Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Unusual six-connected self-catenated network with 5-fold interpenetrated $CdSO_4$ subnets: Stepwise synthesis, topology analysis and fluorescence properties

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Additional experiments

Entry **1**: A buffer layer of component solvent (H_2O:CH_3OH = 1:1, 8 mL) was carefully layered over a mixed solution of NH_4Cl (0.06 mmol) and $Cd(ClO_4)_2·6H_2O$ (0.03 mmol) in H_2O (6 mL). Then a solution of **L** (0.06 mmol) in CH_3OH (6 mL) was layered over the buffer layer, and the resultant reaction was left to stand at room temperature. After ca. four weeks, bulky flocculent deposit appeared at the boundary, which was not proved to be complex **2** by the XRPD analysis.

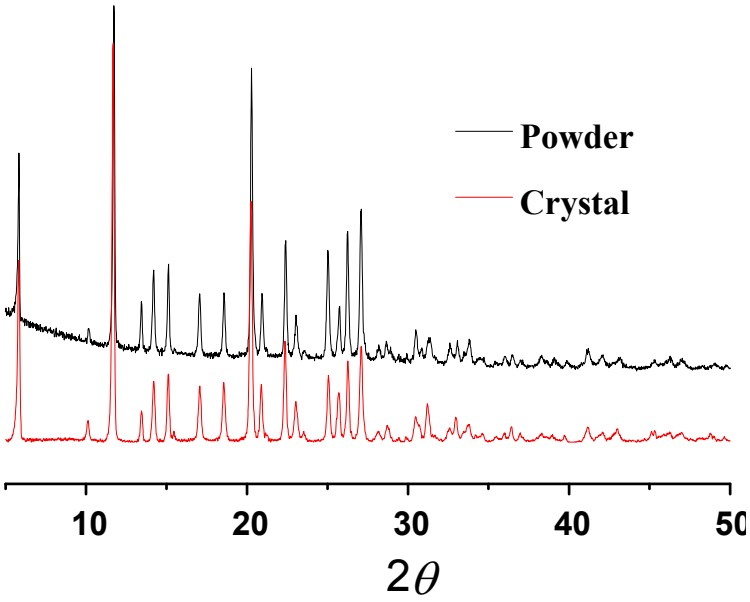
Entry **2**: A buffer layer of component solvent ($CHCl_3$:CH_3OH = 1:1, 8 mL) was carefully layered over a solution of **L** (0.06 mmol) in $CHCl_3$ (6 mL). Then a mixed solution of NH_4Cl (0.06 mmol) in H_2O (1 mL) and $Cd(ClO_4)_2·6H_2O$ (0.03 mmol) in CH_3OH (5 mL) was layered over the buffer layer, and the resultant reaction was left to stand at room temperature. After ca. four weeks, bulky flocculent deposit appeared at the boundary, which was not proved to be complex **2** by the XRPD analysis, either.

Entry **3**: A buffer layer of component solvent (H_2O:CH_3OH = 1:1, 8 mL) was carefully layered over a solution of $Cd(ClO_4)_2·6H_2O$ (0.03 mmol) in H_2O (6 mL). Then a mixed solution of NH_4Cl (0.06 mmol) in H_2O (1 mL) and **L** (0.06 mmol) in CH_3OH (5 mL) was layered over the buffer layer, and the resultant reaction was left to stand at room temperature. After ca. four weeks, bulky flocculent deposit appeared at the boundary, which was not complex **2** proved by the XRPD analysis.

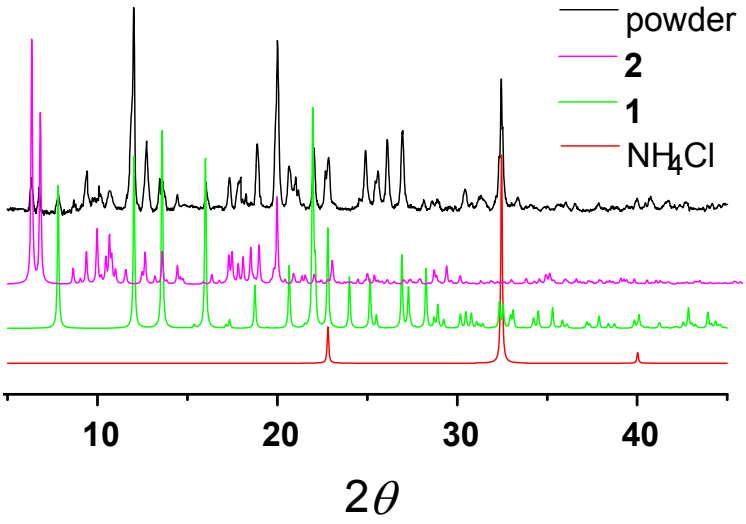
Table S1. Selected Bond Lengths [Å] and Angles [º] for complexes **1** and **2**.

		1	
Cd(1)-N(1)	2.303(4)	Cd(1)-N(1)#1	2.303(4)
Cd(1)-N(1)#2	2.303(4)	Cd(1)-N(1)#3	2.303(4)
Cd(1)-O(1)	2.414(7)	Cd(1)-O(1)#1	2.414(7)
Cd(1)-O(1)#2	2.414(7)	Cd(1)-O(1)#3	2.414(7)
O(1)-O(1')	0		
N(1)-Cd(1)-N(1)#1	87.26(19)	N(1)-Cd(1)-N(1)#2	92.74(19)
N(1)-Cd(1)-N(1)#3	180	N(1)#1-Cd(1)-N(1)#2	180
N(1)#1-Cd(1)-N(1)#3	92.74(19)	N(1)#2-Cd(1)-N(1)#3	87.26(19)
O(1)-Cd(1)-O(1)#3	180	O(1)#2-Cd(1)-O(1)#1	180
N(1)-Cd(1)-O(1)	82.62(19)	N(1)-Cd(1)-O(1)#1	81.77(19)
N(1)-Cd(1)-O(1)#2	98.23(19)	N(1)-Cd(1)-O(1)#3	97.38(19)
N(1)#1-Cd(1)-O(1)	81.77(19)	N(1)#1-Cd(1)-O(1)#1	82.62(19)
N(1)#1-Cd(1)-O(1)#2	97.38(19)	N(1)#1-Cd(1)-O(1)#3	98.23(19)
N(1)#2-Cd(1)-O(1)	98.23(19)	N(1)#2-Cd(1)-O(1)#1	97.38(19)
N(1)#2-Cd(1)-O(1)#2	82.62(19)	N(1)#2-Cd(1)-O(1)#3	81.77(19)
N(1)#3-Cd(1)-O(1)	97.38(19)	N(1)#3-Cd(1)-O(1)#1	98.23(19)
N(1)#3-Cd(1)-O(1)#2	81.77(19)	N(1)#3-Cd(1)-O(1)#3	82.62(19)
		2	
Cd(1)-N(1)	2.308(5)	Cd(1)-N(3)	2.304(5)
Cd(1)-N(5)	2.331(5)	Cd(1)-N(7)	2.271(5)
Cd(1)-Cl(1)	2.6843(8)	Cd(1)-Cl(2)	2.6743(7)
N(3)-Cd(1)-N(1)	94.6(2)	N(5)-Cd(1)-N(1)	176.15(17)
N(7)-Cd(1)-N(1)	88.49(18)	N(5)-Cd(1)-N(3)	89.23(19)
N(7)-Cd(1)-N(3)	176.77(19)	N(7)-Cd(1)-N(5)	87.65(17)
Cl(2)-Cd(1)-Cl(1)	177.79(4)	N(1)-Cd(1)-Cl(1)	93.62(13)
N(3)-Cd(1)-Cl(1)	89.21(14)	N(5)-Cd(1)-Cl(1)	86.44(13)
N(7)-Cd(1)-Cl(1)	91.46(13)	N(1)-Cd(1)-Cl(2)	88.53(13)
N(3)-Cd(1)-Cl(2)	90.11(14)	N(5)-Cd(1)-Cl(2)	91.45(13)
N(7)-Cd(1)-Cl(2)	89.11(13)		

*Symmetry mode for **1**: #1, -x+1, -y, -z+1; #2, x, -y, z; #3, -x+1, y, -z+1.

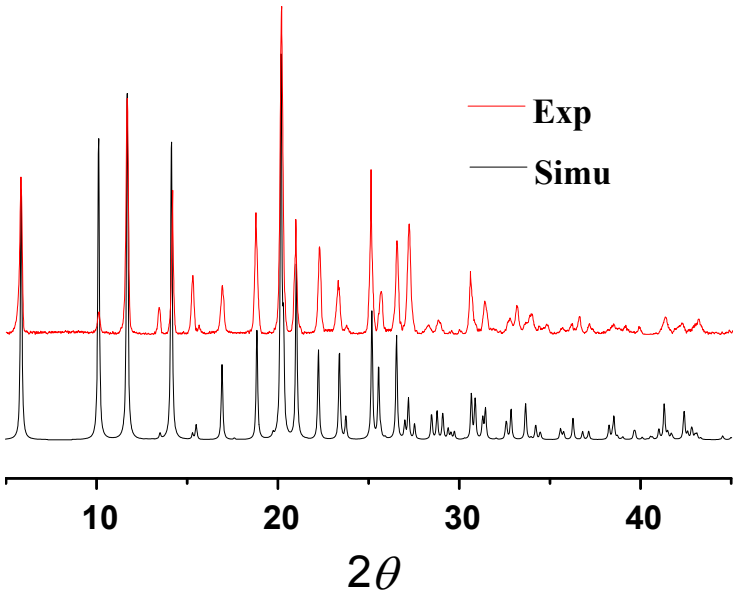


(a)

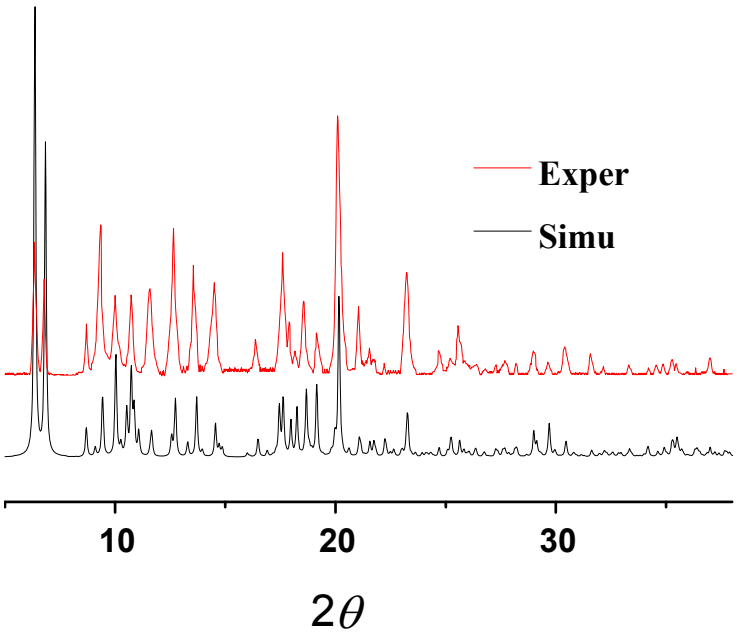


(b)

Figure S1 XRPD data of powder samples in the preparation of: (a) **1**; (b) **2**.

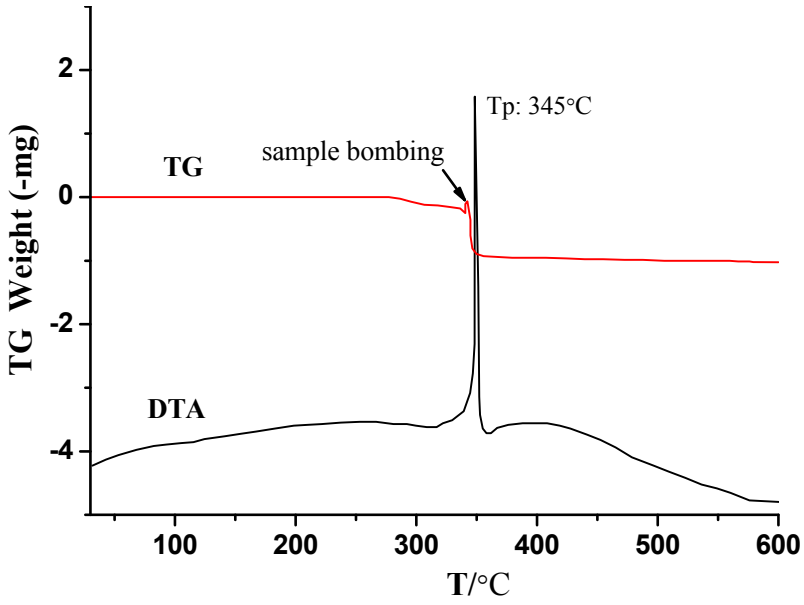


(a)

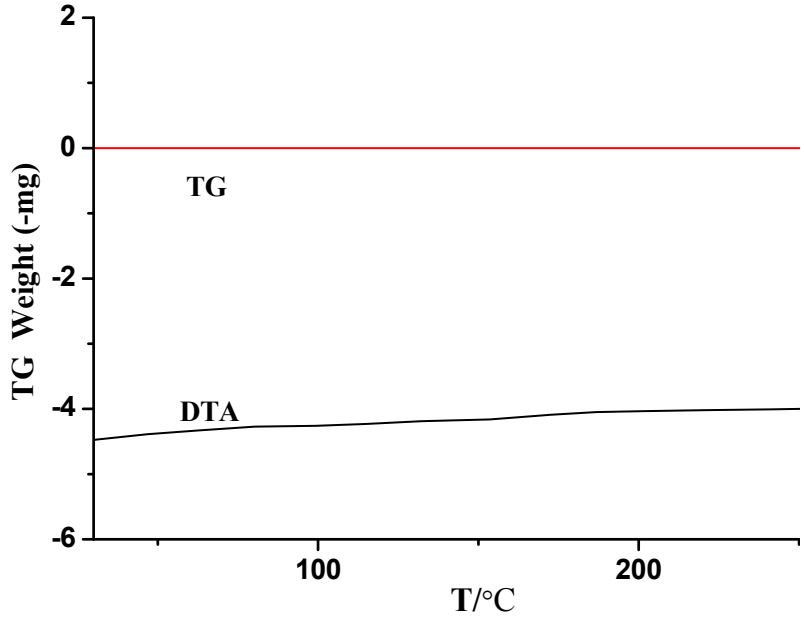


(b)

Figure S2 XRPD experimental and calculated patterns for complexes: (a) **1**; (b) **2**.

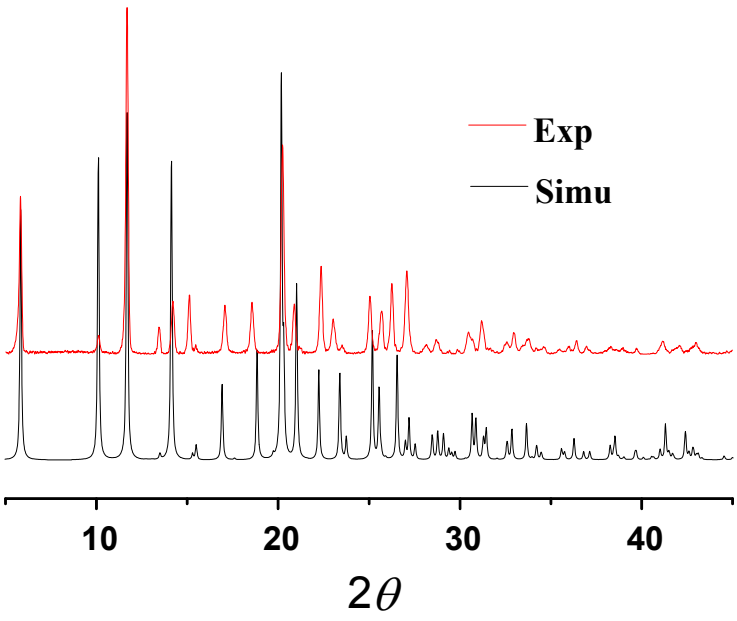


(a)

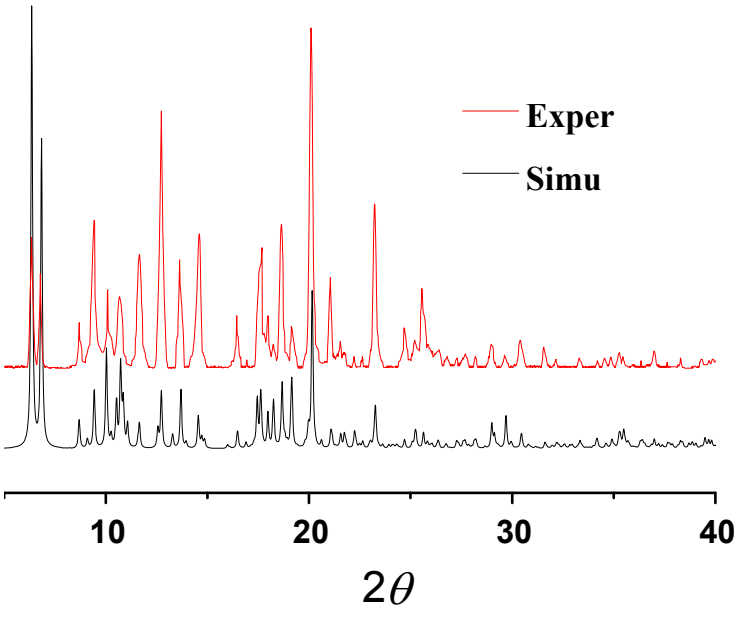


(b)

Figure S3 TGA data of degassed samples for: (a) **1′**; (b) **2′**. When **1′** was conducted a TGA experiment, a rapid mass loss with slightly explosive was observed at about 340 °C due to the perchlorate ion. The balance was disturbed and the sample was splashed out. To avoid the explosion, the TGA experiment of **2′** was carried out up to 250 °C. For the two TGA data, no obvious weigh lost was found until 250 °C, which proved that there were no guest molecules in the two samples.



(a)



(b)

Figure S4 XRPD experimental and calculated patterns of degassed samples for: (a) **1′**; (b) **2′**.

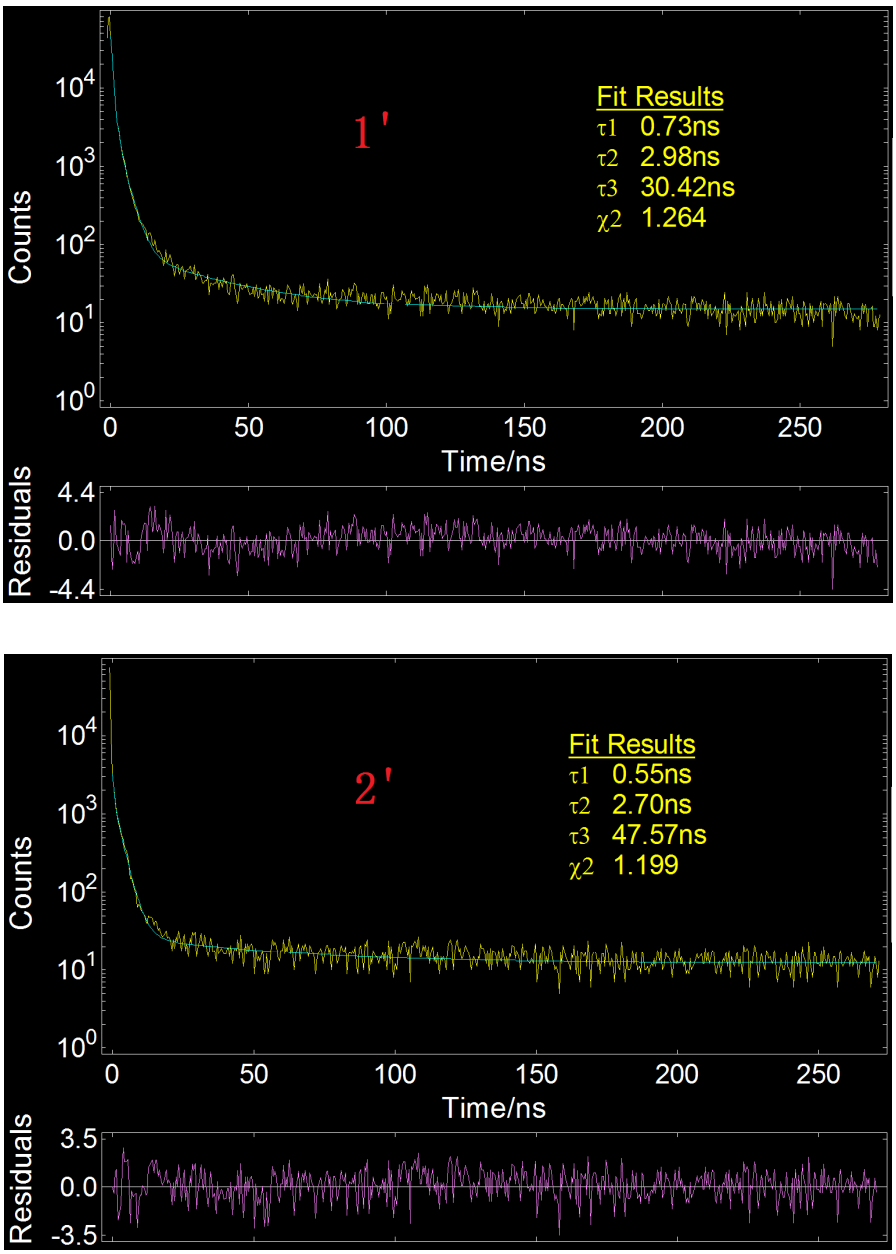


Figure S5 The luminescence decay of **1′** and **2′**.