Syntheses, crystal structures, surface photovoltage, luminescence and molecular recognition properties of Zinc(II) and Iron(II) carboxyphosphonates with 2D and 3D supramolecular structures

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Supplementary Materials

BVS calculations for compounds **1** and **2**

Compound **1**

Fe 1

		Fe^{2+}			Fe^{3+}
1.734	2.001	0.48596	1.759	2.001	0.51993
1.734	2.129	0.34384	1.759	2.129	0.36788
1.734	2.149	0.32575	1.759	2.149	0.34852
1.734	2.157	0.31878	1.759	2.157	0.34107
1.734	2.327	0.20135	1.759	2.327	0.21543
1.86	2.281	0.32051	1.86	2.281	0.32051
		1.99619			2.11334

Fe 2

		Fe^{2+}			Fe^{3+}
1.734	2.033	0.44570	1.759	2.033	0.47686
1.734	2.001	0.48596	1.759	2.001	0.51993
1.734	2.115	0.35710	1.759	2.115	0.38207
1.734	2.075	0.39787	1.759	2.075	0.42569
1.734	2.115	0.35710	1.759	2.115	0.38207
		2.04373			2.18689

Compound **2**

Fe1

		Fe^{2+}			Fe^{3+}
1.734	2.094	0.37796	1.759	2.094	0.40438
1.734	2.094	0.37796	1.759	2.094	0.40438
1.734	2.154	0.32138	1.759	2.154	0.34384
1.734	2.154	0.32138	1.759	2.154	0.34384
1.734	2.162	0.31450	1.759	2.162	0.33649
1.734	2.162	0.31450	1.759	2.162	0.33649
		2.02768			2.16942

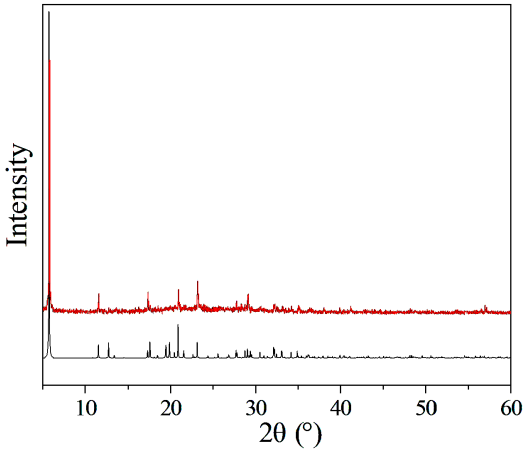

Fig S1. The experimental powder XRD patterns and the simulated XRD patterns of compound **1**.

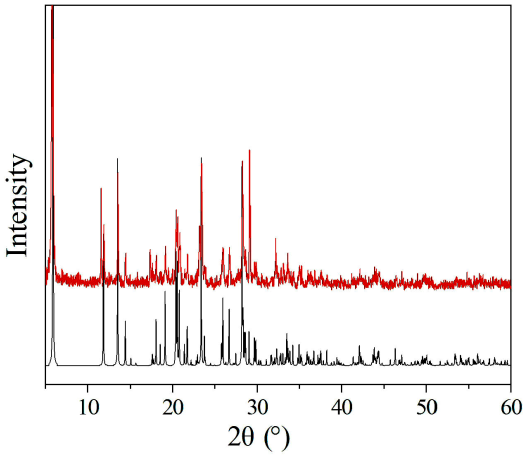

Fig S2. The experimental powder XRD patterns and the simulated XRD patterns of compound **2**.

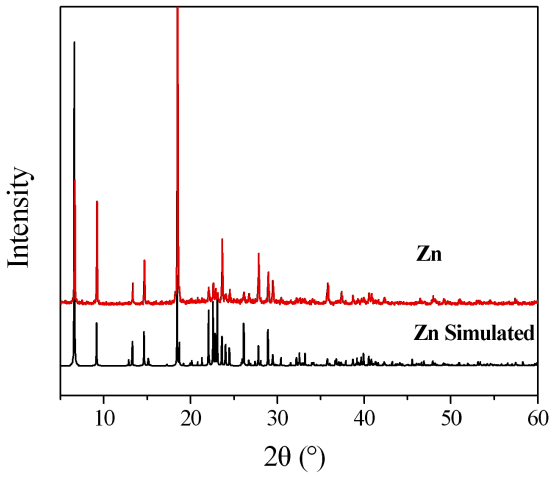

Fig S3. The experimental powder XRD patterns and the simulated XRD patterns of compound **3**.

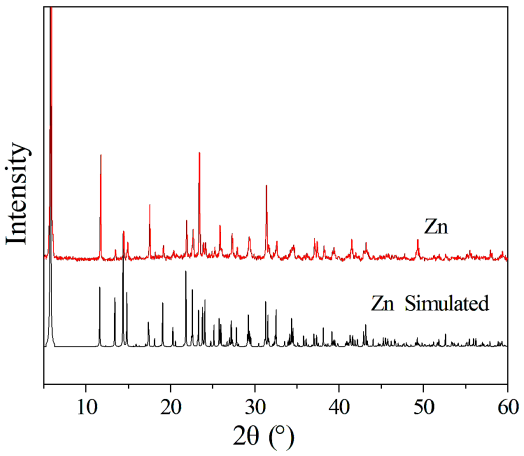

Fig S4. The experimental powder XRD patterns and the simulated XRD patterns of compound **4**.

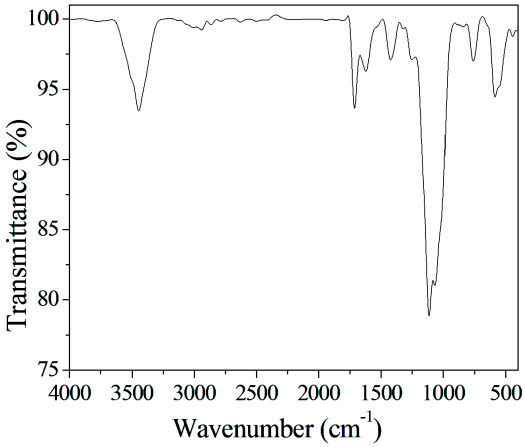

Fig S5. The IR spectrum of compound **1**.

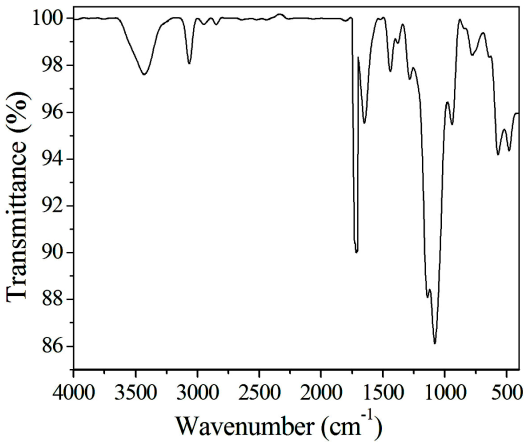

Fig S6. The IR spectrum of compound **2**.

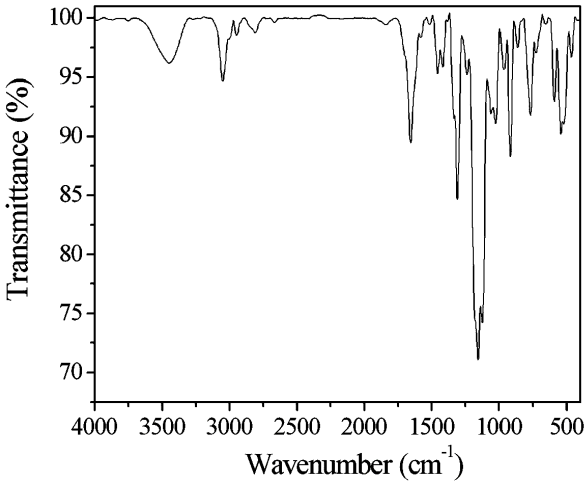

Fig S7. The IR spectrum of compound **3**.

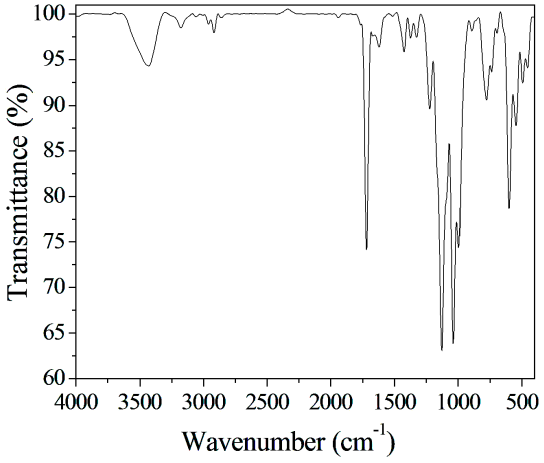

Fig S8. The IR spectrum of compound **4**.

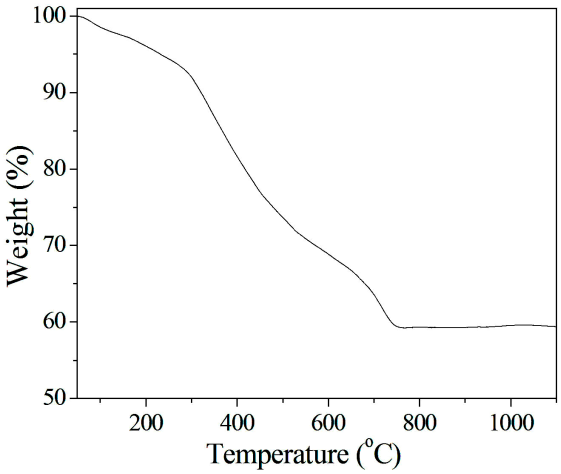

Fig S9. The TGA curve of compound **1**.

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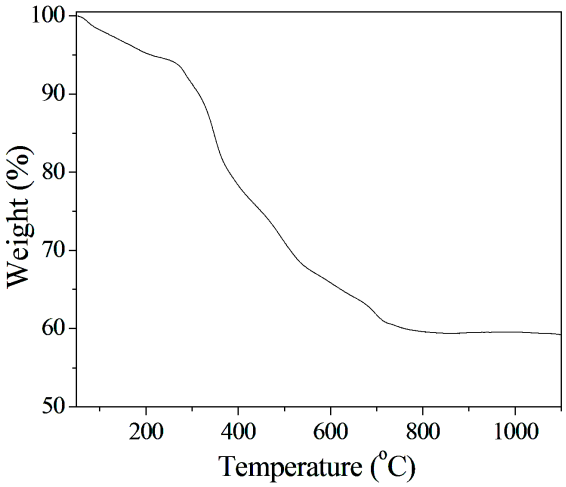

Fig S10. The TGA curve of compound **2**.

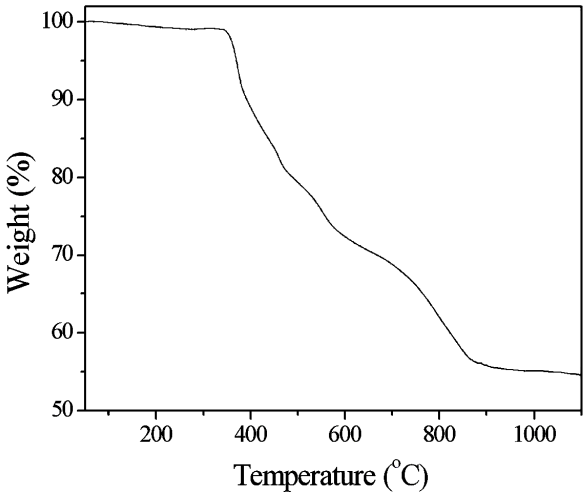

Fig S11. The TGA curve of compound **3**.

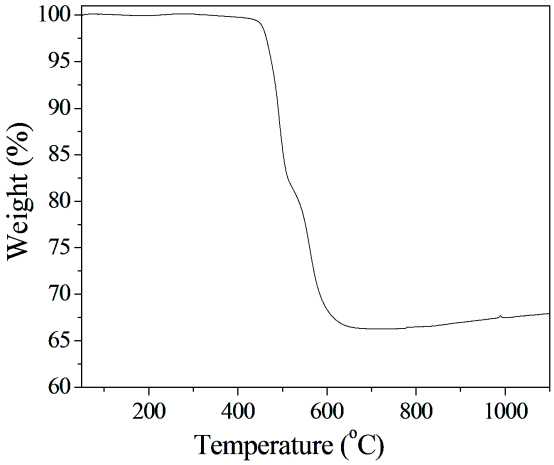

Fig S12. The TGA curve of compound **4**.

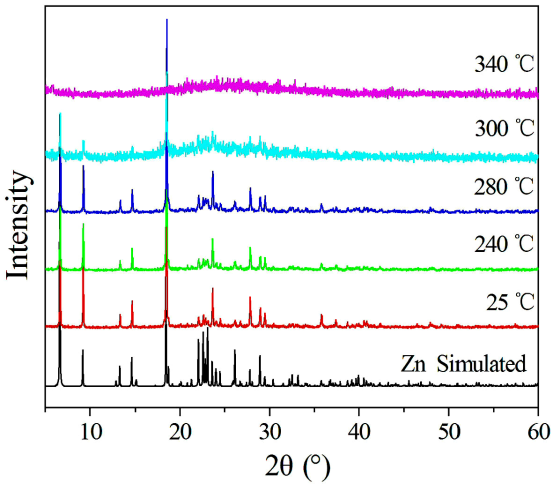

Fig S13. The PXRD patterns for compound **3** on heating from 25–340 °C.

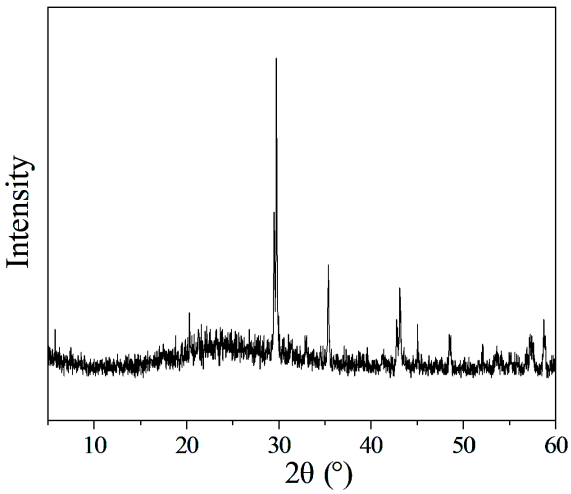

Fig S14. The X–ray power diffraction patterns of the final products in the thermal decomposition for compound **4**.

The final product is $Zn_2P_2O_7$ (JCPDS 00-007-0153)

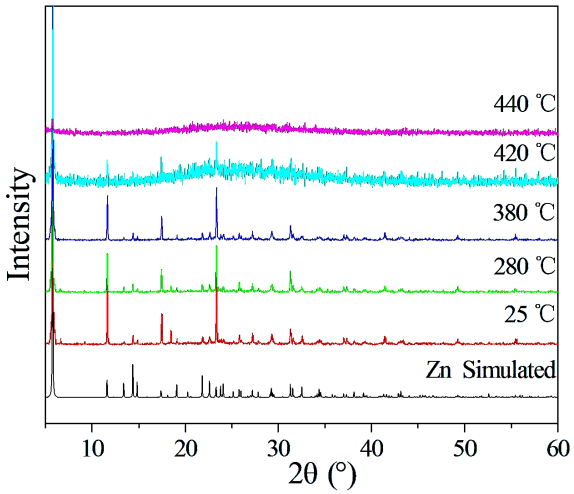

Fig S15. The PXRD patterns for compound **4** on heating from 25–440 °C.

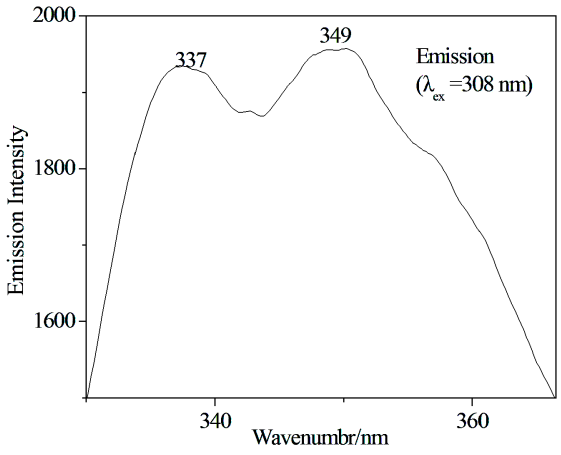

Fig S16. Solid–state emission spectrum of H_5L at room temperature.

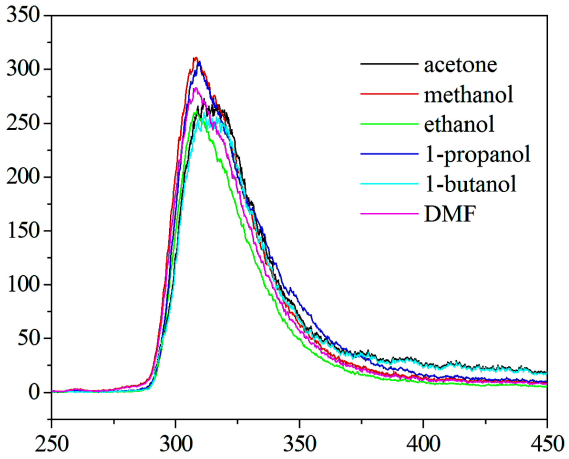

Fig S17. Emission spectrum of compound **3** in various pure solvents when excited at 240 nm.

Table S1 Selected bond lengths (Å) and angles (deg) for compound **1**[a]

Fe(1)–O(1)#1	2.001(3)	O(5)–Fe(2)#3	1.938(3)
Fe(1)–O(4)	2.129(3)	O(6)–Fe(2)	2.033(3)
Fe(1)–O(4)#2	2.149(3)	P(1)–O(2)	1.511(3)
Fe(1)–O(3)	2.157(3)	P(1)–O(1)	1.527(3)
Fe(1)–N(1)	2.281(3)	P(1)–O(3)	1.543(3)
Fe(1)–O(9)	2.327(3)	O(1)–Fe(1)#4	2.001(3)
P(2)–O(5)	1.497(3)	O(2)–Fe(2)#5	2.075(3)
P(2)–O(4)	1.536(3)	O(3)–Fe(2)#2	2.115(3)
P(2)–O(6)	1.536(3)	Fe(2)–O(5)#6	1.938(3)
P(2)–C(2)	1.802(4)	Fe(2)–O(2)#7	2.075(3)
O(4)–Fe(1)#2	2.149(3)	Fe(2)–O(3)#2	2.115(3)
O(1)#1–Fe(1)–O(4)	168.91(12)	O(5)–P(2)–O(4)	112.60(17)
O(1)#1–Fe(1)–O(4)#2	106.96(11)	O(5)–P(2)–O(6)	114.50(18)
O(4)–Fe(1)–O(4)#2	75.56(11)	O(4)–P(2)–O(6)	108.80(15)
O(1)#1–Fe(1)–O(3)	98.84(11)	O(2)–P(1)–O(1)	110.95(16)
O(4)–Fe(1)–O(3)	91.68(11)	O(2)–P(1)–O(3)	115.46(16)
O(4)#2–Fe(1)–O(3)	94.08(11)	O(1)–P(1)–O(3)	109.99(16)
O(1)#1–Fe(1)–N(1)	95.67(12)	O(5)#6–Fe(2)–O(6)	133.64(14)
O(4)–Fe(1)–N(1)	81.81(11)	O(5)#6–Fe(2)–O(2)#7	95.50(12)
O(4)#2–Fe(1)–N(1)	157.27(11)	O(6)–Fe(2)–O(2)#7	88.71(12)
O(3)–Fe(1)–N(1)	84.35(11)	O(5)#6–Fe(2)–O(3)#2	112.00(12)
O(1)#1–Fe(1)–O(9)	89.33(11)	O(6)–Fe(2)–O(3)#2	113.88(12)
O(4)–Fe(1)–O(9)	80.91(10)	O(2)#7–Fe(2)–O(3)#2	92.72(11)
O(4)#2–Fe(1)–O(9)	74.42(11)	O(5)#6–Fe(2)–O(9)	88.12(12)
O(3)–Fe(1)–O(9)	167.52(11)	O(6)–Fe(2)–O(9)	91.89(11)
N(1)–Fe(1)–O(9)	104.34(12)	O(2)#7–Fe(2)–O(9)	174.39(12)
O(3)#2–Fe(2)–O(9)	81.94(11)		

[a] Symmetry transformations used to generate equivalent atoms: #1 x, -y + 3/2, z + 1/2; #2 -x + 1, -y + 1, -z + 2; #3 x, -y + 1/2, z - 1/2; #4 x, -y + 3/2, z - 1/2; #5 x, y + 1, z; #6 x, -y + 1/2, z + 1/2; #7 x, y - 1, z.

Table S2 Selected bond lengths (Å) and angles (deg) for compound **2**[a]

Fe(1)–O(1)	2.094(2)	P(1)–O(2)	1.574(2)
Fe(1)–O(1)#1	2.094(2)	P(1)–C(1)	1.833(3)
Fe(1)–O(4)#1	2.154(2)	P(2)–O(4)	1.487(2)
Fe(1)–O(4)	2.154(2)	P(2)–O(6)	1.518(2)
Fe(1)–O(3)#2	2.162(2)	P(2)–O(5)	1.571(2)
Fe(1)–O(3)#3	2.162(2)	P(2)–C(2)	1.834(3)
P(1)–O(3)	1.501(2)	O(3)–Fe(1)#4	2.162(2)
P(1)–O(1)	1.507(2)		
O(1)#1–Fe(1)–O(4)	89.20(9)	O(4)#1–Fe(1)–O(3)#2	96.78(9)
O(4)#1–Fe(1)–O(4)	180.0	O(4)–Fe(1)–O(3)#2	83.22(9)
O(1)–Fe(1)–O(3)#2	92.37(9)	O(1)–Fe(1)–O(3)#3	87.63(9)
O(1)#1–Fe(1)–O(3)#2	87.63(9)	O(1)#1–Fe(1)–O(3)#3	92.37(9)
O(4)#1–Fe(1)–O(3)#2	96.78(9)	O(4)#1–Fe(1)–O(3)#3	83.22(9)
O(4)–Fe(1)–O(3)#2	83.22(9)	O(4)–Fe(1)–O(3)#3	96.78(9)
O(1)–Fe(1)–O(3)#3	87.63(9)	O(3)#2–Fe(1)–O(3)#3	180.00(12)
O(1)#1–Fe(1)–O(3)#3	92.37(9)	O(3)–P(1)–O(1)	114.79(13)
O(4)#1–Fe(1)–O(3)#3	83.22(9)	O(3)–P(1)–O(2)	111.84(13)
O(4)–Fe(1)–O(3)#3	96.78(9)	O(1)–P(1)–O(2)	109.16(14)
O(3)#2–Fe(1)–O(3)#3	180.00(12)	O(3)–P(1)–C(1)	110.16(13)
O(1)–Fe(1)–O(1)#1	180.00(12)	O(1)–P(1)–C(1)	108.90(14)
O(1)–Fe(1)–O(4)#1	89.20(9)	O(2)–P(1)–C(1)	101.10(14)
O(1)#1-Fe(1)-O(4)#1	90.80(9)	O(4)–P(2)–O(6)	117.35(14)
O(1)–Fe(1)–O(4)	90.80(9)	O(4)–P(2)–O(5)	108.12(13)
O(1)#1–Fe(1)–O(4)	89.20(9)	O(6)–P(2)–O(5)	110.24(14)
O(4)#1–Fe(1)–O(4)	180.0	O(4)–P(2)–C(2)	112.36(14)
O(1)–Fe(1)–O(3)#2	92.37(9)	O(6)–P(2)–C(2)	100.99(15)
O(1)#1–Fe(1)–O(3)#2	87.63(9)	O(5)–P(2)–C(2)	107.26(15)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x + 2, -y, -z; #2 -x + 2, y - 1/2, -z + 1/2; #3 x, -y + 1/2, z - 1/2; #4 -x + 2, y + 1/2, -z + 1/2.

Table S3 Selected bond lengths (Å) and angles (deg) for compound **3**[a]

Zn(1)–O(2)#1	1.871(13)	P(2)–O(6)	1.487(6)
Zn(1)–O(1)#2	1.877(9)	P(2)–O(4)	1.493(6)
Zn(1)–O(3)#3	1.939(13)	P(2)–O(5)	1.572(6)
Zn(1)–O(6)	1.961(6)	P(2)–C(2)	1.840(8)
P(1)–O(2)	1.448(13)	O(1)–Zn(1)#4	1.877(9)
P(1)–O(1)	1.454(8)	O(2)–Zn(1)#5	1.871(13)
P(1)–C(1)	1.827(8)	O(3)–Zn(1)#6	1.939(13)
O(2)#1–Zn(1)–O(1)#2	117.9(5)	O(6)–P(2)–O(4)	115.8(4)
O(2)#1–Zn(1)–O(3)#3	90.5(5)	O(6)–P(2)–O(5)	110.4(4)
O(1)#2–Zn(1)–O(3)#3	127.7(5)	O(4)–P(2)–O(5)	111.2(3)
O(2)#1–Zn(1)–O(6)	110.0(4)	O(6)–P(2)–C(2)	110.4(4)
O(1)#2–Zn(1)–O(6)	105.8(3)	O(4)–P(2)–C(2)	107.1(4)
O(3)#3–Zn(1)–O(6)	103.4(4)	O(5)–P(2)–C(2)	100.9(4)
O(2)–P(1)–O(1)	114.8(7)	P(1)–O(1)–Zn(1)#4	144.9(6)
O(2)–P(1)–C(1)	107.4(6)	P(1)–O(2)–Zn(1)#5	145.4(9)
O(1)–P(1)–C(1)	104.4(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 x, -y + 1/2, z – 1/2; #2 -x + 1/2, y, z - 1/2 #3 x, y, z - 1; #4 -x + 1/2, y, z + 1/2; #5 x, -y + 1/2, z + 1/2; #6 x, y, z + 1.

Table S4 Selected bond lengths (Å) and angles (deg) for compound **4**[a]

Zn(1)–O(6)#1	1.938(3)	P(2)–O(4)	1.507(4)
Zn(1)–O(5)	2.040(3)	P(2)–O(6)	1.510(3)
Zn(1)–O(1)	2.045(3)	P(2)–O(5)	1.554(3)
Zn(1)–O(1)#2	2.076(3)	P(2)–C(2)	1.811(4)
Zn(1)–N(1)	2.195(4)	N(1)–C(1)	1.494(6)
Zn(2)–O(2)#3	1.911(3)	N(1)–C(2)	1.502(5)
Zn(2)–O(4)#1	1.926(3)	N(1)–C(3)	1.501(6)
Zn(2)–O(5)#2	1.988(3)	O(5)–Zn(2)#2	1.988(3)
Zn(2)–O(3)	1.994(3)	O(4)–Zn(2)#4	1.926(3)
P(1)–O(2)	1.509(3)	O(6)–Zn(1)#4	1.938(3)
P(1)–O(3)	1.531(3)	O(1)–Zn(1)#2	2.076(3)
P(1)–O(1)	1.531(3)	O(2)–Zn(2)#5	1.911(3)
P(1)–C(1)	1.835(5)		
O(6)#1–Zn(1)–O(5)	123.55(13)	O(4)–P(2)–O(6)	113.0(2)
O(6)#1–Zn(1)–O(1)	130.75(13)	O(4)–P(2)–O(5)	111.9(2)
O(5)–Zn(1)–O(1)	105.49(13)	O(6)–P(2)–O(5)	110.90(19)
O(6)#1–Zn(1)–O(1)#2	93.37(13)	O(4)–P(2)–C(2)	108.6(2)
O(5)–Zn(1)–O(1)#2	95.03(12)	O(6)–P(2)–C(2)	107.1(2)
O(1)–Zn(1)–O(1)#2	77.01(13)	O(5)–P(2)–C(2)	104.81(19)
O(6)#1–Zn(1)–N(1)	100.25(14)	C(1)–N(1)–C(2)	109.8(3)
O(5)–Zn(1)–N(1)	89.41(13)	C(1)–N(1)–C(3)	111.6(4)
O(1)–Zn(1)–N(1)	83.17(13)	C(2)–N(1)–C(3)	112.8(3)
O(1)#2–Zn(1)–N(1)	160.17(13)	C(1)–N(1)–Zn(1)	108.3(3)
O(2)#3–Zn(2)–O(4)#1	104.99(15)	C(2)–N(1)–Zn(1)	103.7(3)
O(2)#3–Zn(2)–O(5)#2	125.27(13)	C(3)–N(1)–Zn(1)	110.3(3)
O(4)#1–Zn(2)–O(5)#2	109.36(14)	P(2)–O(5)–Zn(2)#2	127.63(18)
O(2)#3–Zn(2)–O(3)	108.75(14)	P(2)–O(5)–Zn(1)	113.69(17)
O(4)#1–Zn(2)–O(3)	103.53(14)	Zn(2)#2–O(5)–Zn(1)	114.01(15)
O(5)#2–Zn(2)–O(3)	103.06(13)	P(1)–O(3)–Zn(2)	116.46(18)
O(2)–P(1)–O(3)	112.72(19)	P(2)–O(4)–Zn(2)#4	156.2(2)
O(2)–P(1)–O(1)	112.00(19)	P(2)–O(6)–Zn(1)#4	115.93(19)
O(3)–P(1)–O(1)	110.28(18)	P(1)–O(1)–Zn(1)	120.14(18)
O(2)–P(1)–C(1)	109.6(2)	P(1)–O(1)–Zn(1)#2	133.0(2)
O(3)–P(1)–C(1)	107.4(2)	Zn(1)–O(1)–Zn(1)#2	102.99(13)
O(1)–P(1)–C(1)	104.4(2)	P(1)–O(2)–Zn(2)#5	136.9(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 x, -y + 1/2, z + 1/2; #2 -x + 1, -y, -z + 1; #3 x, -y - 1/2, z + 1/2; #4 x, -y + 1/2, z - 1/2; #5 x, -y - 1/2, z - 1/2.