Supplementary materials

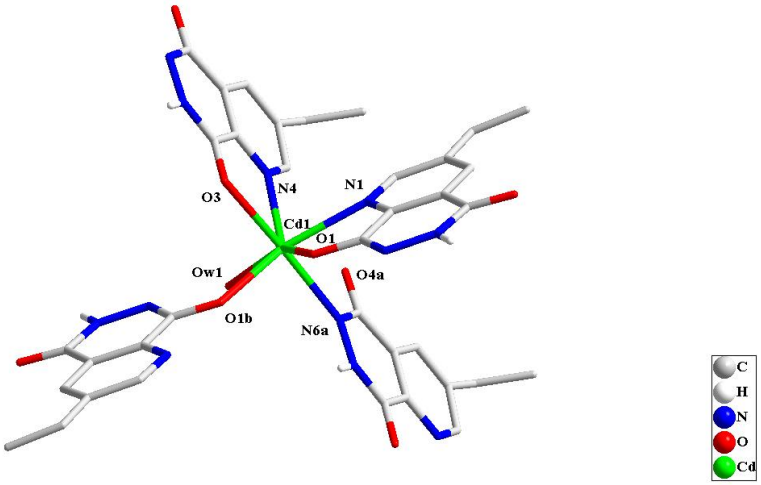


Fig. S1 The coordination environment around Cd1 in compound **1** (a: *x*+1, *y*, *z*; b: -*x*+3, -*y*+3, -*z*+2).

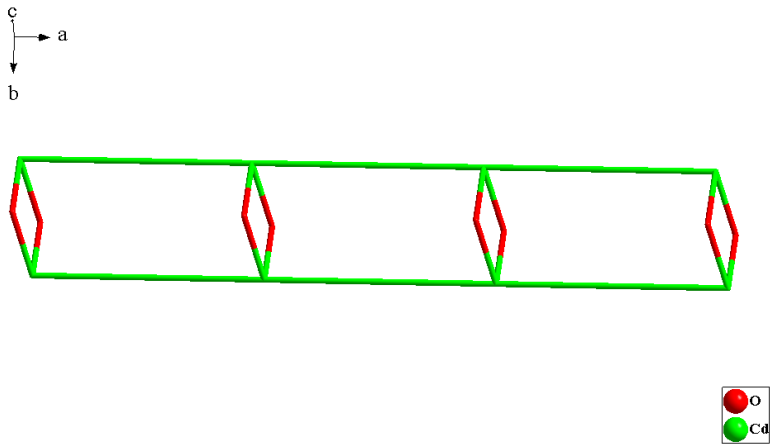


Fig. S2 The columnar structure of compound **1**.

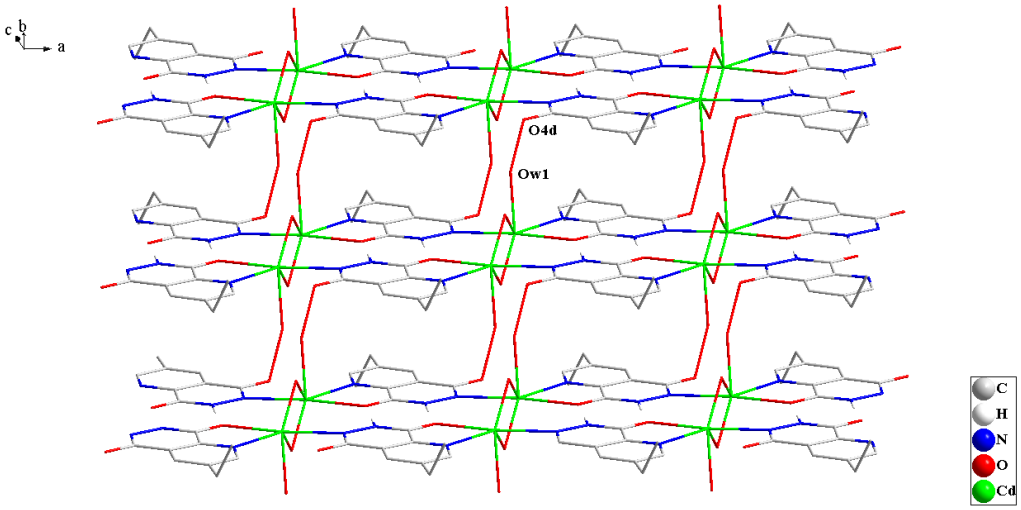


Fig. S3 The interactions between the layers for compound **1** (EPDH I is omitted for clarity; d: -*x*+2, -*y*+2, -*z*+2).

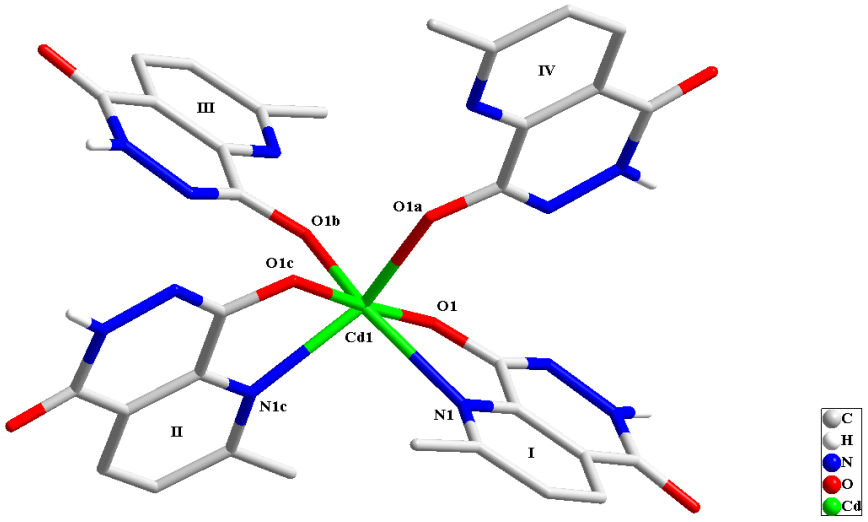


Fig. S4 The coordination environment around Cd1 in compound **2** (a/IV: *x*, *-y*, *z*-1/2; b/III: *-x*, *-y*, *-z*+1; c/II: *-x*, *y*, *-z*+1/2).

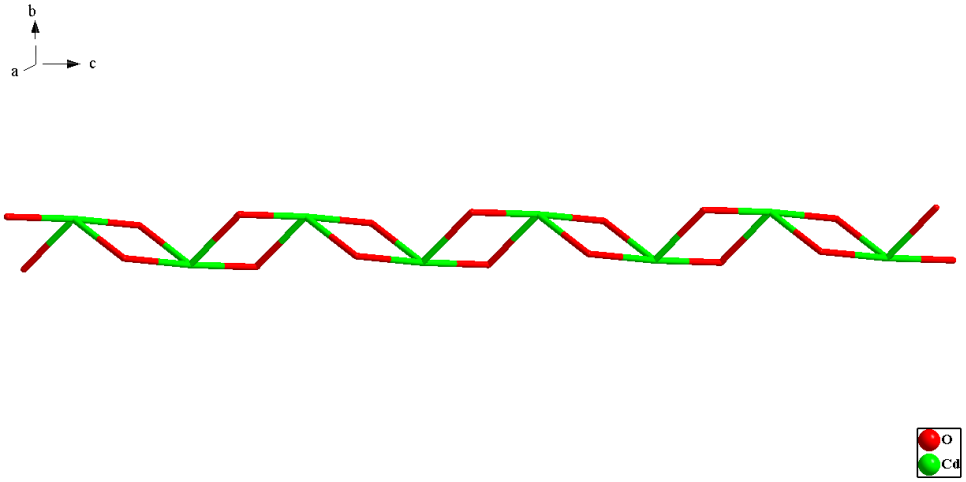


Fig. S5 The 1-D zigzag chain based on Cd_2O_2 units in compound **2**.

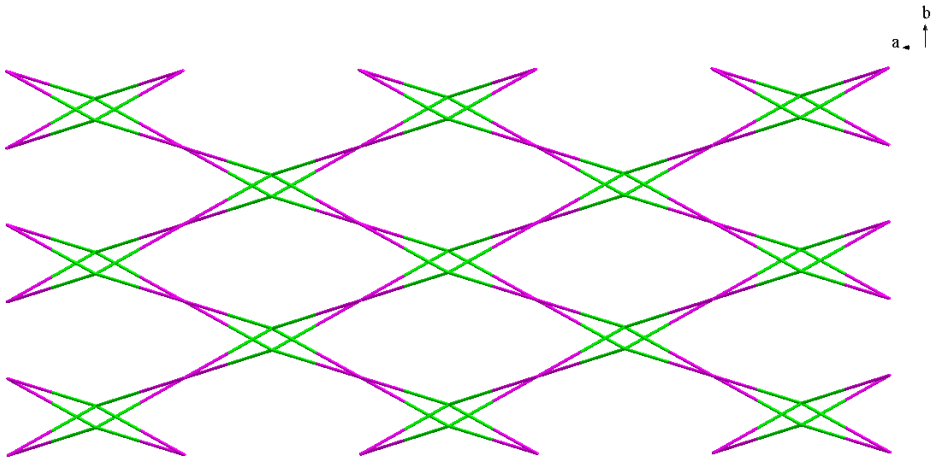


Fig. S6 The topological structure of the 3-D hydrogen-bonded network for compound **2**.

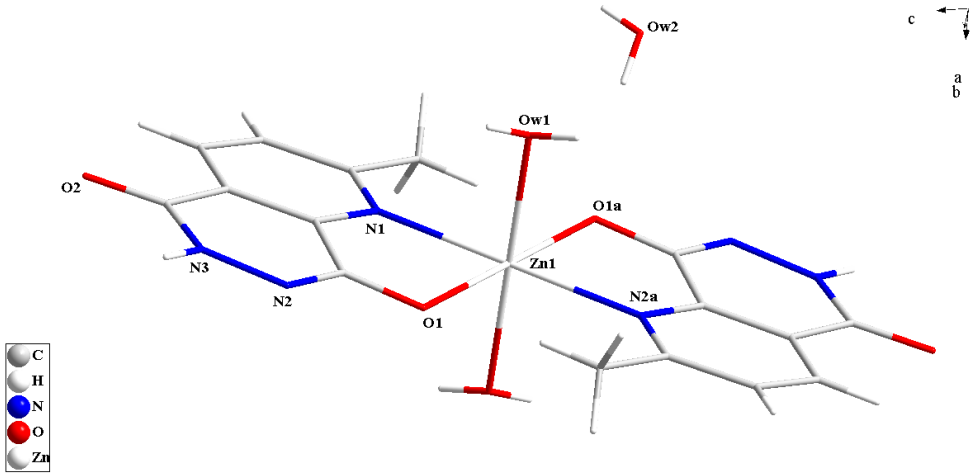


Fig. S7 The coordination environment around Zn1 for compound **3** (a: -*x*, -*y*+2, -*z*+2).

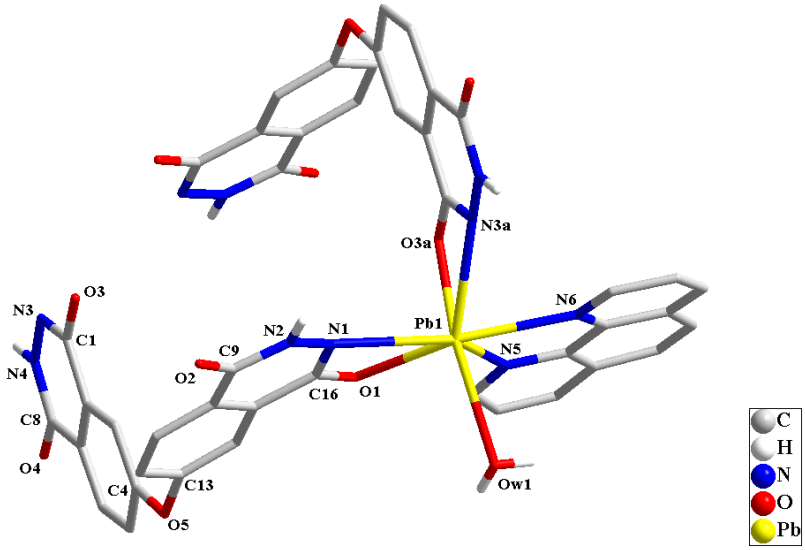


Fig. S8 The coordination environment around Pb1 in compound **4** (a: -*x*+1, -*y*+1, -*z*+1).

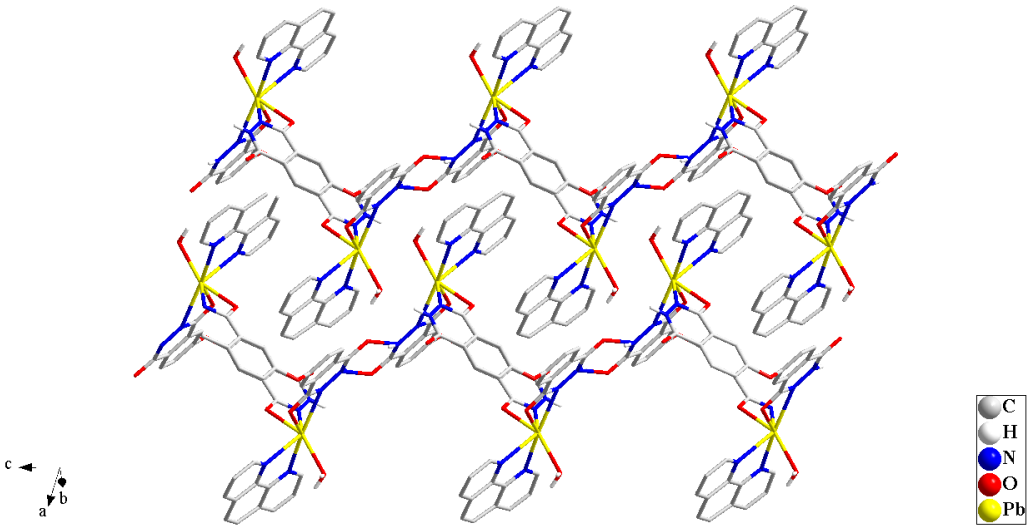


Fig. S9 The interactions between the supramolecular layers in compound **4**.

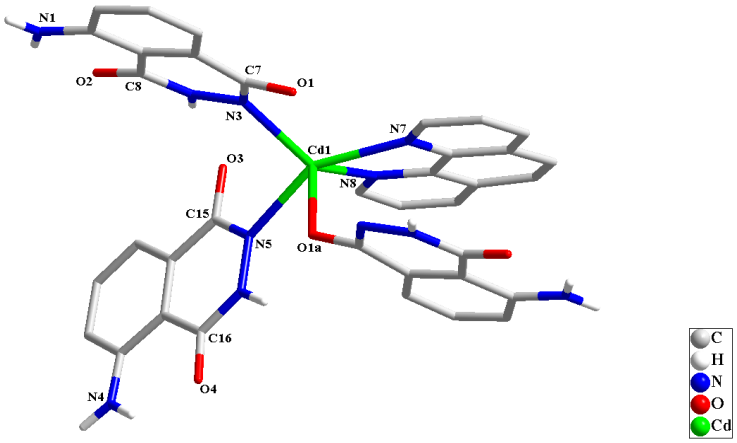
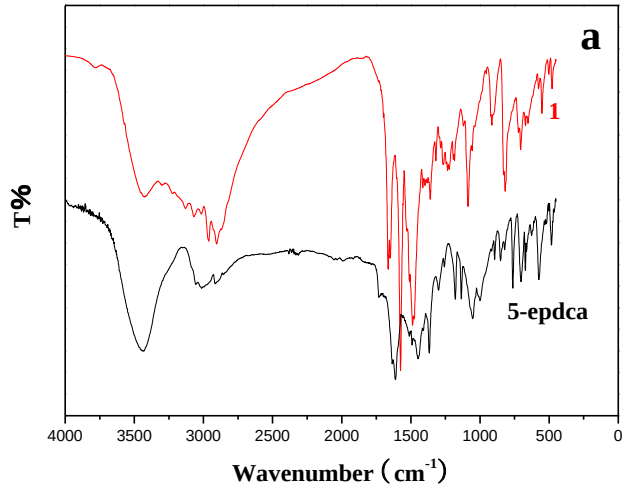
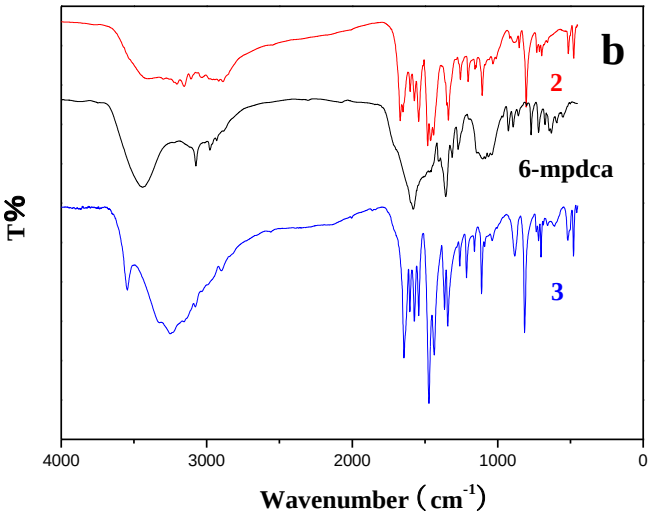


Fig. S10 The coordination environment around Cd1 in compound **5** (a: *-x*, *-y*, *-z*).





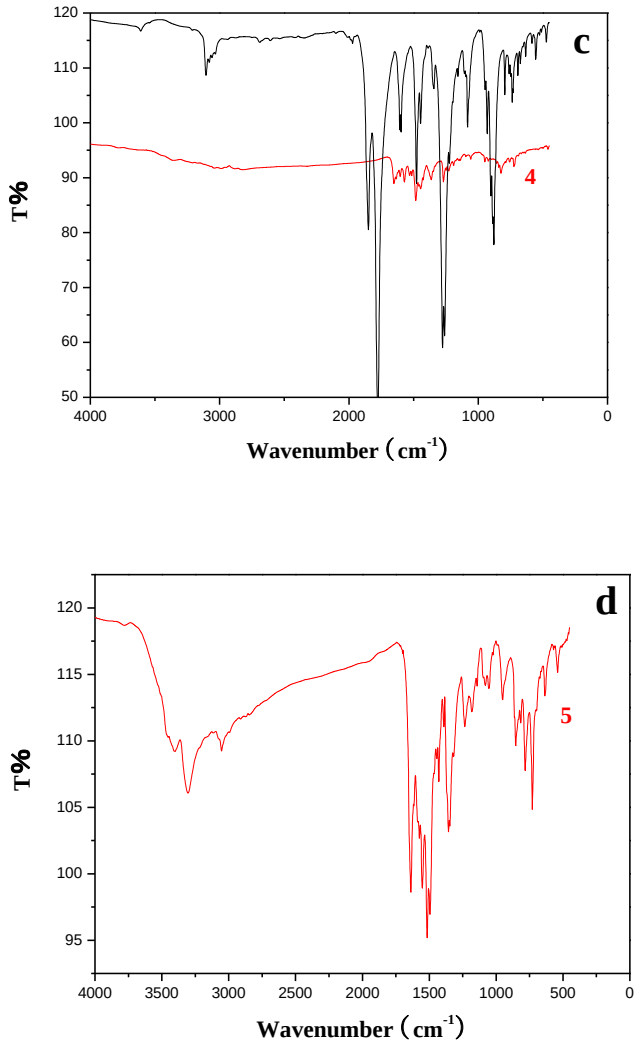
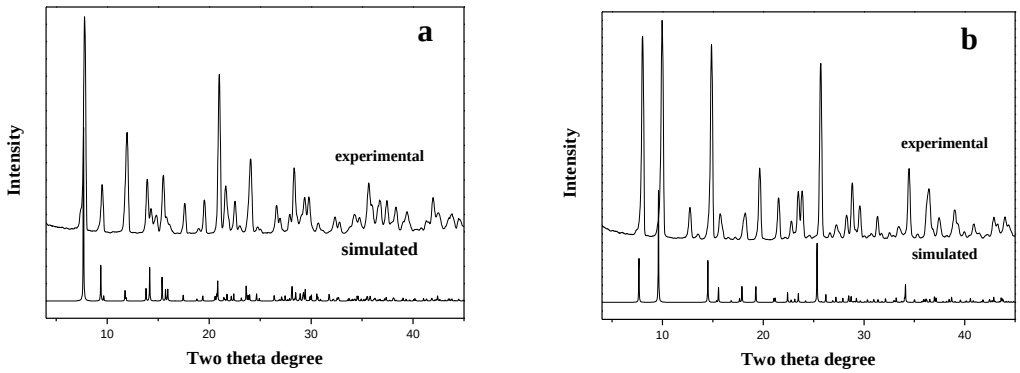


Fig. S11 The IR spectra of 5-epdca, 6-mpdca, 4,4´-odpha and compounds **1** (a), **2**-**3** (b), **4** (c), **5** (d).



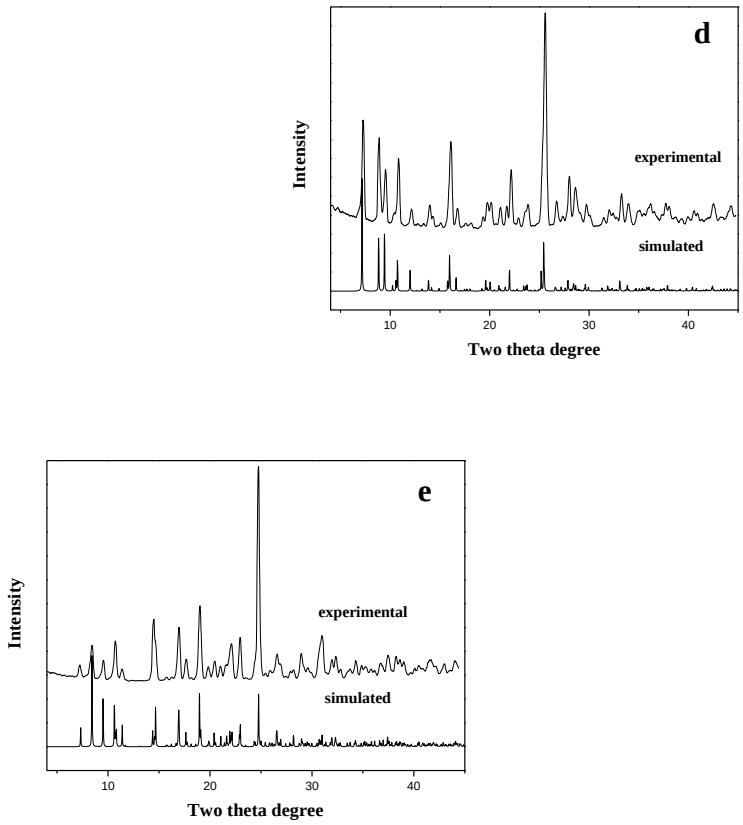


Fig. S12 The experimental and simulated powder XRD patterns for compounds **1** (a), **2** (b), **4** (d) and **5** (e).

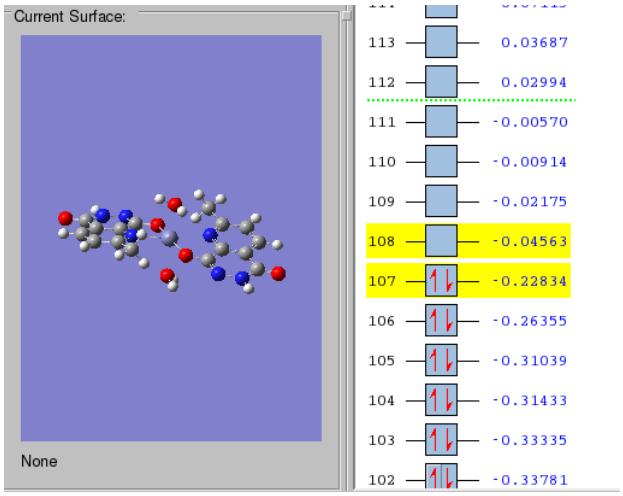


Fig. S13 The first singlet excited state structure of the molecular unit for compound **3**.

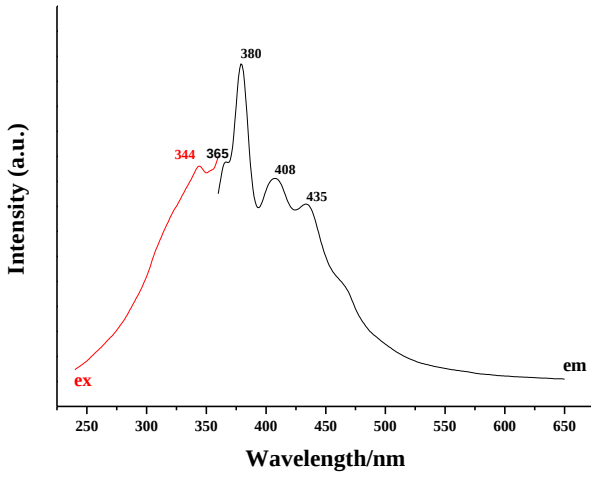


Fig. S14 The solid-state excitation and emission spectra of organic phen molecule.

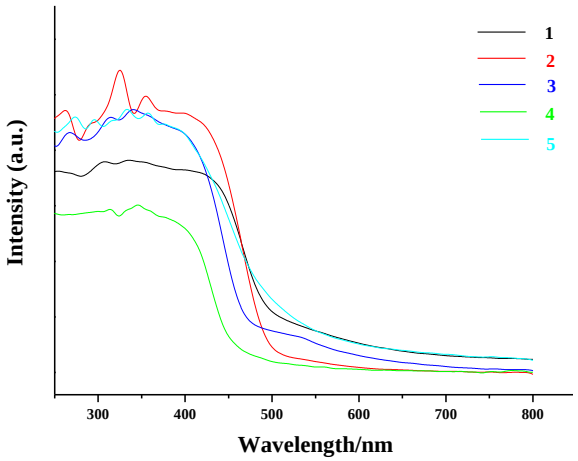


Fig. S15 The solid-state UV-vis absorption spectra of compounds **1**-**5**.

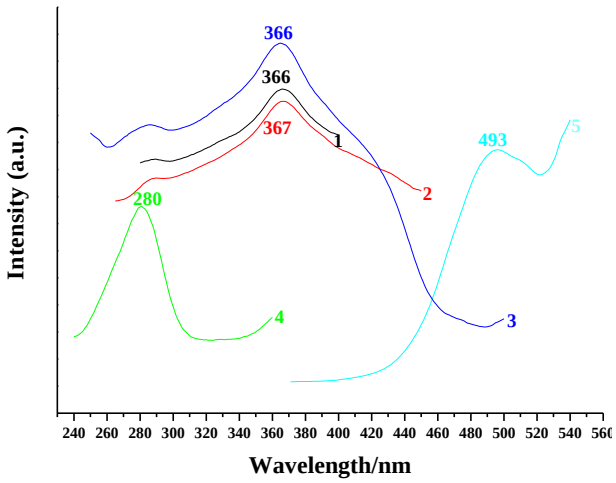


Fig. S16 The solid-state photoluminescence excitation spectra of compounds **1**-**5**.

Computational details for DFT calculations

In this paper, the optimized geometric structure for the excited states of the molecular structure of compound **3** was performed with the CIS method.[1] The calculations for non Zn atoms was carried out with 6-311** basis set,[2] while for Zn atom with LanLDZ basis set.[3] The first singlet excited state structures and emission spectra were obtained using the time-dependent density functional theory TD-CAMB3LYP.[4] All calculations were performed with the GAUSSIAN 09 (revision A.02) program package.[5] The molecular orbitals were plotted with the GaussView program.[6]

1 J. B. Foresman, M. Head-Gordon, J. A. Pople and M. J. Frisch, *J. Phys. Chem.*, 1992, **96**, 135.

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3 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

4 (*a*) R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454; (*b*) M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439 (*c*) T. Yanai, D. Tew and N. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.

5 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

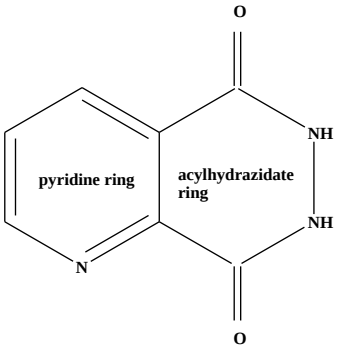
6 R. II. Dennington, K. Todd, J. Millam, K. Eppinnett, W. L. Hovell and R. Gilliland, GaussView, version 5.08, Semichem, Inc Shawnee Mission, KS, 2003.

Table S1 TD-CAMB3LYP calculated fluorescence emission wavelengths (λ/nm), oscillator strengths (*f*), transitions assignment and main CI coefficients.

	Transitions	CI coeff	λ/nm (E/eV)	oscillator	Assignment
Molecular unit	HOMO→LUMO	0.70552	501 (2.48)	0.0647	Intra-ligand ring-to-ring
Observed			517		

Table S2 The molecular orbital compositions in the excited states of the molecular unit for compound **3**.

Molecular unit	HOMO (%)	LUMO (%)
π orbit of acylhydrazidate ring	91	
π* orbit of acylhydrazidate ring		33
s orbital of methyl		2
p orbit of pyridine ring	8	
π* orbit of pyridine ring		64
H_2O	1	1



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