

Electronic Supplementary Information for CrystEngComm

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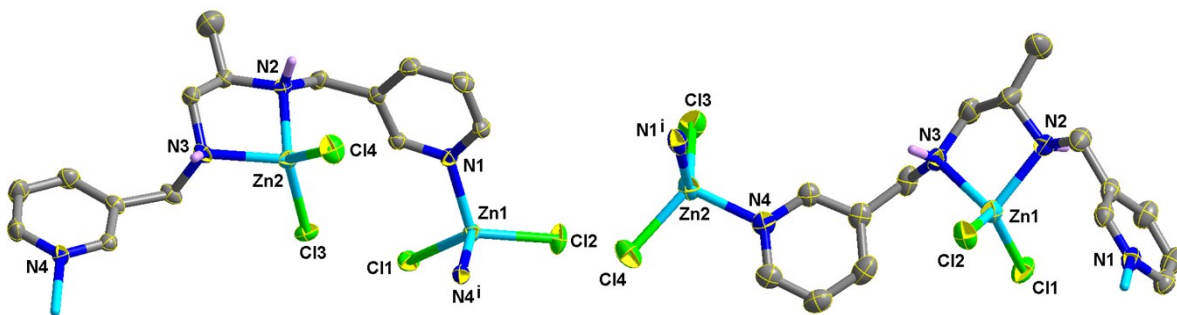
**A Series of Helical Coordination Polymers Based on Two Racemic
Bis(pyridylmethylene) Propane-1,2-Diamine Ligands:
Relationship of Conformations, Structures and Properties**

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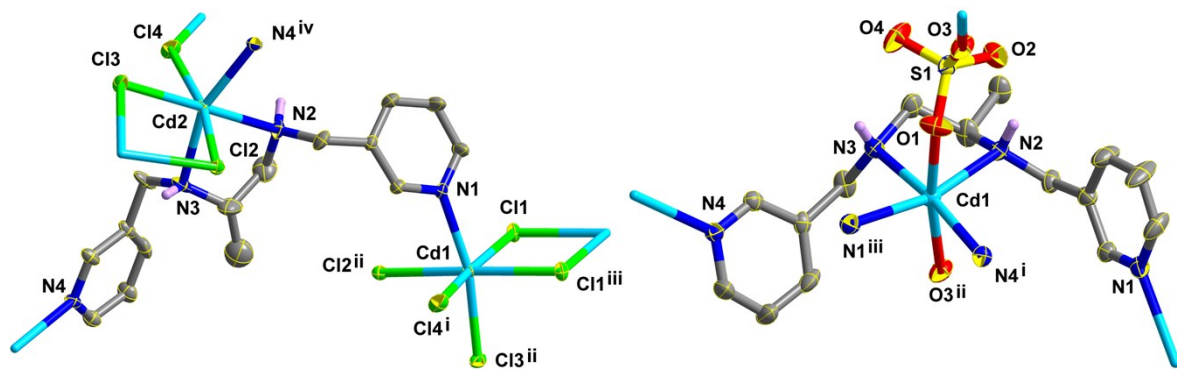
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Syntheses of ligands L1 and L2. A solution of 4-pyridinecarboxaldehyde /3-pyridinecarboxaldehyde (100 mmol, 10.7 g) and 1,2-propanediamine (50 mmol, 3.7 g) in methanol (100 mL) was heated under reflux for 5 h. Then, the solution was left to cool to room temperature followed by adding sodium borohydride in batches. After stirring for 24 h, saturated NH_4Cl was added to the solution under 70 °C water bath until no gas being released. The solution was then extracted with 30 mL chloroform for three times. Yellow oily products for these two ligands were obtained after rotary evaporation under vacuum. In order to determine whether they are racemic or enantiomerically pure, we carried out the measurement of optical rotation. After examination on WXG-4 polarimeter (Shanghai, China), the obtained optical rotation values for the two compounds are $\sim 0.2^\circ$, indicating that the two ligands are racemic.



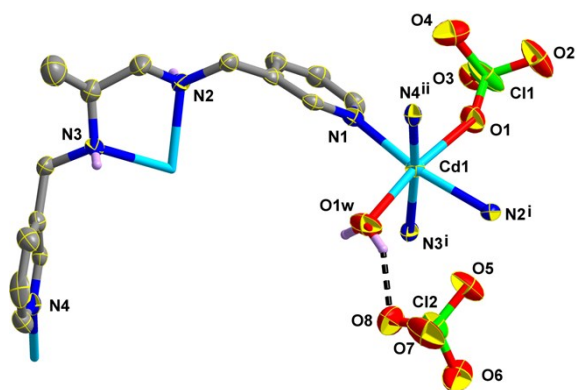
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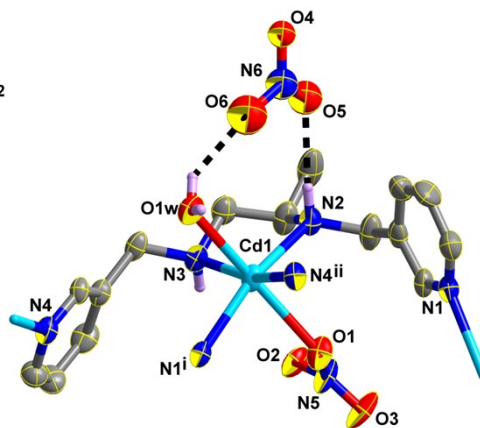


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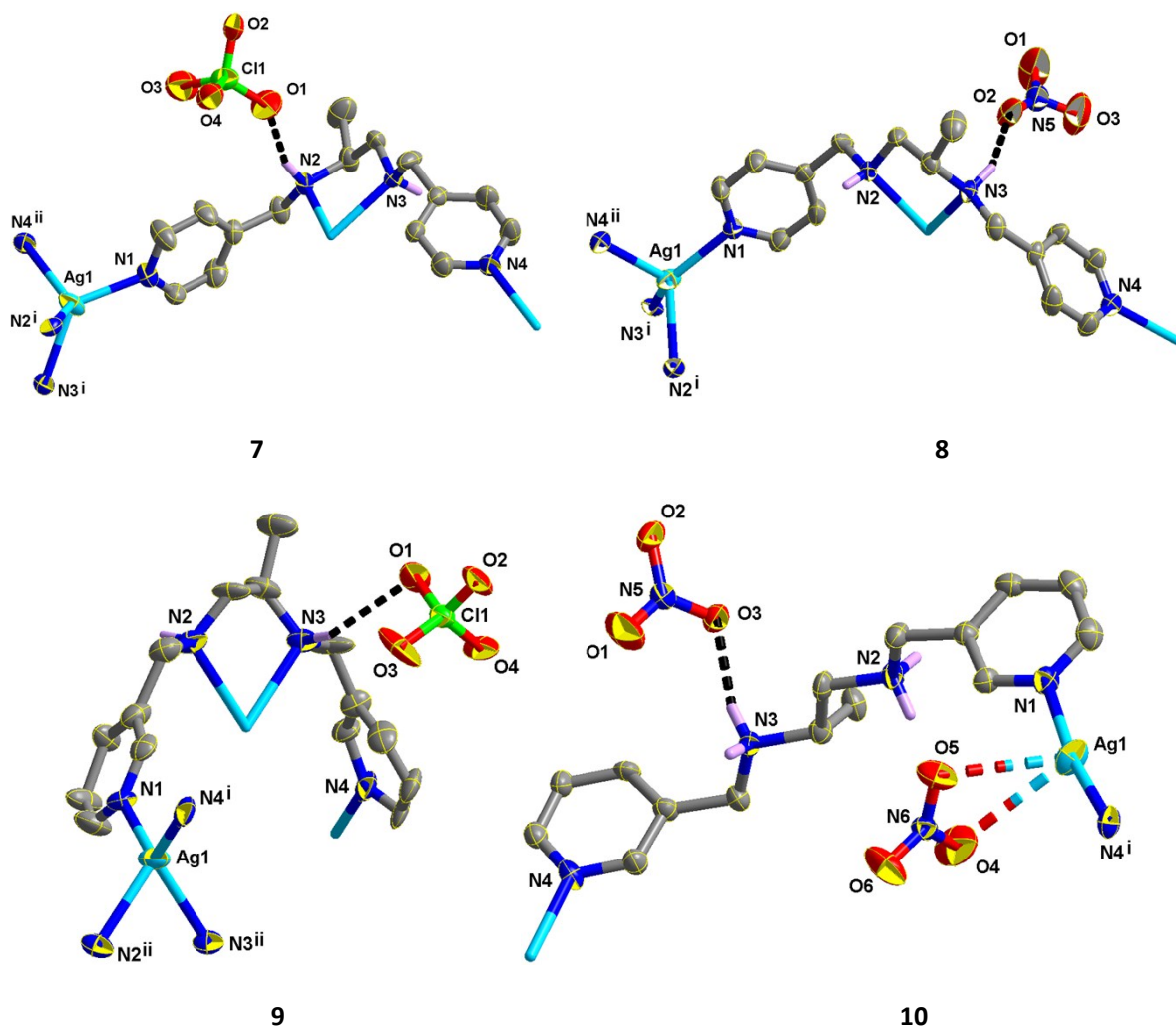


Fig. S1 Molecular structures of **1-10** with 30% probability ellipsoid for the non-H atoms. Lattice water molecules in **8** and **10**, as well as one of the free nitrate anion in **10** were omitted for clarity.

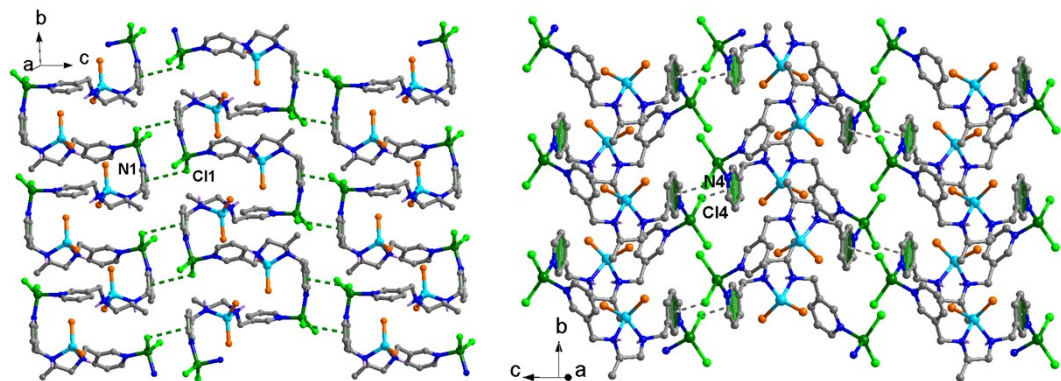


Fig. S2 The anion $\cdots\pi$ interaction (green dashed lines) in complex 1 (left) and long contact (gray dashed lines) between Cl4 anion and N4-pyridyl ring in complex 2 (right).

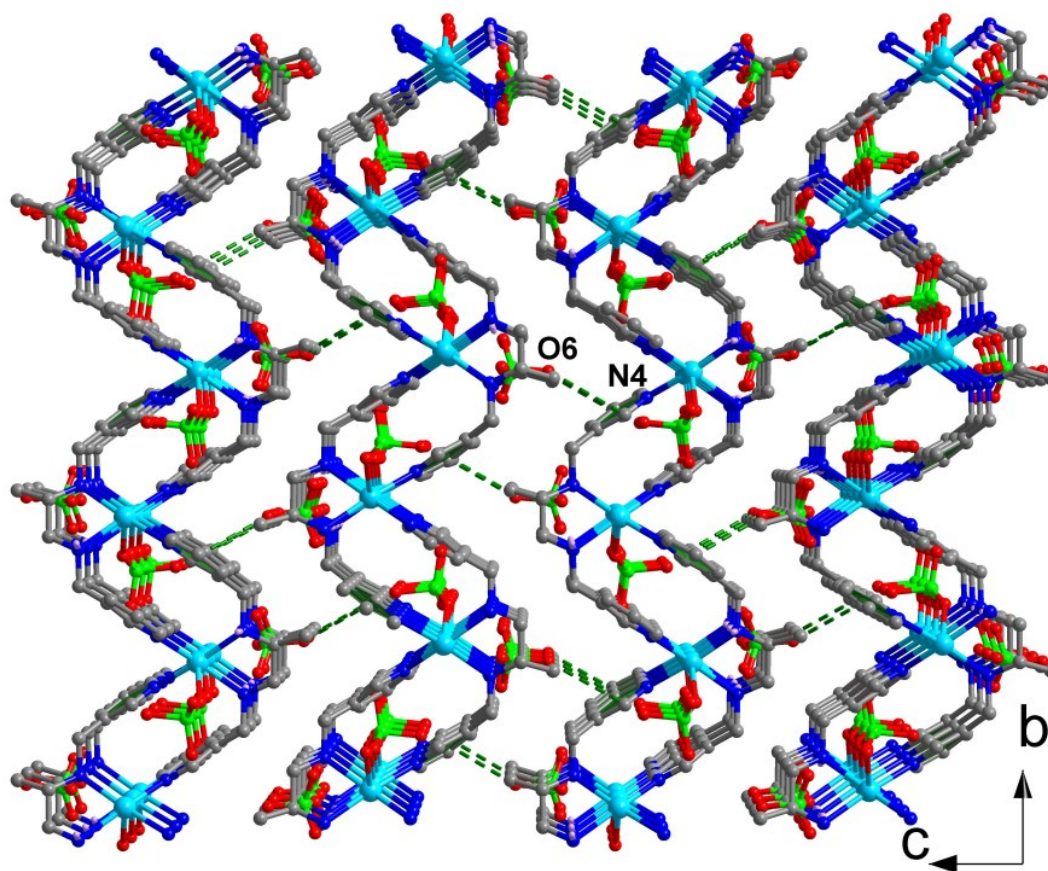


Fig. S3 The 3D supramolecular network of complex 5 extended by anion $\cdots\pi$ interactions (green dashed lines).

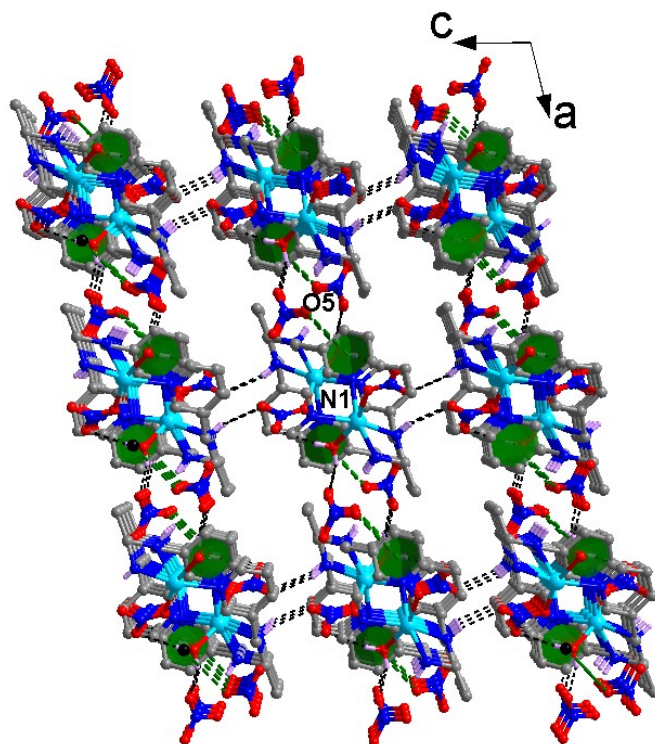


Fig. S4 The 3D supramolecular network of complex **6** extended by anion $\cdots\pi$ interactions (green dashed lines).

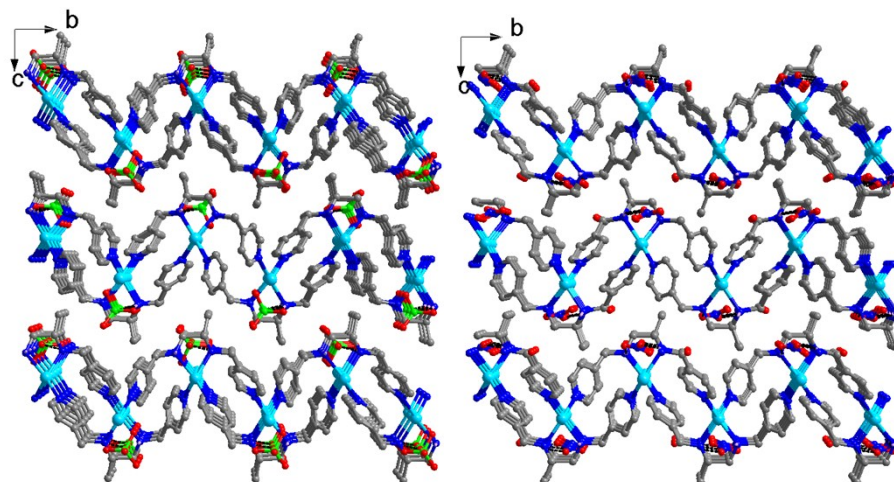


Fig. S5 The 3D supramolecular networks of complexes **7** and **8**. The hydrogen bonds were denoted as black dashed lines.

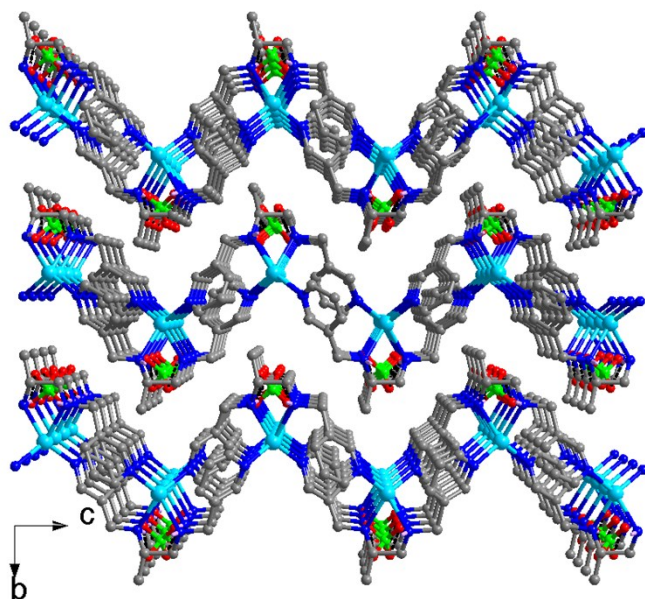


Fig. S6 The 3D supramolecular network of complex **9**. The hydrogen bonds were denoted as black dashed lines.

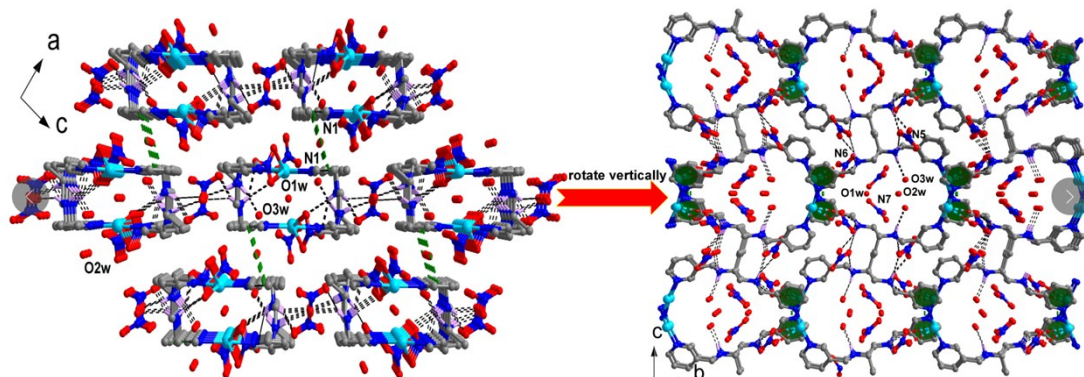


Fig. S7 The 3D supramolecular network of complex **10** viewing along the *b*- (left) and *a*-axis (right).

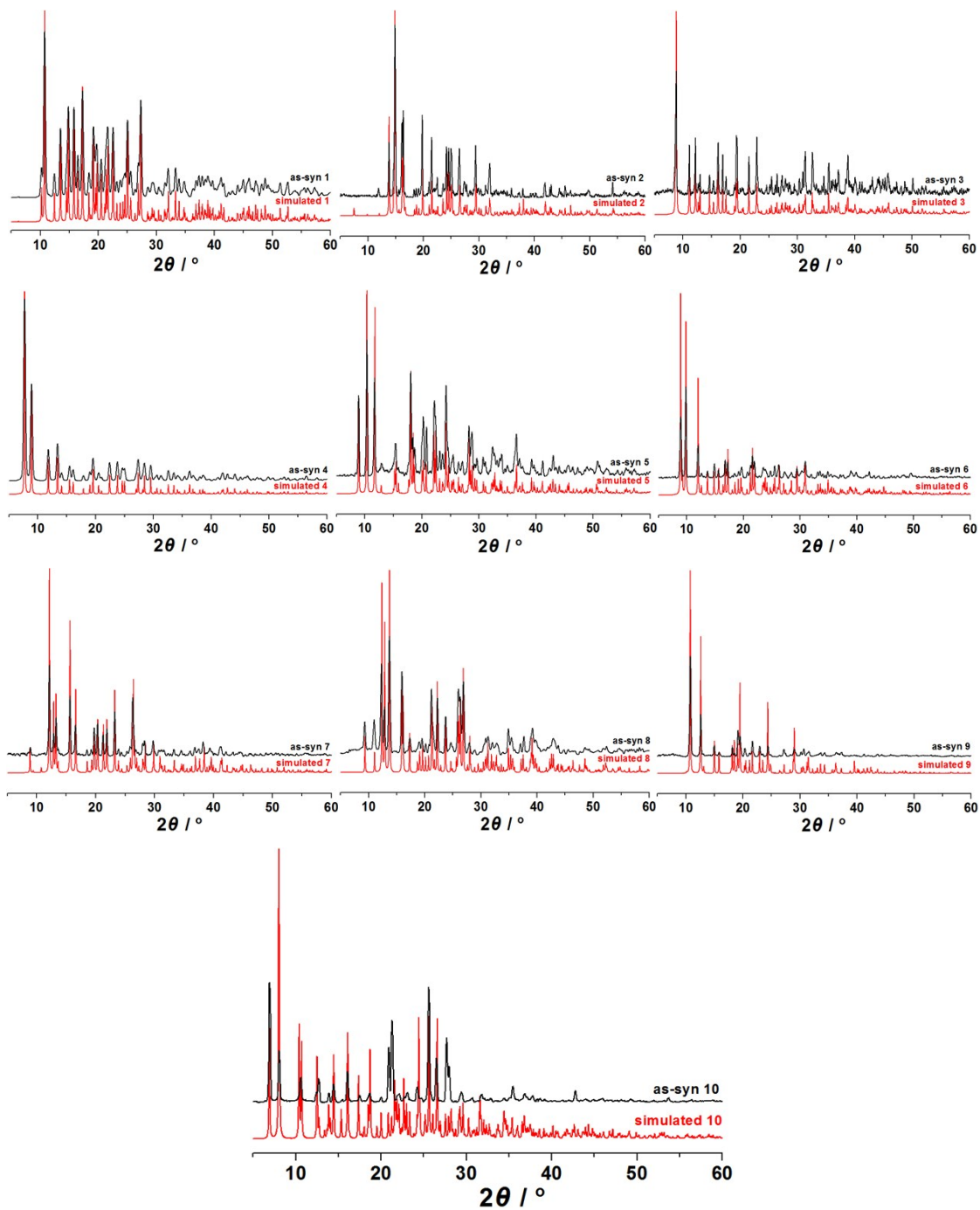


Fig. S8 PXRD patterns of complexes 1-10.

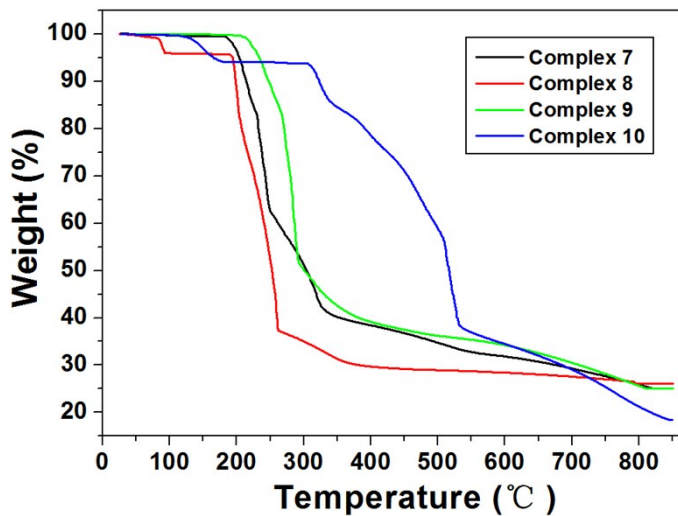
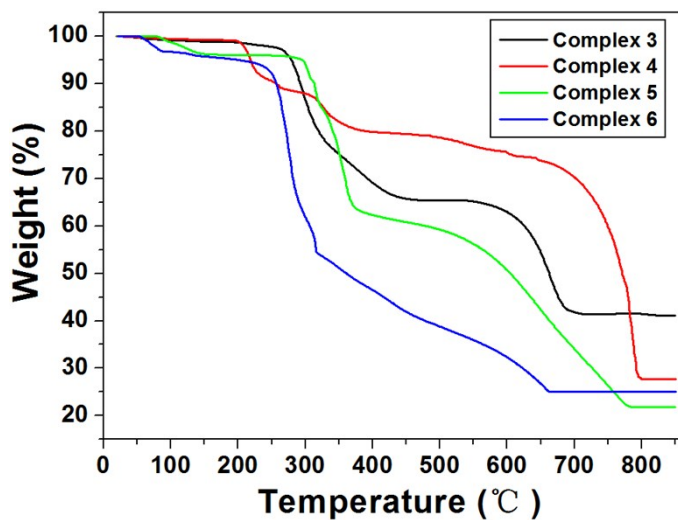
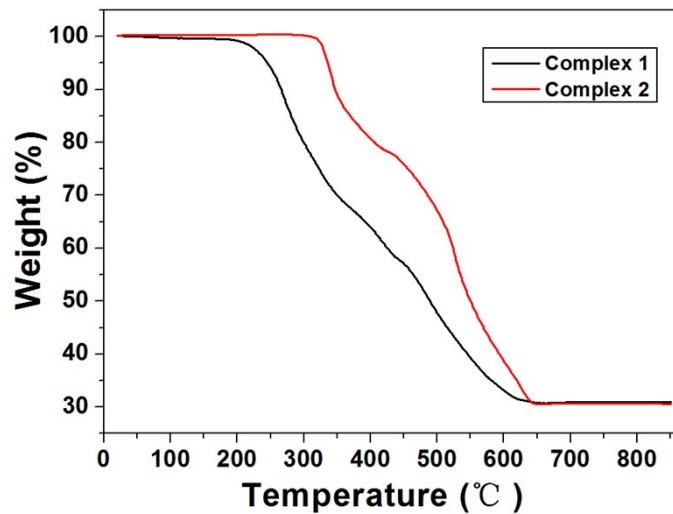


Fig. S9 TG curves of complexes 1-10.

Powder X-Ray diffraction and thermogravimetric analyses (TGA). The purity of complexes **1-10** were confirmed by comparison of their experimental powder X-ray diffraction (PXRD) patterns with the reference powder diffractograms (calculated on the basis of single-crystal X-ray diffraction data). As illustrated in Fig. S8, the experimental PXRD patterns of these complexes are nearly consistent with their simulated ones, which indicate that the as-synthesized complexes are pure and their single crystal structures are really representative of the bulk of the corresponding samples. And the differences in intensity are due to the preferred orientation of the powder samples. The stability of these complexes was analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 850 °C at a rate of 10 °C min⁻¹, under N₂ atmosphere. As illustrated in Fig. S9, for the anhydrous complexes **1-4**, **7** and **9**, only one weight loss step is observed, which begin at 209 °C for **1**, 321 °C for **2**, 240 °C for **3**, 190 °C for **4**, 186 °C for **7** and 213 °C for **9**, corresponding to the collapse of their network. Then, the ZnO (**1** and **2**), CdO (**3** and **4**) and Ag (**7** and **9**) residues have been obtained with their experimental percentages being close to calculated values (obsrd: 30.89%, calcd: 30.77% for **1**; obsrd: 30.76%, calcd: 30.77% for **2**; obsrd: 41.39%, calcd: 41.23% for **3**; obsrd: 27.74%, calcd: 27.63% for **4**; obsrd: 23.99%, calcd: 23.26% for **7**; obsrd: 23.64%, calcd: 23.26% for **9**). In comparison, the hydrous complexes **5**, **6**, **8** and **10** exhibit at least two weight loss steps. The first step corresponds to the release of various coordinated or lattice water molecules with the observed weight loss of 3.65% in **5** (89-142 °C), 3.41% in **6** (60-96°C), 4.11% in **8** (80-94 °C) and 6.01% in **10** (118-170 °C) being reasonably close to their calculated value (3.08% in **5**, 3.53% in **6**, 4.07% in **8** and 6.17% in **10**). Then, the following weight losses for these four complexes indicate the decomposition of the resulting solvent-free networks. All of the residual components are corresponding to CdO (**5** and **6**) and Ag (**8** and **10**) with different percentages (obsrd: 21.79%; calcd: 21.92% for **5**, obsrd: 25.40%; calcd: 25.14% for **6**, obsrd: 25.09%; calcd: 24.28% for **8** and obsrd: 18.77%; calcd: 18.46% for **10**).

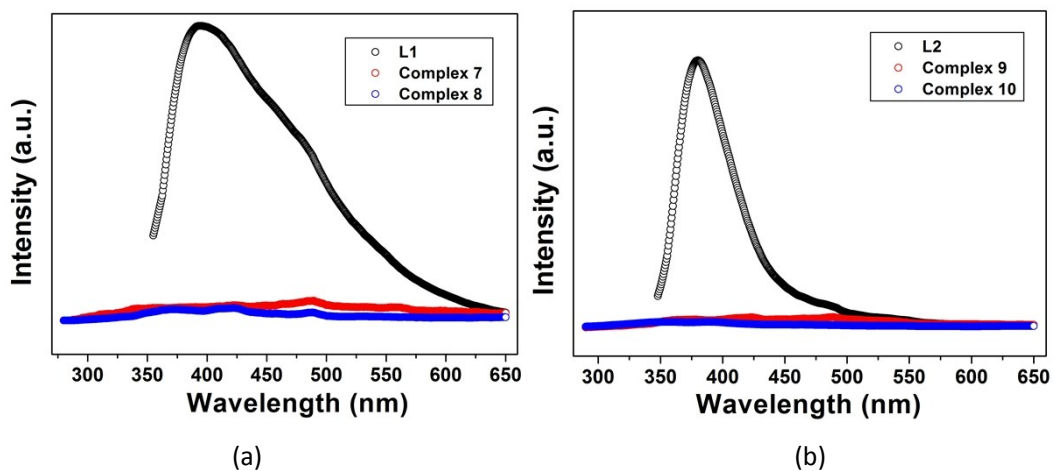


Fig. S10 Emission spectra of L1, L2 and complexes 7-10 in the solid state at room temperature.

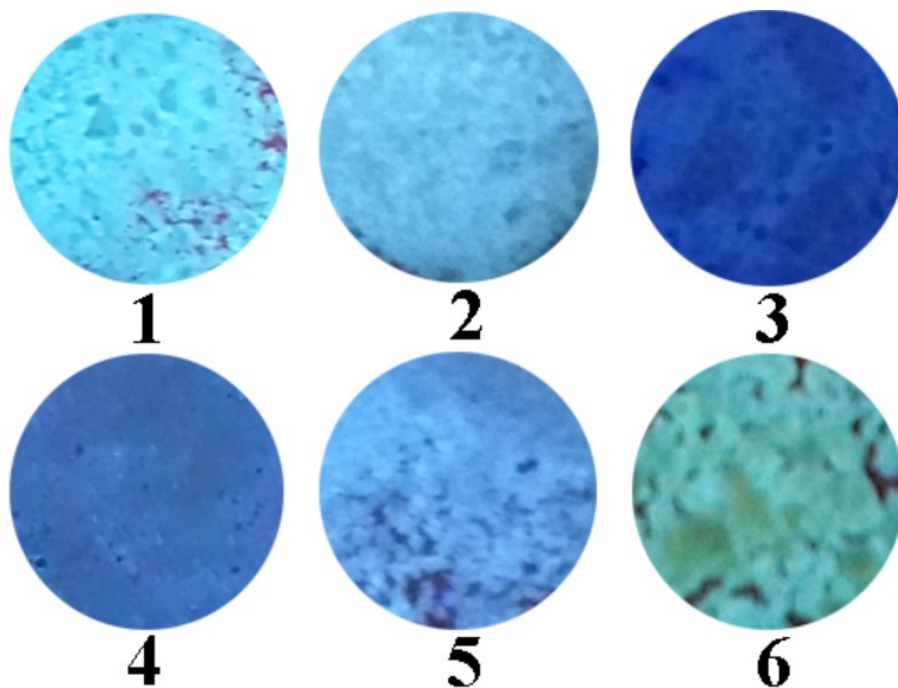


Fig. S11 Photographs for sample powders of complexes 1-6 under UV source ($\lambda = 310$ nm).

Photographs illustration. The luminescent photographs of **1-6** were obtained by placing the solid samples in a dark box (ZF-90 dark box ultraviolet transilluminator, Shanghai, China) with the fixed excitation wavelength of 310 nm. This wavelength is not the optimal excitation wavelength for these complexes, and their emission intensity are totally different. Therefore, chromatic aberration is observed among these photographs. However, these photographs demonstrate that these complexes exhibit luminescent emission in the solid state at room temperature.

Table S1 Selected Bond Lengths (Å) for Complexes **1-10^o**

Complex 1			
Zn(1)-N(1)	2.040(5)	Zn(2)-N(2)	2.074(5)
Zn(1)-N(4) ⁱ	2.070(5)	Zn(2)-N(3)	2.096(4)
Zn(1)-Cl(2)	2.2051(16)	Zn(2)-Cl(4)	2.2056(19)
Zn(1)-Cl(1)	2.2241(16)	Zn(2)-Cl(3)	2.2217(16)
Complex 2			
Zn(1)-N(2)	2.082(4)	Zn(2)-N(4)	2.048(4)
Zn(1)-N(3)	2.082(4)	Zn(2)-N(1) ⁱ	2.049(5)
Zn(1)-Cl(2)	2.2030(17)	Zn(2)-Cl(3)	2.2032(15)
Zn(1)-Cl(1)	2.2103(18)	Zn(2)-Cl(4)	2.2086(16)
Complex 3			
Cd(1)-N(1)	2.344(5)	Cd(2)-N(2)	2.375(5)
Cd(1)-Cl(4) ⁱ	2.5800(16)	Cd(2)-N(4) ^{iv}	2.394(5)
Cd(1)-Cl(3) ⁱⁱ	2.5894(15)	Cd(2)-N(3)	2.428(5)
Cd(1)-Cl(1)	2.6406(15)	Cd(2)-Cl(3)	2.5760(16)
Cd(1)-Cl(1) ⁱⁱⁱ	2.6647(15)	Cd(2)-Cl(4)	2.6231(16)
Cd(1)-Cl(2) ⁱⁱ	2.7175(16)	Cd(2)-Cl(2)	2.6333(16)
Complex 4			
Cd(1)-O(1)	2.306(11)	Cd(1)-O(3) ⁱⁱ	2.364(10)
Cd(1)-N(3)	2.310(11)	Cd(1)-N(2)	2.365(12)
Cd(1)-N(4) ⁱ	2.322(11)	Cd(1)-N(1) ⁱⁱⁱ	2.407(12)
Complex 5			
Cd(1)-N(1)	2.323(13)	Cd(1)-O(1W)	2.366(13)

Cd(1)-N(2) ⁱ	2.324(13)	Cd(1)-N(3) ⁱ	2.377(13)
Cd(1)-N(4) ⁱⁱ	2.350(13)	Cd(1)-O(1)	2.395(9)
Complex 6			
Cd(1)-N(1) ⁱ	2.307(6)	Cd(1)-N(4) ⁱⁱ	2.400(5)
Cd(1)-N(2)	2.352(6)	Cd(1)-N(3)	2.401(5)
Cd(1)-O(1W)	2.393(5)	Cd(1)-O(1)	2.434(5)
Complex 7			
Ag(1)-N(1)	2.307(9)	Ag(1)-N(2) ⁱ	2.359(8)
Ag(1)-N(3) ⁱ	2.348(8)	Ag(1)-N(4) ⁱⁱ	2.361(9)
Complex 8			
Ag(1)-N(1)	2.299(7)	Ag(1)-N(4) ⁱⁱ	2.338(8)
Ag(1)-N(3) ⁱ	2.327(7)	Ag(1)-N(2) ⁱ	2.371(7)
Complex 9			
Ag(1)-N(4) ⁱ	2.284(18)	Ag(1)-N(3) ⁱⁱ	2.399(17)
Ag(1)-N(1)	2.302(18)	Ag(1)-N(2) ⁱⁱ	2.408(17)
Complex 10			
Ag(1)-N(4) ⁱ	2.136(7)	Ag(1)-N(1)	2.172(7)

^aSymmetry codes: For **1**, i -x+2,y+1/2,-z+1/2. For **2**, i -x+1,y+1/2,-z+1/2. For **3**, i x+1,y,z; ii -x+1,y+1/2,-z+1/2; iii -x+2,-y+1,-z+1; iv x,-y+1/2,z+1/2. For **4**, i -y+1,x-y+1,z-1/3; ii x-y+1,-y+1,-z+4/3; iii -x+y,-x+1,z+1/3. For **5**, i -x+1,y-1/2,-z+1/2; ii x,y-1,z. For **6**, i -x+1,y+1/2,-z+3/2; ii -x+1,y-1/2,-z+3/2. For **7**, i x+1/2,-y+1/2,-z; ii x+1,y+1,z. For **8**, i x-1/2,-y+3/2,-z+1; ii x-1,y+1,z. For **9**, i x,y,z+1; ii x,-y+3/2,z+1/2. For **10**, i -x+1,y+1,-z+3/2.