Supplementary information

New 2D zinc phosphonates with heptanuclear units, reversible dehydration-hydration and bright luminescence

Ruibiao Fu*, Shengmin Hu, Xintao Wu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian, 350002 China

- Corresponding author. E-mail: furb@fjirsm.ac.cn

.

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

Zn(1)-O(3)	2.117(5)	Zn(10)-O(42)	2.043(5)
Zn(1)-O(8)	2.079(4)	Zn(11)-N(16)	1.999(7)
Zn(1)-O(13)	2.153(4)	Zn(11)-O(27)	2.022(5)
Zn(1)-O(18)	2.125(4)	Zn(11)-O(32)^{e}	2.007(5)
Zn(1)-O(23)	2.089(5)	Zn(11)-O(37)^{d}	1.959(5)
Zn(1)-O(28)	2.151(4)	Zn(12)-O(33)	2.225(8)
Zn(2)-N(1)	2.127(6)	Zn(12)-O(33)^{d}	1.973(8)
Zn(2)-O(1)	2.082(5)	Zn(12)-O(38)	2.274(7)
Zn(2)-O(3)	2.240(4)	Zn(12)-O(38)^{d}	2.004(7)
Zn(2)-O(9)	1.930(4)	Zn(12)-O(43)	2.354(8)
Zn(2)-O(30)	1.948(5)	Zn(12)-O(43)^{d}	1.975(8)
Zn(3)-N(2)	2.137(5)	Zn(13)-N(7)	2.144(9)
Zn(3)-O(6)	2.112(5)	Zn(13)-O(31)	2.109(6)
Zn(3)-O(8)	2.159(4)	Zn(13)-O(33)	2.149(6)
Zn(3)-O(14)	1.936(4)	Zn(13)-O(40)^{d}	1.967(9)
Zn(3)-O(20)	1.982(4)	Zn(13)-O(44)	1.963(6)
Zn(4)-N(3)	2.290(6)	Zn(14)-N(8)	2.138(8)
Zn(4)-O(4)	1.951(5)	Zn(14)-O(34)	1.936(6)
Zn(4)-O(11)	2.000(5)	Zn(14)-O(36)	2.087(5)
Zn(4)-O(13)	2.033(4)	Zn(14)-O(38)	2.219(5)
Zn(4)-O(25)	1.993(6)	Zn(14)-O(45)^{d}	1.969(8)
Zn(5)-N(4)	2.112(6)	Zn(15)-N(9)	2.314(10)
Zn(5)-O(15)	1.955(5)	Zn(15)-O(35)^{d}	1.985(9)
Zn(5)-O(16)	2.102(5)	Zn(15)-O(39)	1.947(6)
Zn(5)-O(18)	2.218(4)	Zn(15)-O(41)	2.014(6)
Zn(5)-O(24)	1.946(5)	Zn(15)-O(43)	2.047(6)
Zn(6)-N(5)	2.196(6)	Zn(16)-O(48)	2.140(7)
Zn(6)-O(5)	1.987(6)	Zn(16)-O(48)^{b}	2.140(7)
Zn(6)-O(21)	2.094(5)	Zn(16)-O(53)	2.081(6)

Zn(6)-O(23)	2.127(5)	Zn(16)-O(53)[b]	2.081(6)
Zn(6)-O(29)	1.953(5)	Zn(16)-O(58)	2.123(5)
Zn(7)-N(6)	2.272(6)	Zn(16)-O(58)[b]	2.123(5)
Zn(7)-O(10)	1.997(5)	Zn(17)-N(10)	2.250(9)
Zn(7)-O(19)	1.968(5)	Zn(17)-O(46)	2.042(6)
Zn(7)-O(26)	2.033(5)	Zn(17)-O(48)	2.055(6)
Zn(7)-O(28)	2.064(5)	Zn(17)-O(55)[b]	1.980(8)
Zn(8)-N(13)	2.012(8)	Zn(17)-O(59)	1.958(6)
Zn(8)-O(17)	1.965(5)	Zn(18)-N(11)	2.172(9)
Zn(8)-O(22)[a]	2.006(5)	Zn(18)-O(50)	1.959(6)
Zn(8)-O(47)[b]	2.022(5)	Zn(18)-O(51)	2.087(6)
Zn(9)-N(14)	1.996(8)	Zn(18)-O(53)	2.120(6)
Zn(9)-O(12)	2.029(6)	Zn(18)-O(60)[b]	1.959(8)
Zn(9)-O(52)[c]	2.012(6)	Zn(19)-N(12)	2.145(7)
Zn(9)-O(57)	1.969(5)	Zn(19)-O(49)[b]	1.934(7)
Zn(10)-N(15)	2.023(7)	Zn(19)-O(54)	1.918(6)
Zn(10)-O(2)	1.956(5)	Zn(19)-O(56)	2.091(5)
Zn(10)-O(7)[c]	2.015(5)	Zn(19)-O(58)	2.229(5)
O(3)-Zn(1)-O(8)	93.23(17)	N(16)-Zn(11)-O(37)[d]	124.3(3)
O(3)-Zn(1)-O(13)	93.35(17)	O(27)-Zn(11)-O(32)[e]	106.2(2)
O(3)-Zn(1)-O(18)	178.24(16)	O(27)-Zn(11)-O(37)[d]	103.8(2)
O(3)-Zn(1)-O(23)	87.09(18)	O(32)[e]-Zn(11)-O(37)[d]	102.5(2)
O(3)-Zn(1)-O(28)	86.37(17)	O(33)-Zn(12)-O(33)[d]	166.21(15)
O(8)-Zn(1)-O(13)	91.86(17)	O(33)-Zn(12)-O(38)	86.0(3)
O(8)-Zn(1)-O(18)	86.71(17)	O(33)-Zn(12)-O(38)[d]	85.8(3)
O(8)-Zn(1)-O(23)	179.36(18)	O(33)-Zn(12)-O(43)	82.3(3)
O(8)-Zn(1)-O(28)	88.61(16)	O(33)-Zn(12)-O(43)[d]	90.1(3)
O(13)-Zn(1)-O(18)	84.89(17)	O(33)[d]-Zn(12)-O(38)	85.1(3)
O(13)-Zn(1)-O(23)	88.68(18)	O(33)[d]-Zn(12)-O(38)[d]	100.9(3)
O(13)-Zn(1)-O(28)	179.47(17)	O(33)[d]-Zn(12)-O(43)	86.5(3)
O(18)-Zn(1)-O(23)	92.98(18)	O(33)[d]-Zn(12)-O(43)[d]	99.6(3)
O(18)-Zn(1)-O(28)	95.39(17)	O(38)-Zn(12)-O(38)[d]	166.73(17)
O(23)-Zn(1)-O(28)	90.86(17)	O(38)-Zn(12)-O(43)	85.9(3)
N(1)-Zn(2)-O(1)	80.1(2)	O(38)-Zn(12)-O(43)[d]	85.5(3)
N(1)-Zn(2)-O(3)	80.80(19)	O(38)[d]-Zn(12)-O(43)	82.8(3)
N(1)-Zn(2)-O(9)	119.6(2)	O(38)[d]-Zn(12)-O(43)[d]	104.8(3)
N(1)-Zn(2)-O(30)	124.4(2)	O(43)-Zn(12)-O(43)[d]	168.9(2)
O(1)-Zn(2)-O(3)	160.88(18)	N(7)-Zn(13)-O(31)	79.9(3)
O(1)-Zn(2)-O(9)	93.84(19)	N(7)-Zn(13)-O(33)	82.6(3)
O(1)-Zn(2)-O(30)	100.9(2)	N(7)-Zn(13)-O(40)[d]	126.4(3)
O(3)-Zn(2)-O(9)	96.84(18)	N(7)-Zn(13)-O(44)	117.1(4)
O(3)-Zn(2)-O(30)	88.67(18)	O(31)-Zn(13)-O(33)	161.0(2)
O(9)-Zn(2)-O(30)	115.8(2)	O(31)-Zn(13)-O(40)[d]	96.8(3)

N(2)-Zn(3)-O(6)	80.40(19)	O(31)-Zn(13)-O(44)	94.3(2)
N(2)-Zn(3)-O(8)	82.20(18)	O(33)-Zn(13)-O(40)[d]	87.7(3)
N(2)-Zn(3)-O(14)	118.4(2)	O(33)-Zn(13)-O(44)	100.2(2)
N(2)-Zn(3)-O(20)	125.32(19)	O(40)[d]-Zn(13)-O(44)	116.5(3)
O(6)-Zn(3)-O(8)	161.81(17)	N(8)-Zn(14)-O(34)	117.2(3)
O(6)-Zn(3)-O(14)	94.13(19)	N(8)-Zn(14)-O(36)	80.6(2)
O(6)-Zn(3)-O(20)	96.37(19)	N(8)-Zn(14)-O(38)	81.1(3)
O(8)-Zn(3)-O(14)	98.76(17)	N(8)-Zn(14)-O(45)[d]	127.0(3)
O(8)-Zn(3)-O(20)	89.38(17)	O(34)-Zn(14)-O(36)	92.9(2)
O(14)-Zn(3)-O(20)	116.30(19)	O(34)-Zn(14)-O(38)	96.5(2)
N(3)-Zn(4)-O(4)	112.4(2)	O(34)-Zn(14)-O(45)[d]	115.7(3)
N(3)-Zn(4)-O(11)	78.0(2)	O(36)-Zn(14)-O(38)	161.6(2)
N(3)-Zn(4)-O(13)	82.15(19)	O(36)-Zn(14)-O(45)[d]	101.1(2)
N(3)-Zn(4)-O(25)	134.6(2)	O(38)-Zn(14)-O(45)[d]	89.0(3)
O(4)-Zn(4)-O(11)	103.7(2)	N(9)-Zn(15)-O(35)[d]	130.0(3)
O(4)-Zn(4)-O(13)	105.76(18)	N(9)-Zn(15)-O(39)	114.5(3)
O(4)-Zn(4)-O(25)	112.6(2)	N(9)-Zn(15)-O(41)	78.0(3)
O(11)-Zn(4)-O(13)	149.04(19)	N(9)-Zn(15)-O(43)	82.8(3)
O(11)-Zn(4)-O(25)	85.8(2)	O(35)[d]-Zn(15)-O(39)	115.2(3)
O(13)-Zn(4)-O(25)	91.6(2)	O(35)[d]-Zn(15)-O(41)	86.0(3)
N(4)-Zn(5)-O(15)	124.9(2)	O(35)[d]-Zn(15)-O(43)	89.8(3)
N(4)-Zn(5)-O(16)	80.3(2)	O(39)-Zn(15)-O(41)	102.8(3)
N(4)-Zn(5)-O(18)	81.47(19)	O(39)-Zn(15)-O(43)	105.2(2)
N(4)-Zn(5)-O(24)	117.7(2)	O(41)-Zn(15)-O(43)	150.8(2)
O(15)-Zn(5)-O(16)	98.9(2)	O(48)-Zn(16)-O(48)[b]	180.0(4)
O(15)-Zn(5)-O(18)	90.31(18)	O(48)-Zn(16)-O(53)	92.2(3)
O(15)-Zn(5)-O(24)	117.4(2)	O(48)-Zn(16)-O(53)[b]	87.8(3)
O(16)-Zn(5)-O(18)	161.69(18)	O(48)-Zn(16)-O(58)	94.4(2)
O(16)-Zn(5)-O(24)	91.7(2)	O(48)-Zn(16)-O(58)[b]	85.6(2)
O(18)-Zn(5)-O(24)	98.12(19)	O(48)[b]-Zn(16)-O(53)	87.8(3)
N(5)-Zn(6)-O(5)	128.8(2)	O(48)[b]-Zn(16)-O(53)[b]	94.4(2)
N(5)-Zn(6)-O(21)	80.2(2)	O(48)[b]-Zn(16)-O(58)	85.6(2)
N(5)-Zn(6)-O(23)	82.7(2)	O(48)[b]-Zn(16)-O(58)[b]	92.2(3)
N(5)-Zn(6)-O(29)	115.6(2)	O(53)-Zn(16)-O(53)[b]	180.000(3)
O(5)-Zn(6)-O(21)	92.1(2)	O(53)-Zn(16)-O(58)	93.1(2)
O(5)-Zn(6)-O(23)	89.2(2)	O(53)-Zn(16)-O(58)[b]	86.9(2)
O(5)-Zn(6)-O(29)	115.7(2)	O(53)[b]-Zn(16)-O(58)	86.9(2)
O(21)-Zn(6)-O(23)	158.96(19)	O(53)[b]-Zn(16)-O(58)[b]	93.1(2)
O(21)-Zn(6)-O(29)	97.2(2)	O(58)-Zn(16)-O(58)[b]	180.000(2)
O(23)-Zn(6)-O(29)	101.20(18)	N(10)-Zn(17)-O(46)	78.9(3)
N(6)-Zn(7)-O(10)	125.3(2)	N(10)-Zn(17)-O(48)	83.3(3)
N(6)-Zn(7)-O(19)	118.1(2)	N(10)-Zn(17)-O(55)[b]	130.2(3)
N(6)-Zn(7)-O(26)	78.49(19)	N(10)-Zn(17)-O(59)	115.9(3)
N(6)-Zn(7)-O(28)	83.41(19)	O(46)-Zn(17)-O(48)	152.6(2)

O(10)-Zn(7)-O(19)	116.27(19)	O(46)-Zn(17)-O(55)[b]	85.8(3)
O(10)-Zn(7)-O(26)	86.17(19)	O(46)-Zn(17)-O(59)	100.9(2)
O(10)-Zn(7)-O(28)	88.90(19)	O(48)-Zn(17)-O(55)[b]	90.0(3)
O(19)-Zn(7)-O(26)	101.19(19)	O(48)-Zn(17)-O(59)	105.5(2)
O(19)-Zn(7)-O(28)	104.19(18)	O(55)[b]-Zn(17)-O(59)	113.5(3)
O(26)-Zn(7)-O(28)	153.66(18)	N(11)-Zn(18)-O(50)	115.8(4)
N(13)-Zn(8)-O(17)	125.7(3)	N(11)-Zn(18)-O(51)	80.7(3)
N(13)-Zn(8)-O(22)[a]	106.8(3)	N(11)-Zn(18)-O(53)	81.6(3)
N(13)-Zn(8)-O(47)[b]	111.7(3)	N(11)-Zn(18)-O(60)[b]	127.5(3)
O(17)-Zn(8)-O(22)[a]	101.2(2)	O(50)-Zn(18)-O(51)	95.6(2)
O(17)-Zn(8)-O(47)[b]	104.3(2)	O(50)-Zn(18)-O(53)	99.6(2)
O(22)[a]-Zn(8)-(47)[b]	105.0(2)	O(50)-Zn(18)-O(60)[b]	116.7(3)
N(14)-Zn(9)-O(12)	116.2(3)	O(51)-Zn(18)-O(53)	160.4(2)
N(14)-Zn(9)-O(52)[c]	106.3(3)	O(51)-Zn(18)-O(60)[b]	95.2(2)
N(14)-Zn(9)-O(57)	125.3(3)	O(53)-Zn(18)-O(60)[b]	89.1(3)
O(12)-Zn(9)-O(52)[c]	104.7(2)	N(12)-Zn(19)-O(49)[b]	124.5(3)
O(12)-Zn(9)-O(57)	101.2(2)	N(12)-Zn(19)-O(54)	119.6(3)
O(52)[c]-Zn(9)-O(57)	100.5(2)	N(12)-Zn(19)-O(56)	80.1(2)
N(15)-Zn(10)-O(2)	125.1(2)	N(12)-Zn(19)-O(58)	81.7(2)
N(15)-Zn(10)-O(7)[c]	104.5(2)	O(49)[b]-Zn(19)-O(54)	115.9(3)
N(15)-Zn(10)-O(42)	117.3(3)	O(49)[b]-Zn(19)-O(56)	100.4(3)
O(2)-Zn(10)-O(7)[c]	101.3(2)	O(49)[b]-Zn(19)-O(58)	88.9(2)
O(2)-Zn(10)-O(42)	100.6(2)	O(54)-Zn(19)-O(56)	92.8(2)
O(7)[c]-Zn(10)-O(42)	105.9(2)	O(54)-Zn(19)-O(58)	97.2(2)
N(16)-Zn(11)-O(27)	112.3(2)	O(56)-Zn(19)-O(58)	161.8(2)
N(16)-Zn(11)-O(32)[e]	106.1(2)		

Symmetry codes: a x + 1, y, z; b - x + 1, - y, - z + 2; c x - 1, y, z; d - x - 1, - y + 1, - z + 1; e - x, - y + 1, - z + 1.

Table S2. Selected bond lengths (Å) and angles (°) for **2**

Zn(1)-O(1)	2.142(2)	Zn(3)-O(6)	2.116(2)
Zn(1)-O(1)[a]	2.142(2)	Zn(3)-O(9)	2.133(2)
Zn(1)-O(6)	2.117(2)	Zn(3)-O(12)[a]	1.965(2)
Zn(1)-O(6)[a]	2.117(2)	Zn(4)-N(1)[a]	2.183(3)
Zn(1)-O(11)	2.110(2)	Zn(4)-O(1)[a]	2.168(2)
Zn(1)-O(11)[a]	2.110(2)	Zn(4)-O(4)[a]	2.103(2)
Zn(2)-N(3)	2.134(3)	Zn(4)-O(8)	1.959(2)
Zn(2)-O(2)	1.953(2)	Zn(4)-O(13)	1.956(2)
Zn(2)-O(7)	1.951(2)	Zn(5)-N(4)	2.083(4)
Zn(2)-O(11)	2.203(2)	Zn(5)-N(5)	2.082(3)
Zn(2)-O(14)	2.072(2)	Zn(5)-N(6)	2.219(4)
Zn(3)-N(2)	2.152(3)	Zn(5)-O(5)[b]	1.981(3)
Zn(3)-O(3)	1.952(2)	Zn(5)-O(10)	2.126(3)
O(1)-Zn(1)-O(1)[a]	180.00(15)	N(2)-Zn(3)-O(12)[a]	127.17(10)
O(1)-Zn(1)-O(6)	91.11(8)	O(3)-Zn(3)-O(6)	95.39(9)
O(1)-Zn(1)-O(6)[a]	88.89(8)	O(3)-Zn(3)-O(9)	100.40(10)
O(1)-Zn(1)-O(11)	92.65(8)	O(3)-Zn(3)-O(12)[a]	124.56(10)
O(1)-Zn(1)-O(11)[a]	87.35(8)	O(6)-Zn(3)-O(9)	160.25(9)
O(1)[a]-Zn(1)-O(6)	88.89(8)	O(6)-Zn(3)-O(12)[a]	94.16(9)
O(1)[a]-Zn(1)-O(6)[a]	91.11(8)	O(9)-Zn(3)-O(12)[a]	86.64(9)
O(1)[a]-Zn(1)-O(11)	87.35(8)	N(1)[a]-Zn(4)-O(1)[a]	83.23(8)
O(1)[a]-Zn(1)-O(11)[a]	92.65(8)	N(1)[a]-Zn(4)-O(4)[a]	77.92(9)
O(6)-Zn(1)-O(6)[a]	180.00(11)	N(1)[a]-Zn(4)-O(8)	141.29(10)
O(6)-Zn(1)-O(11)	89.37(8)	N(1)[a]-Zn(4)-O(13)	106.23(9)
O(6)-Zn(1)-O(11)[a]	90.63(8)	O(1)[a]-Zn(4)-O(4)[a]	160.13(8)
O(6)[a]-Zn(1)-O(11)	93.69(10)	O(1)[a]-Zn(4)-O(8)	95.40(9)
O(6)[a]-Zn(1)-O(11)[a]	86.31(10)	O(1)[a]-Zn(4)-O(13)	94.31(9)
O(11)-Zn(1)-O(11)[a]	180.00(11)	O(4)[a]-Zn(4)-O(8)	95.40(10)
N(3)-Zn(2)-O(2)	127.42(10)	O(4)[a]-Zn(4)-O(13)	96.92(10)
N(3)-Zn(2)-O(7)	111.39(10)	O(8)-Zn(4)-O(13)	112.43(10)
N(3)-Zn(2)-O(11)	84.27(9)	N(4)-Zn(5)-N(5)	129.19(17)
N(3)-Zn(2)-O(14)	79.31(10)	N(4)-Zn(5)-N(6)	80.04(16)
O(2)-Zn(2)-O(7)	121.08(10)	N(4)-Zn(5)-O(5)[b]	123.69(15)
O(2)-Zn(2)-O(11)	89.60(9)	N(4)-Zn(5)-O(10)	91.41(16)
O(2)-Zn(2)-O(14)	93.89(10)	N(5)-Zn(5)-N(6)	81.11(14)
O(7)-Zn(2)-O(11)	92.92(9)	N(5)-Zn(5)-O(5)[b]	105.39(12)
O(7)-Zn(2)-O(14)	100.59(11)	N(5)-Zn(5)-O(10)	99.49(13)
O(11)-Zn(2)-O(14)	161.66(10)	N(6)-Zn(5)-O(5)[b]	97.95(12)
N(2)-Zn(3)-O(3)	107.88(10)	N(6)-Zn(5)-O(10)	169.12(12)
N(2)-Zn(3)-O(6)	86.46(9)	O(5)[b]-Zn(5)-O(10)	92.37(11)
N(2)-Zn(3)-O(9)	77.47(9)		

Symmetry codes: a - x, - y, - z; b - x- 1/2, y + 1/2, - z +1/2.

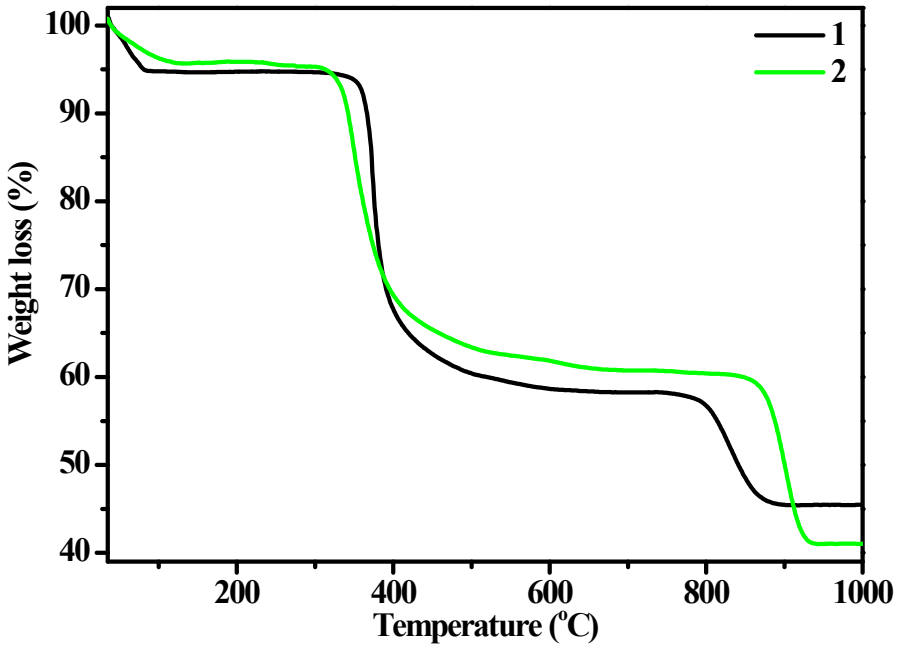

Fig. S1 TGA curves of compounds **1**-**2**.

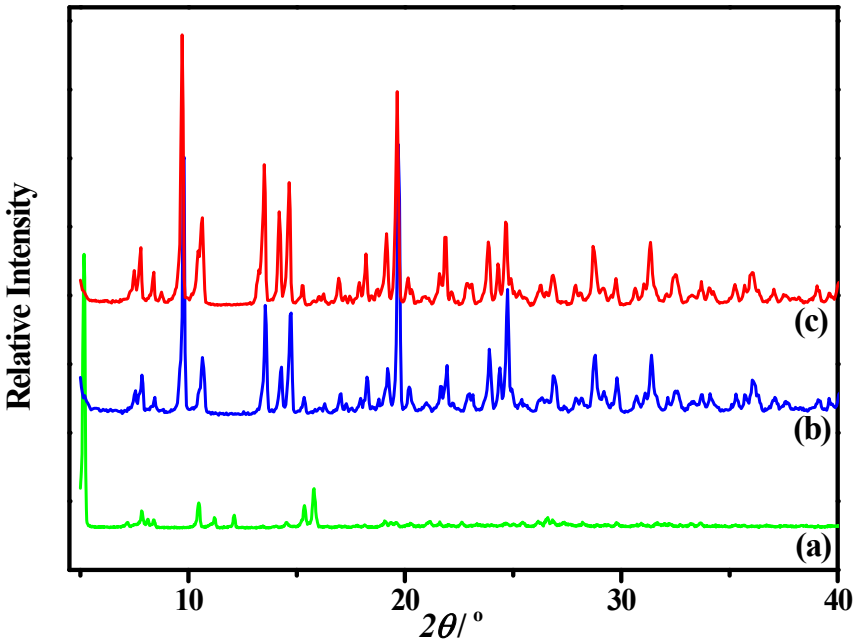

Fig. S2 Powder XRD patterns of as-prepared **1** (a), solids **1**-**100** (b) and **1**-**250** (c).

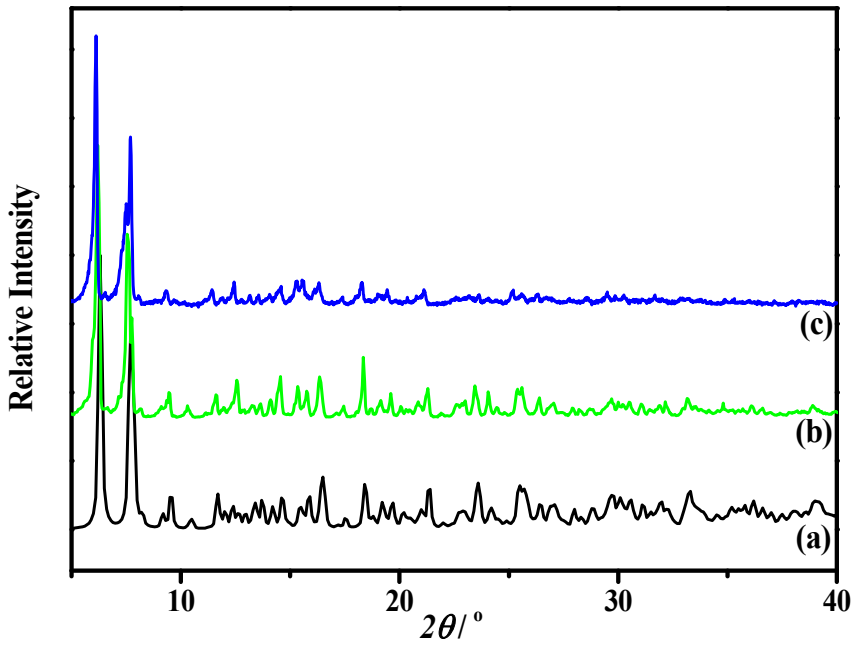

Fig. S3 Powder XRD patterns of compound **2** (a) simulated from single-crystal X-ray data, and experimental data for as-prepared **2** (b) and solid **2-250** (c)

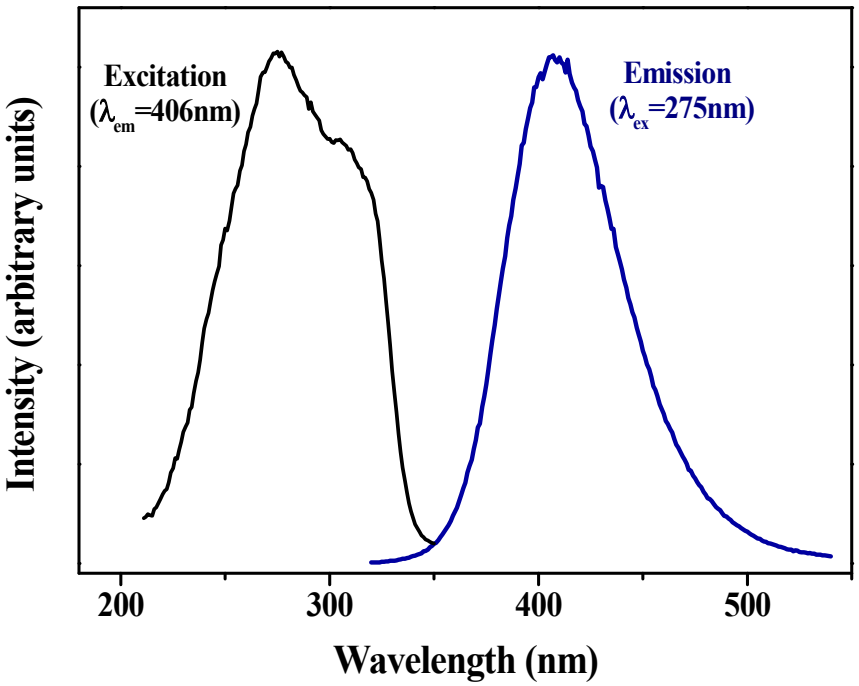

Fig. S4 Emission and excitation spectra for solid **1** at room temperature.

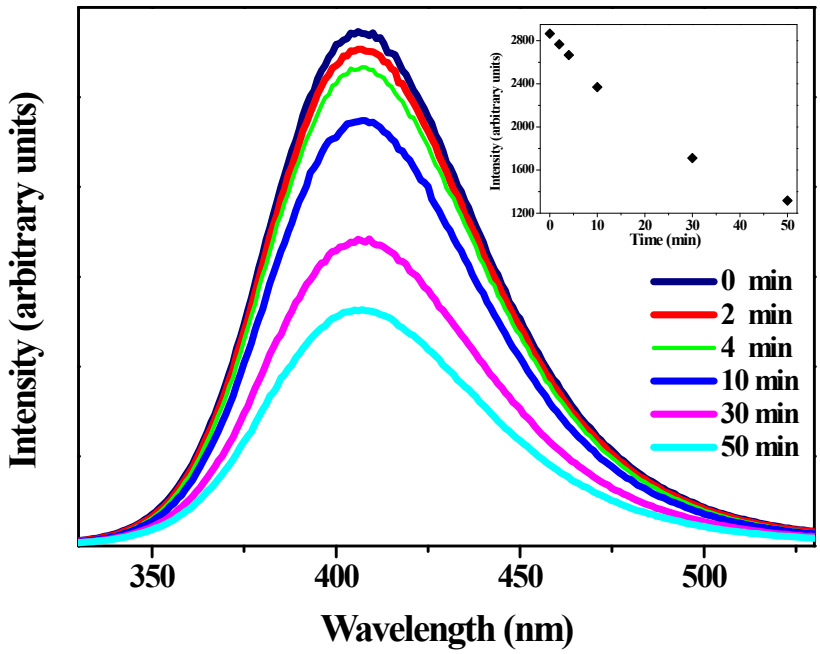

Fig. S5 Fluorescent spectra for solid **1-250** with different UV irradiation time at 270 nm. Inset: fluorescent intensity at $\lambda_{max(em)}$ as a function of UV irradiation time at 270 nm.

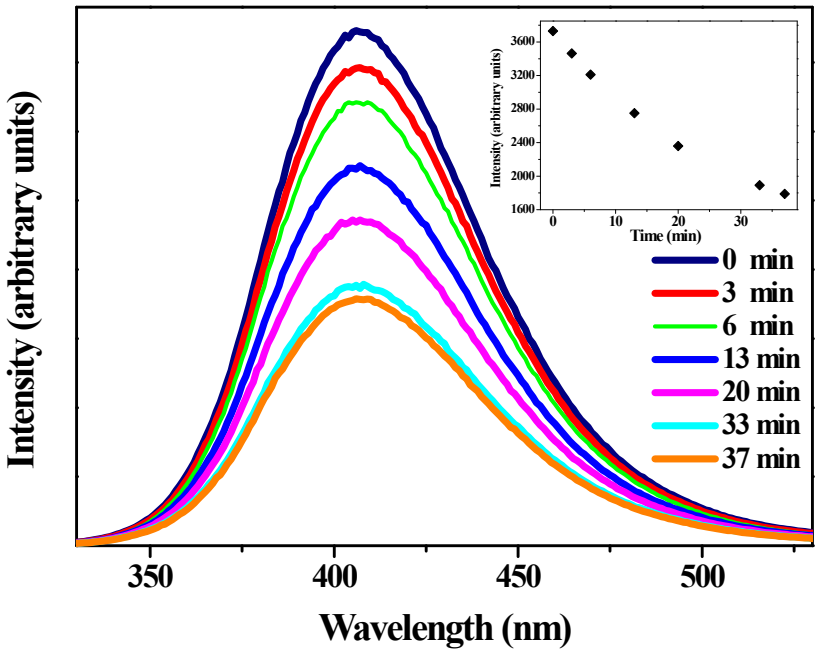

Fig. S6 Fluorescent spectra for solid **1-100D** with different UV irradiation time at 273 nm. Inset: fluorescent intensity at $\lambda_{max(em)}$ as a function of UV irradiation time at 273 nm.

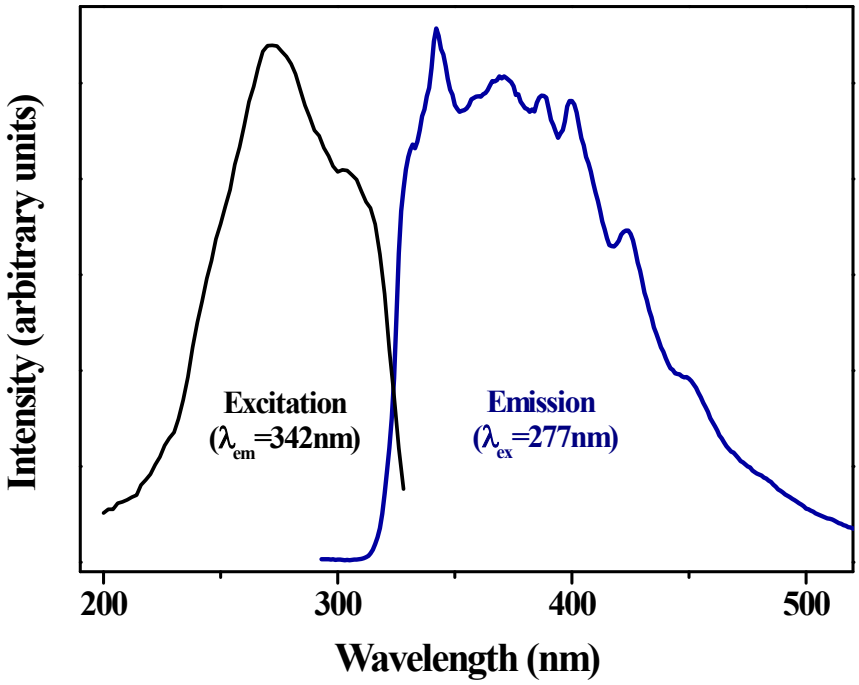

Fig. S7 Emission and excitation spectra for compound **2** at room temperature.

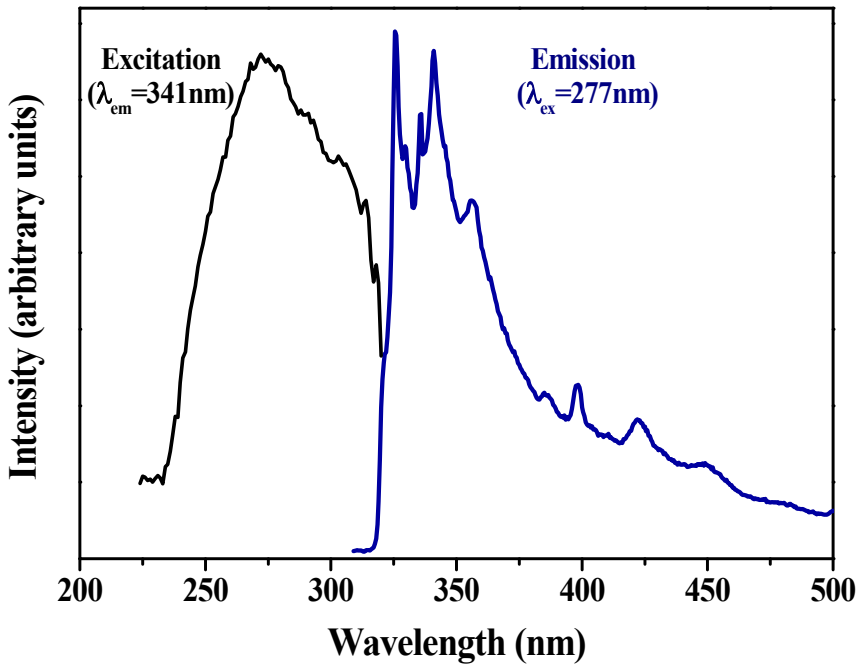

Fig. S8 Emission and excitation spectra for compound **2** at 10 K.

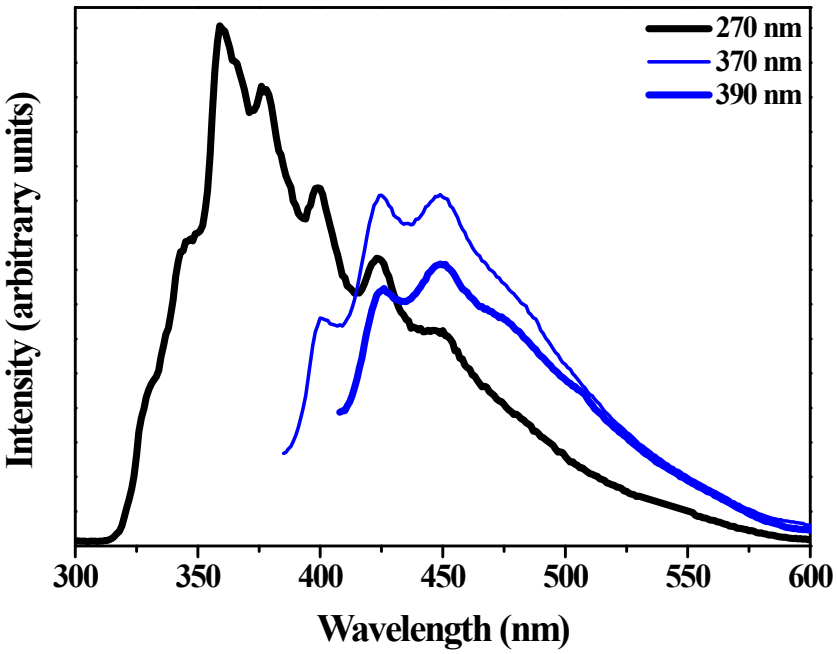

Fig. S9 Emission spectra for solid **2-150** upon different wavelength of excited light at room temperature.

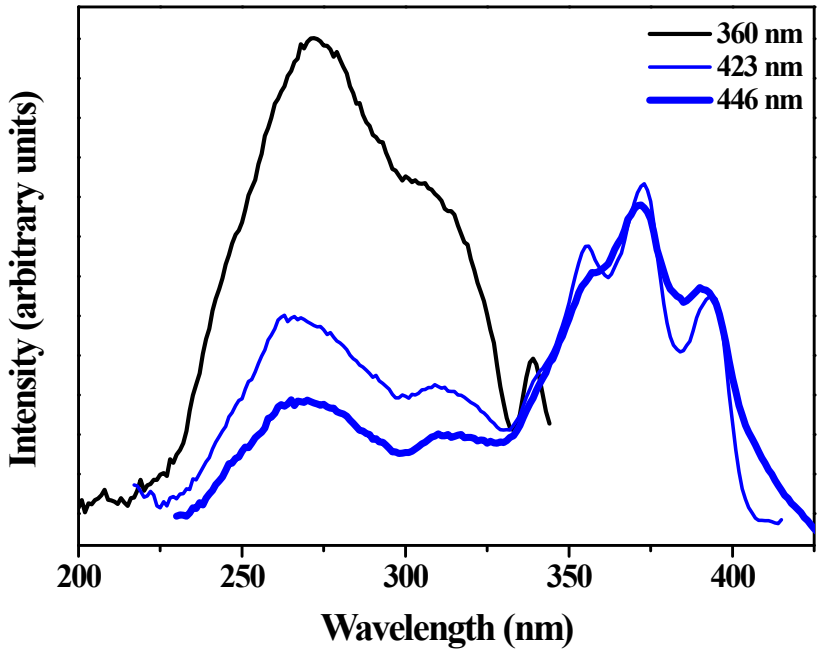

Fig. S10 Excitation spectra for solid **2-150** upon emission fixed at 360, 423 and 446 nm under room temperature, respectively.

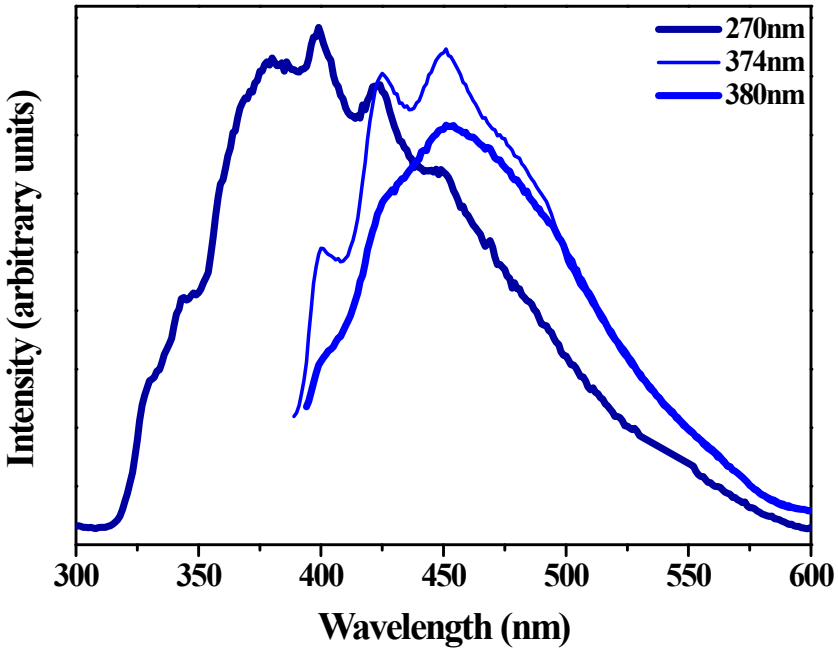

Fig. S11 Emission spectra for solid **2-200** upon different wavelengths of excited light at room temperature.

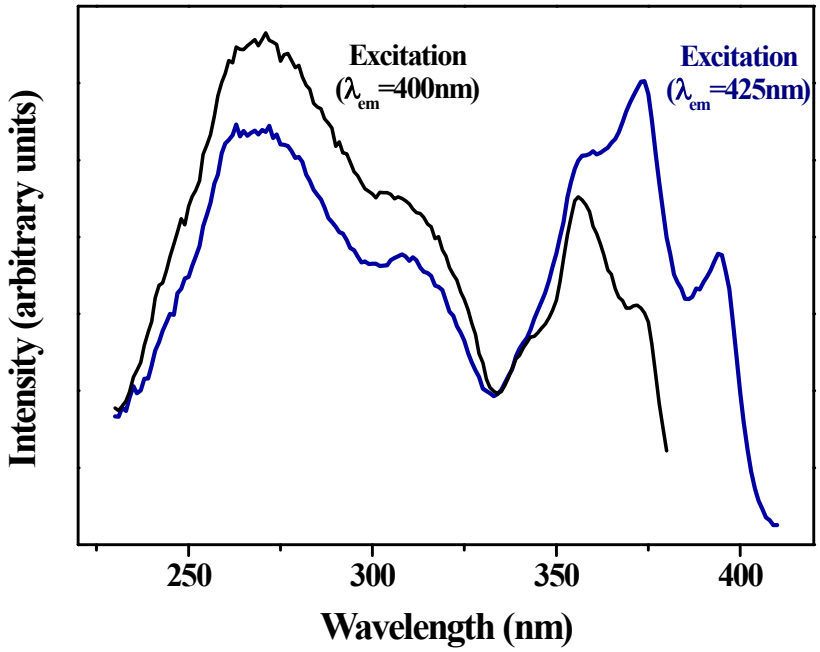

Fig. S12 Excitation spectra for solid **2-200** upon emission fixed at 400 and 425 nm under room temperature, respectively.

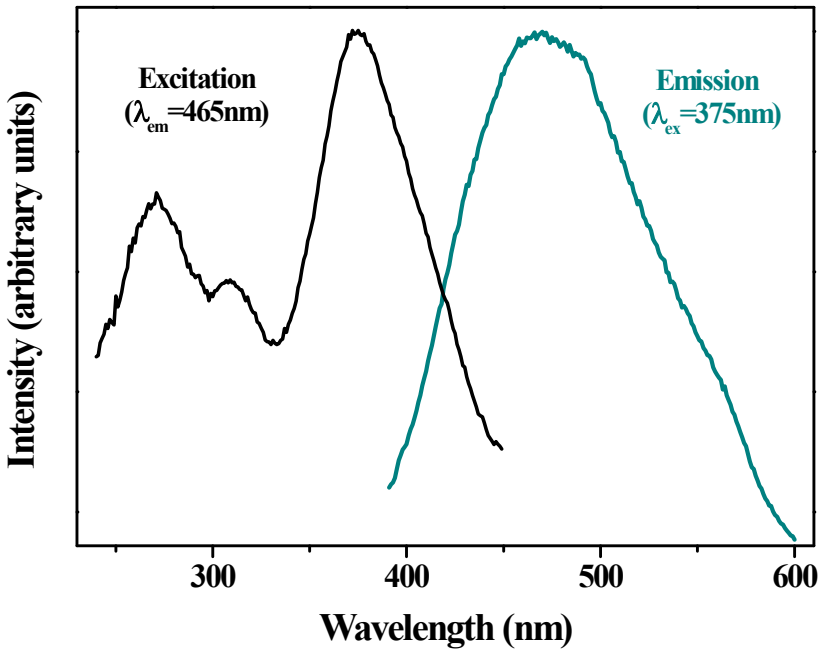

Fig. S13 Emission and excitation spectra for solid **2-250** at room temperature.