Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Solvent-assisted Construction of Diverse Mg-TDC Coordination Polymers

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Table S1. Temperature and solvent effects on the syntheses of compounds **1-4** under solvothermal conditions.

Number	Metal source	Solvent	Temperature	Results
1				
1-1	$Mg(NO_3)_2 \cdot 6H_2O$[a]	3mL EG[c] + 3mL acetonitrile	150 ˚C[b]	**1**
1-2	$Mg(NO_3)_2 \cdot 6H_2O$	3mL EG + 3mL acetonitrile	160 ˚C	**1**
1-3	$Mg(NO_3)_2 \cdot 6H_2O$	3mL EG	150 ˚C	Solution
1-4	$Mg(NO_3)_2 \cdot 6H_2O$	3mL EG + 3mL acetone	150 ˚C	**1**
1-5	$Mg(NO_3)_2 \cdot 6H_2O$	3mL EG + 3mL methanol	150 ˚C	**1**
1-6	$Mg(NO_3)_2 \cdot 6H_2O$	3mL EG + 3mL ethanol	160 ˚C	**1**
1-7	$MgCl_2 \cdot 6H_2O$	3mL EG + 3mL acetonitrile	150 ˚C	Unknown solids
1-8	$MgCl_2 \cdot 6H_2O$	3mL EG + 3mL acetonitrile	160 ˚C	**1**
2				
2-1	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL methanol	120 ˚C	Unknown crystals
2-2	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL methanol	140 ˚C	**2**
2-3	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL methanol	150 ˚C	**2**
2-4	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL methanol	160 ˚C	Unknown powders
2-5	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL methanol	170 ˚C	$MgSO_4$
2-6	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO	150 ˚C	**2**
2-7	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL ethanol	150 ˚C	**2**
2-8	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL acetonitrile	150 ˚C	**2**
2-9	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL DMF	150 ˚C	**2**
2-10	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 2mL benzene	150 ˚C	**2**
2-11	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMSO + 1mL DMF + 1mL H_2O	120 ˚C	**2**
3				
3-1	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMA	120 ˚C	**3**
3-2	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMA	140 ˚C	**3**
3-3	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMA	150 ˚C	**3**
3-4	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMA	160 ˚C	Unknown crystals
3-5	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMA + 0.1 mL H_2O	150 ˚C	**3**
3-6	$Mg(NO_3)_2 \cdot 6H_2O$	4mL DMA + 0.1mL methanol	150 ˚C	**3**
4				
4-1	$Mg(NO_3)_2 \cdot 6H_2O$	5mL DMF + 1mL ethanol + 0.5mL H_2O	100 ˚C	**4**
4-2	$Mg(NO_3)_2 \cdot 6H_2O$	5mL DMF + 1mL ethanol + 0.5mL H_2O	120 ˚C	Mg-formate[d]
4-3	$Mg(NO_3)_2 \cdot 6H_2O$	5mL DMF + 1mL ethanol + 0.5mL H_2O	130 ˚C	Mg-formate

4-4	$Mg(NO_3)_2·6H_2O$	5mL DMF + 1mL ethanol + 0.5mL H_2O	140 ˚C	Mg-formate
4-5	$Mg(NO_3)_2·6H_2O$	5mL DMF + 1mL ethanol + 0.5mL H_2O	160 ˚C	Mg-formate
4-6	$Mg(NO_3)_2·6H_2O$	5mL DMF + 1mL ethanol +0.1mL H_2O	100 ˚C	**4**
4-7	$Mg(NO_3)_2·6H_2O$	5mL DMF + 1mL ethanol	100 ˚C	Unknown solids

Noting that:

[a] The reaction amount of $Mg(NO_3)_2·6H_2O$ was 1 mmol in **1**, **2** and **4** while it was 0.39 mmol in **3** and that of H_2TDC was 1.5 mmol in **1**, **2** and **4** while it was 0.39 mmol in **3**.

[b] The reaction time was 3 days for **1**, **2** and **3** while it was 3.5 days for **4**; for obtaining crystals with large size, programmed cooling process was needed for **3** and **4**.

[c] H_2TDC = 2, 5-thiophenedicarboxylic acid, EG = ethylene glycol, DMSO = dimethyl sulfoxide, DMA = *N, N'*-dimethyl-acetamide, DMF = *N, N'*-dimethyl-formamide.

[d] Chemical formula, $(Me_2NH_2)[Mg(HCOO)_3]$[1].

References:

1 A. Rossin, A. Ienco, F. Costantino, T. Montini, B. Di Credico, M. Caporali, L. Gonsalvi, P. Fornasiero and M. Peruzzini, *Cryst. Growth Des.*, 2008, **8**, 3302-3308.

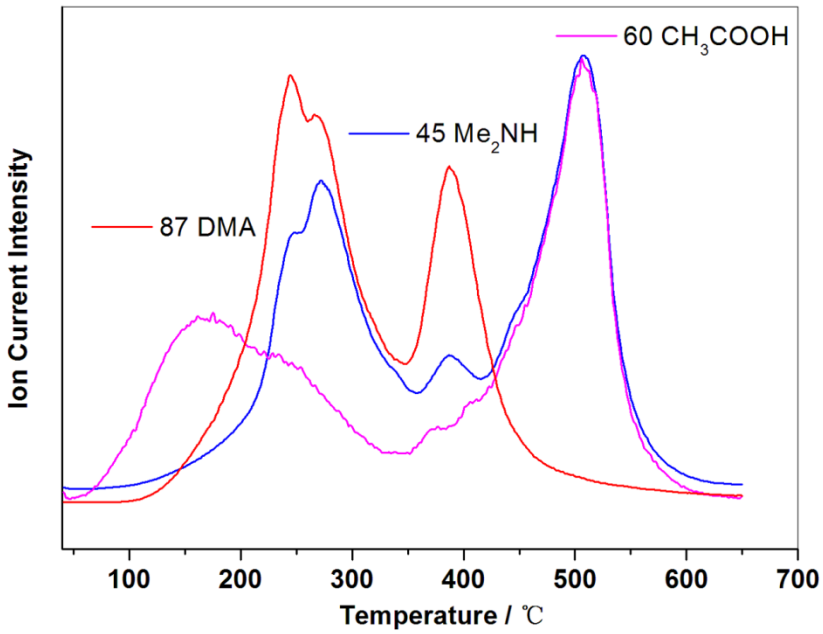

Fig. S1 The TGA-MS characterizations of compound **3** verified the existence of DMA, $[Me_2NH_2]^+$ and CH_3COO^- in the structure.

More structural figures.

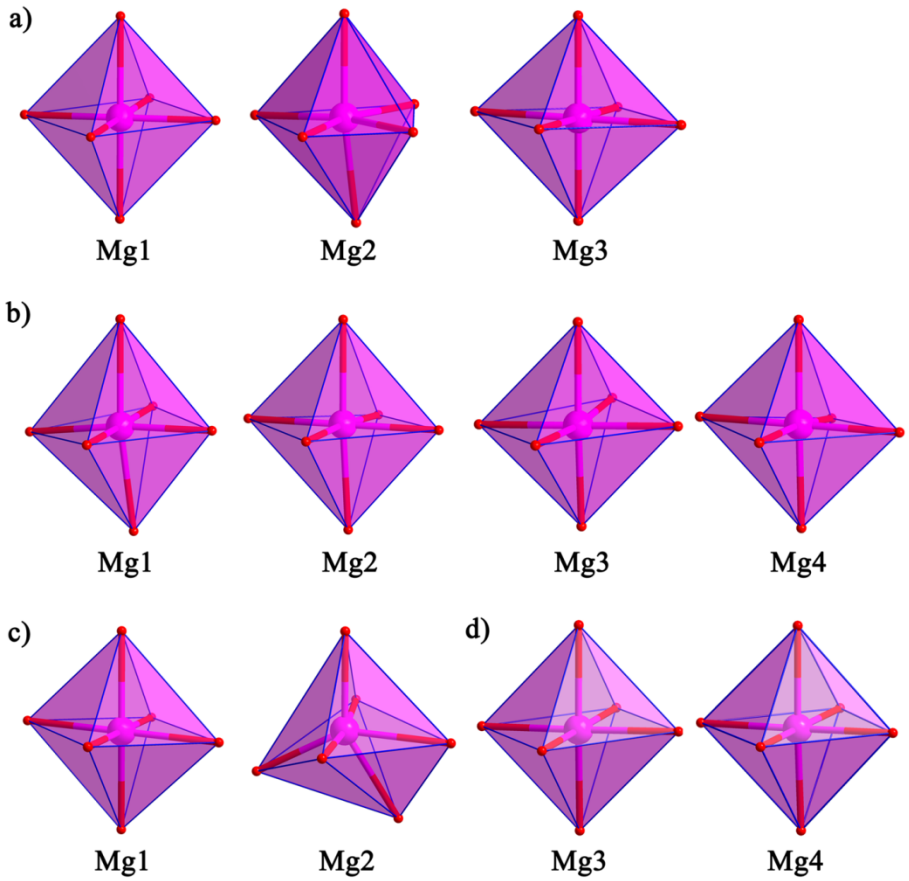

Fig. S2 The [MgO_6] polyhedra in the structures of **1** (a), **2** (b), **3** (c) and **4** (d).

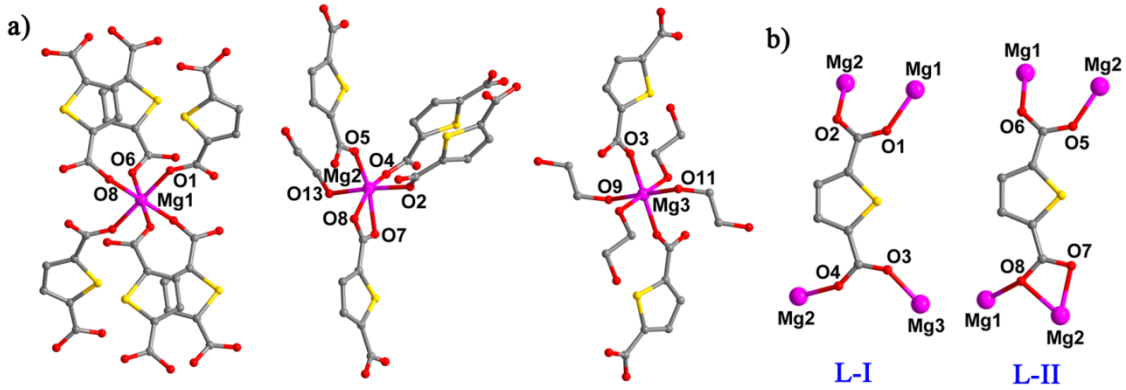

Fig. S3 The coordination environments of independent Mg^{2+} ions (a) and TDC^{2-} ligands (b) in **1**.

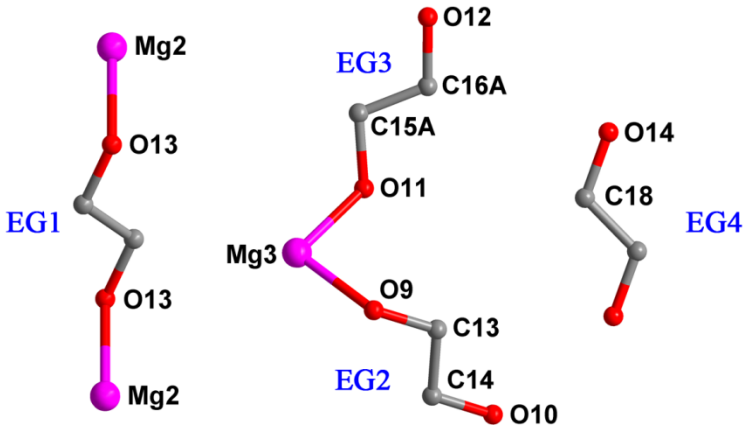

Fig. S4 The four independent EG molecules existing in the structure of **1**.

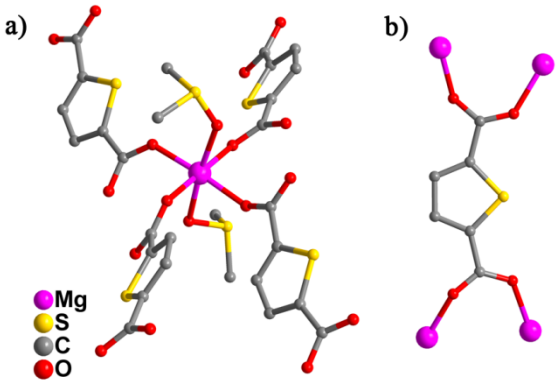

Fig. S5 The similar coordination modes of four independent Mg^{2+} ions (a) and four unique TDC^{2-} ligands (b) in **2**.

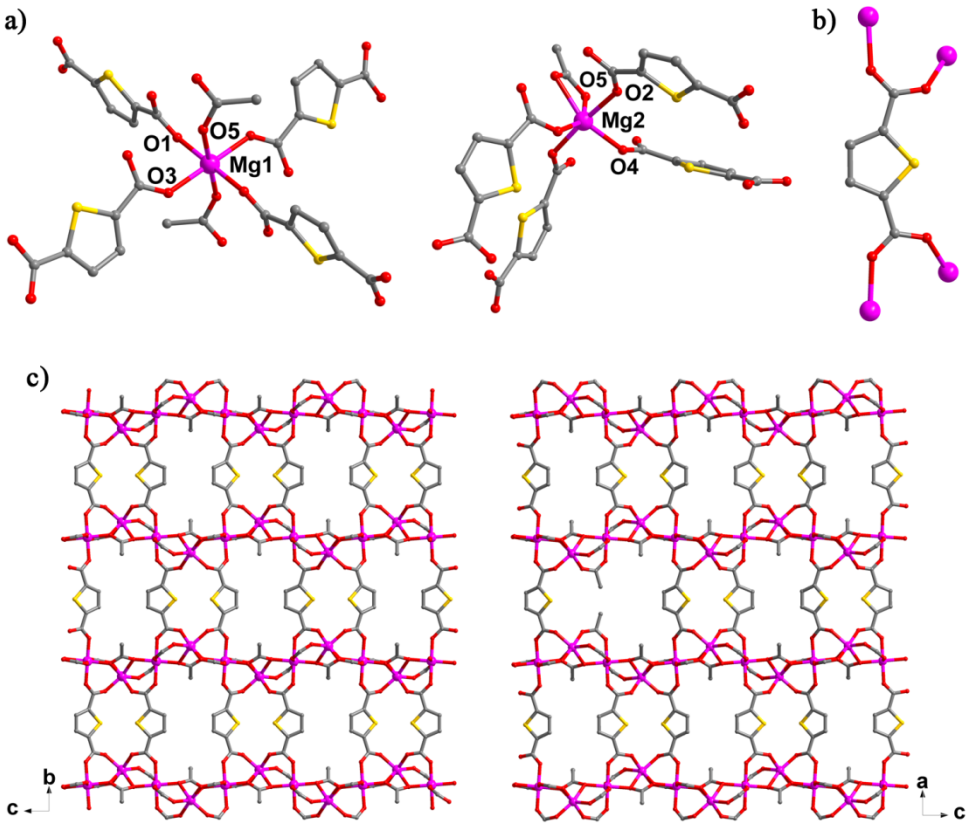

Fig. S6 (a) and (b) show the coordination modes of two unique Mg^{2+} centers and TDC^{2-} ligand, respectively. (c) View of the layers formed by linking TDC^{2-} ligands and [Mg-AC] chains along the *bc* and *ac* planes, respectively in **3**.

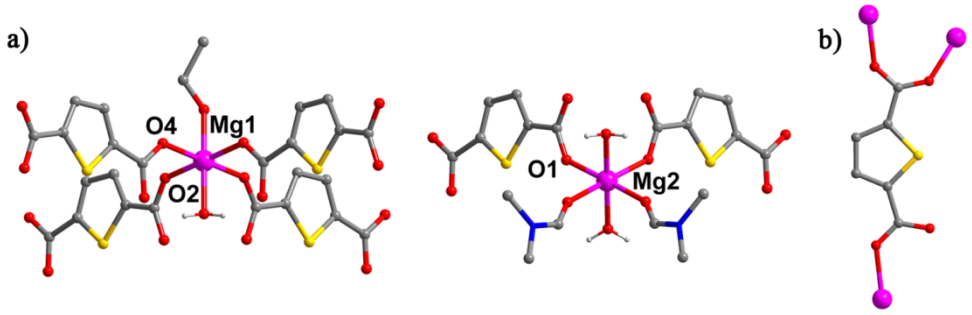

Fig. S7 The coordination environment of two unique Mg^{2+} centers (a) and TDC^{2-} ligand (b) in **4**.

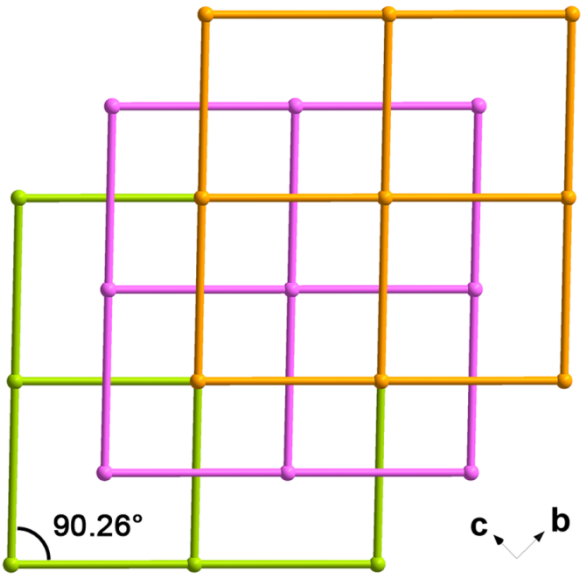

Fig. S8 View of the simplified rhombic topology in **4**.

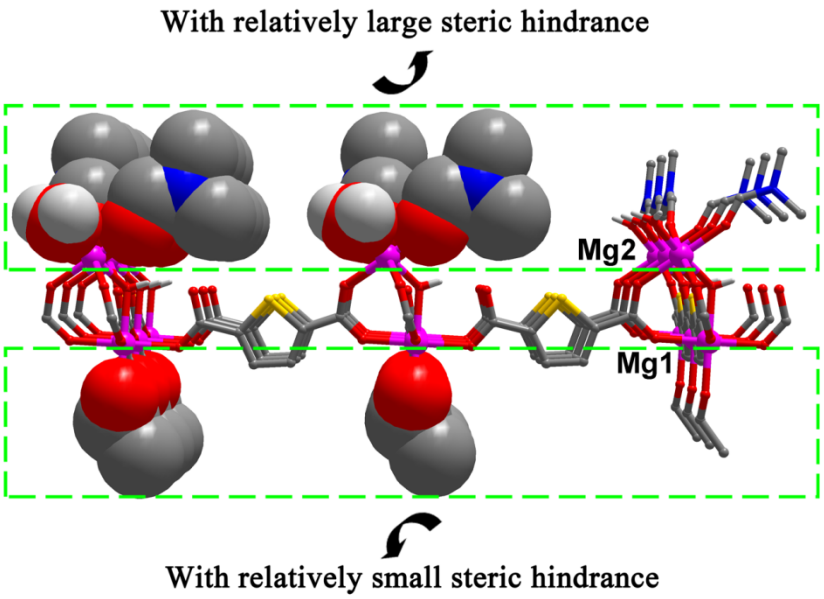

Fig. S9 View of a layer of **4** showing the difference of steric hindrance in both sides of a layer in **4**. Clearly, the side with two DMF and one H_2O molecule coordinated to Mg2 has larger steric hindrance than the other side with one ethanol molecule binding to Mg1.

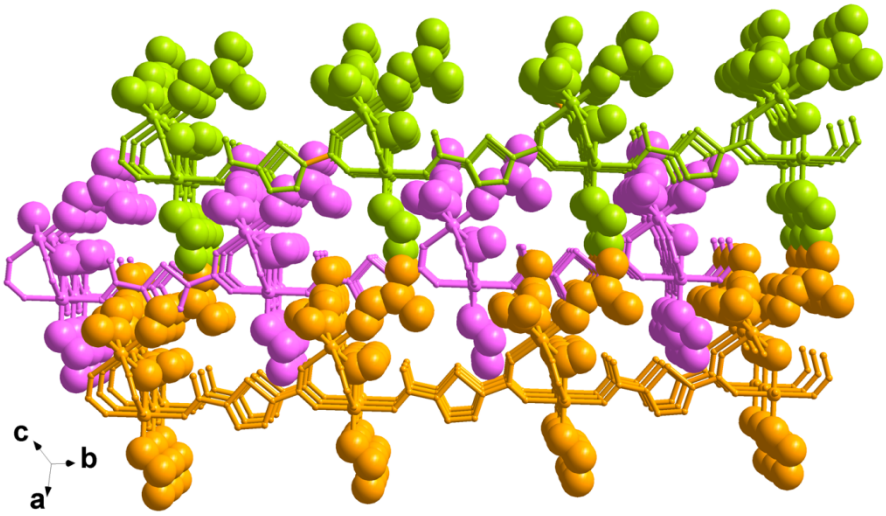

Fig. S10 View of the packing diagram of **4** showing the "head to tail" packing favourable for the maximal filling of the void space. Solvent molecules are drawn in a space-filling mode. The free DMF molecules are omitted for clarity.

CIE chromaticity diagram.

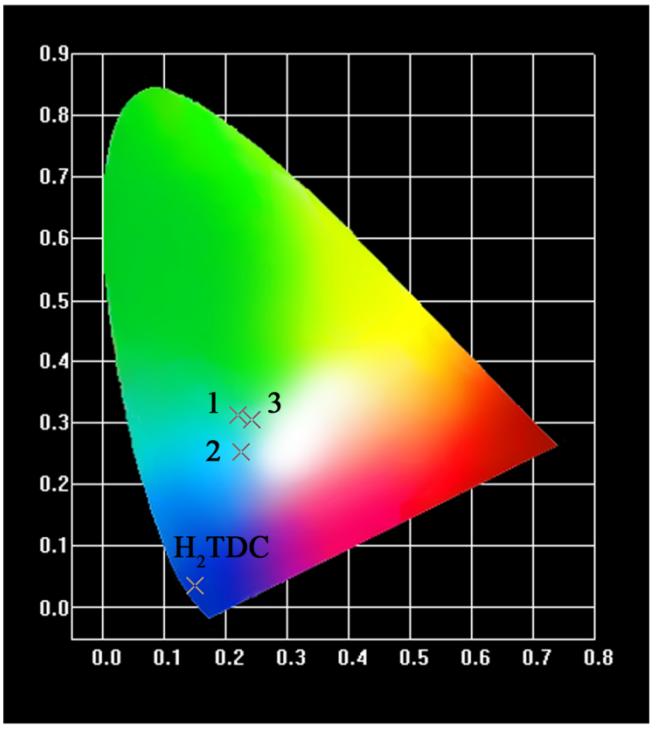

Fig. S11 CIE chromaticity diagram of the emission colors of compounds **1-3** and H_2TDC ligand.

SHG characterization.

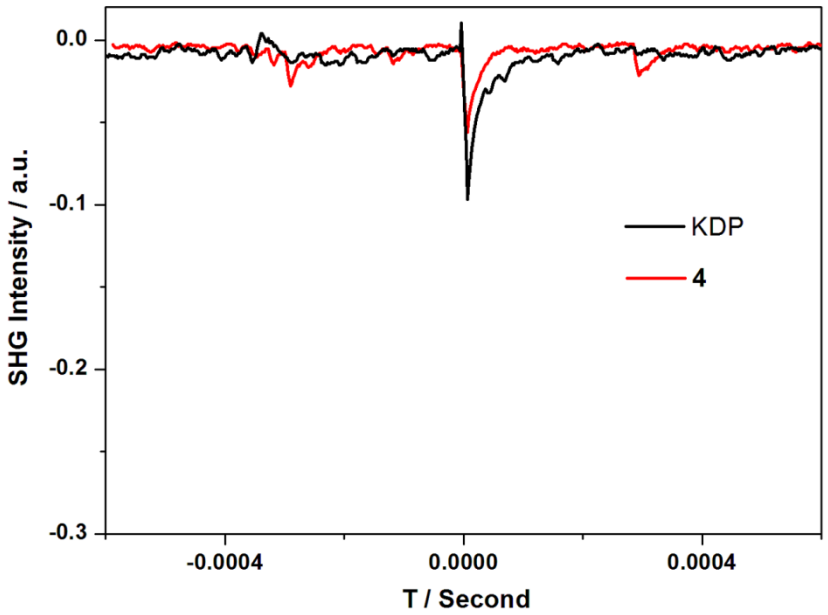

Fig. S12 Oscilloscope traces of the SHG signals of **4** and KDP at the same particle size.

IR Spectra.

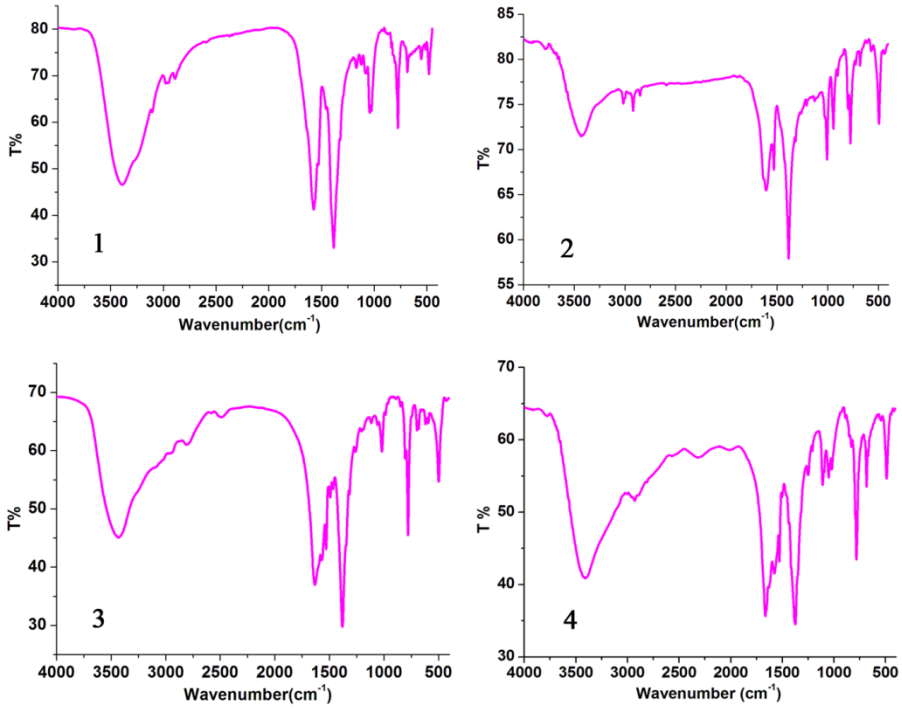

Fig. S13 FT-IR spectra of compounds **1-4**.