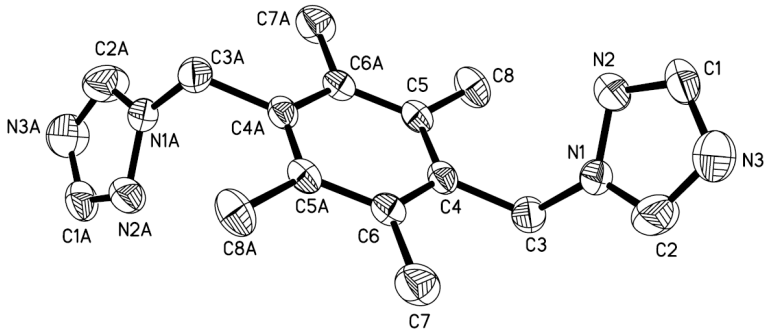

Figure S1a. Crystal structure of the free ligand btmx with atom numbering, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Symmetry code: A = 1-x, 1-y, 2-z.

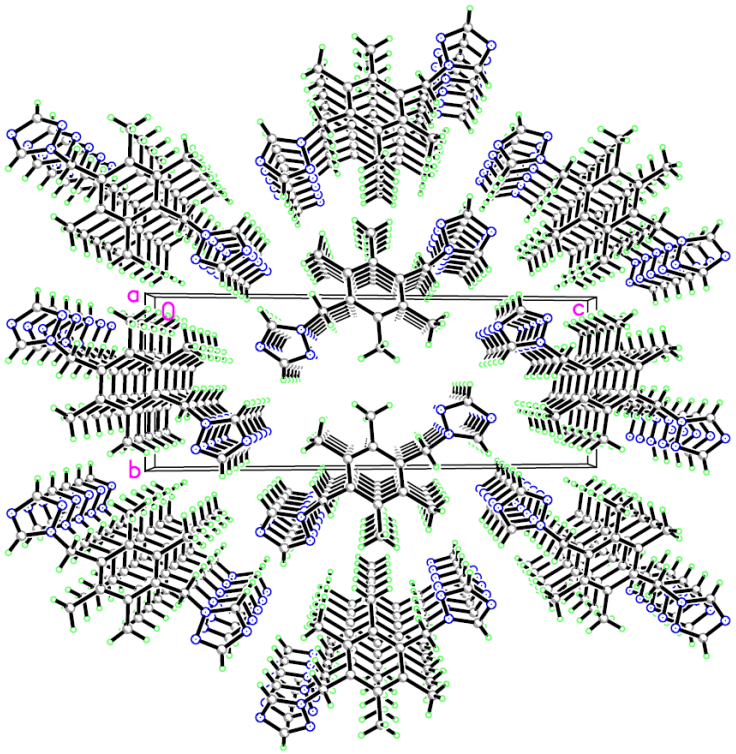

Figure S1b. A 3D packing perspective view of ligand btmx along *a* axis.

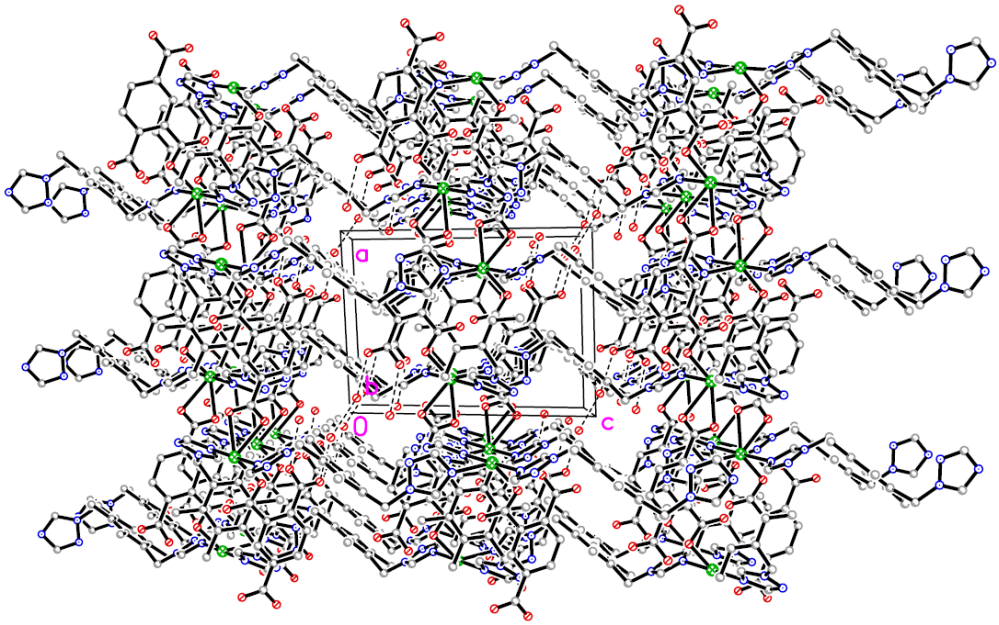

Figure S2. The 3D supramolecular structure of **2**.

Thermal analyses

To estimate the stability of the coordination architectures, thermogravimetric analyses (TGA) were carried out (Figure S3). The TGA curve of **1** shows that the first weight loss of 5.10% appeared from 145 to 228 °C, which corresponded to the loss of one lattice water molecule and one coordinated water molecule (calcd: 6.32%). At above 293 °C, the framework begins to decompose slowly and the remaining weight is attributed to the formation of CdO (obsd: 23.51%, calcd: 22.79%). Complex **2** showed the first weight loss of 5.46% from 85–195 °C corresponding to the release of two lattice water molecules (calcd: 4.50%). The anhydrous composition begins to decompose at 251 °C. Finally a plateau region is observed from 632–750 °C with CdO as the residue (obsd: 14.61%, calcd: 16.02%). As for **3**, the first step weight loss attributed to the gradual release of two lattice water molecules is observed in the range 98–142 °C (obsd: 5.46%, calcd: 6.01%). The second step weight loss from 324–470 °C corresponds to the decomposition of btmx and $HBTC^{2-}$, leading to the formation of Co_2O_3 as the residue (obsd: 14.95%, calcd: 13.84 %). For **4**, the whole framework is stable up to 369 °C and then suffers a sharp weight loss that ends at 496 °C. The remaining weight corresponds to the formation of Co_2O_3 (obsd: 16.33%, calcd: 15.96%).

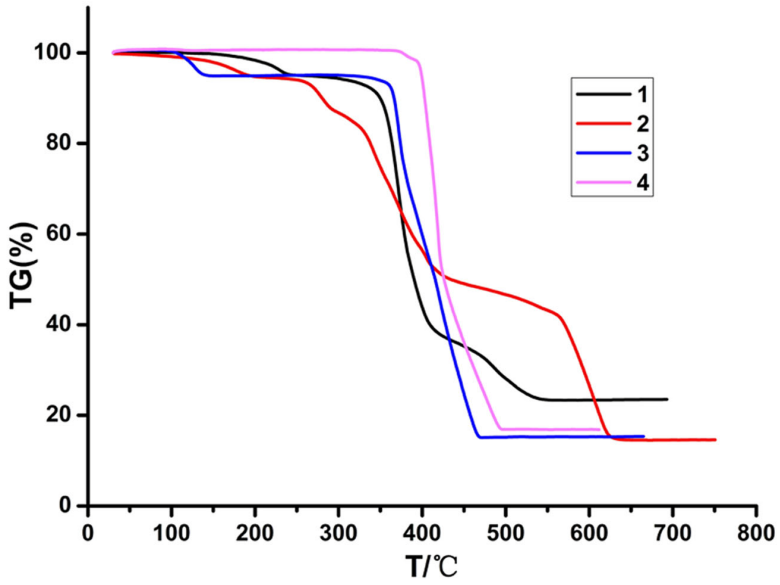

Figure S3. TG plots of complexes **1**–**4**.

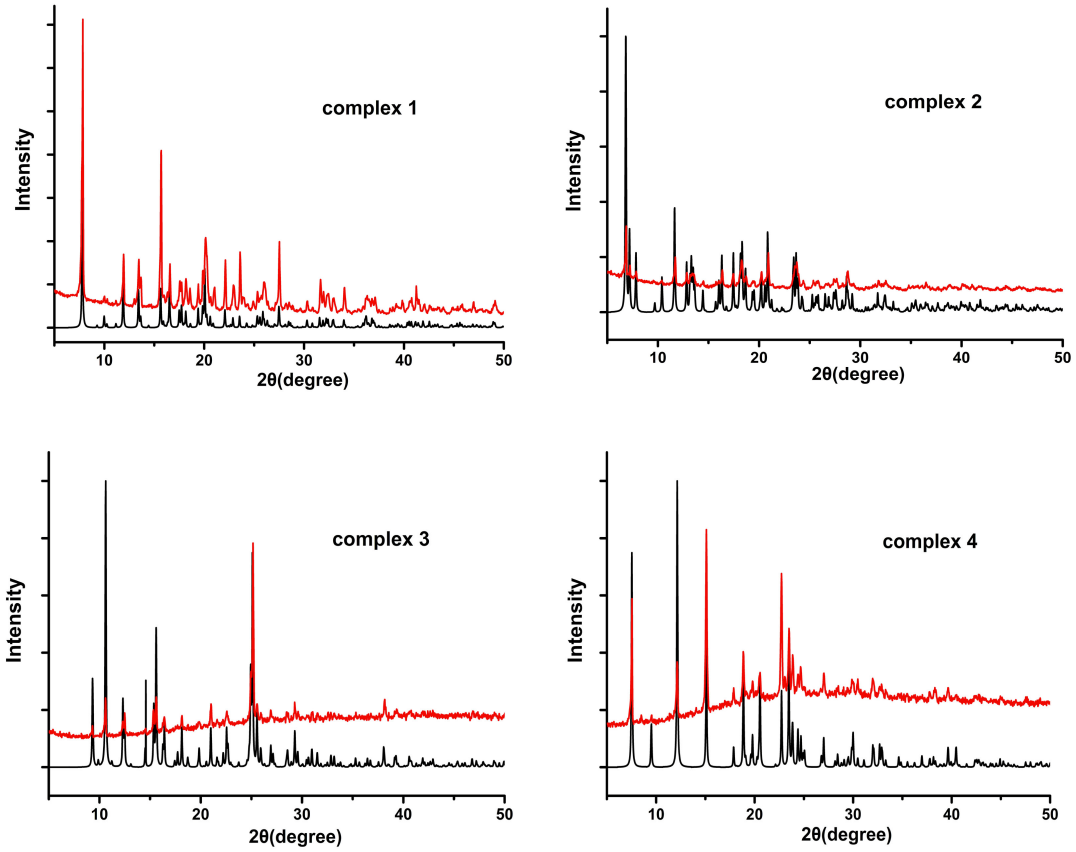

Figure S4**.** Experimental (red) and simulated (black) PXRD patterns of **1**–**4**.

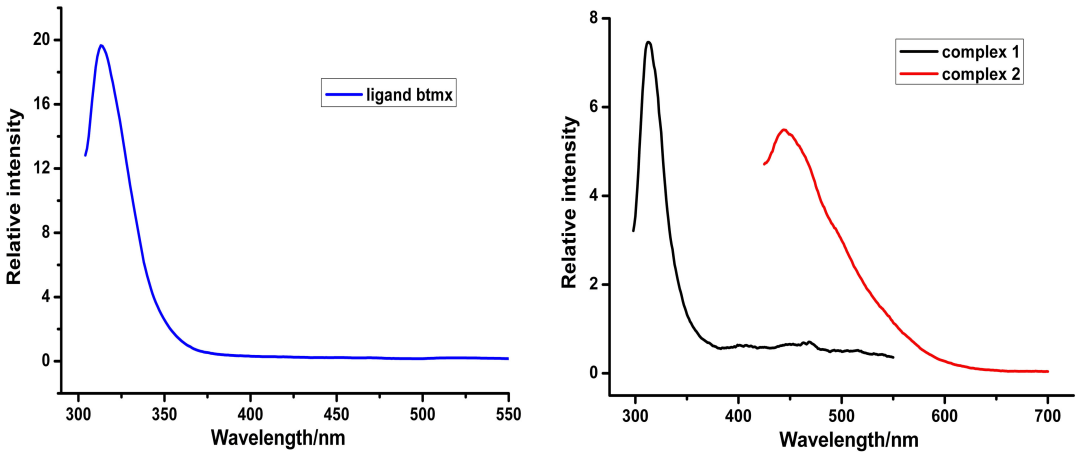

Figure S5. Solid-state emission spectra of ligand btmx (left) and complexes **1** and **2** (right) at room temperature.