Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2016

"Electronic Supplementary Information (ESI)"

Halide ion-driven self-assembly of Zn(II) compounds derived from an asymmetrical hydrazone-pyridine building block: Combined experimental and theoretical study

Ghodrat Mahmoudi[a],*Farhad Akbari Afkhami[b], Himanshu Sekhar Jena[c], Parisa Nematollahi[a], Mehdi D. Esrafili[a], Piotr Garczarek[d], Kristof Van Hecke[e], Masoumeh Servati Gargari[b] and Alexander M. Kirillov[f]

Contents:

Fig. S1 Molecular structure of complex **2**.

Fig. S2 A comparison of dihedral angle between coordinating pyridine group and other hanging group in ligand and illustration of tetrahedral distortion around Zn(II) center in H_2L (a), and complexes **1** (b) and **2** (c).

Fig. S3 Illustration of H-bonding interaction in H_2L and complex **1** and their lattice arrangement.

Fig. S4 Illustration of localized and non-localized π···π stacking interactions in **1** (top) and **2** (bottom).

Fig. S5 (a) Illustration of trigonal bipyramidal geometry for Zn(II) atom and (b) molecular square arrangement of adjacent Zn(II) atoms in **3**.

Fig. S6 Illustrationof various weak and classical H-bonding interactions as well as type-I halogen interaction and slipped π-stacking interactions in **3**.

Fig. S7 Hirshfeld surface of H_2L mapped with shape index function. Arrow indicates 'bow-tie' patterns.

Fig. S8 Decomposed fingerprint plots of H_2L: (a) H···H, (b) H···O, (c) H···N.

Fig. S9 Hirshfeld surface of **1** mapped with shape index function.

Fig. S10 Decomposed fingerprint plots of **1**: (a) H···H, (b) H···O, (c) H···C.

Fig. S11 Hirshfeld surface of **3** mapped with shape index function. Arrows indicate 'bow-tie' patterns.

Fig. S12 Decomposed fingerprint plots of **3**: (a) H···H, (b) H···O, (c) H···Cl, (d) C···C.

Fig S13 Topological representation of a 2D H-bonded underlying network in the H_2L structure showing a uninodal 4-connected layer with the **sql** [Shubnikov tetragonal plane net] topology.

Fig. S14 Absorption spectra of H_2L and complexes **1-3** in DMSO: 1×10^{-5} M.

Fig. S15 Optimized gas phase structures of **1-3**.

Table S1 Selected bond lengths (Å) and angles (^{o}) for complexes **1-3**.

Table S2 Hydrogen-bond geometries (Å, ^{o}) for complexes **1-3**.

Table S3 IR spectral assignments (cm^{-1}) for H_2L and complexes **1-3**.

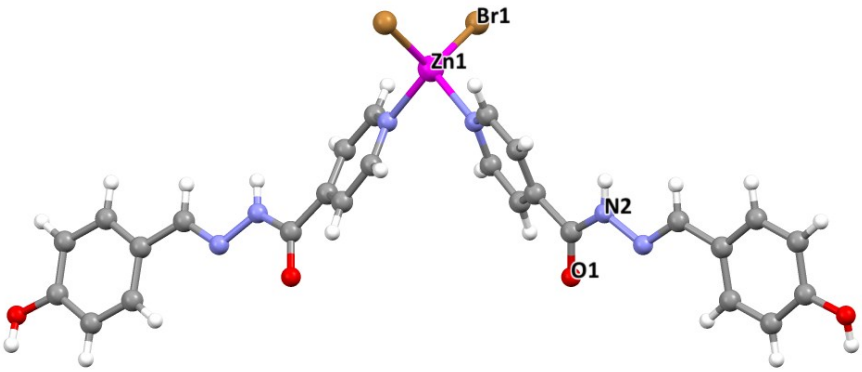
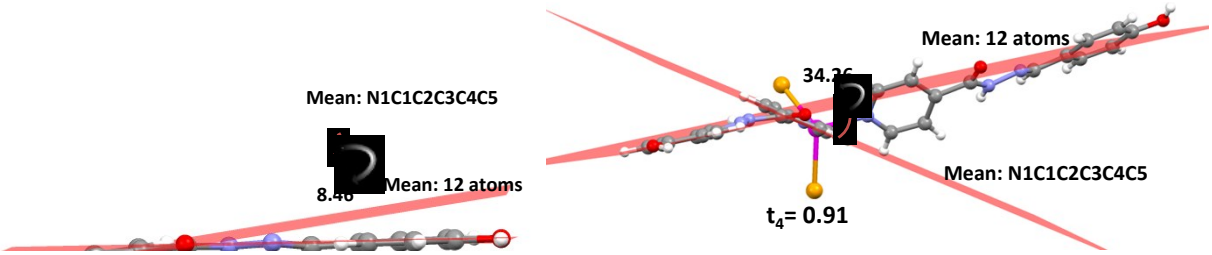
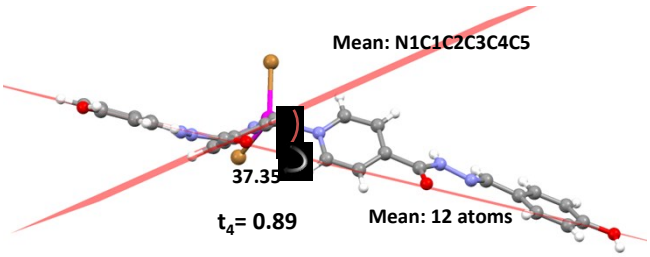


Fig. S1 Molecular structure of complex **2**.



(a)(b)



(c)

Fig. S2 A comparison of dihedral angle between coordinating pyridine group and other hanging group in ligand and illustration of tetrahedral distortion around Zn(II) center in H_2L (a), and complexes **1** (b) and **2** (c).

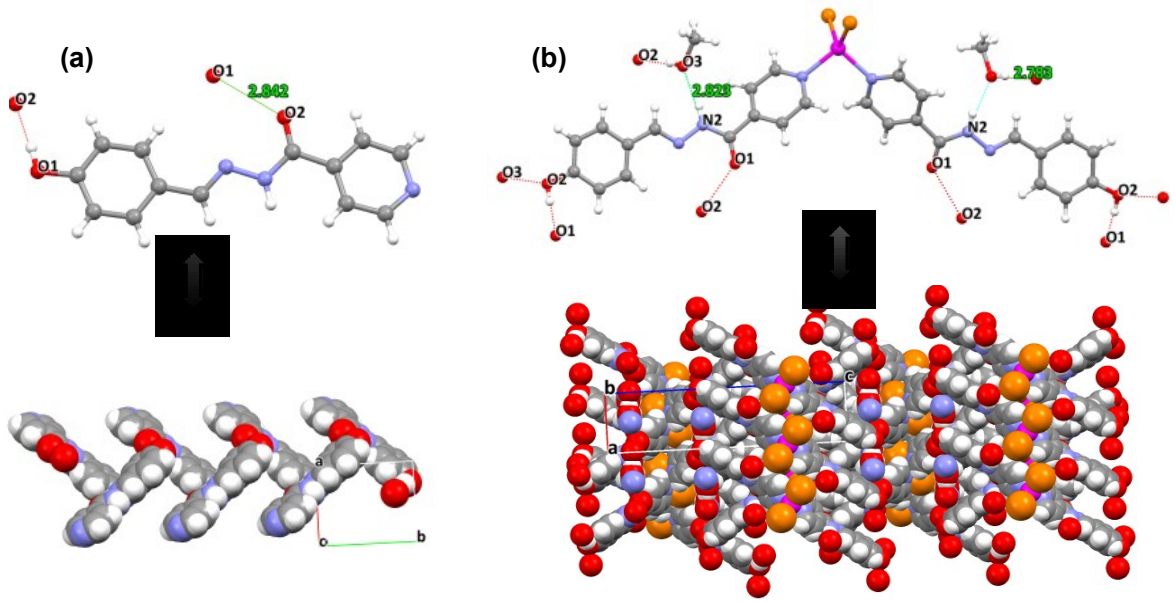


Fig. S3 Illustration of H-bonding interaction in H_2L and complex **1** and their lattice arrangement.

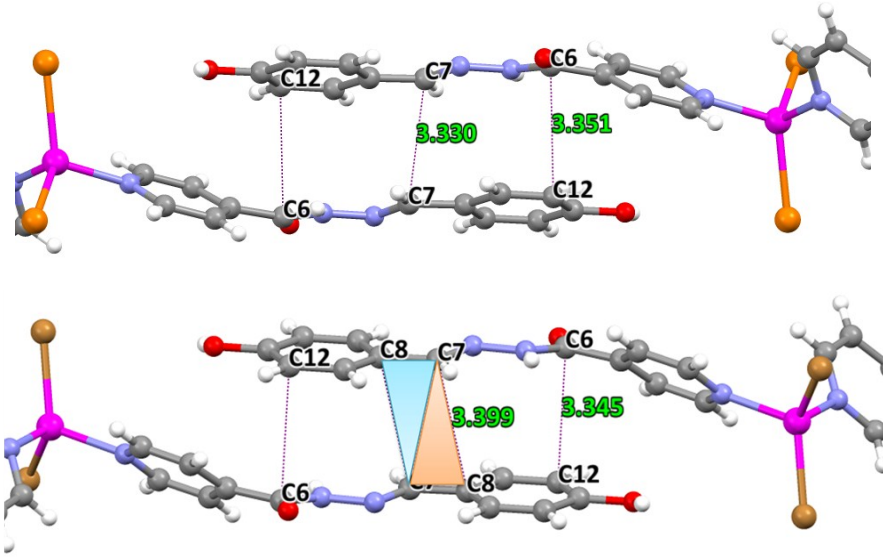
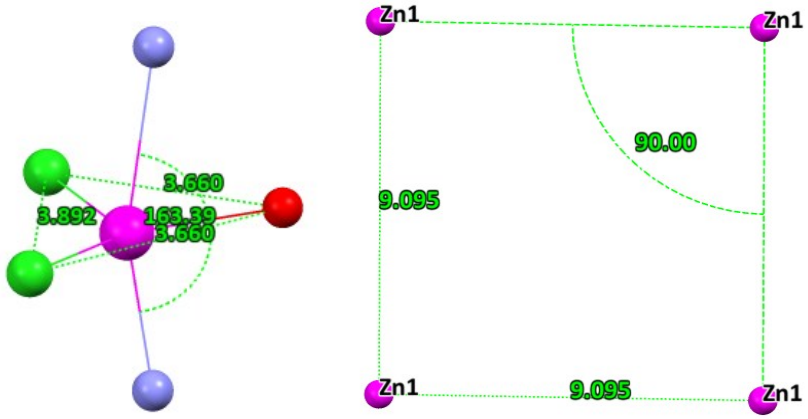
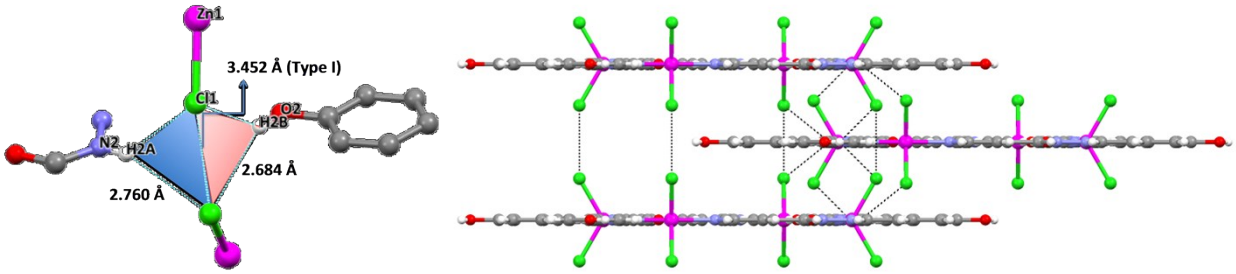


Fig. S4 Illustration of localized and non-localized π···π stacking interactions in **1** (top) and **2** (bottom).



a **b**

Fig. S5 (a) Illustration of trigonal bipyramidal geometry for Zn(II) atom and (b) molecular square arrangement of adjacent Zn(II) atoms in **3**.



(a) (b)

Fig. S6 Illustration of various weak and classical H-bonding interactions as well as type-I halogen interaction and slipped π-stacking interactions in **3**.

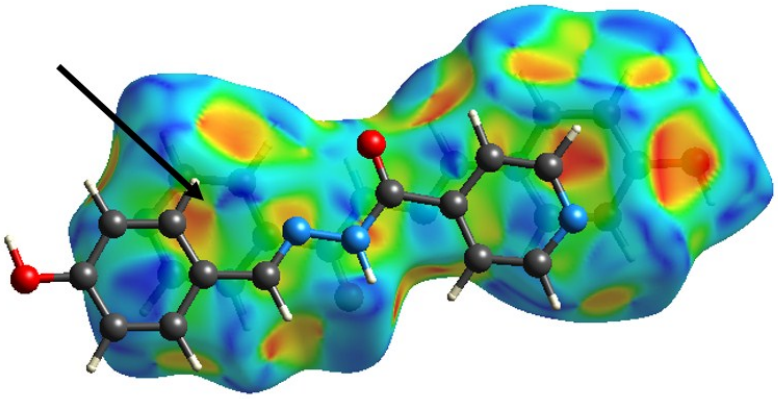


Fig. S7 Hirshfeld surface of H_2L mapped with shape index function. Arrow indicates 'bow-tie' patterns.

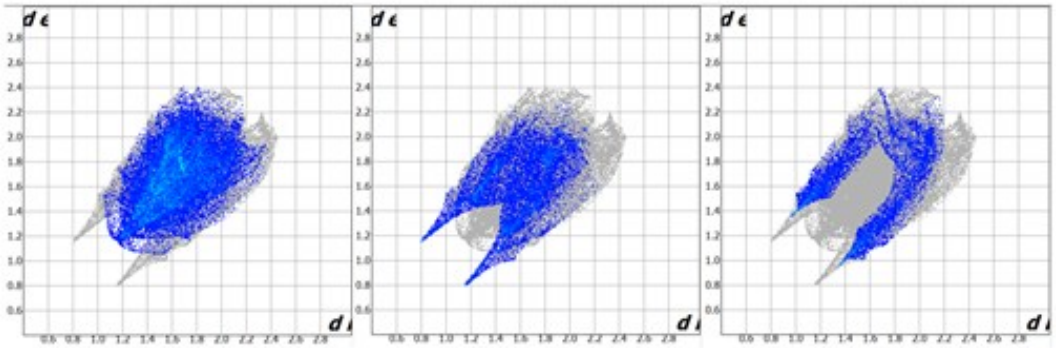


Fig. S8 Decomposed fingerprint plots of H_2L: (a) H···H, (b) H···O, (c) H···N.

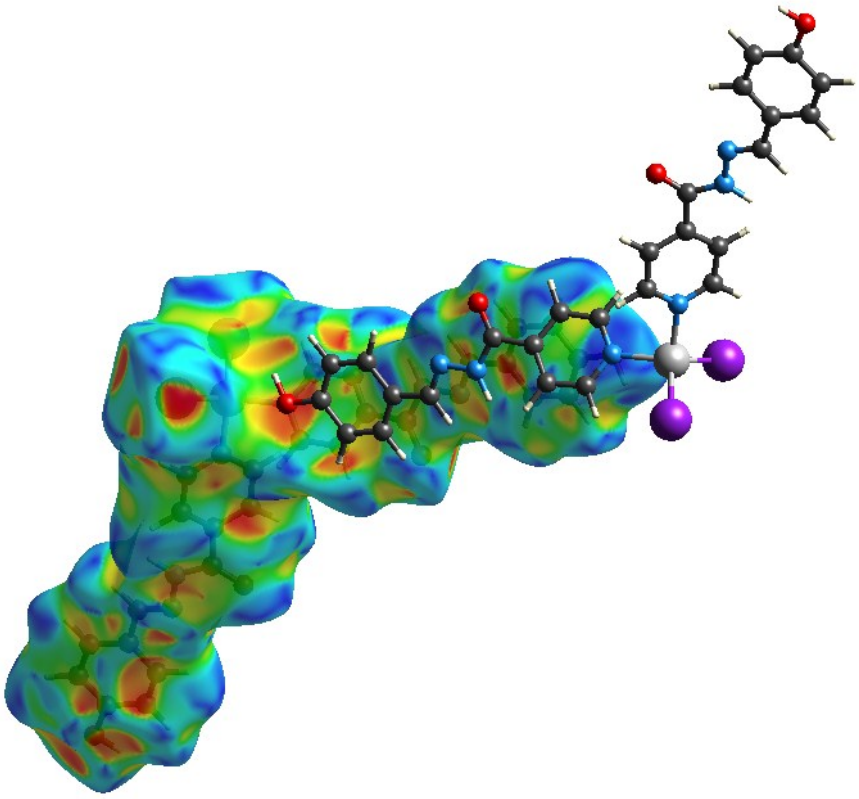


Fig. S9 Hirshfeld surface of **1** mapped with shape index function.

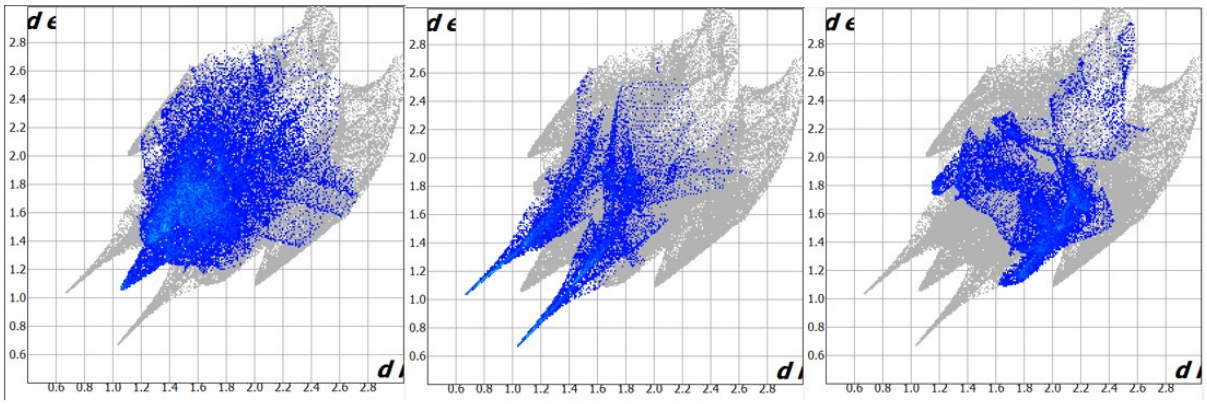


Fig. S10 Decomposed fingerprint plots of **1**: (a) H···H, (b) H···O, (c) H···C.

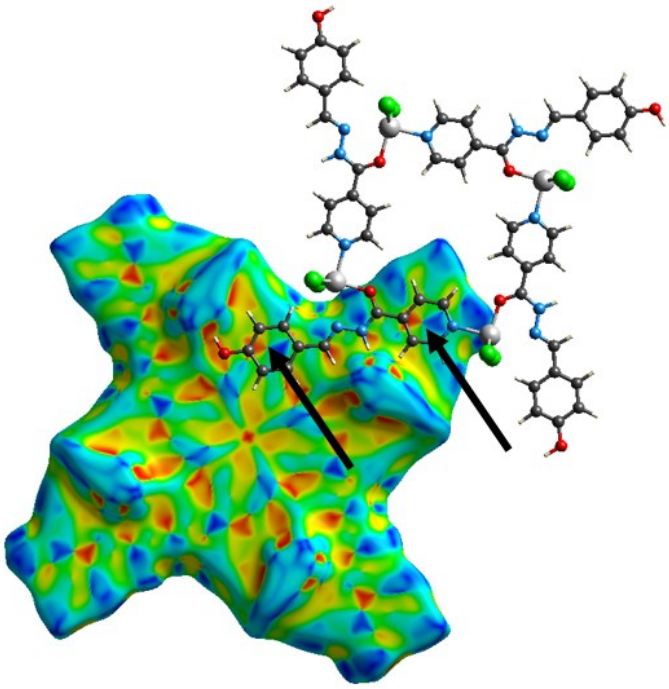


Fig. S11 Hirshfeld surface of **3** mapped with shape index function. Arrows indicate 'bow-tie' patterns.

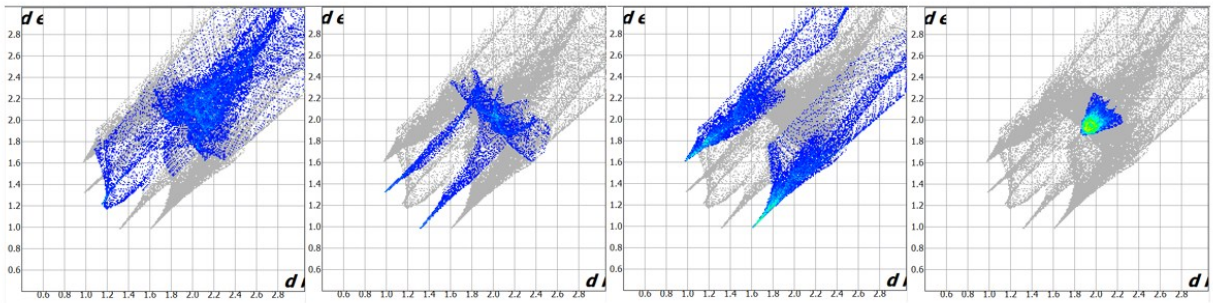


Fig. S12 Decomposed fingerprint plots of **3**: (a) H···H, (b) H···O, (c) H···Cl, (d) C···C.

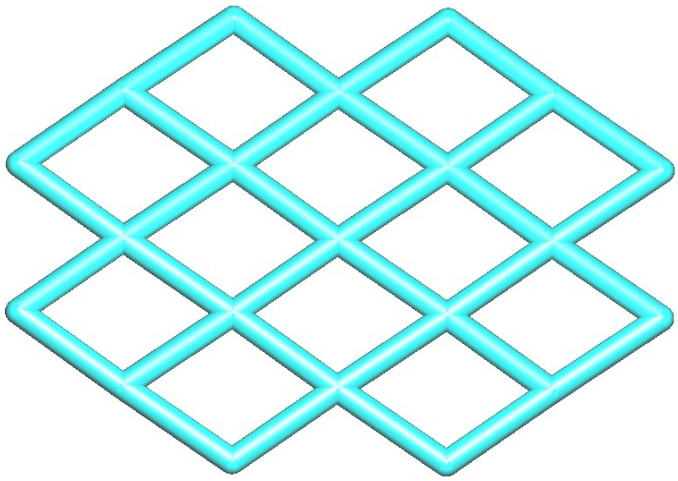


Fig S13 Topological representation of a 2D H-bonded underlying network in the H_2Lstructure showing a uninodal 4-connected layer with the **sql** [Shubnikov tetragonal plane net] topology. View along the *a* axis; centroids of 4-connected [H_2L] nodes (cyan).

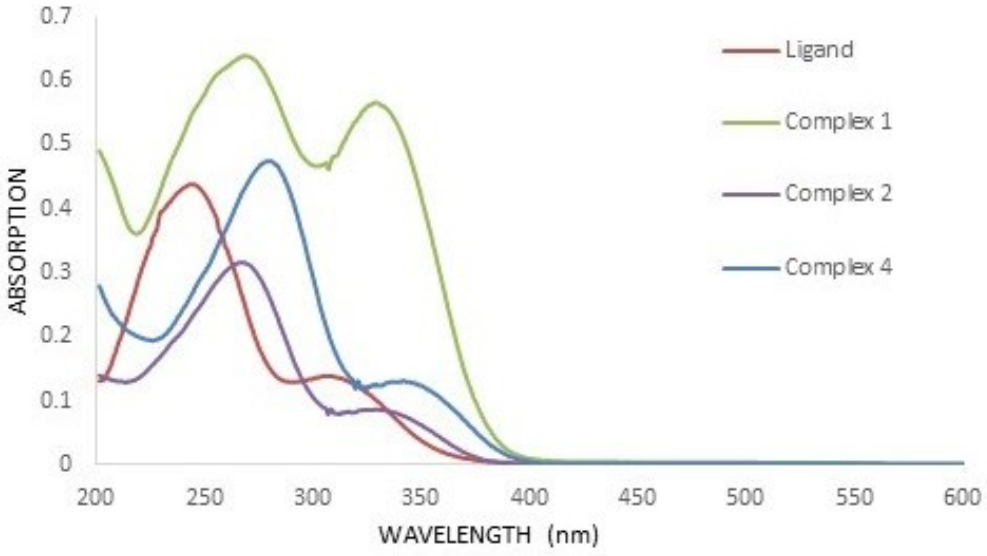
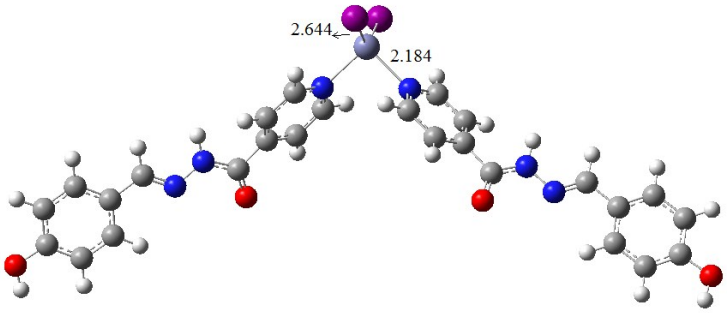
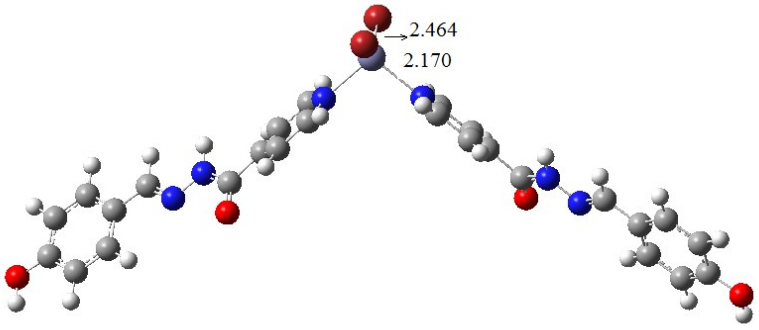


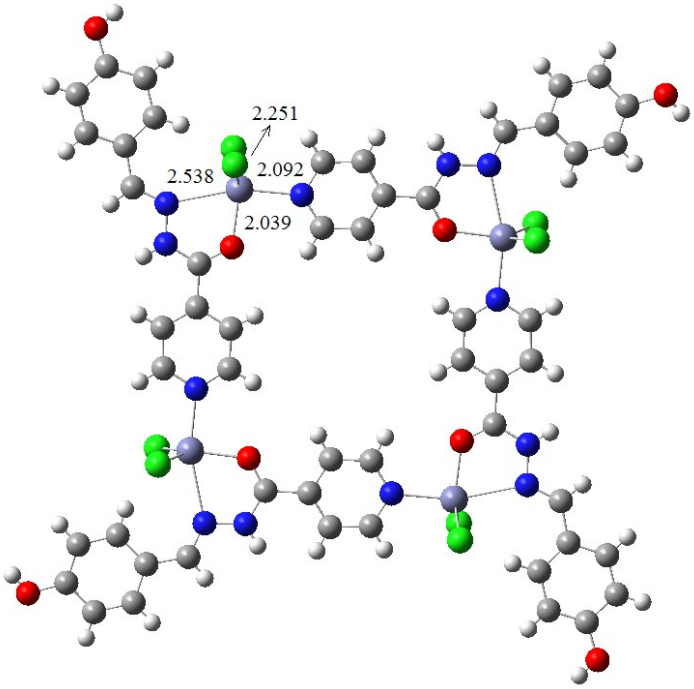
Fig. S14 Absorption spectra of H_2L and complexes **1-3** in DMSO: 1×10^{-5} M.



1



2



3

Fig. S15 Optimized gas phase structures of **1**-**3**.

Table S1 Selected bond lengths (Å) and angles (°) for complexes **1-3**.

1		**2**		**3**	
Zn(1) N(1)	2.072(4)	Zn(1) N(1)	2.071(2)	Zn(1) N(1)	2.128(2)
Zn(1) N(1A)	2.072(4)	Zn(1) N(1A)	2.071(2)	Zn(1) N(3)	2.517(3)
Zn(1) I(1)	2.5490(5)	Zn(1) Br(1)	2.3587(4)	Zn(1) O(1)	2.006(2)
Zn(1) I(1)	2.5490(5)	Zn(1) Br(1)	2.3587(4)	Zn(1) Cl(1)	2.2475(7)
				Zn(1) Cl(1)	2.2475(7)
O(1) C(6)	1.235(6)	O(1) C(6)	1.235(3)	O(1) C(6)	1.242(3)
C(6) N(2)	1.344(6)	C(6) N(2)	1.340(3)	C(6) N(2)	1.320(4)
N(2) N(3)	1.395(5)	N(2) N(3)	1.391(3)	N(2) N(3)	1.385(3)
N(3) C(7)	1.278(6)	N(3) C(7)	1.281(3)	N(3) C(7)	1.272(4)
C(11) O(2)	1.353(5)	C(11) O(2)	1.362(3)	C(11) O(2)	1.351(4)
I(1) Zn(1) I(1)	118.97(4)	Br(1) Zn(1)Br(1)	119.40(3)	Cl(1) Zn(1)Cl(1)	119.95(4)
N(1) Zn(1) I(1)	112.48(11)	N(1) Zn(1)Br(1)	113.96(6)	N(1) Zn(1)Cl(1)	97.25(4)
N(1) Zn(1) I(1)	105.89(11)	N(1) Zn(1)Br(1)	105.59(6)	O(1) Zn(1)Cl(1)	118.66(2)
N(1) Zn(1) I(1)	112.48(11)	N(1) Zn(1)Br(1)	113.96(6)	Cl(1) Zn(1) N(3)	91.00(3)
N(1) Zn(1) I(1)	105.89(11)	N(1) Zn(1)Br(1)	105.59(6)	O(1) Zn(1) N(1)	91.93(9)
N(1) Zn(1) N(1)	99.50(2)	N(1) Zn(1) N(1)	96.06(12)	O(1) Zn(1) N(3)	71.46(8)
				N(1)Zn(1)N(3)	163.39(1)

Table S2 Hydrogen-bond geometry (Å, °) for complexes **1**-**3**.

D—H…A	*d*(D—H)	*d*(H…A)	*d*(D…A)	<DHA	Symmetry codes
1					
O(2)-(H2B)…O(1)	0.840(3)	1.824(3)	2.645(4)	165.10(2)	-x+1/2, -y-1/2, z-1/2
C(14)-(H14C)…O(1)	0.979(5)	2.598(3)	3.476(6)	149.17(3)	x-1/2, y-1/2, -z+1/2
N(2)-H(2A)…O(3)	0.877(3)	1.959(3)	2.823(5)	168.42(4)	x-1/2, y-1/2, -z+1/2
2					
O(2)-(H2B)…O(1)	0.839(2)	1.791(2)	2.610(2)	164.91(1)	-x+1/2, -y+1/2, z-1/2
C(14)-(H14C)…O(1)	0.981(3)	2.559(2)	3.437(3)	149.14(2)	x-1/2, y +1/2, -z+1/2
N(2)-H(2A)…O(3)	0.860(3)	1.973(3)	2.814(3)	165.67(3)	x-1/2, y +1/2, -z+1/2
3					
C(13)-H(13)…O(2)	0.929(4)	2.425(3)	3.339(5)	168.21(2)	-x+1, -y+1, z
N(2)-H(2A)…Cl(1)	0.861(2)	2.760(7)	3.454(2)	138.79(2)	-x+3/2, -y+1/2, -z+1/2
O(2)-H(2B)…Cl(1)	0.819(4)	2.684(4)	3.352(2)	139.86(4)	-x+3/2, -y+1/2, -z+1/2

Table S3 IR spectral assignments (cm^{-1}) for H_2L and **1**-**3**.

Compound	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{N-N}
H_2L	3243	1652	1597	1161
1	3240	1656	1597	1159
2	3243	1656	1601	1167
3	3231	1622	1592	1170