Electronic Supplementary Material (ESI) for Dalton Transactions.

Anion-Dependent Self-Assembly of Copper Coordination Polymers based on Pyrazole-3,5-dicarboxylate and 1,2-di(4-pyridyl)ethylene

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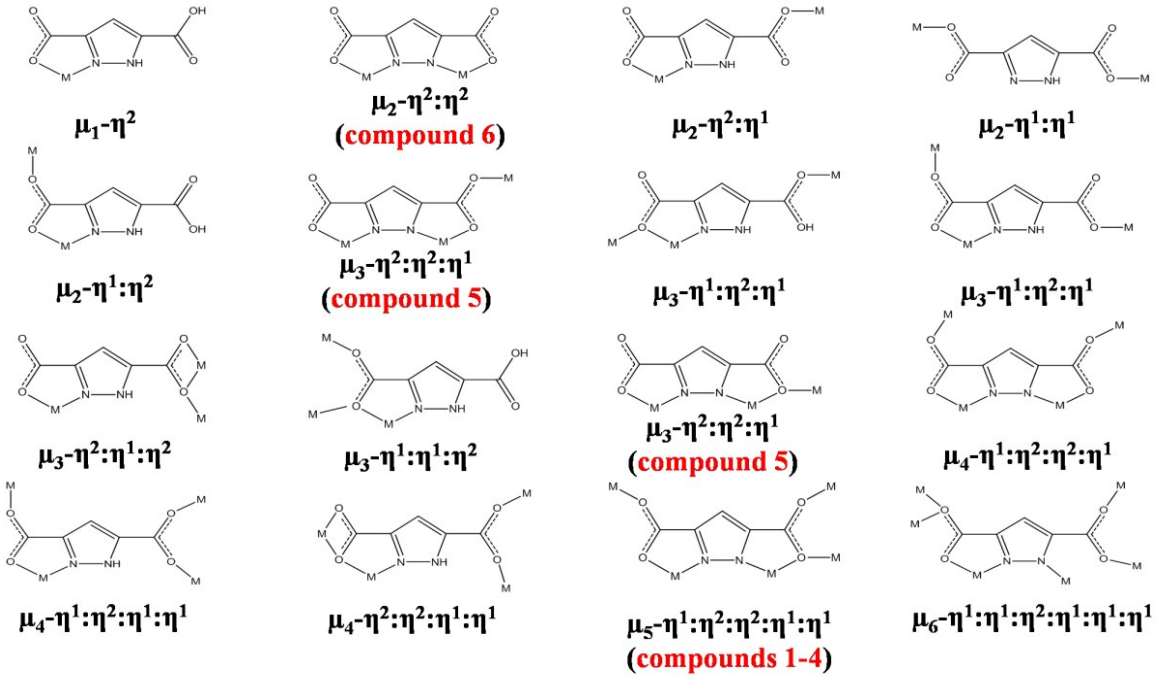

Figure S1. Diverse coordination modes of pyrazole-3,5-dicarboxylate.

Table S1. The selected bond lengths (Å) and angles (°) for compounds **1-6**.

Compound **1**[a] (100 K)			
Cu1—O1	1.949(4)	$N1^{i}$—Cu1—$N4^{ii}$	96.71(9)
Cu1—$N1^{i}$	2.019(3)	N1—Cu1—$N4^{ii}$	96.71(9)
Cu1—N1	2.019(3)	$O3^{ii}$—Cu1—$N4^{ii}$	79.75(15)
Cu1—$O3^{ii}$	2.043(4)	N3—Cu2—$O4^{iii}$	156.89(15)
Cu1—$N4^{ii}$	2.173(4)	N3—Cu2—$N2^{iv}$	92.44(9)
Cu2—N3	1.981(5)	$O4^{iii}$—Cu2—$N2^{iv}$	89.23(9)
Cu2—$O4^{iii}$	1.990(4)	N3—Cu2—$N2^{v}$	92.44(9)
Cu2—$N2^{iv}$	2.025(3)	$O4^{iii}$—Cu2—$N2^{v}$	89.23(9)
Cu2—$N2^{v}$	2.025(3)	$N2^{iv}$—Cu2—$N2^{v}$	171.00(18)
Cu2—$O2^{vi}$	2.305(4)	N3—Cu2—$O2^{vi}$	88.30(16)
Cu2—O1	2.425(4)	$O4^{iii}$—Cu2—$O2^{vi}$	114.81(14)
O1—Cu1—$N1^{i}$	90.44(9)	$N2^{iv}$—Cu2—$O2^{vi}$	86.30(9)
O1—Cu1—N1	90.44(9)	$N2^{v}$—Cu2—$O2^{vi}$	86.30(9)
$N1^{i}$—Cu1—N1	164.79(18)	N3—Cu2—O1	74.38(15)
O1—Cu1—$O3^{ii}$	165.54(14)	$O4^{iii}$—Cu2—O1	82.51(13)
$N1^{i}$—Cu1—$O3^{ii}$	87.68(9)	$N2^{iv}$—Cu2—O1	94.30(9)
N1—Cu1—$O3^{ii}$	87.68(9)	$N2^{v}$—Cu2—O1	94.30(9)
O1—Cu1—$N4^{ii}$	114.71(16)	$O2^{vi}$—Cu2—O1	162.68(14)
Compound **2**[b]			
Cu1—O1	1.957(7)	$N4^{i}$—Cu1—$N2^{iii}$	96.7(2)
Cu1—$N4^{i}$	2.003(6)	$N4^{ii}$—Cu1—$N2^{iii}$	96.7(2)
Cu1—$N4^{ii}$	2.003(6)	$O3^{iii}$—Cu1—$N2^{iii}$	78.7(3)
Cu1—$O3^{iii}$	2.121(8)	N1—Cu2—N3	93.87(19)
Cu1—$N2^{iii}$	2.157(9)	N1—Cu2—$N3^{iv}$	93.87(19)
Cu2—N1	2.008(8)	N3—Cu2—$N3^{iv}$	165.9(4)
Cu2—N3	2.008(6)	N1—Cu2—$O4^{v}$	156.4(3)
Cu2—$N3^{iv}$	2.008(6)	N3—Cu2—$O4^{v}$	88.79(19)
Cu2—O1	2.492(8)	$N3^{iv}$—Cu2—$O4^{v}$	88.79(19)
Cu2—O2	2.504(8)	$N3^{iv}$—Cu2—O2	84.29(19)
Cu2—$O4^{v}$	2.030(8)	N3—Cu2—O2	84.29(19)
O1—Cu1—$N4^{i}$	89.2(2)	$N3^{iv}$—Cu2—O1	96.74(18)
O1—Cu1—$N4^{ii}$	89.2(2)	N3—Cu2—O1	96.74(18)
$N4^{i}$—Cu1—$N4^{ii}$	164.8(4)	O1—Cu2—O2	160.76(26)
O1—Cu1—$O3^{iii}$	157.6(3)	O1—Cu2—N1	72.83(28)
$N4^{i}$—Cu1—$O3^{iii}$	87.9(2)	O2—Cu2—N1	87.93(30)
$N4^{ii}$—Cu1—$O3^{iii}$	87.9(2)	O1—Cu2—$O4^{v}$	83.61(27)
O1—Cu1—$N2^{iii}$	123.7(3)	O2—Cu2—$O4^{v}$	115.63(29)
Compound **3**[c]			
Cu1—O1	1.954(5)	N1—Cu1—$N4^{ii}$	96.82(15)
Cu1—N1	2.008(4)	$N1^{i}$—Cu1—$N4^{ii}$	96.82(15)
Cu1—$N1^{i}$	2.008(4)	$O4^{ii}$—Cu1—$N4^{ii}$	78.9(2)
Cu1—$O4^{ii}$	2.094(5)	$N3^{iii}$—Cu2—$N2^{iv}$	93.64(13)
Cu1—$N4^{ii}$	2.167(6)	$N3^{iii}$—Cu2—$N2^{v}$	93.64(13)
Cu2—$N3^{iii}$	1.996(6)	$N2^{iv}$—Cu2—$N2^{v}$	167.4(3)
Cu2—$N2^{iv}$	2.014(4)	$N3^{iii}$—Cu2—O3	156.6(2)
Cu2—$N2^{v}$	2.014(4)	$N2^{iv}$—Cu2—O3	88.70(13)
Cu2—O1	2.473(5)	$N2^{v}$—Cu2—O3	88.70(13)
Cu2—O2	2.464(5)	$N2^{v}$—Cu2—O1	95.95(15)
Cu2—O3	2.027(5)	$N2^{iv}$—Cu2—O1	95.95(15)
O1—Cu1—N1	89.32(14)	$N2^{v}$—Cu2—O2	84.99(14)
O1—Cu1—$N1^{i}$	89.32(14)	$N2^{iv}$—Cu2—O2	84.99(14)
N1—Cu1—$N1^{i}$	164.7(3)	$N3^{iii}$—Cu2—O1	73.24(19)
O1—Cu1—$O4^{ii}$	159.2(2)	$N3^{iii}$—Cu2—O2	88.31(20)
N1—Cu1—$O4^{ii}$	87.93(14)	O1—Cu2—O3	83.32(19)
$N1^{i}$—Cu1—$O4^{ii}$	87.93(14)	O2—Cu2—O3	115.12(20)
$N1^{i}$—Cu1—N2	99.13(15)	O1—Cu2—O2	161.55(17)
O1—Cu1—$N4^{ii}$	121.9(2)		

Table S1. The selected bond lengths (Å) and angles (°) for compounds **1-6**. (Cont.)

Compound **4**[d]			
Cu1—O1	1.959(6)	$N1^{i}$—Cu1—$N4^{ii}$	96.80(18)
Cu1—$N1^{i}$	2.002(5)	N1—Cu1—$N4^{ii}$	96.80(18)
Cu1—N1	2.002(5)	$O4^{ii}$—Cu1—$N4^{ii}$	78.6(3)
Cu1—$O4^{ii}$	2.073(7)	O3—Cu2—$N3^{iii}$	157.6(3)
Cu1—$N4^{ii}$	2.163(8)	O3—Cu2—$N2^{iv}$	88.55(16)
Cu2—O1	2.462(6)	$N3^{iii}$—Cu2—$N2^{iv}$	93.42(16)
Cu2—O2	2.452(6)	O3—Cu2—$N2^{v}$	88.55(16)
Cu2—O3	1.984(6)	$N3^{iii}$—Cu2—$N2^{v}$	93.42(16)
Cu2—$N3^{iii}$	2.003(7)	$N2^{iv}$—Cu2—$N2^{v}$	168.7(3)
Cu2—$N2^{iv}$	2.017(5)	O1—Cu2—$N2^{iv}$	95.27(18)
Cu2—$N2^{v}$	2.017(5)	O1—Cu2—$N2^{v}$	95.27(18)
O1—Cu1—$N1^{i}$	89.32(17)	O2—Cu2—$N2^{iv}$	85.60(18)
O1—Cu1—N1	89.32(17)	O2—Cu2—$N2^{v}$	85.60(18)
$N1^{i}$—Cu1—N1	164.8(4)	O1—Cu2—O2	162.22(22)
O1—Cu1—$O4^{ii}$	159.9(3)	O1—Cu2— $N3^{iii}$	73.45(26)
$N1^{i}$—Cu1—$O4^{ii}$	88.05(17)	O2—Cu2— $N3^{iii}$	88.77(28)
N1—Cu1—$O4^{ii}$	88.05(17)	O1—Cu2—O3	84.11(23)
O1—Cu1—$N4^{ii}$	121.4(3)	O2—Cu2—O3	113.67(25)
Compound **5**[e]			
Cu1—N1	1.929(4)	N1—Cu1—O5	162.55(16)
Cu1—N3	1.921(4)	O1—Cu1—O5	101.38(15)
Cu1—N9	2.250(4)	N3—Cu1—N9	97.46(16)
Cu1—O1	2.010(3)	N1—Cu1—N9	96.56(17)
Cu1—O5	2.030(3)	O1—Cu1—N9	100.99(15)
Cu2—N2	1.934(4)	O5—Cu1—N9	100.32(15)
Cu2—N4	1.931(4)	N2—Cu2—N4	93.22(18)
Cu2—N11	2.264(4)	N2—Cu2—O3	80.03(16)
Cu2—O3	1.997(3)	N4—Cu2—O3	163.56(16)
Cu2—O7	2.012(4)	N2—Cu2—O7	160.62(16)
Cu3—N5	1.923(4)	N4—Cu2—O7	79.80(17)
Cu3—N7	1.938(4)	O3—Cu2—O7	101.69(15)
Cu3—N12	2.246(4)	N2—Cu2—N11	95.72(17)
Cu3—O9	2.048(4)	N4—Cu2—N11	97.09(17)
Cu3—O13	1.974(4)	O3—Cu2—N11	98.48(15)
Cu4—N6	1.934(4)	O7—Cu2—N11	103.04(16)
Cu4—N8	1.931(4)	N5—Cu3—N7	93.37(19)
Cu4—N10	2.246(4)	N5—Cu3—O13	161.58(16)
Cu4—O11	2.006(4)	N7—Cu3—O13	80.59(17)
Cu4—O15	2.016(4)	N5—Cu3—O9	79.57(17)
Cu5—N13	1.930(4)	N7—Cu3—O9	159.98(15)
Cu5—$N14^{i}$	1.926(4)	O13—Cu3—O9	100.23(15)
Cu5—O2	2.227(4)	N5—Cu3—N12	96.49(17)
Cu6—N15	1.912(4)	N7—Cu3—N12	96.80(17)
Cu6—$N16^{ii}$	1.911(4)	O13—Cu3—N12	101.48(16)
Cu6—O6	2.293(4)	O9—Cu3—N12	102.57(15)
Cu7—N17	1.923(4)	N8—Cu4—N6	93.29(19)
Cu7—$N18^{i}$	1.935(4)	N8—Cu4—O11	161.98(16)
Cu7—O16	2.201(4)	N6—Cu4—O11	80.08(17)
Cu8—N19	1.905(4)	N8—Cu4—O15	79.55(16)
Cu8—$N20^{iii}$	1.901(4)	N6—Cu4—O15	160.97(16)
Cu8—O9	2.345(4)	O11—Cu4—O15	101.36(15)
N3—Cu1—N1	93.62(18)	N8—Cu4—N10	97.52(17)
N3—Cu1—O1	160.93(16)	N6—Cu4—N10	98.42(17)
N1—Cu1—O1	79.56(16)	O11—Cu4—N10	100.01(16)
N3—Cu1—O5	79.87(16)	O15—Cu4—N10	99.98(15)

Table S1. The selected bond lengths (Å) and angles (°) for compounds **1-6**. (Cont.)

Compound **5**[e]			
N14^{i}—Cu5—N13	150.46(19)	N17—Cu7—N18^{i}	150.51(19)
N14^{i}—Cu5—O2	106.54(16)	N17—Cu7—O16	106.83(16)
N13—Cu5—O2	102.73(17)	N18^{i}—Cu7—O16	102.36(16)
N15—Cu6—N16^{ii}	155.1(2)	N20^{iii}—Cu8—N19	156.7(2)
N15—Cu6—O6	99.57(17)	N20^{iii}—Cu8—O9	99.66(16)
N16^{ii}—Cu6—O6	104.70(17)	N19—Cu8—O9	103.40(16)
Compound **6**[f]			
Cu1—O5	1.957(2)	O1—Cu1—N3	88.78(12)
Cu1—N1	1.968(3)	O5—Cu1—O5^{i}	79.52(10)
Cu1—O1	1.991(3)	N1—Cu1—O5^{i}	101.82(11)
Cu1—N3	2.010(3)	O1—Cu1—O5^{i}	103.29(11)
Cu1—O5^{i}	2.382(2)	N3—Cu1—O5^{i}	89.64(11)
Cu2—O6	1.898(3)	O6—Cu2—O3	164.58(12)
Cu2—O3	1.944(3)	O6—Cu2—N2	95.87(12)
Cu2—N2	1.948(3)	O3—Cu2—N2	82.49(12)
Cu2—N5	2.011(3)	O6—Cu2—N5	94.75(15)
Cu3—O7^{ii}	1.890(3)	O3—Cu2—N5	88.87(15)
Cu3—O7	1.890(3)	N2—Cu2—N5	167.75(15)
Cu3—N4	2.029(3)	O7^{ii}—Cu3—O7	180
Cu3—N4^{ii}	2.029(3)	O7^{ii}—Cu3—N4	92.79(12)
O5—Cu1—N1	95.01(10)	O7—Cu3—N4	87.21(12)
O5—Cu1—O1	175.05(11)	O7^{ii}—Cu3—N4^{ii}	87.21(12)
N1—Cu1—O1	80.46(11)	O7—Cu3—N4^{ii}	92.79(12)
O5—Cu1—N3	95.35(12)	N4—Cu3—N4^{ii}	180
N1—Cu1—N3	165.77(12)		

[a]Symmetry codes for **1**: (i) *x*, 0.5-*y*, *z*; (ii) -0.5+*x*, *y*, 0.5-*z*; (iii) *x*, *y*, 1+*z*; (iv) 1-*x*, 1-*y*, 1-*z*; (v) 1-*x*, -0.5+*y*, 1-*z*; (vi) 0.5+*x*, *y*, 0.5-*z*. [b]For **2**: (i) 1-*x*, -0.5+*y*, -*z*; (ii) 1-*x*, 1-*y*, -*z*; (iii) -0.5+*x*, *y*, 0.5-*z*; (iv) *x*, 0.5-*y*, *z*; (v) *x*, *y*, -1+*z*. [c]For **3**: (i) *x*, 1.5-*y*, *z*; (ii) 0.5+*x*, *y*, 0.5-*z*; (iii) *x*, *y*, 1+*z*; (iv) 1-*x*, 1-*y*, 1-*z*; (v) 1-*x*, 0.5+*y*, 1-*z*. [d]For **4**: (i) *x*, 0.5-*y*, *z*; (ii) -0.5+*x*, *y*, 1.5-*z*; (iii) *x*, *y*, 1+*z*; (iv) 2-*x*, 1-*y*, 2-*z*; (v) 2-*x*, -0.5+*y*, 2-*z*. [e]For **5**: (i) -0.5+*x*, 0.5-*y*, -0.5+*z*; (ii) 0.5+*x*, 0.5-*y*, 0.5+*z*; (iii) 0.5+x, 1.5-y, 0.5+z. [f]For **6**: (i) -*x*, 2-*y*, 1-*z*; (ii) -*x*, 1-*y*, 1-*z*.

Table S2. Intermolecular hydrogen bond length/Å angles/° in compounds **1-4**.

		Compound **1**[a]		
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
C2−H2···O6	0.95	2.56	3.279(16)	133
C2−H2···O7^{i}	0.95	2.59	3.406(17)	144
C6−H6···O5	0.95	2.30	3.241(9)	169
C7−H7···O5^{ii}	0.95	2.35	2.943(9)	120
C9−H9···O5	0.95	2.44	3.383(10)	173
C9−H9···O6^{i}	0.95	2.49	3.269(16)	140
		Compound **2**[b]		
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
C9−H9···O5^{i}	0.93	2.49	3.22(4)	135
C11−H11···O6^{ii}	0.93	2.04	2.93(2)	160
C12−H12···O7^{i}	0.93	2.33	3.25(2)	169
C14−H14···O6^{ii}	0.93	2.53	3.35(4)	147
C16−H16···O8^{i}	0.93	2.55	3.26(4)	133
		Compound **3**[c]		
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
C2−H2···F2^{i}	0.93	2.52	3.364(18)	151
C6−H6···F4	0.93	2.22	3.134(14)	169
C6−H6···F2^{ii}	0.93	2.38	2.846(14)	111
C7−H7···F2^{iii}	0.93	2.12	3.009(15)	159
C11−H11···F4	0.93	2.50	3.421(14)	169
		Compound **4**[d]		
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
C6−H6···S1	0.93	2.78	3.610(19)	150

[a]Symmetry codes for **1**: (i) 1-x, 1-y, 2-z; (ii) -0.5+x, y, 1.5-z. [b]For **2**: (i) 1-x, 1-y, 1-z; (ii) 1.5-x, 1-y, -0.5+z. [c]For **3**: (i) 0.5+x, y, 0.5-z; (ii) 1-x, 1-y, -z; (iii) 0.5+x, y, 0.5-z.

Bond Valence Sum (BVS) Studies. The BVS analysis was performed according to the following equations:

$$\mathrm{BVS} = \sum_{i=1}^{n} s_i$$

$$s_i = \exp[(r_0 - r)/0.37]$$

Where r is the experimentally derived bond length for ligand, i and r_0 is a parameter characteristic of the bond, which is a calculated value depending on the geometry and coordination number of the complex. The r_0 values were taken from the literature.[1-3] The values used for r_0 include the Cu(I)–N = 1.571, Cu(I)–O = 1.567, Cu(II)–N = 1.713, and Cu(II)–O = 1.655 Å.

References

1. I. D. Brown and D. Altermatt, *Acta Cryst.*, 1985, **B41**, 244-247.
2. I. D. BROWN, *Acta Cryst.*, 1992, **B48**, 553-572.

3. G. P. Shields, P. R. Raithby, F. H. Allen and W. D. S. Motherwell, *Acta Crystallogr.*, 2000, **B56**, 455-465.

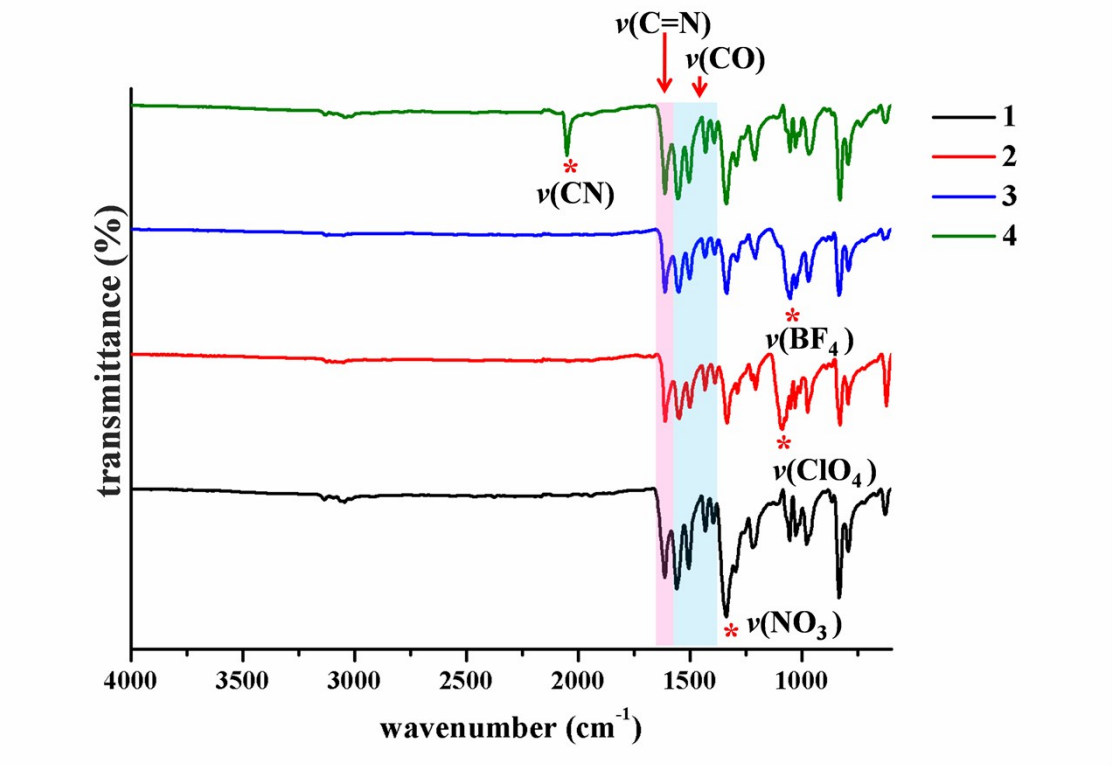

Figure S2. IR spectra of compounds **1-4**.

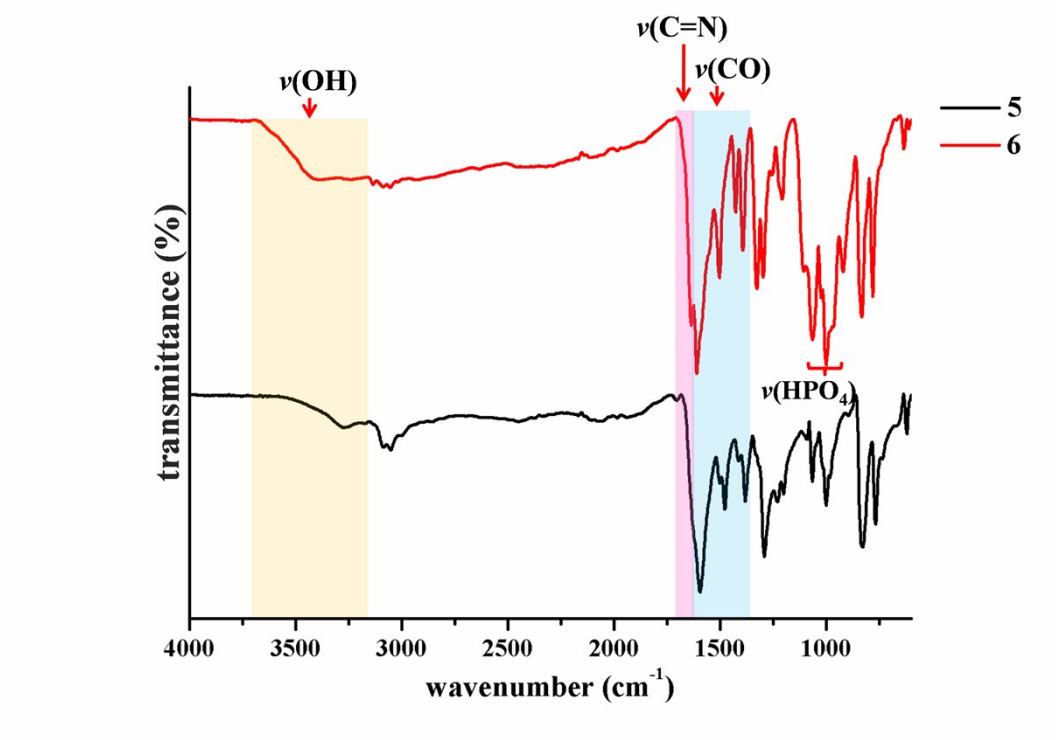

Figure S3. IR spectra of **5** and **6**.

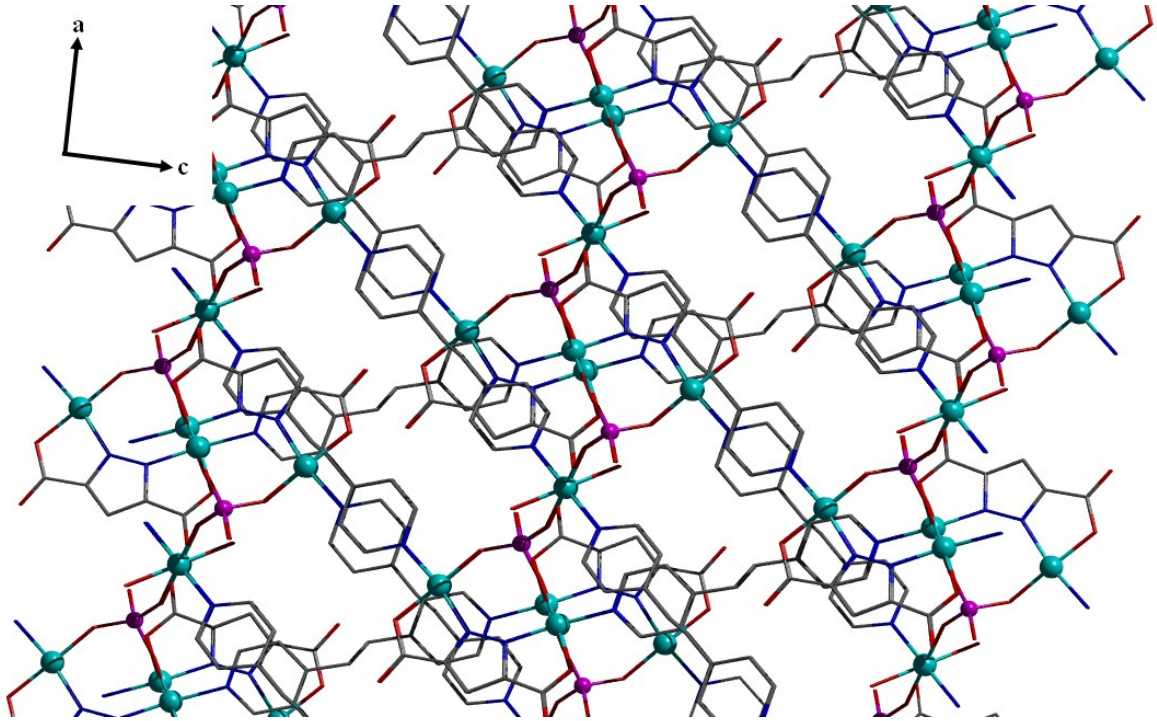

Figure S4. 3D coordination framework of **6** in *ac* crystallographic plane.

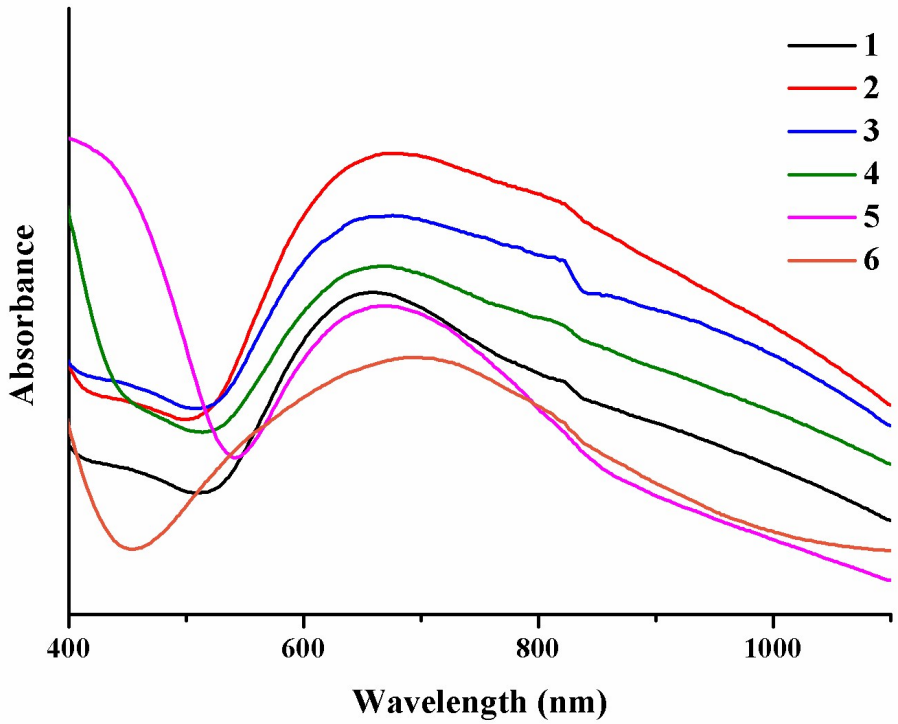

Figure S5. The electronic spectra of **1**-**6**.

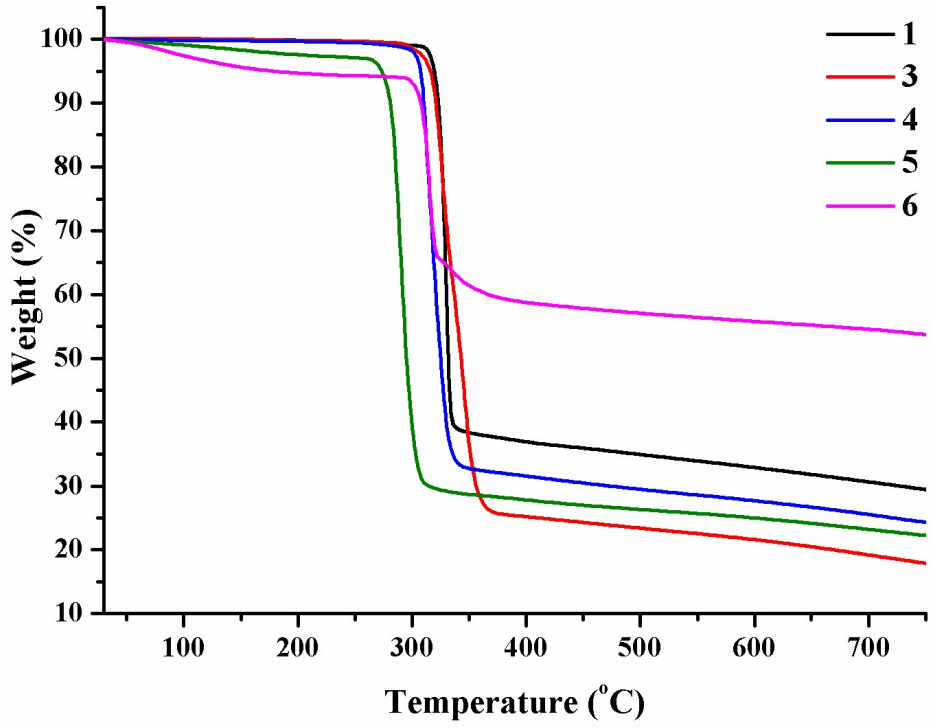

Figure S6. TGA curves of compounds **1** and **3**-**6**.

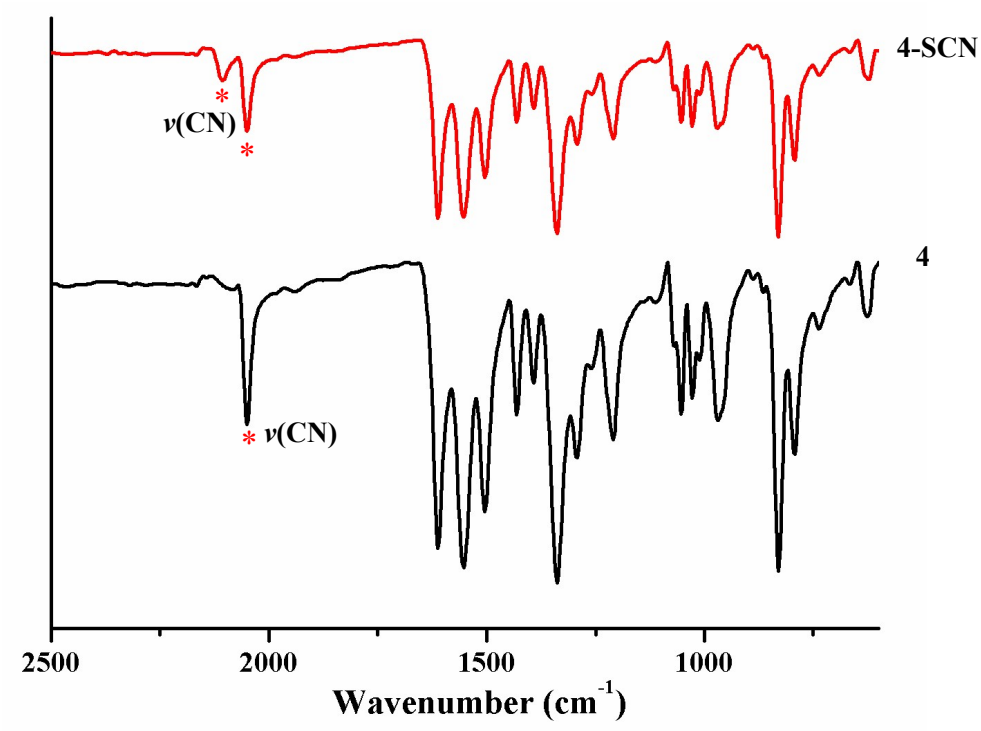

Figure S7. IR spectra of SCN^- chemisorption of compound **4**.

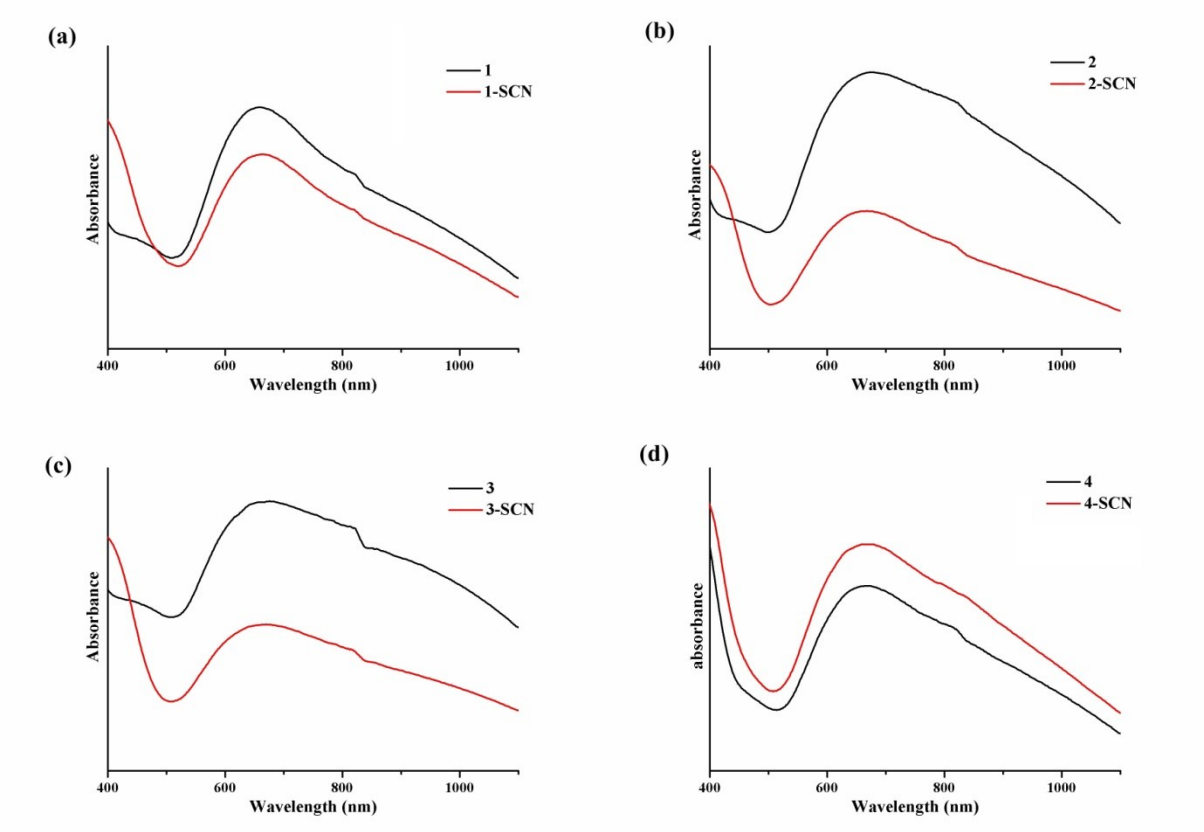

Figure S8. UV-Vis spectra of the anion exchange products with SCN^- anion.

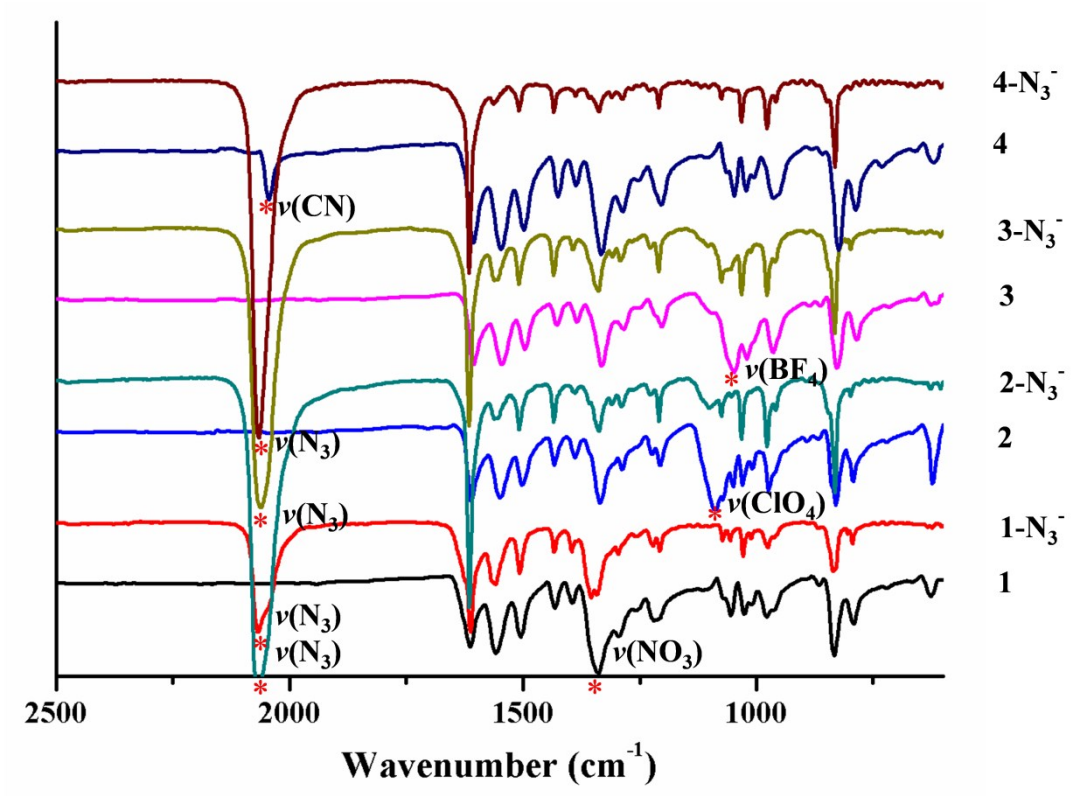

Figure S9. IR spectra of the anion exchange product with N_3^- anion.

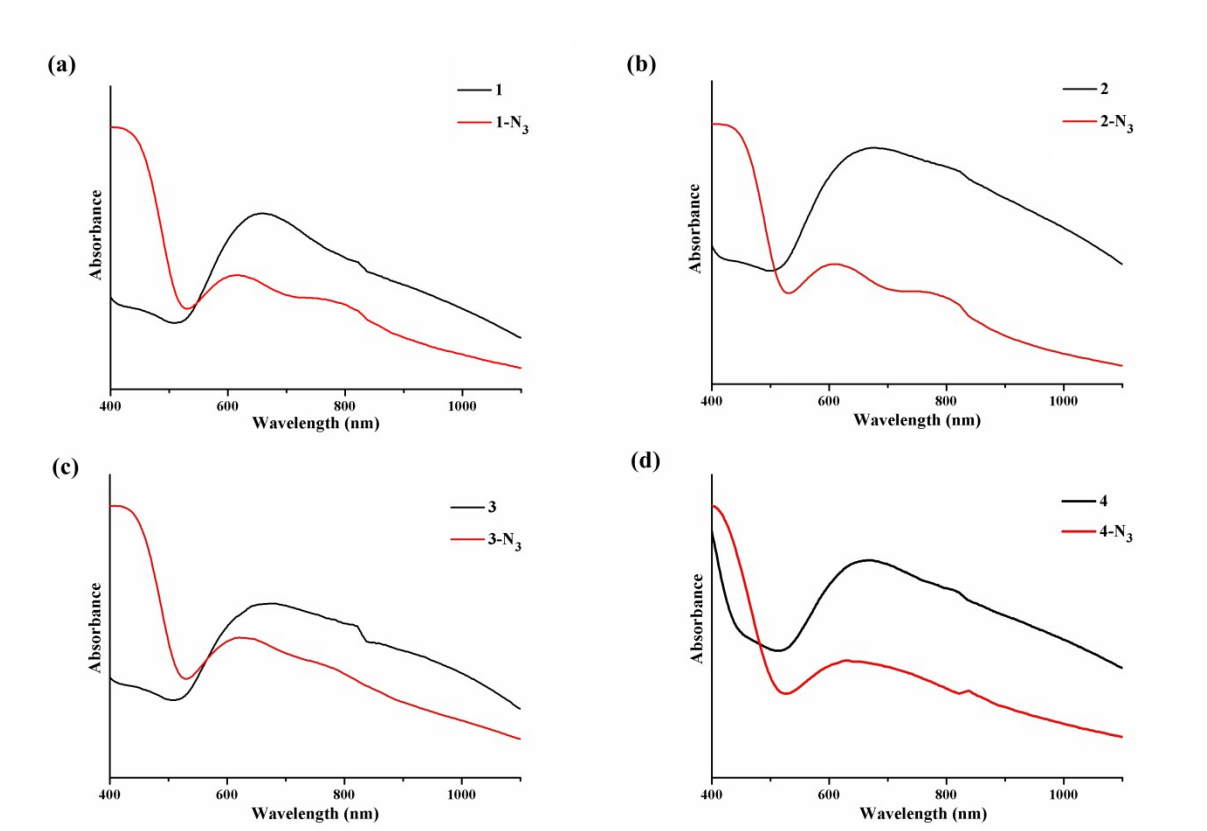

Figure S10. UV-Vis spectra of the anion exchange products with N_3^- anion.

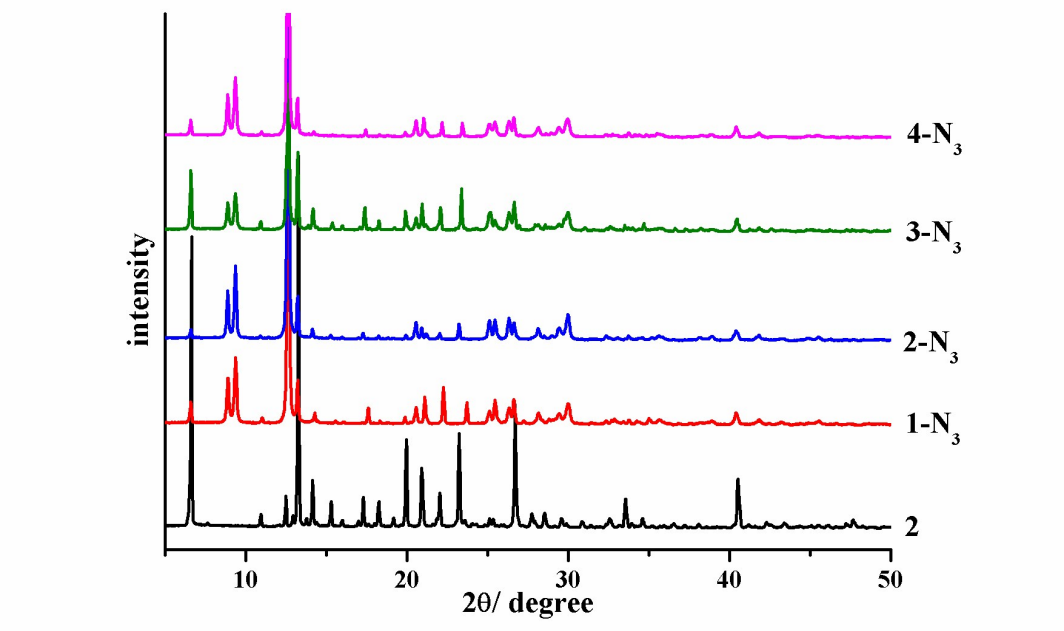

Figure S11. PXRD patterns of the anion exchange products with N_3^- anion.

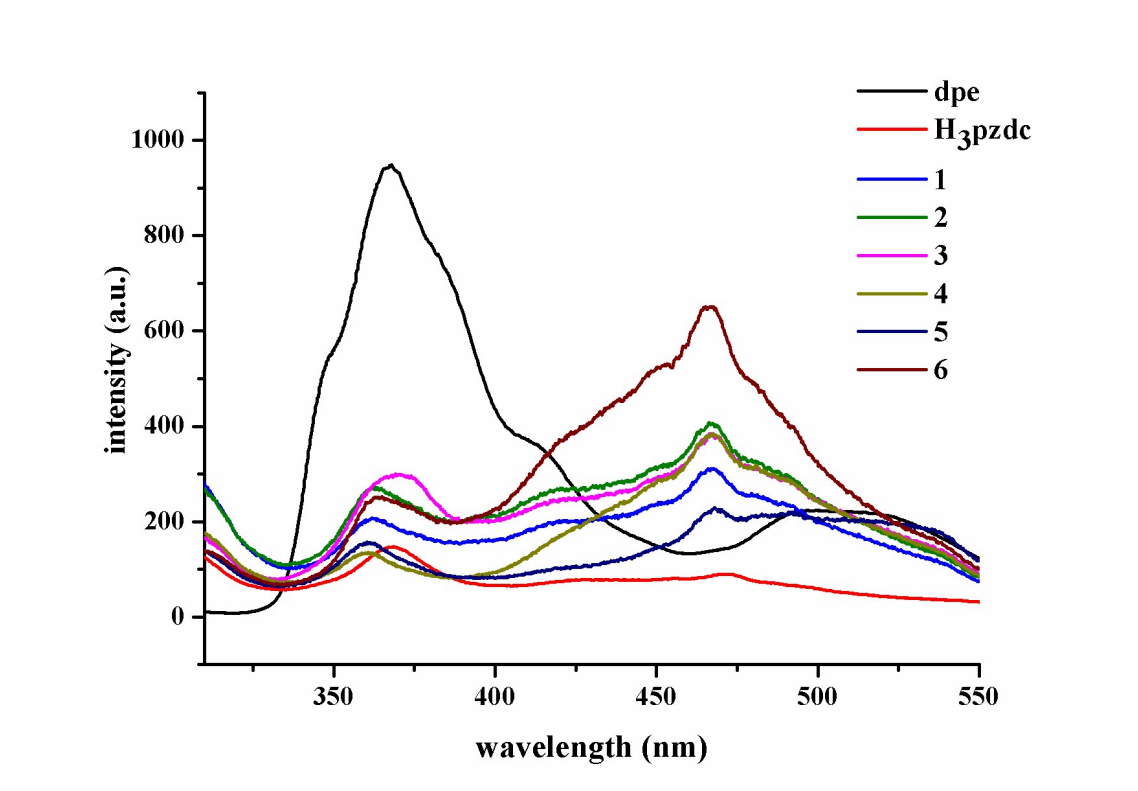

Figure S12. The emission spectra of compounds **1-6**, H_3pzdc, and dpe ligands.

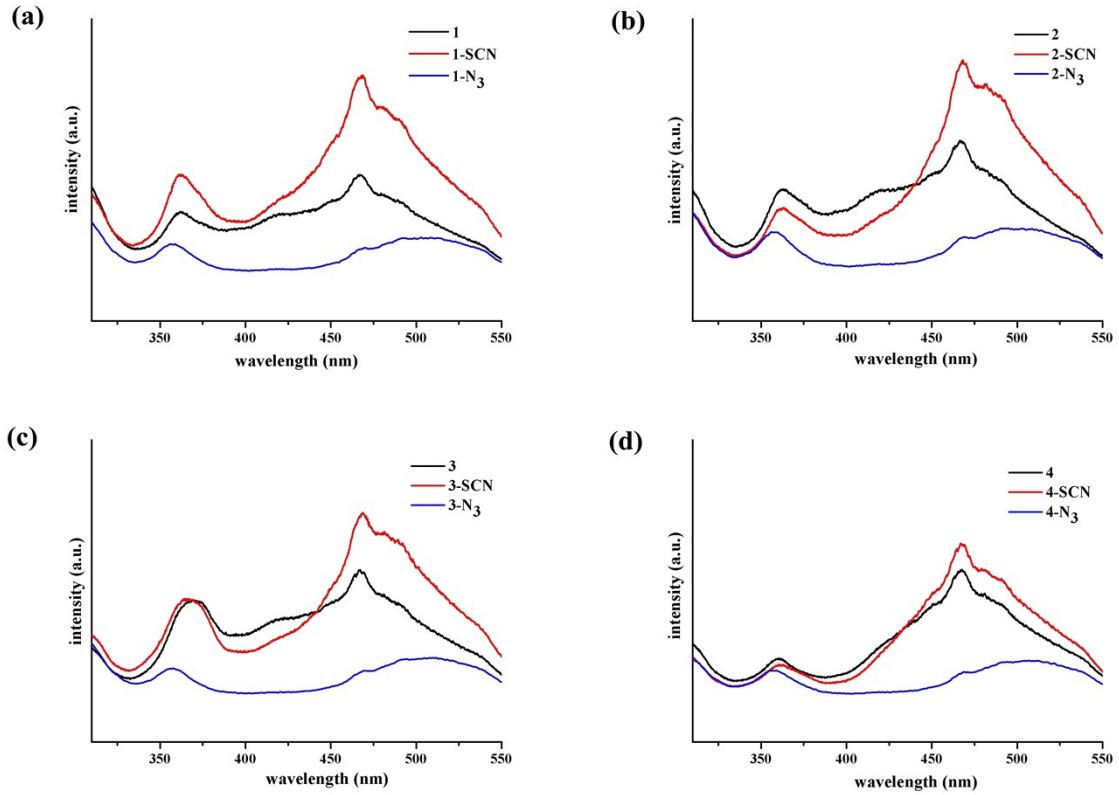

Figure S13. The emission spectra of compounds **1-4** , **1-4-SCN**, and **1-4-N_3**.