25
5	Cl2	H11–C11	1/2-x,1/2-y,1-z	2.689	137.76
6	Cl2	H17–C17	1/2-x,1/2-y,1-z	2.874	136.13
7	Cl2	H16–C16	1/2-x,y-1/2,1/2-z	2.806	152.65
8	Cl3	H136–C136	x,y-1,z	2.681	148.89
	3				
1	Cl1	H133–C133	x+1,y,z	2.948	155.73
2	Cl1	H12A–C12	x+1,y-1,z	2.682	151.11
3	Cl1	H136–C136	x+1,y-1,z	2.938	159.90
4	Cl1	H135–C135	1-x,1-y,1-z	2.898	131.11
5	Cl1	H24–C24	x,y-1,z	2.841	129.62
6	Cl1	H234–C234	-x,1-y,1-z	2.839	139.48
7	Cl2	H15–C15	x+1,y,z	2.686	166.24
8	Cl2	H11–C11	x,y-1,z	2.651	167.67
9	Cl2	H16–C16	1-x,1-y,-z	2.950	154.08

* Symm. op. x,y,z

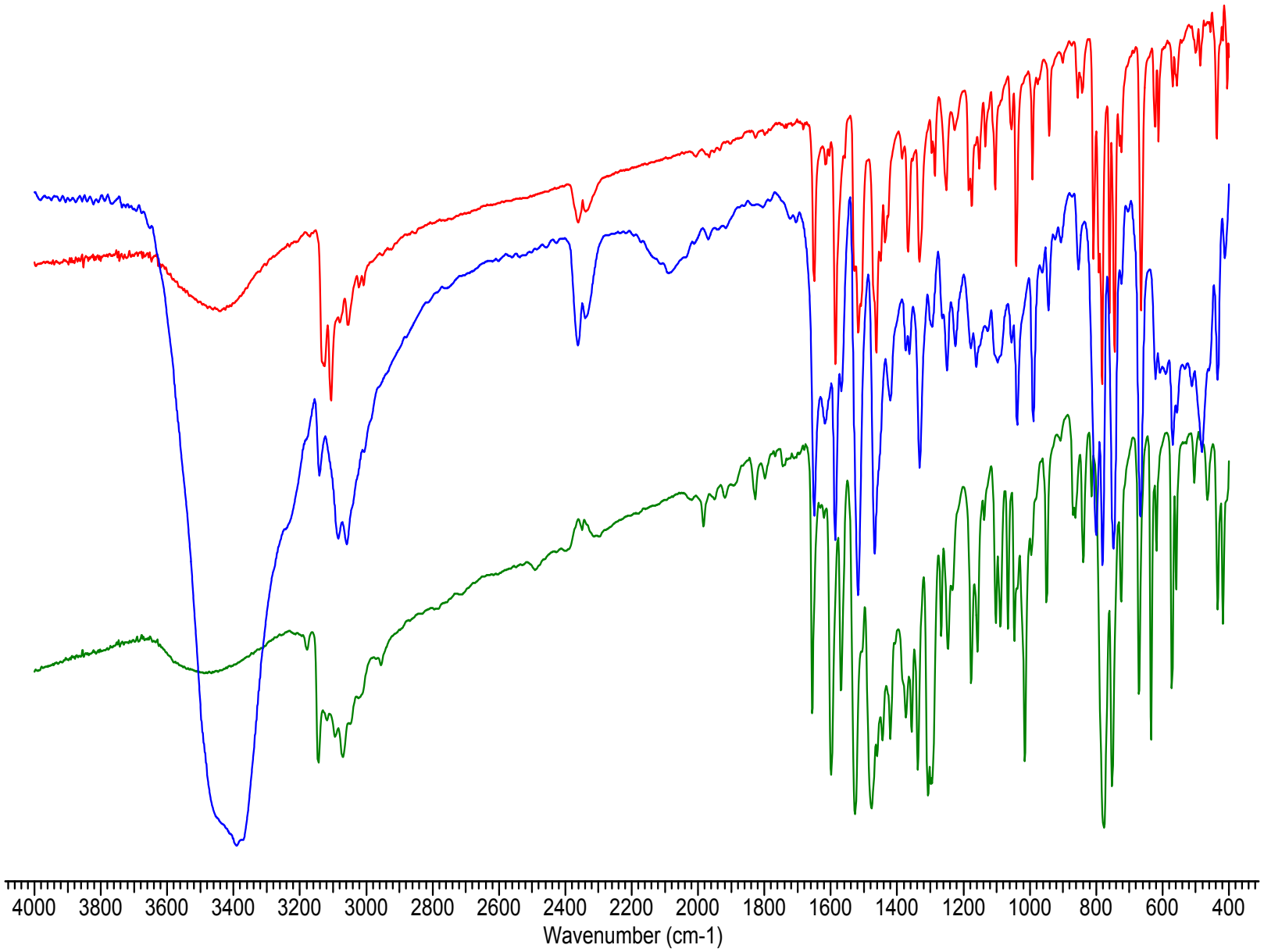

Fig. S1 IR spectra of $[L]_2[ZnCl_4]$ (**1**, green line), $LZnCl_3$ (**2**, red line) and $LCl \cdot 1.5H_2O$ (**3**, blue line) in the 4000–400 cm^{-1} region.

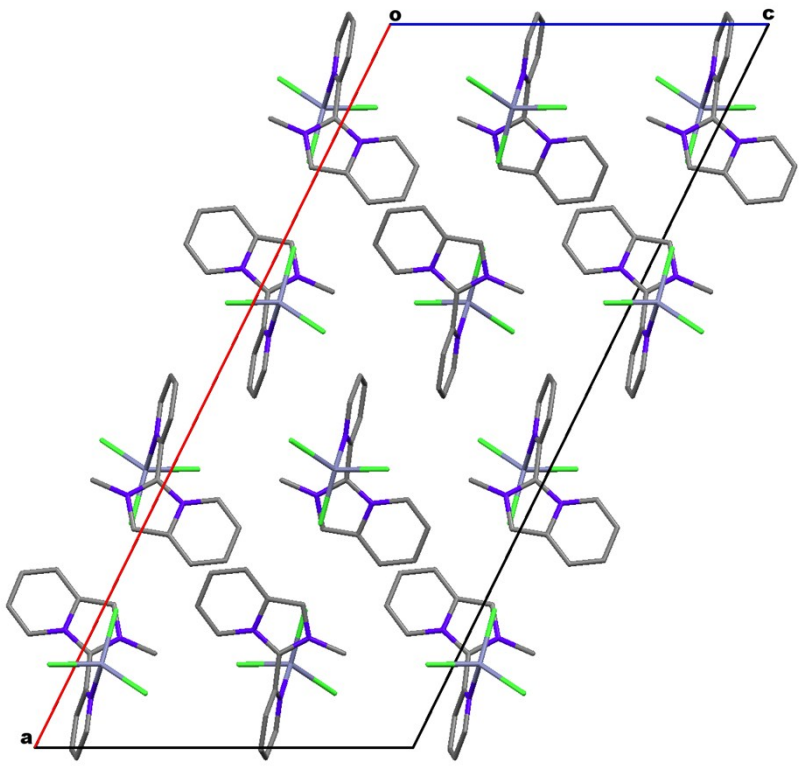

Fig. S2 Fragment of crystal packing of $LZnCl_3$ (**2**). The hydrogen atoms are not shown.

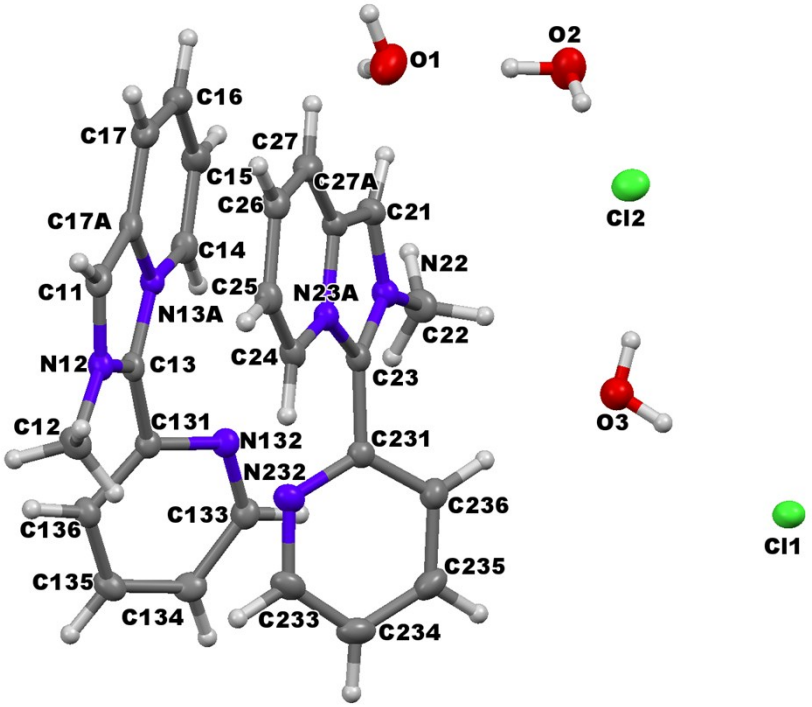

Fig. S3 Molecular structure and labelling of **3** with ellipsoids at the 50% probability level.

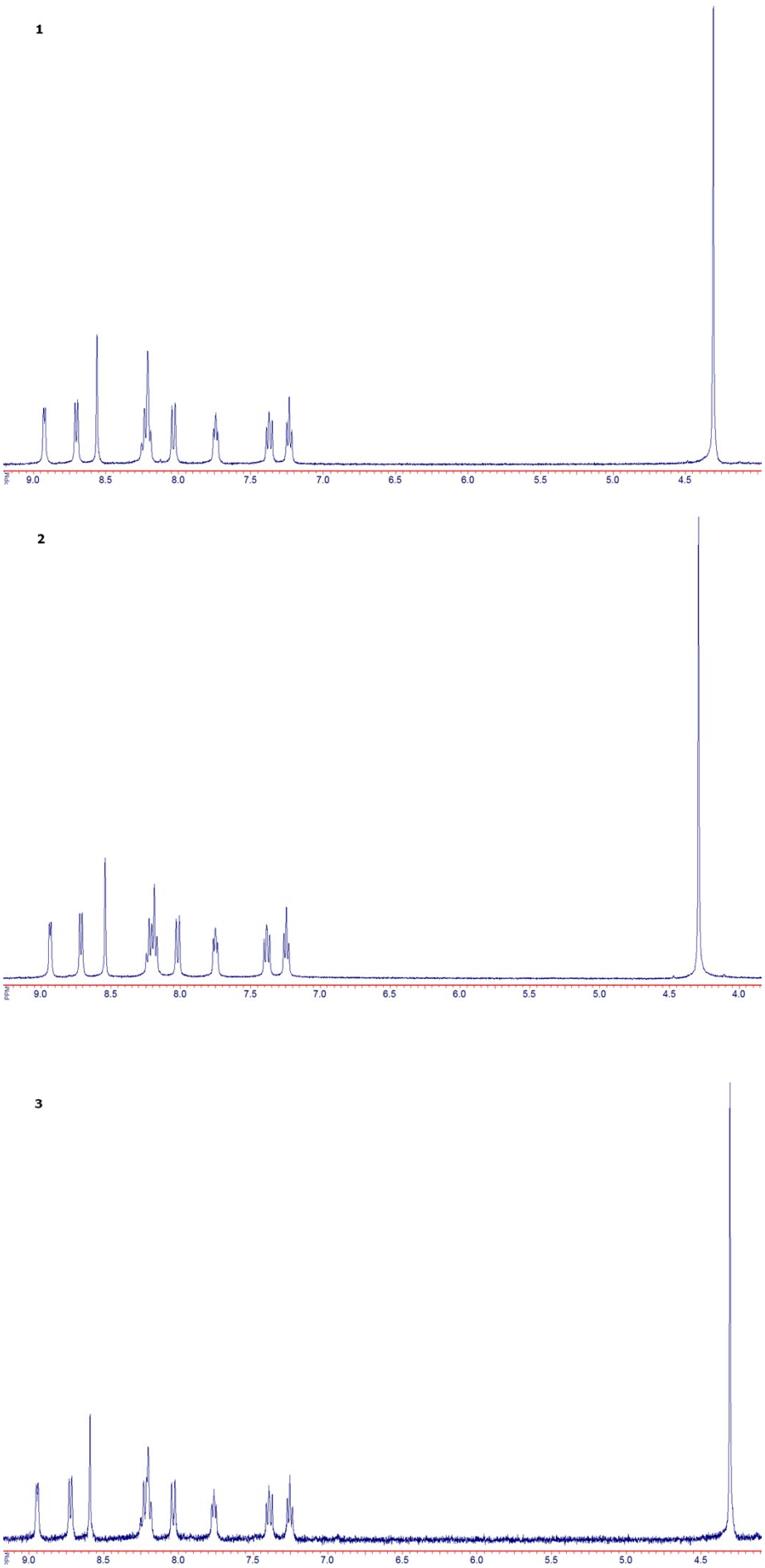

Fig. S4 400 MHz ^{1}HNMR spectra of $[L]_2[ZnCl_4]$ (**1**), $LZnCl_3$ (**2**) and $[L][Cl]\cdot 1.5H_2O$ (**3**) in dmso-d_6 at 293 K.