Supporting materials

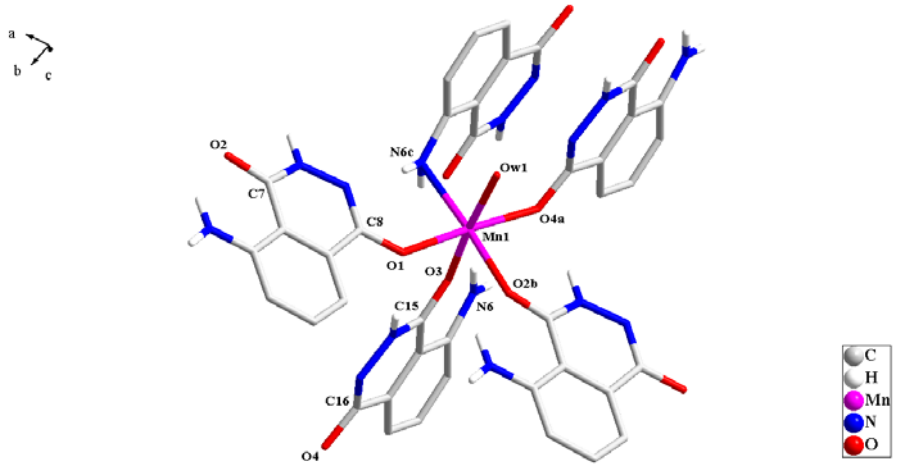


Fig. S1 The coordination environment around Mn1 in compound **1**.

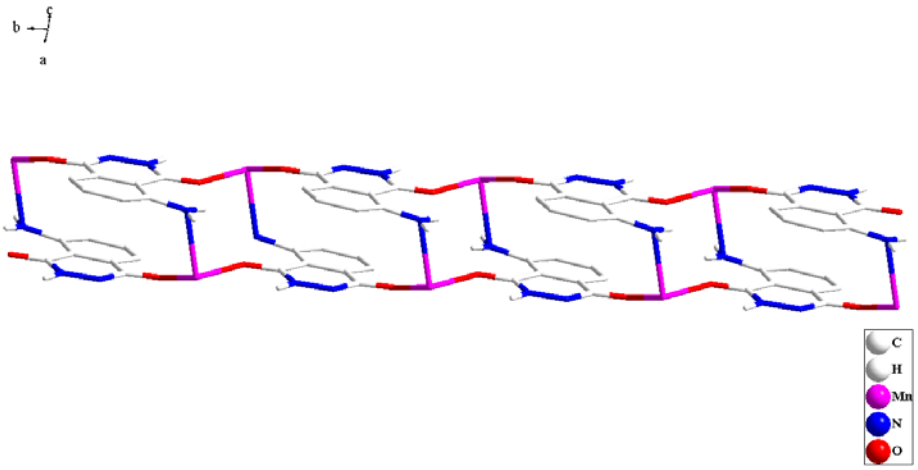


Fig. S2 The 1-D double-chain structure in compound **1**, bridged by APTHs II.

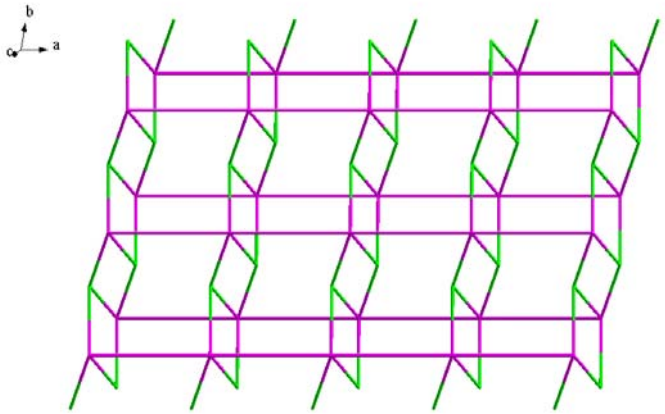


Fig. S3 The topological structure of compound **1**.

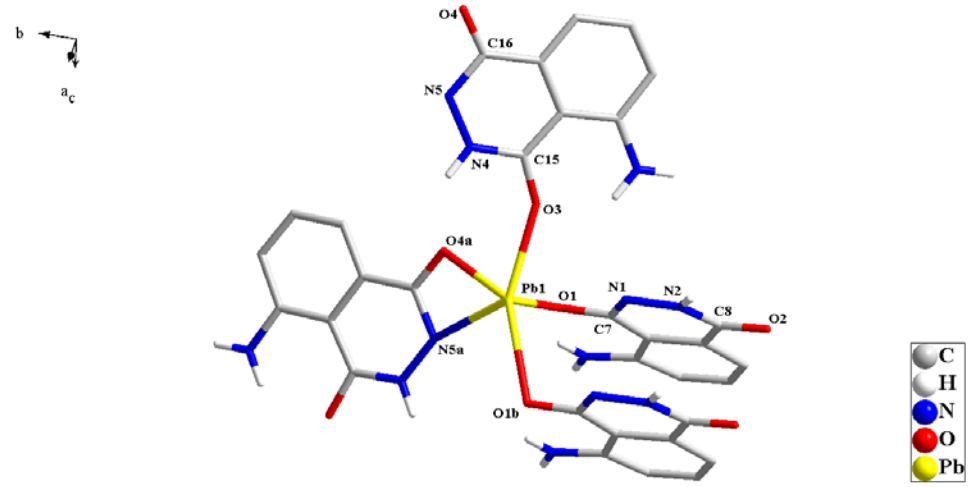


Fig. S4 The coordination environment around Pb1 in compound **2**.

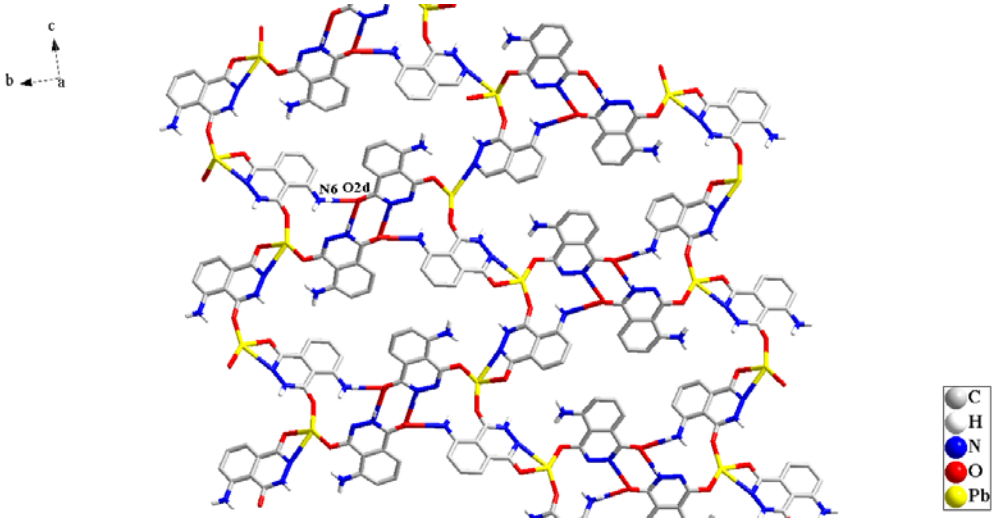
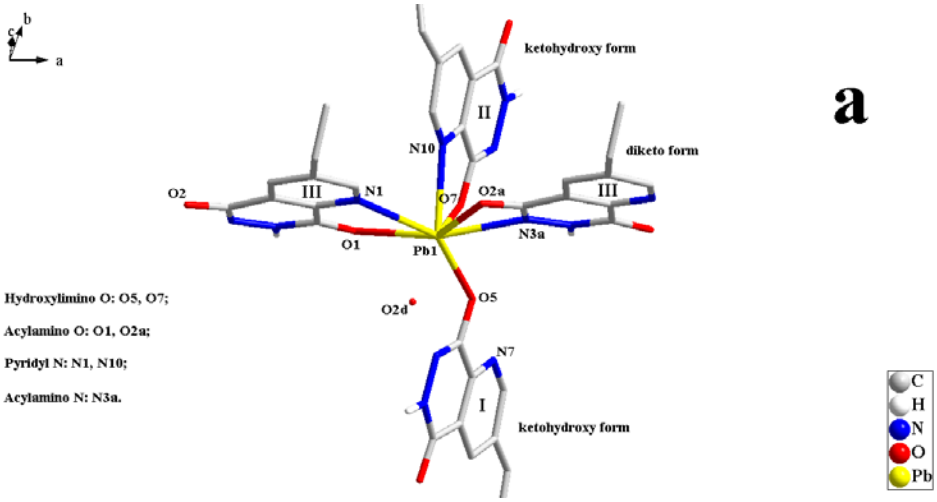


Fig. S5 The 3-D supramolecular network structure of compound **2**.



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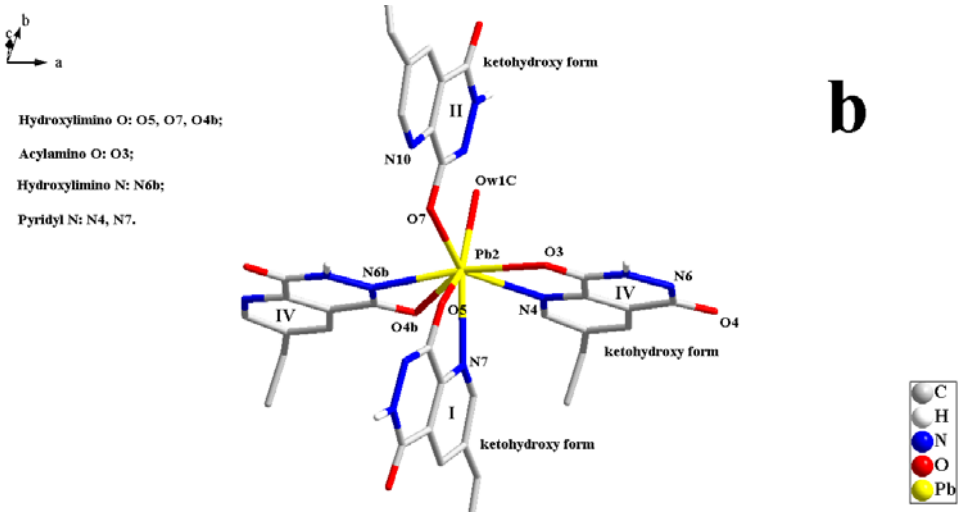


Fig. S6 The coordination environments around Pb1 (a) and Pb2 (b) in compound **3**.

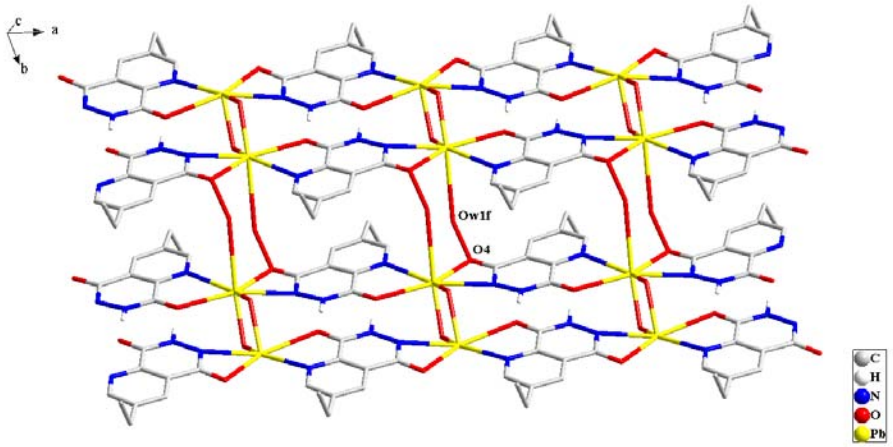
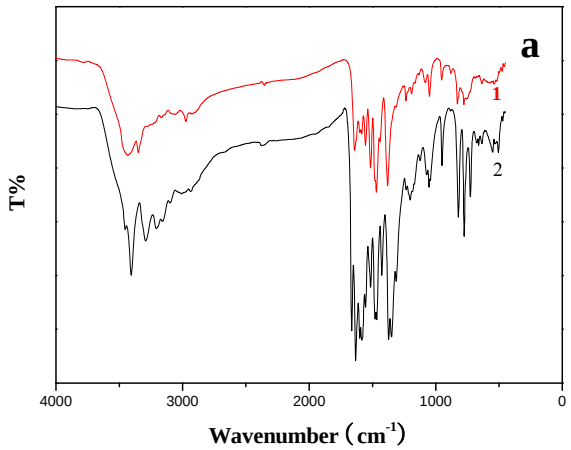
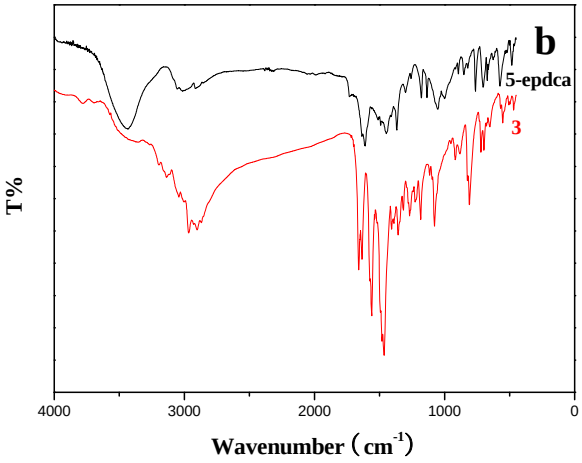


Fig. S7 The 2-D supramolecular double-layer network (EPDHs I, II are omitted for clarity).





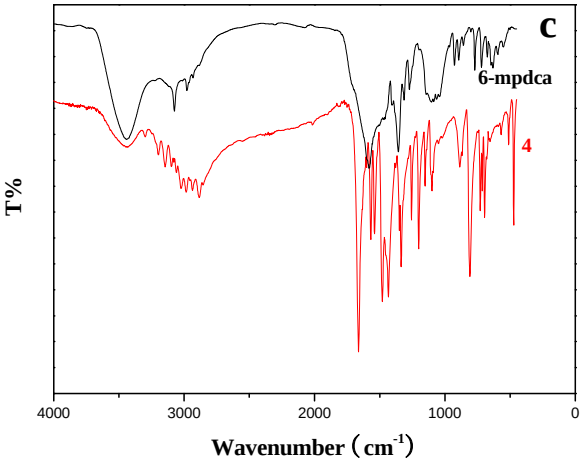
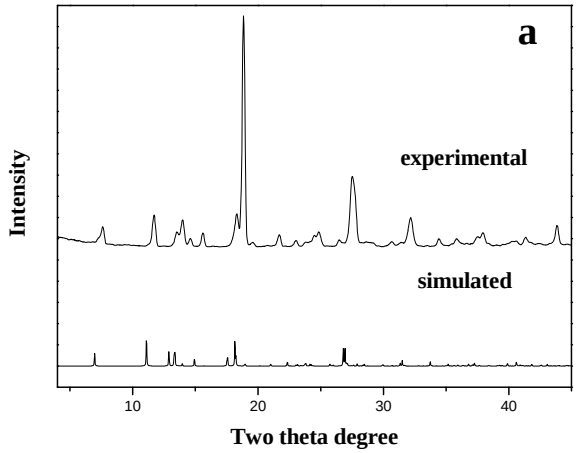


Fig. S8 The IR spectra of epdca, mpdca and the title compounds.



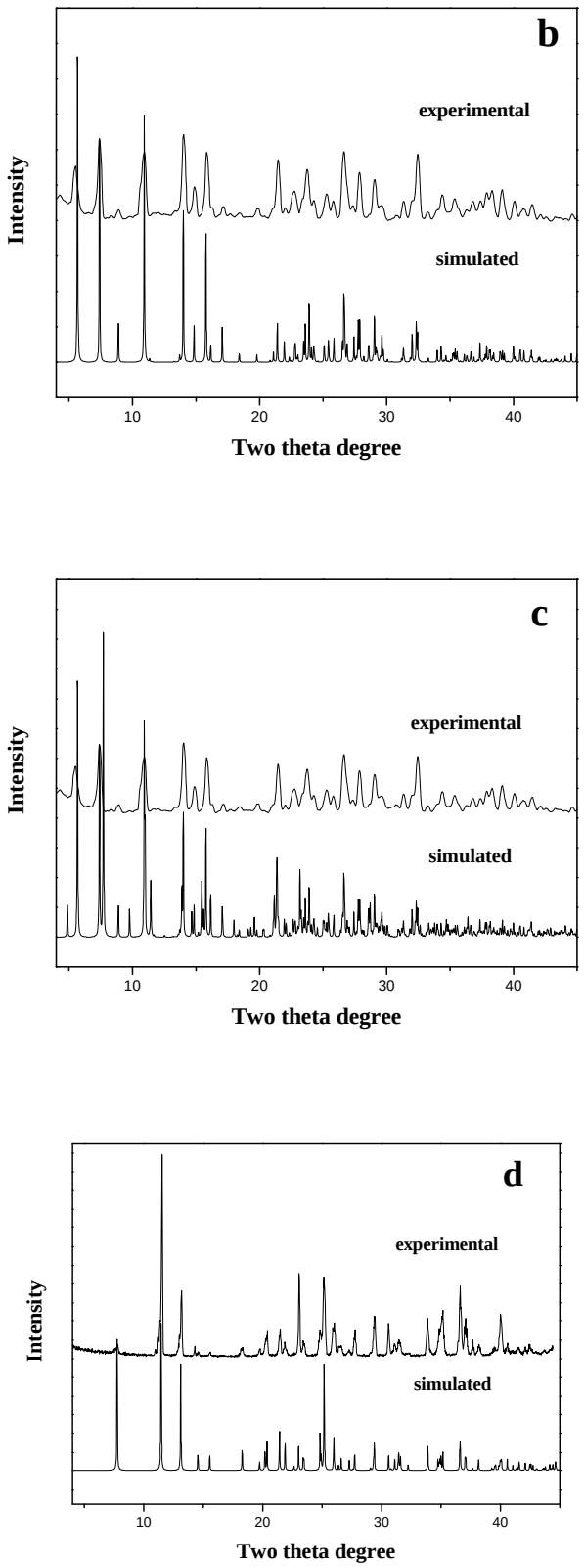


Fig. S9 The experimental and simulated XRD patterns for compounds **1** (a), **2** (b), **3** (c) and **4** (d).

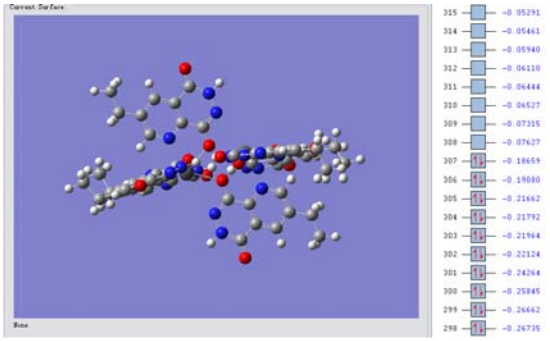
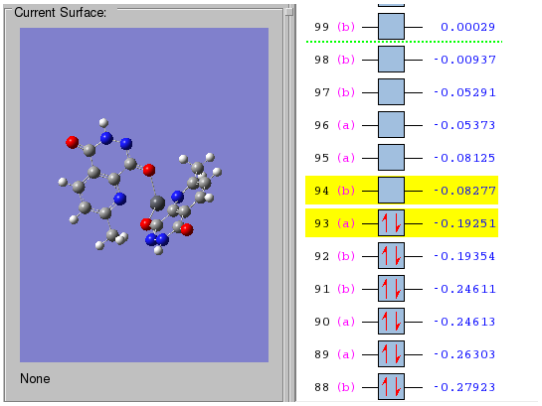


Fig. S10. The first singlet excited state structure of the dinuclear unit for compound **3**.



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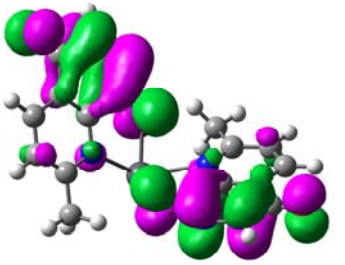

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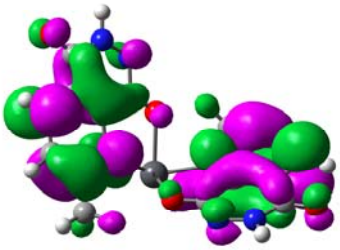

c

Fig. S11. The first singlet excited state structure (a), and the electron density contours of the frontier molecular orbitals of the molecular unit for compound **4** HOMO (b) and LUMO (c).

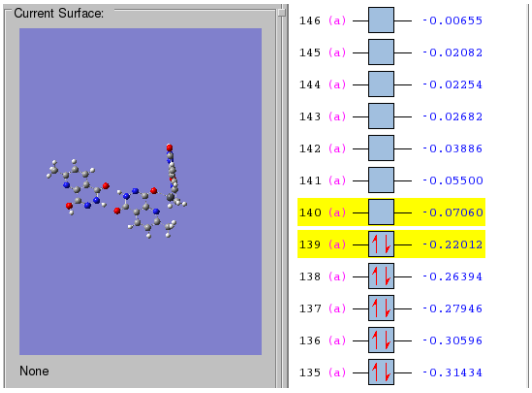

Fig. S12. The first singlet excited state structure of the new unit for compound **4**.

Computational details for DFT calculations for compounds **3** and **4**

Compound **3**

The optimized geometric structure for the excited states of compound **3** was performed with the TD-PBE method.[1] The calculations for non Pb atoms was carried out with 6-31G* basis set,[2] while for Pb atom with LanLDZ basis set.[3] The emission spectra was obtained using the time-dependent density functional theory TD-PBE.[1] All calculations were performed with the GAUSSIAN 09 (revision A.02) program package.[4] The molecular orbitals were plotted with the GaussView program.[5]

Compound **4**

The optimized geometric structure for the excited states of compound **4** was performed with the CIS method.[6] The calculations for non Pb atoms was carried out with 6-311G** basis set,[7] while for Pb atom with LanLDZ basis set.[3] The emission spectra was obtained using the time-dependent density functional theory TD-CAMB3LYP.[8] All calculations were performed with the GAUSSIAN 09 (revision A.02) program package.[4] The molecular orbitals were plotted with the GaussView program.[5]

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Table S1 Calculated fluorescence emission wavelengths (λ/nm), oscillator strengths (*f*), transitions assignment and main CI coefficients.

	Transitions	CI coeff	λ/nm (E/eV)	oscillator
Compound **3**				
Dinuclear unit	HOMO→LUMO HOMO-1→LUMO+1	0.6016 0.6223	556 (2.23)	0.048
Observed			531	

Compound **4**				
Molecular unit	HOMO→LUMO	0.61202	528 (2.35)	0.053
New unit	HOMO→LUMO	0.70357	627 (1.97)	0.026
Observed			600	

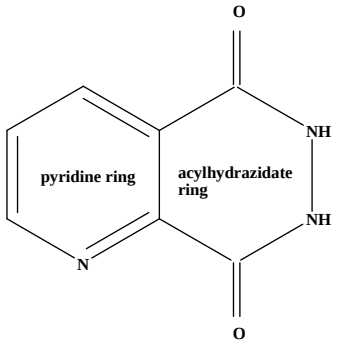
Table S2 Molecular orbital compositions in the excited states of the dinuclear unit for compound **3**.

Dinuclear unit	HOMO (%)	LUMO (%)	HOMO-1 (%)	LUMO+1 (%)
π orbitals of two acylhydrazidate rings	94		97	
π* orbitals of one EPDH ligand		100		100
p orbitals			3	
p orbitals of one acylhydrazidate ring	5			

Table S3 Molecular orbital compositions in the excited states of the monocular unit (up) and the new unit (down) for compound **4**.

Molecular unit	HOMO (%)	LUMO (%)
π orbitals of acylhydrazidate ring	73	
π* orbitals of acylhydrazidate ring		26
p orbitals of =O	11	2
-OH	9	2
p orbitals of pyridine ring	7	
p* orbitals of pyridine ring		70

New unit	HOMO (%)	LUMO (%)
π orbitals of acylhydrazidate ring	74	
π* orbitals of acylhydrazidate ring		20
p orbitals of =O	11	2
-OH	9	2
p orbitals of pyridine ring	6	
π* orbitals of pyridine ring		73
d orbitals of metal		3



Note: The monoacylhydrazidate ligand is composed of two rings: one is pyridine ring (left), the other is acylhydrazidate ring (right).