

Supporting Information

Figure S1. Perspective view of the 3D supramolecular network in **1**, highlighting the channels along the *b* axis. Guest water molecules and free anions included in the channels are omitted for clarity.

Figure S2. ORTEP drawing of **2** with thermal ellipsoids at 50 % probability. Other atoms have been omitted for clarity.

Figure S3. Representation of the coordination number of a $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ polyoxoanion.

Figure S4. View of the 3D framework in **3**, highlighting the channels along the *a* axis. Guest water molecules included in the channels are omitted for clarity.

Figure S5. (a) The XPS spectrum of compound **1**. (b) The XPS spectrum of compound **2**. (c) The XPS spectrum of compound **3**.

Figure S6. ESR spectrum of compound **3**, showing the signal of Cr^{3+} .

Figure S7. (a) The IR spectrum of compound **1**. (b) The IR spectrum of compound **2**. (c) The IR spectrum of compound **3**.

Figure S8. (a) The TG curve of compound **1**. (b) The TG curve of compound **2**. (c) The TG curve of compound **3**.

Table S1. Relevant hydrogen-bonding distances in **1**.

Table S2. Relevant hydrogen-bonding distances in **2**.

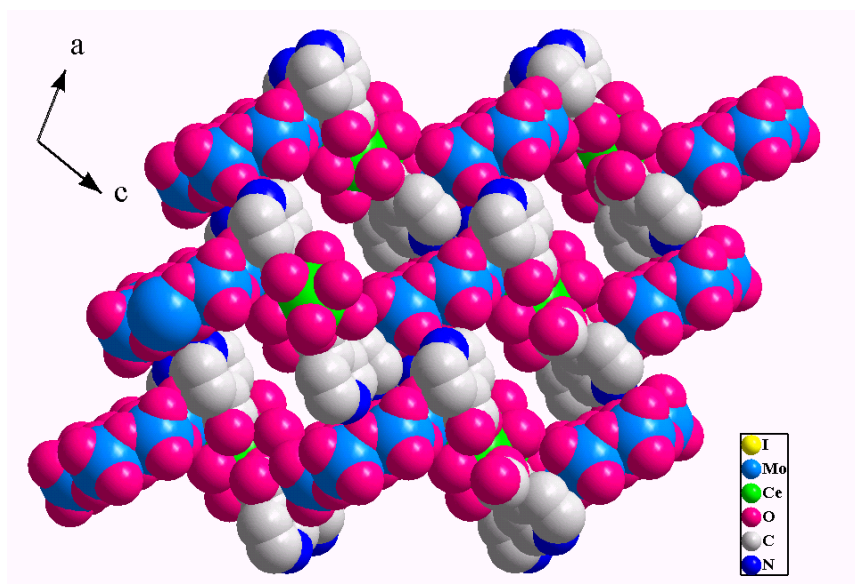


Figure S1

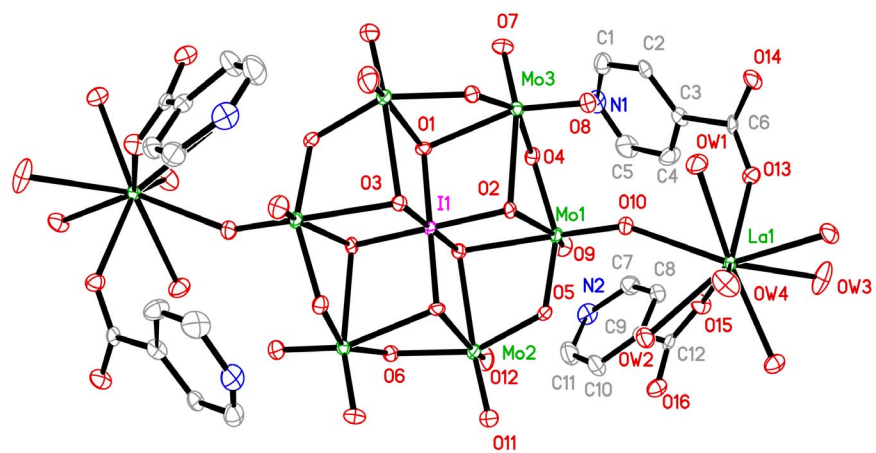


Figure S2

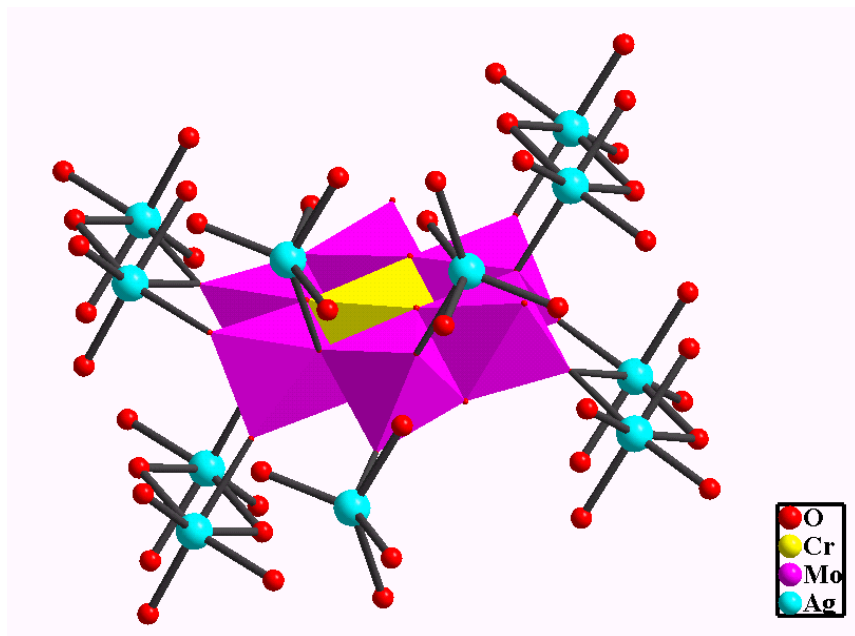


Figure S3

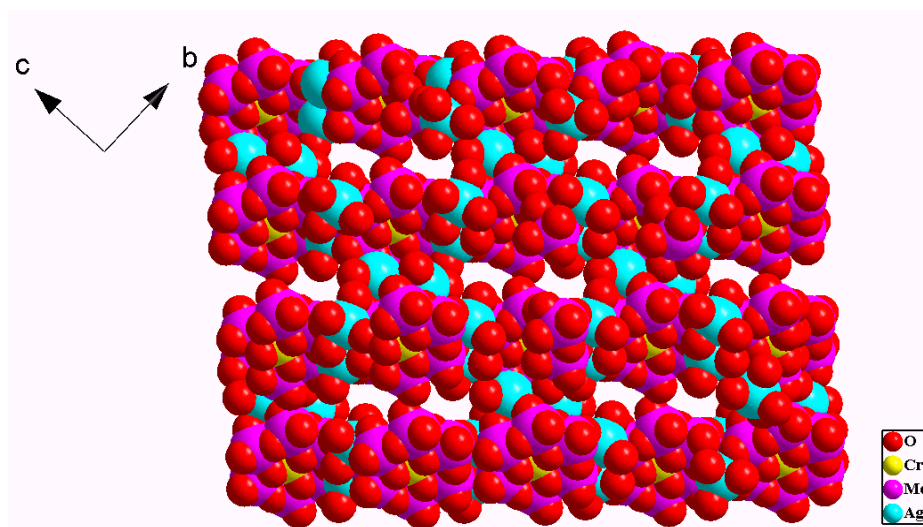


Figure S4

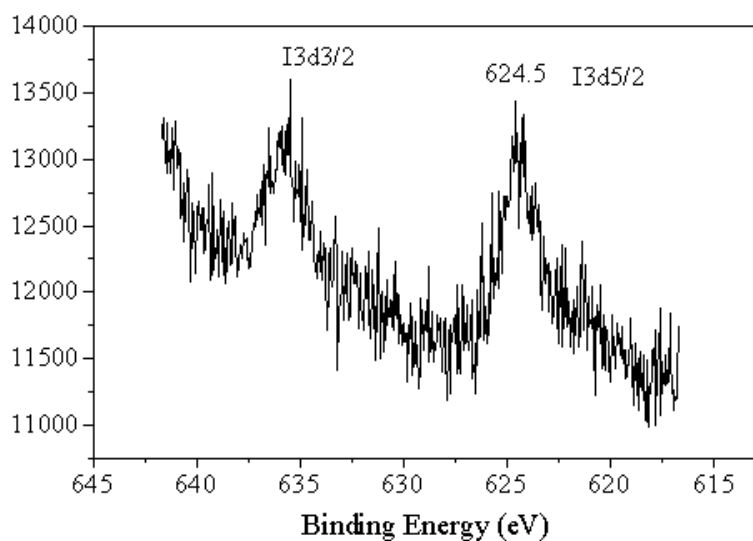
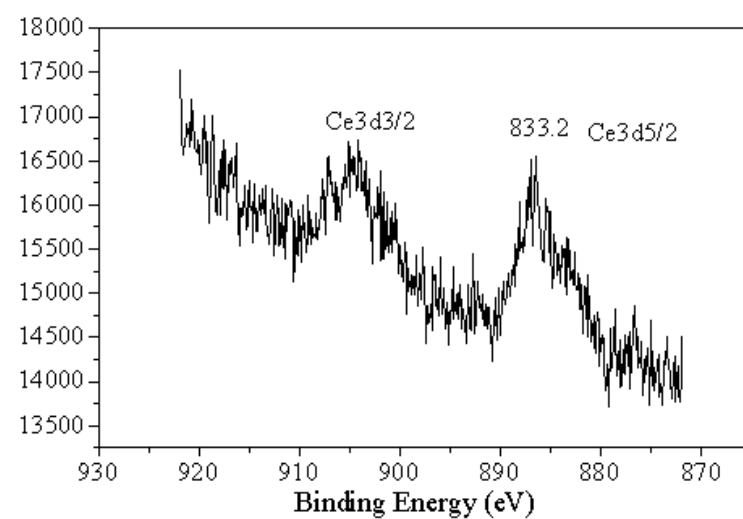
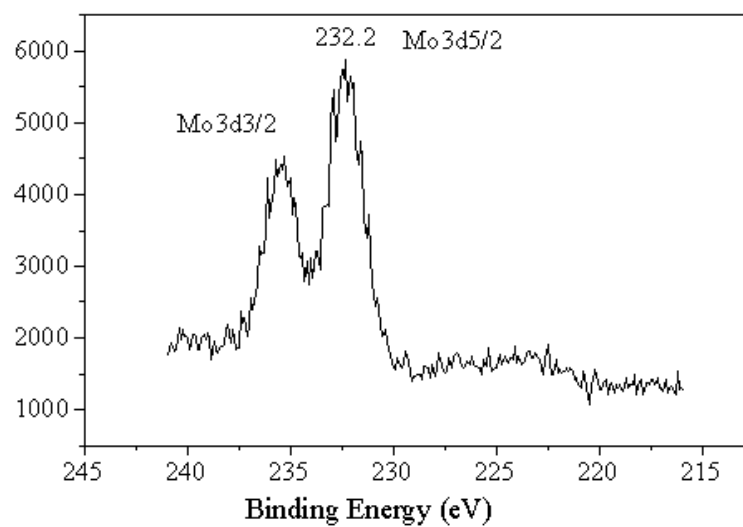


Figure S5a

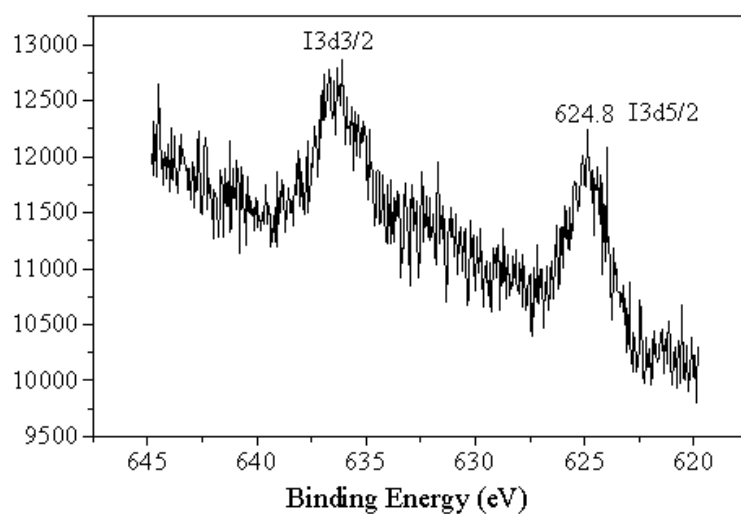
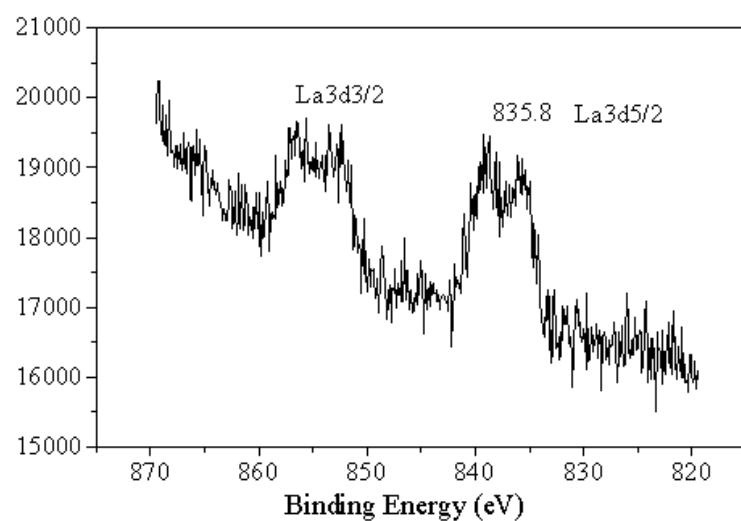
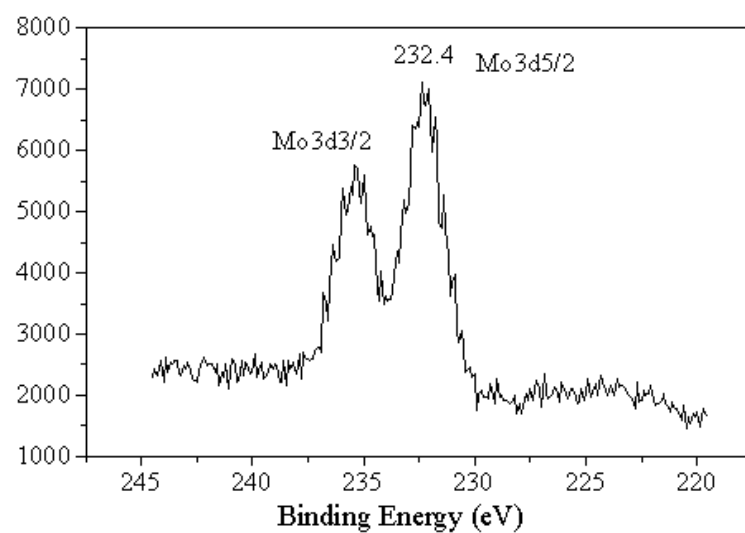


Figure S5b

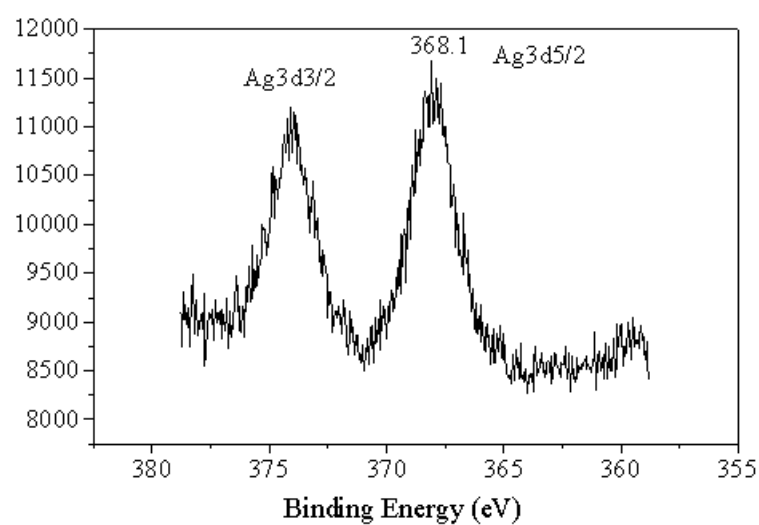
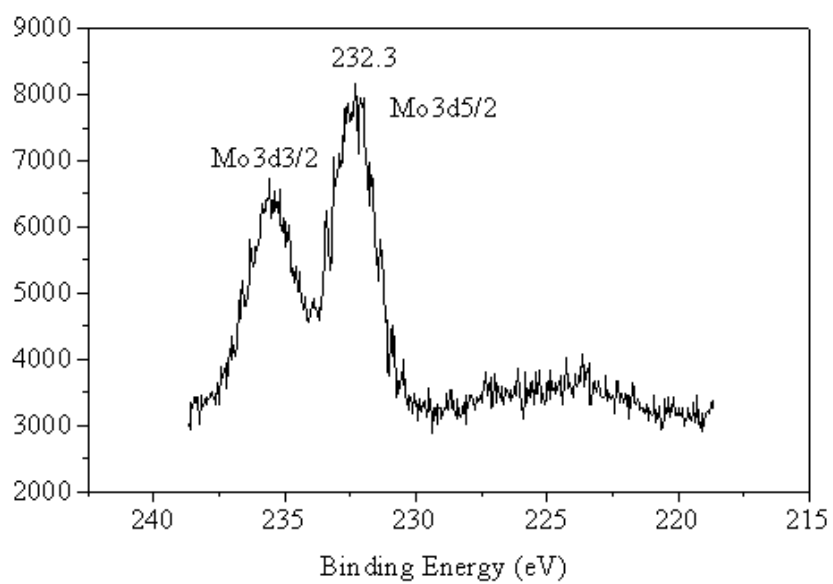


Figure S5c

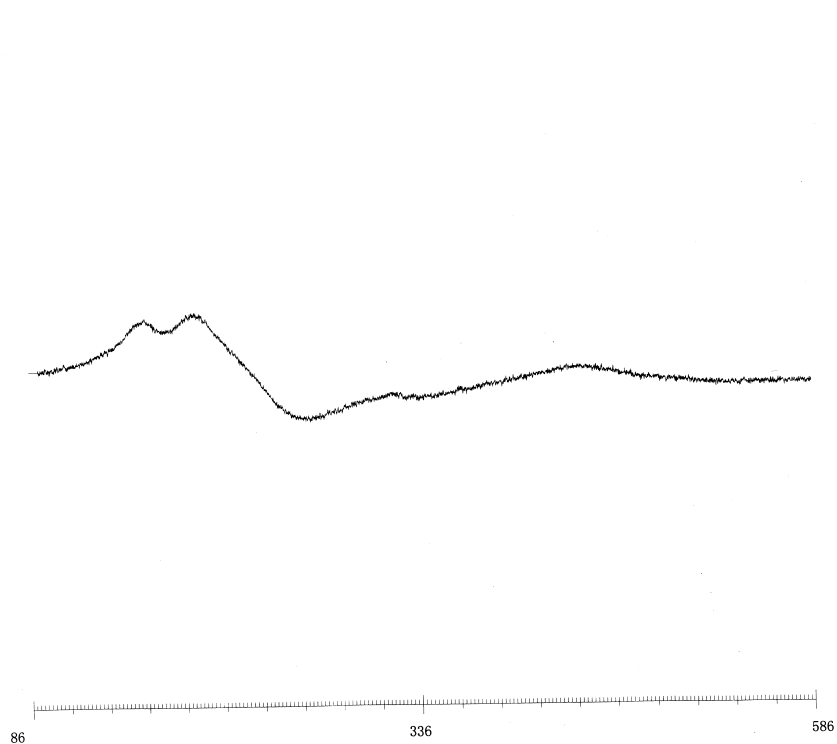


Figure S6

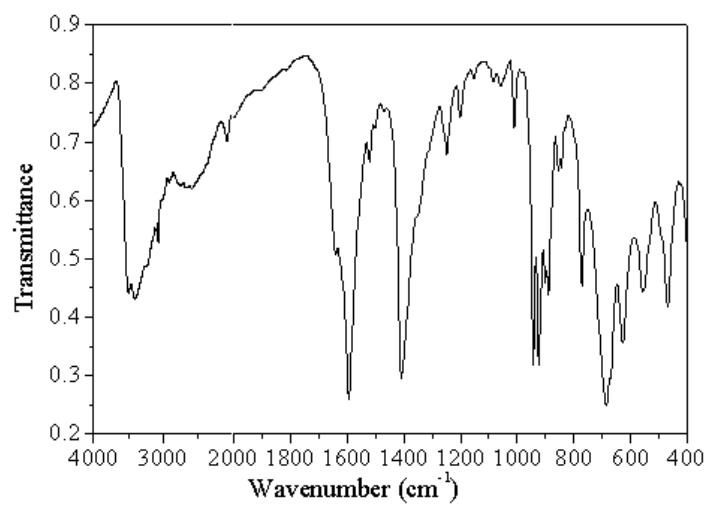


Figure S7a

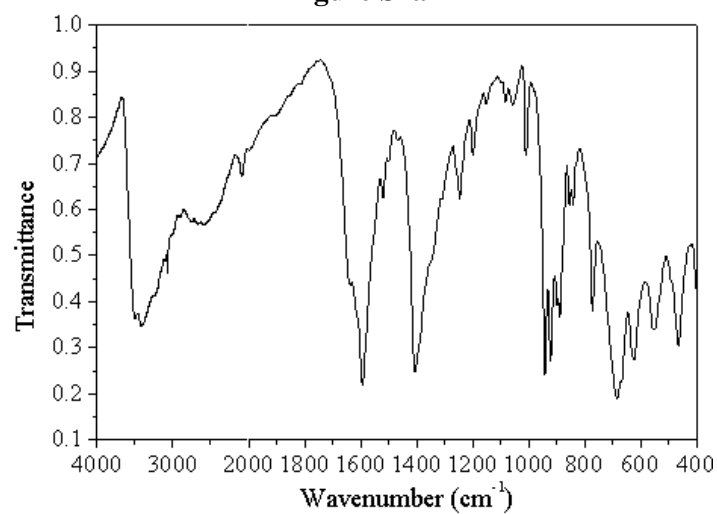


Figure S7b

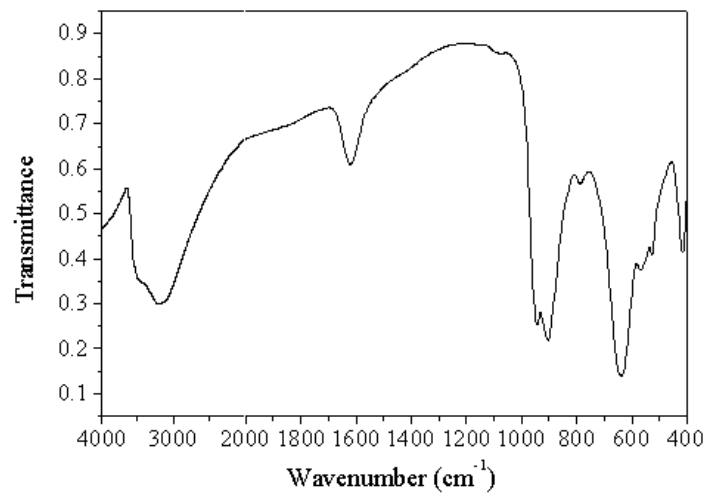


Figure S7c

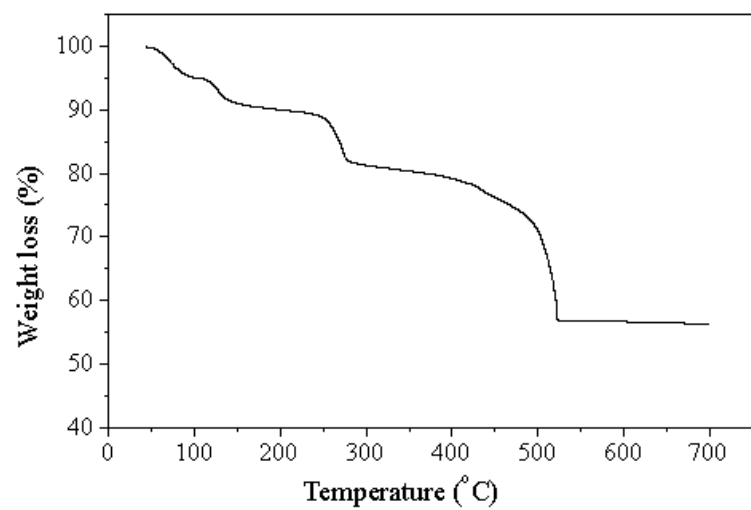


Figure S8a

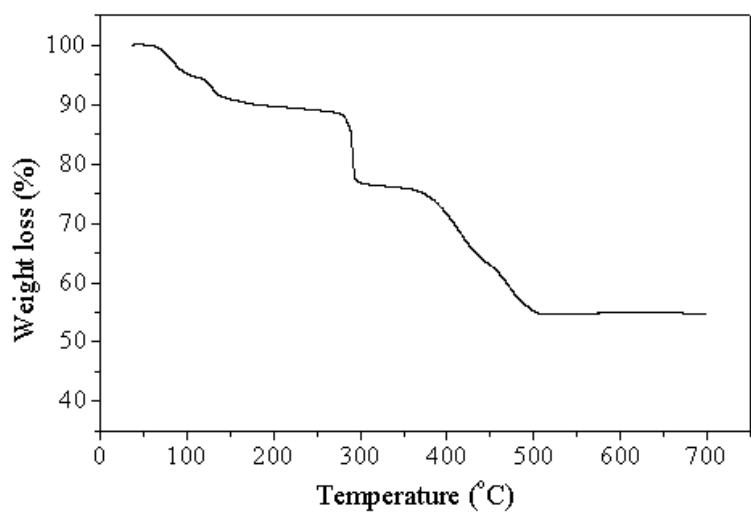


Figure S8b

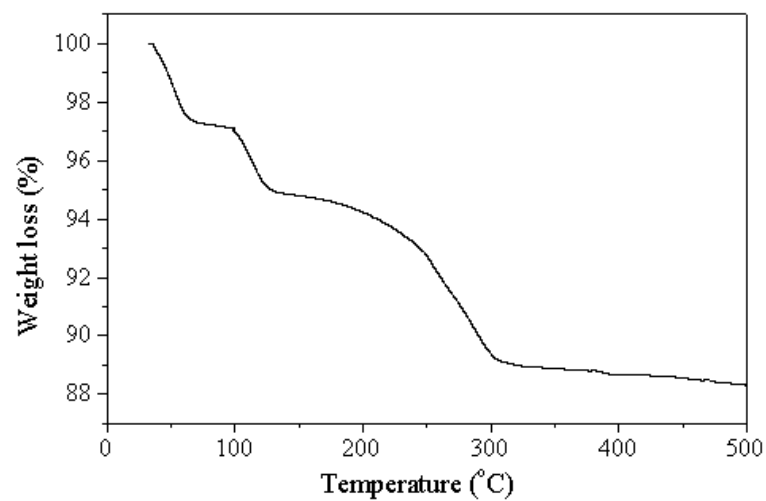


Figure S8c

Table S1. Relevant hydrogen-bonding distances in **1**.

A...B	Distance(Å)	A...B	Distance(Å)
N1...O6	2.660	O1...OW6A	2.805
N2...O5	2.664	O1...OW6B	2.802
O2...OW5	2.800	OW5...OW6A	2.709
		OW5...OW6B	2.703

Table S2. Relevant hydrogen-bonding distances in **2**.

A...B	Distance(Å)	A...B	Distance(Å)
N1...O4	2.669	OW4...OW5	2.749
N2...O6	2.648	OW5...OW6A	2.693
O2...OW6A	2.840	OW5...OW6B	2.718
O2...OW6B	2.765		