Supporting Information

New complexes constructed from *in situ* nitration of (1*H*-tetrazol-5-yl)phenol: synthesis, structures and properties

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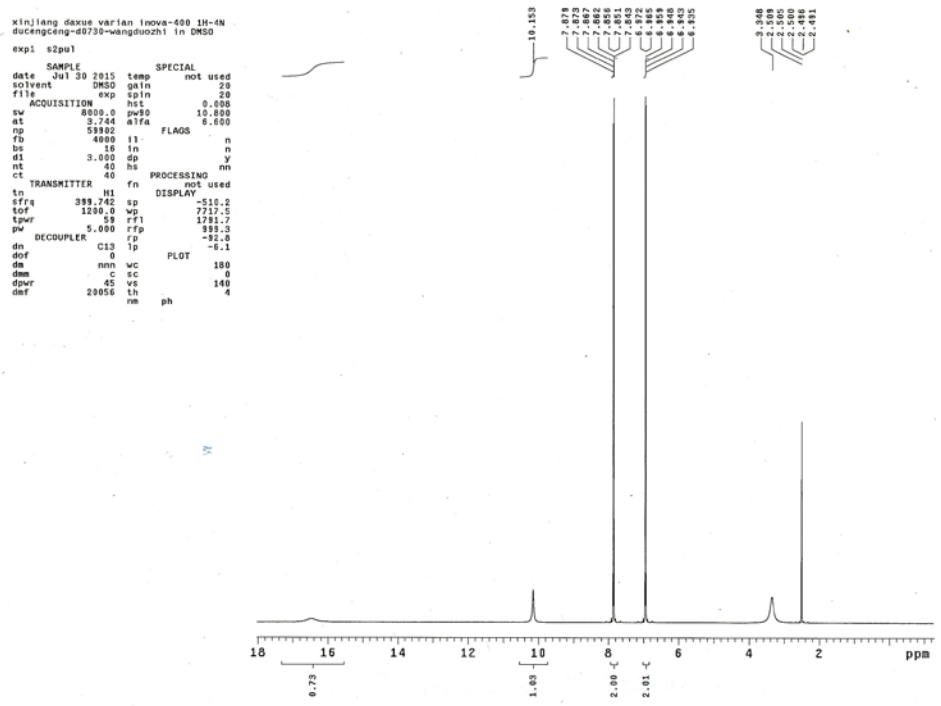
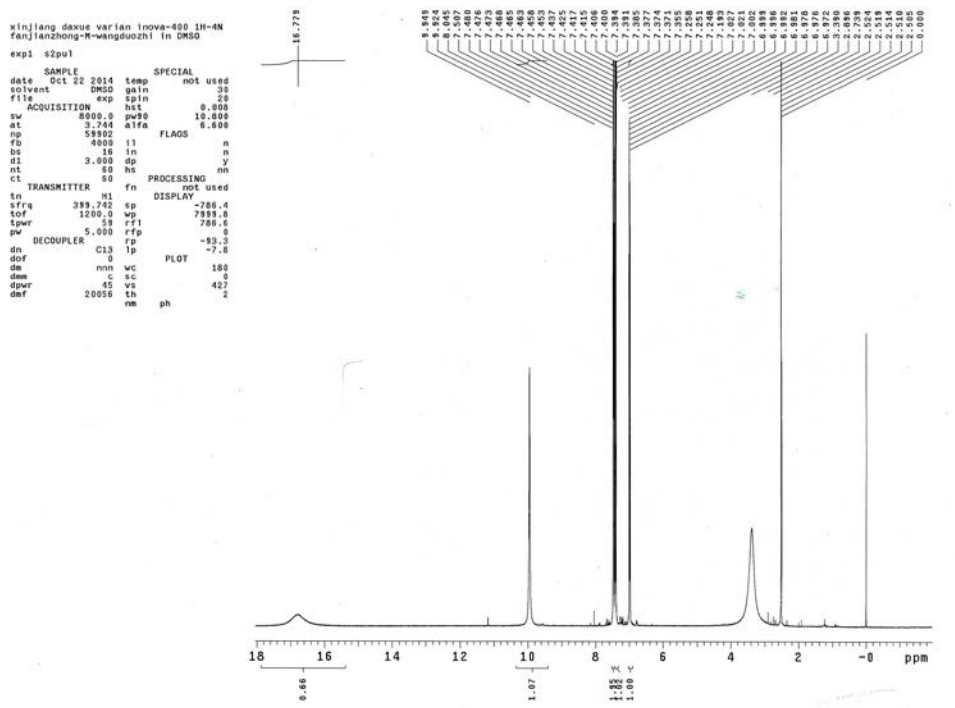
^{1}H NMR spectra for 4-(1*H*-tetrazol-5-yl)phenol

^{1}H NMR (400 MHz, DMSO) δ 16.48 (s, 1H), 10.15 (s, 1H), 7.88-7.84 (m, 2H), 6.97-6.94 (m, 2H).



^{1}H NMR spectra for 3-(1*H*-tetrazol-5-yl)phenol

^{1}H NMR (400 MHz, DMSO) δ 16.78 (s, 1H), 9.95 (s, 1H), 7.49–7.45 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.00–6.97 (m, 1H).



^{1}H NMR spectra for 2-(1*H*-tetrazol-5-yl)phenol

^{1}H NMR (400 MHz, DMSO) δ 15.92 (s, 1H), 10.94 (s, 1H), 8.00–7.98 (m, 1H), 7.43-7.40 (m, 1H), , 7.07 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.02-6.98 (m, 1H)

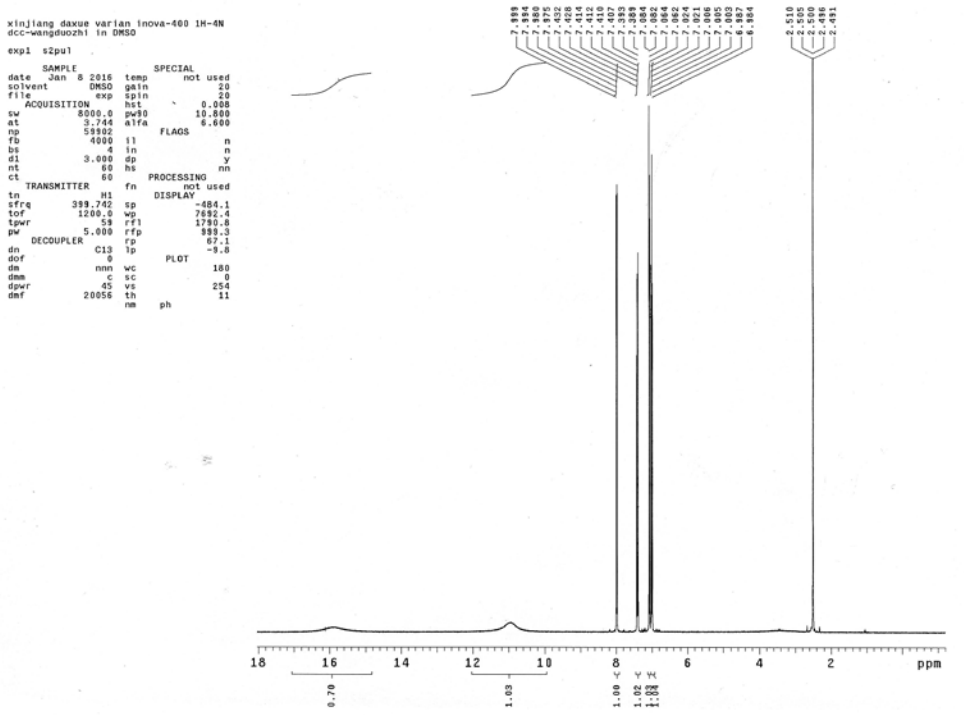
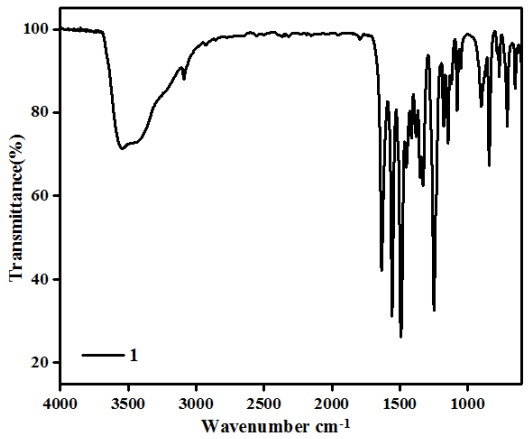
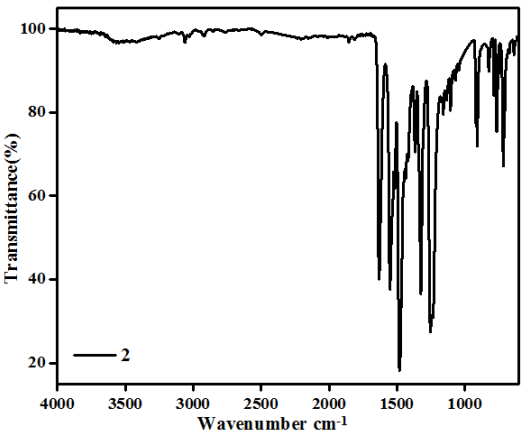


Fig. S1.^{1}H NMR spectra for three precursors ligands


Transmittance(%)
Wavenumber cm-1
1


Transmittance(%)
Wavenumber cm-1
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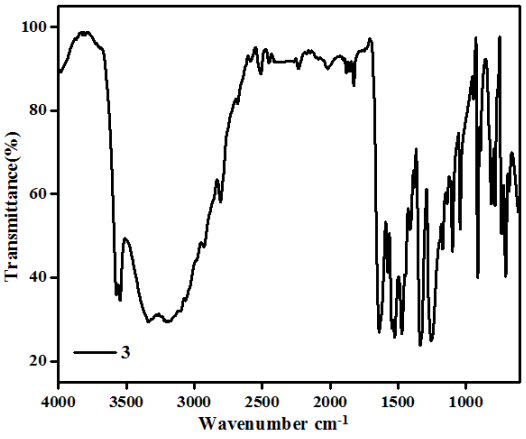
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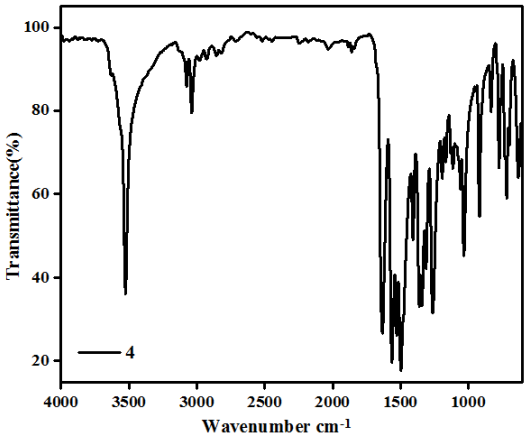
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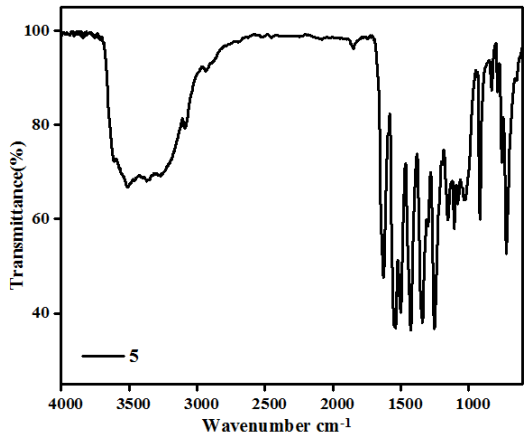
4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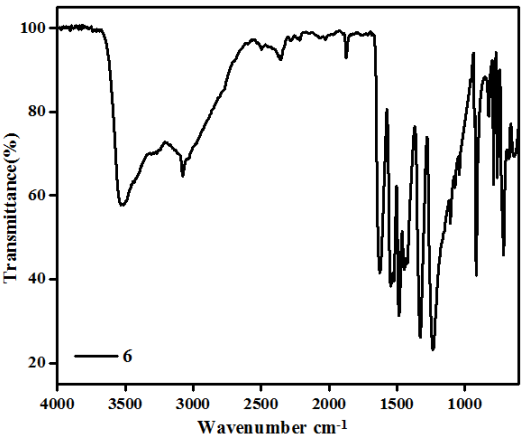
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Wavenumber cm-1
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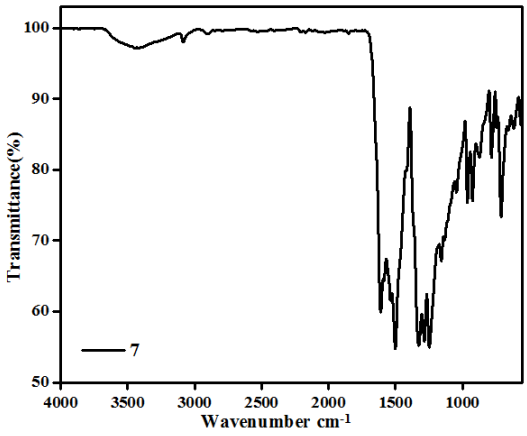
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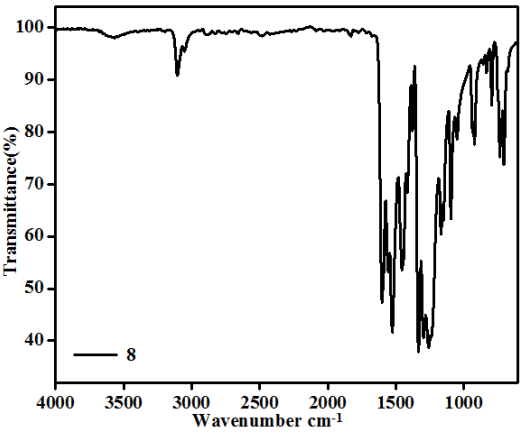
Wavenumber cm-1
7


Transmittance(%)
Wavenumber cm-1
8

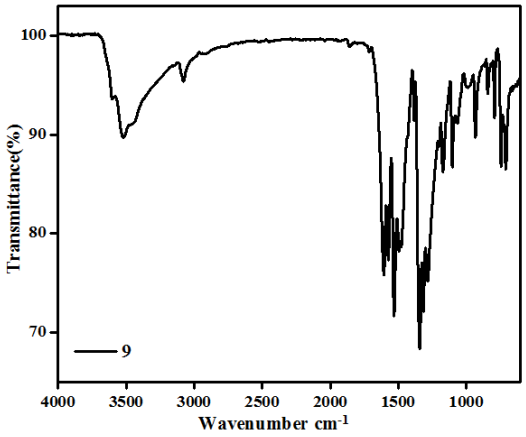


Fig. S2. FT-IR spectra of **1-9**.

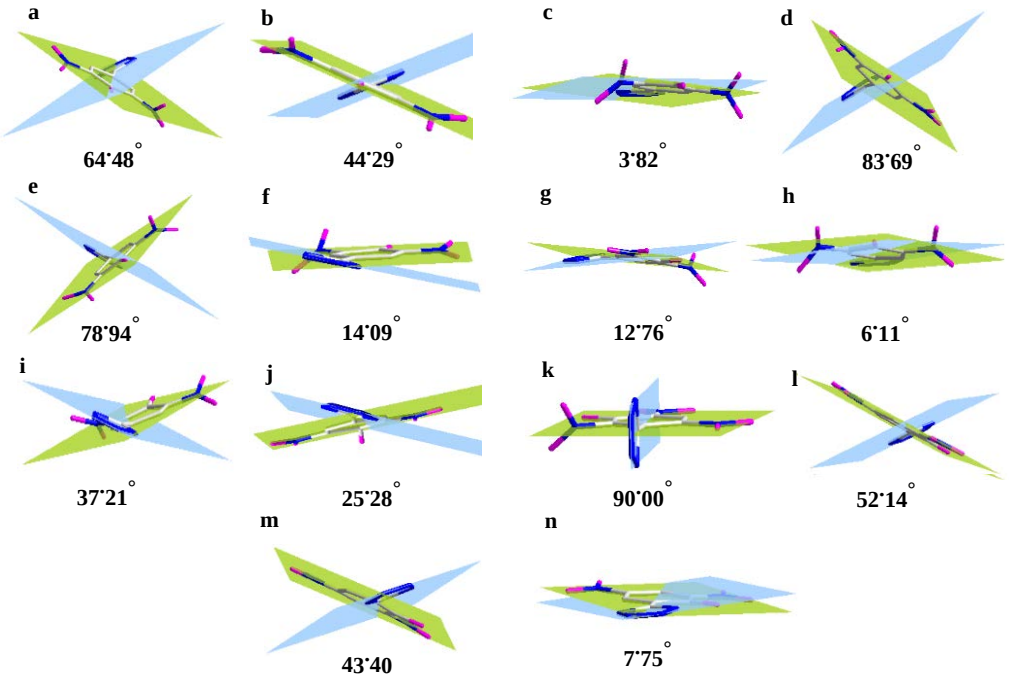
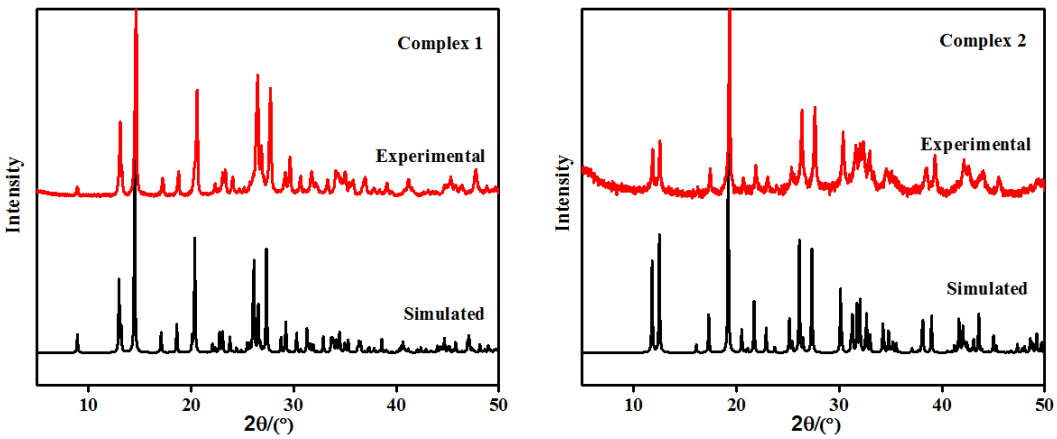
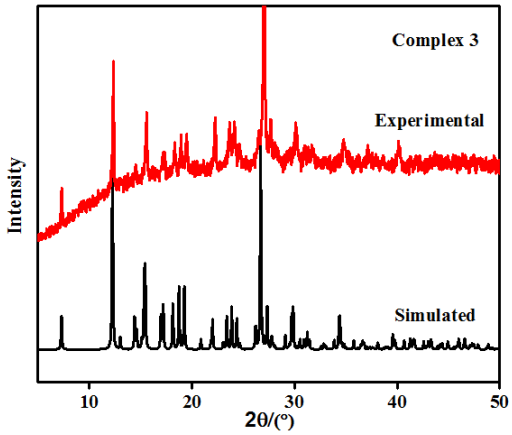
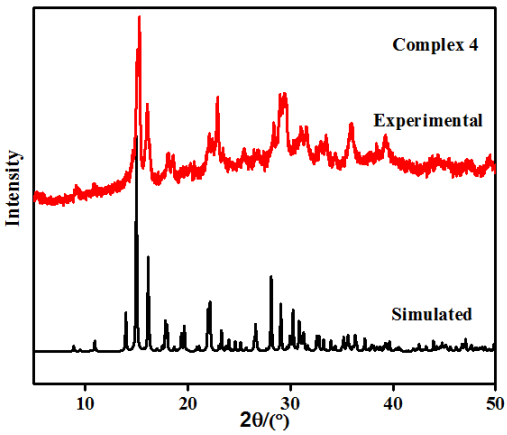


Fig. S3. The dihedral angles between the tetrazole ring and the benzene ring in the ligand.




Complex 3
Experimental
Simulated
Intensity
10
20
30
40
50
2θ/(°)


Complex 4
Experimental
Simulated
Intensity
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30
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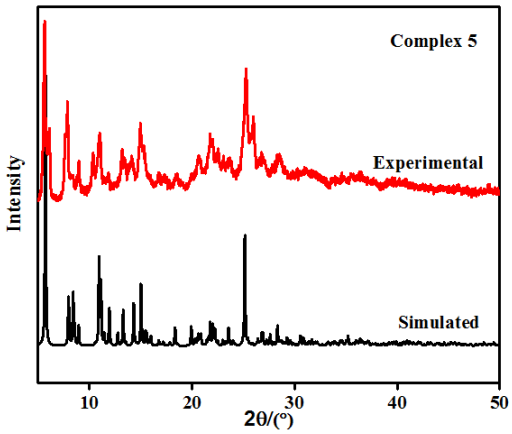
50
2θ/(°)


Complex 5
Experimental
Simulated
Intensity
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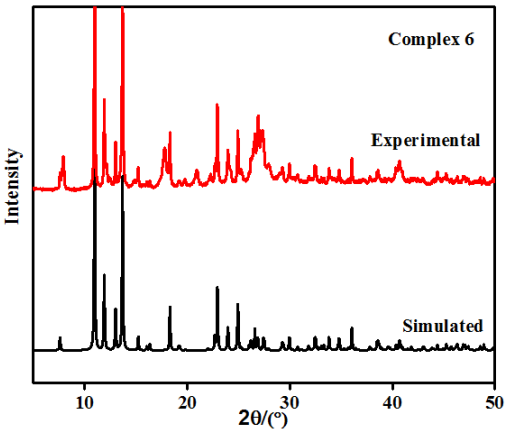
50
2θ/(°)


Complex 6
Experimental
Simulated
Intensity
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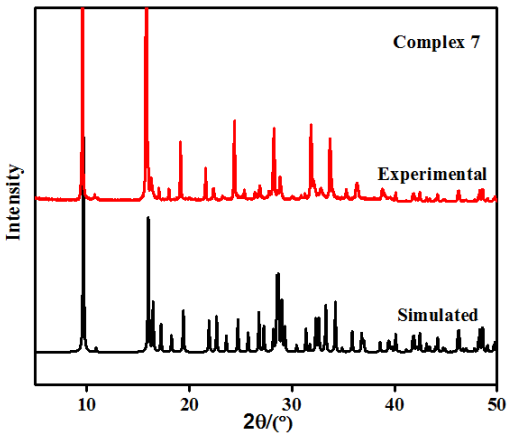
40
50
2θ/(°)


Complex 7
Experimental
Simulated
Intensity
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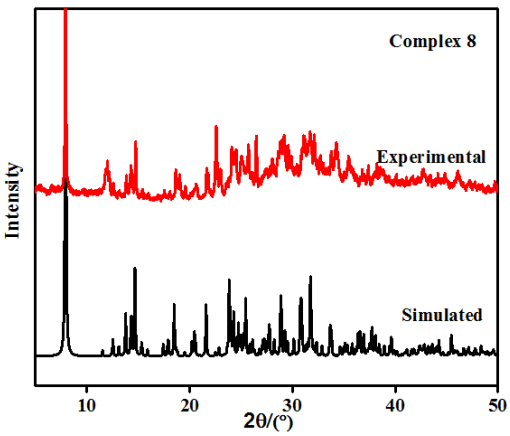
2θ/(°)


Complex 8
Experimental
Simulated
Intensity
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20
30
40
50
2θ/(°)

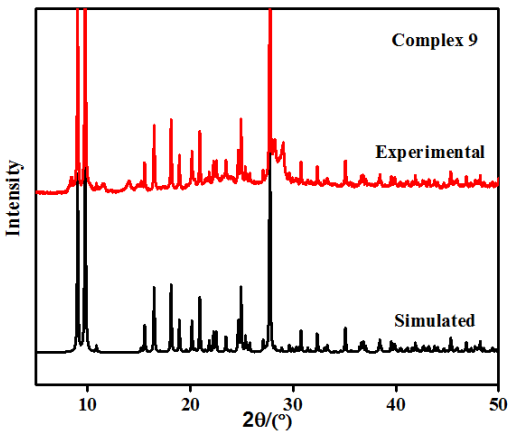

Complex 9
Experimental
Simulated
Intensity
10
20
30
40
50
2θ/(°)

Fig. S4. Experimental and simulated PXRD patterns of **1**-**9**.

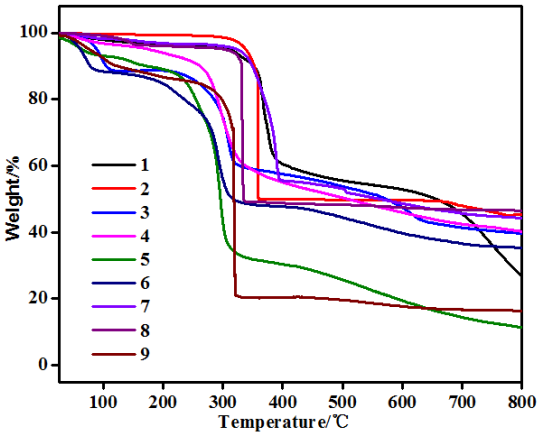
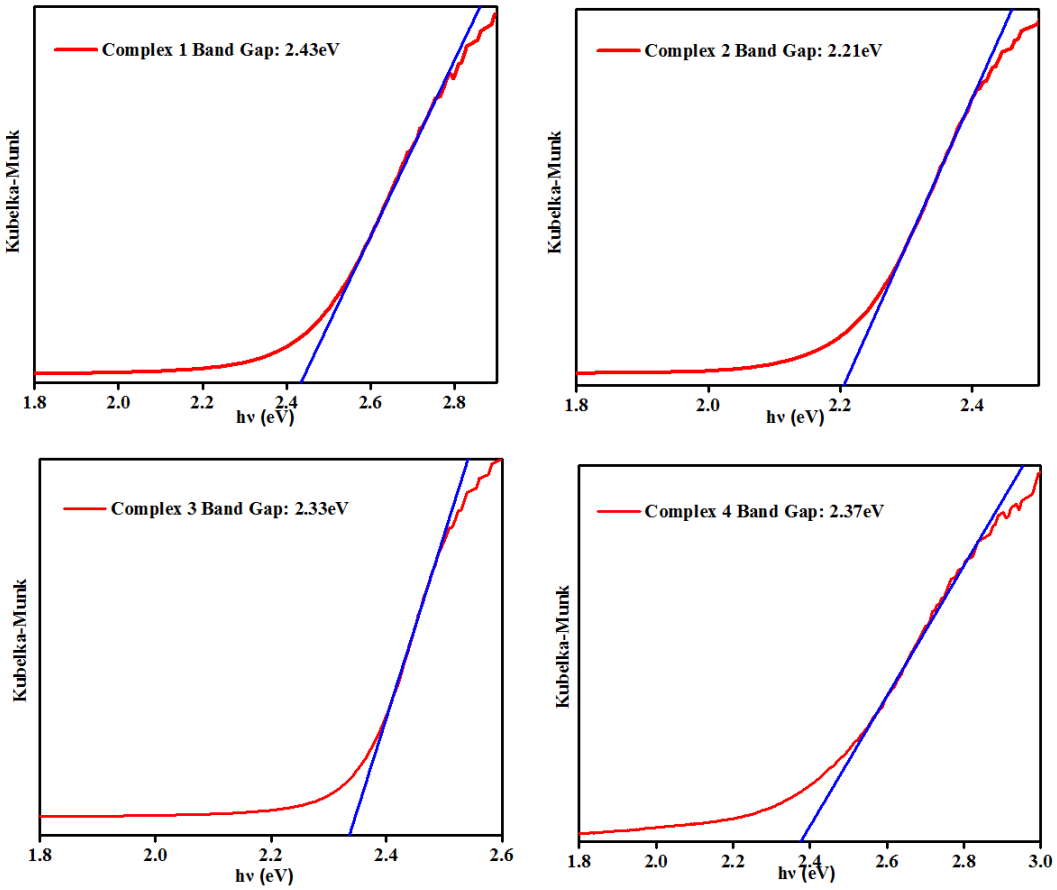


Fig. S5. TGA curves of **1**-**9**.



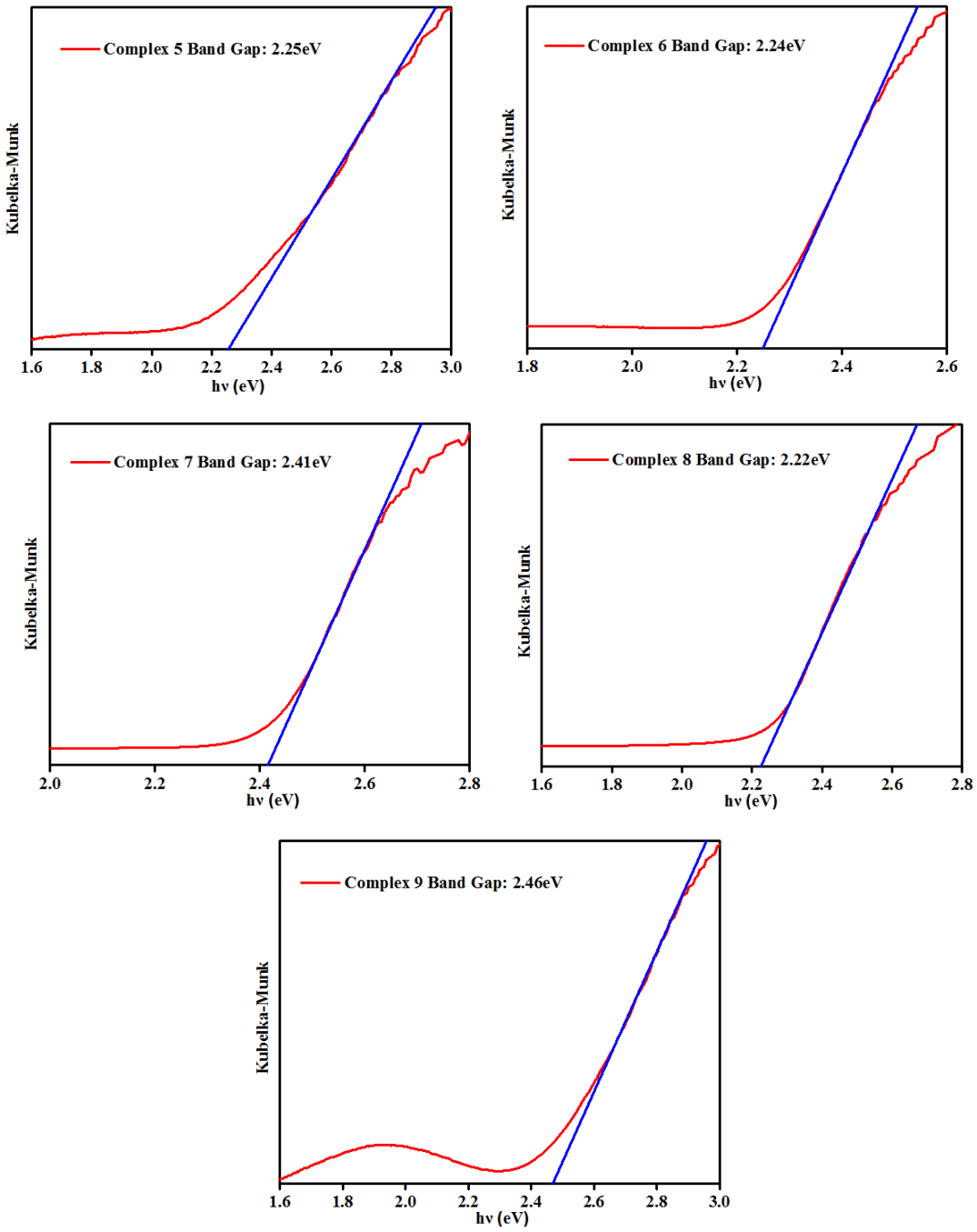


Fig. S6. Diffuse reflectance spectra of K–M functions versus energy (eV) of complexes **1-9** at room temperature.

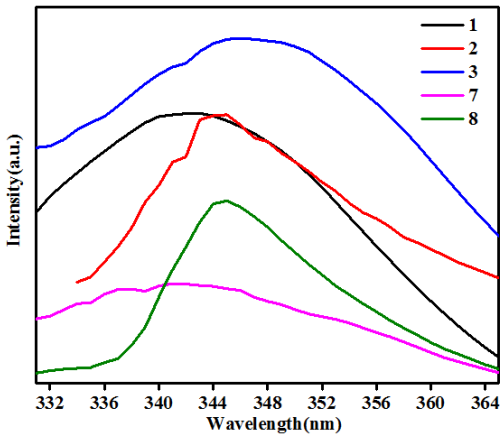
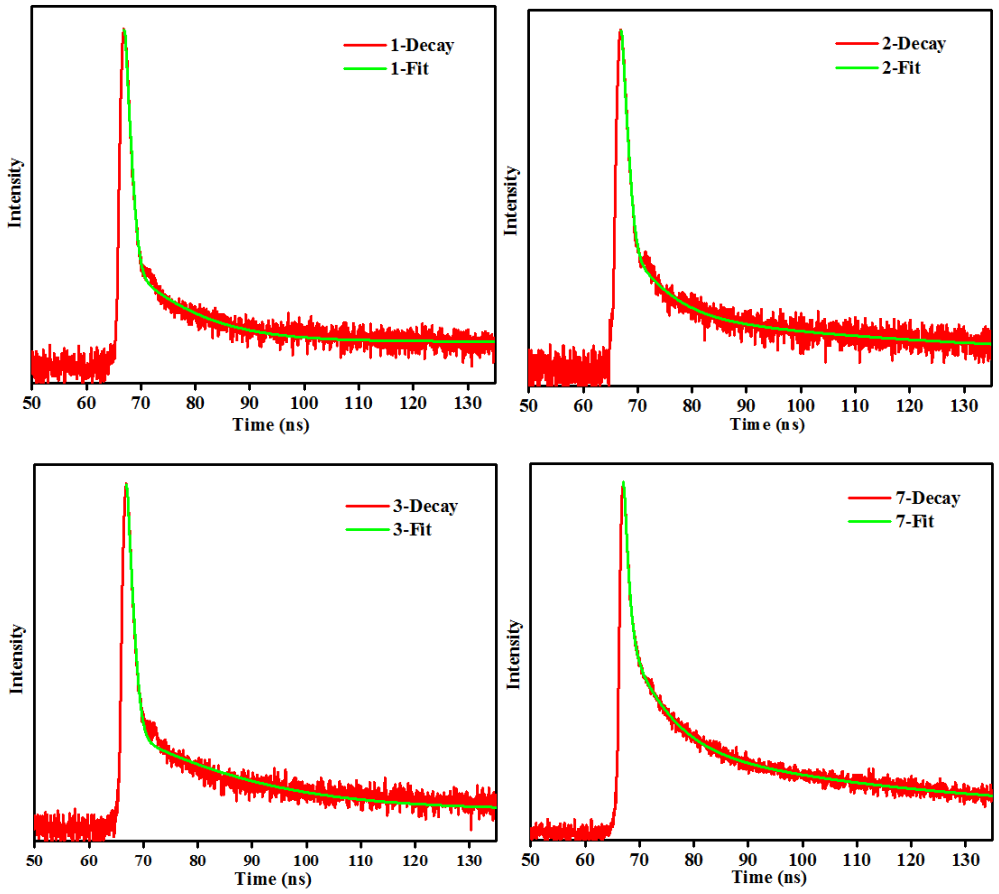


Fig. S7. Excitation spectra of **1-3**, **7** and **8** in solid state at room temperature.



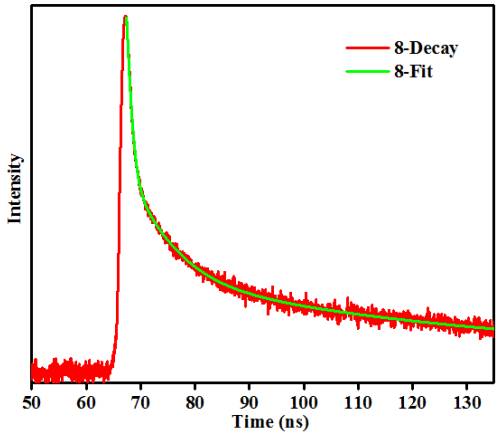


Fig. S8. Luminescence decays of **1-3** ,**7** and **8** at corresponding excitation/emission maxima.

Table S1. Selected Bond Distances (Å) and Angles (°) for Complexes **1-9**

		Complex **1**	
O(1)-Zn(1)	1.9021(18)	N(1)-Zn(1)	2.047(2)
O(1)-Zn(2)	1.9570(19)	O(3)$^{\#4}$-Zn(2)	2.409(2)
O(4)$^{\#4}$-Zn(2)	1.9002(19)	N(4)$^{\#1}$-Zn(2)	2.029(2)
N(2)-Zn(2)	2.107(2)	O(1)-Zn(1)-N(1)	93.02(8)
O(1)-Zn(1)-N(1)$^{\#3}$	111.86(8)	N(1)-Zn(1)-N(1)$^{\#3}$	110.4(12)
O(4)$^{\#4}$-Zn(2)-O(3)$^{\#4}$	77.53(8)	O(1)-Zn(2)-O(4)$^{\#4}$	102.71(8)
O(3)$^{\#4}$-Zn(2)-N(4)$^{\#1}$	86.39(8)	O(1)-Zn(2)-N(4)$^{\#1}$	104.77(9)
O(1)-Zn(2)-N(2)	89.96(8)	O(3)$^{\#4}$-Zn(2)-N(2)	80.22(7)
N(4)$^{\#1}$-Zn(2)-N(2)	98.93(9)		
		Complex **2**	
O(1)-Ag(1)	2.321(5)	O(3)-Ag(1)	2.532(8)
N(2)$^{\#2}$-Ag(1)	2.322(7)	N(3)$^{\#1}$-Ag(1)	2.218(7)
O(1)-Ag(1)-N(2)$^{\#2}$	95.3(2)	O(1)-Ag(1)-O(3)	66.6(2)
N(3)$^{\#1}$-Ag(1)-N(2)$^{\#2}$	111.0(2)	N(3)$^{\#1}$-Ag(1)-O(3)	101.3(3)
		Complex **3**	
O(7)-Co(1)	2.091(8)	O(8)-Co(1)	2.030(8)
N(3)-Co(1)	2.138(8)	O(7)-Co(1)-O(8)$^{\#1}$	89.6(3)
O(7)-Co(1)-O(8)	90.4(3)	O(7)-Co(1)-N(3)	91.4(3)
O(7)-Co(1)-N(3)$^{\#1}$	91.4(3)	O(8)-Co(1)-N(3)$^{\#1}$	87.8(3)
O(8)-Co(1)-N(3)	92.2(3)		
		Complex **4**	
O(3)$^{\#1}$-Cu(1)	1.890(9)	O(4)$^{\#1}$-Cu(1)	2.281(12)
O(12)-Cu(1)	1.867(9)	O(13)-Cu(1)	2.58(2)
N(1)-Cu(1)	2.103(12)	N(5)-Cu(1)	2.148(11)
O(11)$^{\#2}$-Cu(2)	1.902(9)	O(6)$^{\#4}$-Cu(2)	2.505(12)
O(12)-Cu(2)	1.853(9)	N(6)-Cu(2)	1.998(11)
N(3)$^{\#3}$-Cu(2)	1.963(11)	O(1)$^{\#4}$-Cu(3)	2.593(14)
O(7)$^{\#5}$-Cu(3)	2.383(11)	O(11)-Cu(3)	1.905(10)
O(8)$^{\#5}$-Cu(3)	1.930(10)	N(4)$^{\#6}$-Cu(3)	2.123(12)

N(8)-Cu(3)	2.076(11)	O(3)$^{\#1}$-Cu(1)-O(4)$^{\#1}$	80.4(4)
O(12)-Cu(1)-O(4)$^{\#1}$	112.7(4)	O(3)$^{\#1}$-Cu(1)-O(13)	72.3(6)
O(12)-Cu(1)-O(13)	94.1(6)	O(12)-Cu(1)-N(1)	89.2(4)
O(3)$^{\#1}$-Cu(1)-N(1)	93.7(4)	O(12)-Cu(1)-N(5)	83.6(4)
O(3)$^{\#1}$-Cu(1)-N(5)	93.0(4)	O(4)$^{\#1}$-Cu(1)-N(1)	97.2(5)
O(4)$^{\#1}$-Cu(1)-N(5)	86.9(4)	O(13)-Cu(1)-N(1)	93.3(6)
O(13)-Cu(1)-N(5)	85.9(6)	O(12)-Cu(2)-O(6)$^{\#4}$	85.6(4)
O(11)$^{\#2}$-Cu(2)-O(6)$^{\#4}$	94.4(4)	O(12)-Cu(2)-N(3)$^{\#3}$	93.5(4)
O(11)$^{\#2}$-Cu(2)-N(3)$^{\#3}$	85.7(4)	O(12)-Cu(2)-N(6)	84.8(4)
O(11)$^{\#2}$-Cu(2)-N(6)	96.0(4)	O(6)$^{\#4}$-Cu(2)-N(3)$^{\#3}$	95.4(5)
O(6)$^{\#4}$-Cu(2)-N(6)	93.1(4)	O(8)$^{\#5}$-Cu(3)-O(7)$^{\#5}$	79.6(4)
O(11)-Cu(3)-O(7)$^{\#5}$	107.3(4)	O(11)-Cu(3)-O(1)$^{\#4}$	88.7(4)
O(1)$^{\#4}$-Cu(3)-N(4)$^{\#6}$	89.7(5)	O(7)$^{\#5}$-Cu(3)-N(8)	97.5(4)
O(11)-Cu(3)-N(8)	87.9(4)	O(8)$^{\#5}$-Cu(3)-N(8)	91.7(4)
O(11)-Cu(3)-N(4)$^{\#6}$	86.0(4)	O(8)$^{\#5}$-Cu(3)-N(4)$^{\#6}$	93.7(4)
O(7)$^{\#5}$-Cu(3)-N(4)$^{\#6}$	89.7(4)	O(1)$^{\#4}$-Cu(3)-N(8)	84.5(5)
		Complex **5**	
O(7)-Cu(1)	2.002(10)	N(5)-Cu(1)	1.942(13)
N(14)$^{\#1}$-Cu(1)	1.962(12)	N(8)-Cu(1)	1.979(13)
N(15)-Cu(1)	2.253(13)	O(7)-Cu(2)	2.016(10)
O(16)$^{\#2}$-Cu(2)	1.950(9)	O(6)-Cu(2)	2.321(11)
N(21)-Cu(2)	1.969(13)	N(4)-Cu(2)	1.965(12)
O(8)-Cu(3)	1.954(12)	O(7)-Cu(3)	2.031(10)
N(20)-Cu(3)	1.920(12)	N(9)-Cu(3)	1.990(12)
N(16)-Cu(3)	2.297(18)	O(11)-Cu(4)	1.848(14)
O(10)-Cu(4)	2.33(2)	O(7)-Cu(1)-N(15)	86.3(4)
O(7)-Cu(1)-N(5)	88.1(5)	O(7)-Cu(1)-N(8)	89.3(5)
N(14)$^{\#1}$-Cu(1)-N(8)	93.2(5)	N(5)-Cu(1)-N(14)$^{\#1}$	88.9(5)
N(5)-Cu(1)-N(15)	96.5(5)	N(14)$^{\#1}$-Cu(1)-N(15)	104.0(4)
N(8)-Cu(1)-N(15)	86.3(5)	O(7)-Cu(2)-O(6)	88.8(4)
O(16)$^{\#2}$-Cu(2)-O(6)	95.8(4)	O(6)-Cu(2)-N(21)	99.3(5)
O(16)$^{\#2}$-Cu(2)-N(4)	93.7(5)	O(16)$^{\#2}$-Cu(2)-N(21)	92.2(4)
O(7)-Cu(2)-N(4)	87.0(5)	O(7)-Cu(2)-N(21)	86.6(4)
O(6)-Cu(2)-N(4)	87.9(5)	O(8)-Cu(3)-N(16)	101.4(7)
O(7)-Cu(3)-N(16)	85.9(5)	O(8)-Cu(3)-N(20)	92.9(5)
O(8)-Cu(3)-N(9)	89.1(5)	O(7)-Cu(3)-N(9)	89.6(5)
O(7)-Cu(3)-N(20)	86.6(5)	N(9)-Cu(3)-N(16)	91.2(6)
N(20)-Cu(3)-N(16)	102.4(6)	O(11)-Cu(4)-O(10)	95.9(6)
O(11)-Cu(4)-O(10)$^{\#3}$	84.1(6)		
		Complex **6**	
O(7)-Cu(1)	1.986(16)	O(8)-Cu(1)	2.388(15)
N(5)-Cu(1)	2.045(14)	O(8)$^{\#1}$-Cu(2)	2.378(14)
O(6)-Cu(2)	1.983(16)	N(4)-Cu(2)	2.049(15)
O(7)-Cu(1)-O(8)$^{\#1}$	90.4(5)	O(7)-Cu(1)-O(8)	89.6(5)

O(7)-Cu(1)-N(5)	89.0(6)	O(7)-Cu(1)-N(5)$^{\#1}$	91.0(6)
O(8)-Cu(1)-N(5)	95.1(6)	O(8)-Cu(1)-N(5)$^{\#1}$	84.9(6)
O(6)-Cu(2)-O(8)$^{\#1}$	90.8(5)	O(6)-Cu(2)-O(8)$^{\#3}$	89.2(5)
O(6)-Cu(2)-N(4)	88.8(6)	O(8)$^{\#3}$-Cu(2)-N(4)	95.4(6)
O(8)$^{\#1}$-Cu(2)-N(4)	84.6(6)	O(6)-Cu(2)-N(4)$^{\#2}$	91.2(6)
		Complex **7**	
Ag(1)-O(2)$^{\#2}$	2.590(2)	Ag(1)-O(4)	2.587(34)
Ag(1)-O(7)	2.718(33)	Ag(1)-N(4)	2.293(16)
Ag(2)-O(3)$^{\#4}$	2.541(19)	Ag(2)-N(5)	2.188(13)
O(2)$^{\#}$2-Ag(1)-N(4)	98.4(4)	O(3)$^{\#5}$-Ag(2)-N(5)	113.8(6)
O(3)$^{\#4}$-Ag(2)-O(3)$^{\#5}$	83.3(8)	O(3)$^{\#4}$-Ag(2)-N(5)	89.9(6)
		Complex **8**	
Ag(1)-N(6)	2.140(4)	Ag(1)-N(12)	2.160(3)
Ag(2)-N(4)	2.261(4)	Ag(2)-N(5)$^{\#2}$	2.330(4)
Ag(2)-O(6)$^{\#2}$	2.353(3)	Ag(2)-O(7)$^{\#2}$	2.535(5)
Ag(2)-O(5)$^{\#3}$	2.576(3)	Ag(3)-N(9)$^{\#4}$	2.174(3)
Ag(3)-N(3)	2.176(3)	Ag(4)-N(10)	2.183(3)
Ag(4)-O(5)$^{\#5}$	2.303(3)	Ag(4)-O(6)$^{\#6}$	2.403(3)
Ag(4)-O(11)	2.503(11)	N(4)-Ag(2)-N(5)$^{\#2}$	116.15(12)
N(5)$^{\#2}$-Ag(2)-O(6)$^{\#2}$	104.20(13)	N(4)-Ag(2)-O(7)$^{\#2}$	85.53(15)
N(5)$^{\#2}$-Ag(2)-O(7)$^{\#2}$	116.25(17)	O(6)$^{\#2}$-Ag(2)-O(7)$^{\#2}$	67.72(12)
N(4)-Ag(2)-O(5)$^{\#3}$	117.83(13)	N(5)$^{\#2}$-Ag(2)-O(5)$^{\#3}$	78.30(12)
O(6)$^{\#2}$-Ag(2)-O(5)$^{\#3}$	78.09(11)	N(10)-Ag(4)-O(11)	103.5(3)
O(6)$^{\#6}$-Ag(4)-O(11)	75.5(3)	O(5)$^{\#5}$-Ag(4)-O(6)$^{\#6}$	82.68(11)
		Complex **9**	
O(5)-Cu(1)	1.921(9)	O(6)-Cu(1)	2.013(10)
O(7)-Cu(1)	2.403(16)	N(6)-Cu(1)	1.938(10)
N(4)$^{\#1}$-Cu(1)	1.977(10)	O(6)-Cu(1)-O(7)	92.6(6)
O(5)-Cu(1)-O(7)	95.0(5)	O(5)-Cu(1)-N(6)	89.3(4)
O(7)-Cu(1)-N(4)$^{\#1}$	90.4(5)	O(6)-Cu(1)-N(6)	89.4(4)
O(5)-Cu(1)-N(4)$^{\#1}$	91.6(4)	O(7)-Cu(1)-N(6)	100.8(5)
O(6)-Cu(1)-N(4)$^{\#1}$	88.1(4)		

Symmetry codes, for **1**: #1 -x+3/2,y-1/2,-z+3/2; #2 x-1/2,-y+1/2,z-1/2; #3 -x+1,y,-z+3/2; #4 x+1/2,-y+1/2,z+1/2; for **2**: #1 -x+3/2,-y+3/2,-z+1; #2 x,y-1,z; for **4**: #1 -x,-y,-z+2; #2 -x,-y+1,-z+1; #3 -x-1,-y,-z+1; #4 -x,-y+1,-z+2; #5 -x+1,-y+1,-z+2; #6 x+1,y+1,z; for **5**: #1 -x+2,-y,-z; #2 -x+1,-y,-z; #3 -x+3,-y,-z+1; for **6**: #1 -x+1,-y,-z; #2 -x,-y,-z; #3 x-1,y,z; for **7**: #1 -x+1/2,y,z; #2 -x+1,-y+1,z; #3 -x+1,-y+2,z; #4 x,y+1/2,z+1/2; #5 -x+1,-y+3/2,z+1/2; for **8**: #2 -x,-y+2,-z+1; #3 x-1,y,z; #4 x,y,z+1; #5 x,y,z-1; #6 -x+1,-y+2,-z; for **9**: #1 -x+1/2,y-1/2,-z+0.

Table S2. Intermolecular π–π interactions in **3**

ring(I)→ ring(J)	Distance between ring Centroids (I,J), (Å)	dihedral angle (I,J), (deg)	Perpendicular distance of centroid(I) on ring (J), (Å)
Cg(1)→Cg(1)^{i}	3.625(7)	0	3.279(5)
Cg(1)→Cg(1)^{ii}	3.716(7)	0	3.385(5)

Symmetry code: i = 1-X,1-Y,1-Z; ii = 2-X,1-Y,1-Z.
Cg(I)/Cg(J) denotes the I/J ring in the corresponding structure: Cg(1) = C2/C3/C4/C5/C6/C7.