

## Supporting information for

# Synthesis, optical and magnetic properties of hybrid $\alpha,\alpha'$ -oligothiophenecarboxylates / transition metal hydroxide multilayered compounds

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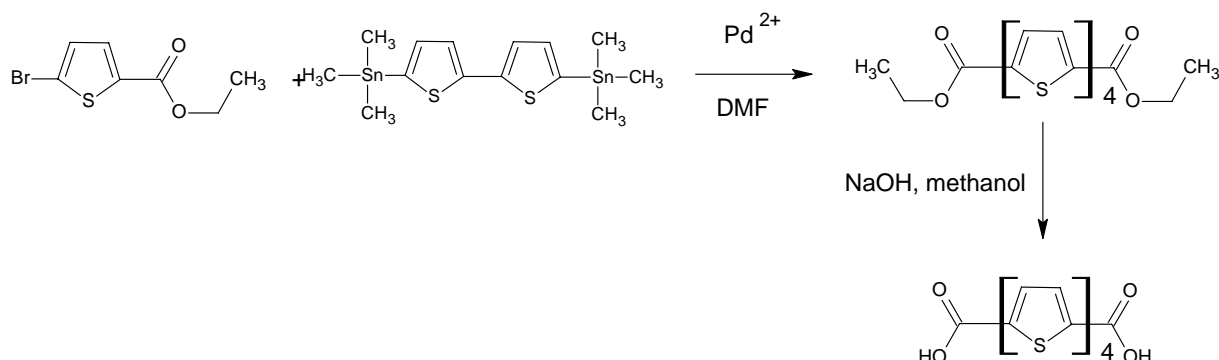
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## Synthesis of the oligothiophene dicarboxylates

[2,2']-bithiophene-5,5'-dicarboxylic acid and [2,2';5',2''] terthiophene-5,5''-dicarboxylic acid were prepared following the procedure reported by Kagan et al.<sup>1</sup> 2,2':5',2'':5'',2'''-Quaterthiophene-5,5'''-dicarboxylate, was obtained following the protocol described below.



**Preparation of diethyl 2,2':5',2'':5'',2'''-Quaterthiophene-5,5'''-dicarboxylate.** 3.3 g of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.0067 mol) were added, under argon atmosphere, to a solution of 4.4 g of ethyl 5-bromothiophene-2-carboxylate (0.0187 mol) in DMF (100 ml) in a three-neck, round-bottomed flask containing 5% of dichlorobis(triphenylphosphine) palladium(II) as catalyst. The reaction mixture was stirred for 15 minutes at room temperature under nitrogen atmosphere, and then heated at 90 °C overnight. The solvent was evaporated under vacuum and the residue was washed with acetone (2 x 100 ml) and filtered. Pure, red powder of 2.2 g of were obtained (70 %), mp > 260 °C.

### Preparation of 2,2':5',2'':5'',2'''-Quaterthiophene-5,5'''-dicarboxylate.

2.2 g of diethyl quaterthiophene dicarboxylic were added to a solution of 25 g of NaOH in a mixture of ethanol water (250-100 ml). The mixture was refluxed for 4h. The red powder obtained was filtered washed with water, methanol, ether, chloroform (1.9 g).

<sup>1</sup>H NMR spectrum (200 MHz, DMSO-D<sub>2</sub>O (2:1)): δ 6.39, 7.31 (d, *J* = 3.4 Hz, 1H, H<sub>4''',3''''</sub>), 7.22 (s, 2H, H<sub>3''',4''''</sub>), 7.15 (d, *J* = 3.4 Hz, 1H, H<sub>3''',4''''</sub>). calc.: C 52.5, H 2.81, O 31.7, S 29.30 % found: C 51.66, H 2.41, O 15.29, S 30.65.

## Reference

1. J. Kagan, S. K. Arora and A. Ustunol, *J. Org. Chem.*, 1983, **48**, 4076.

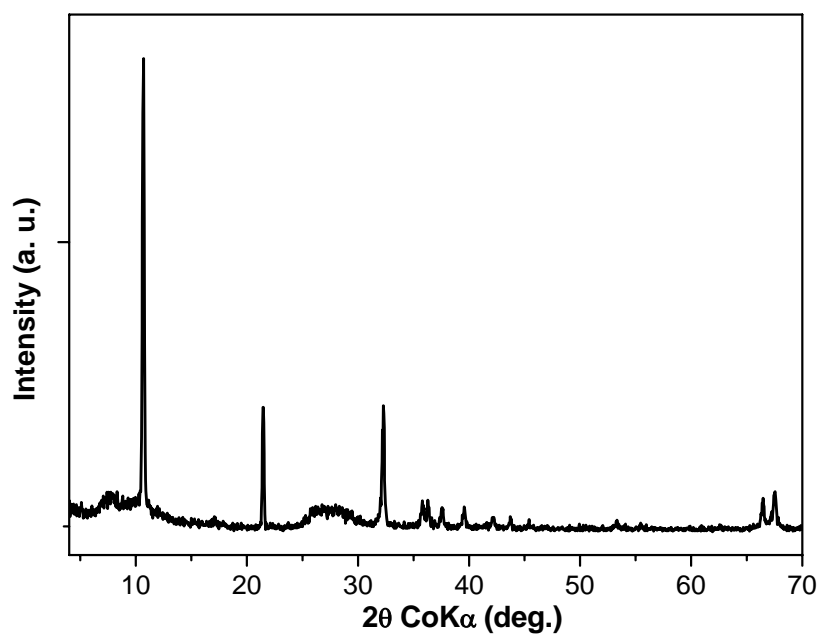


Fig. S1 PXRD pattern of Co-T1 (1).

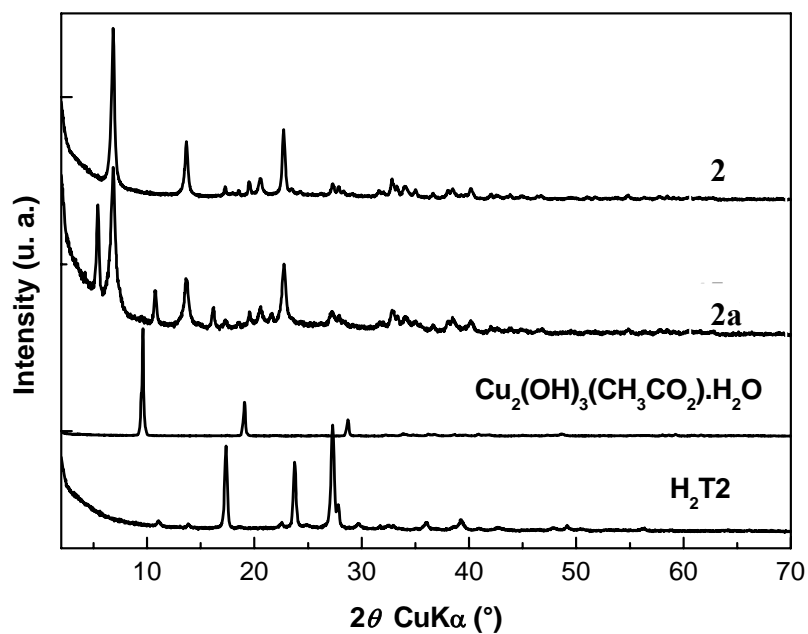
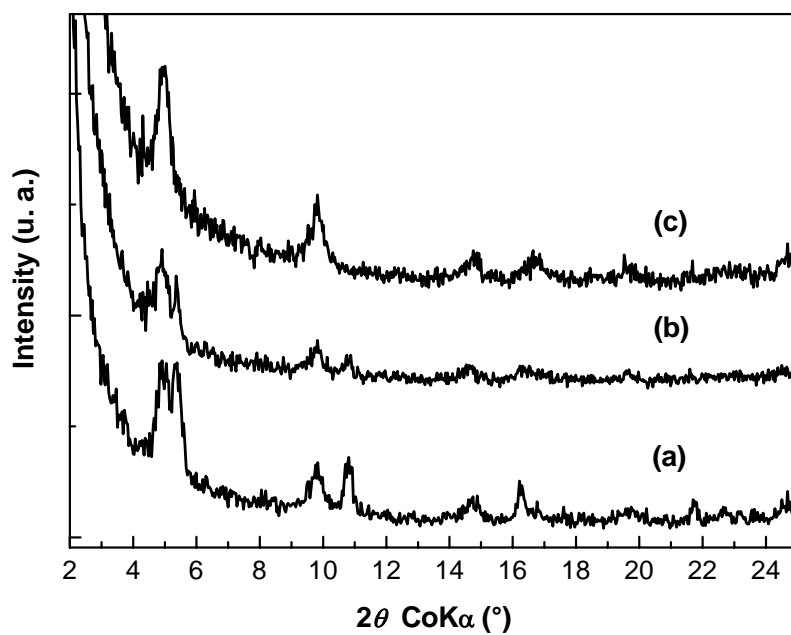
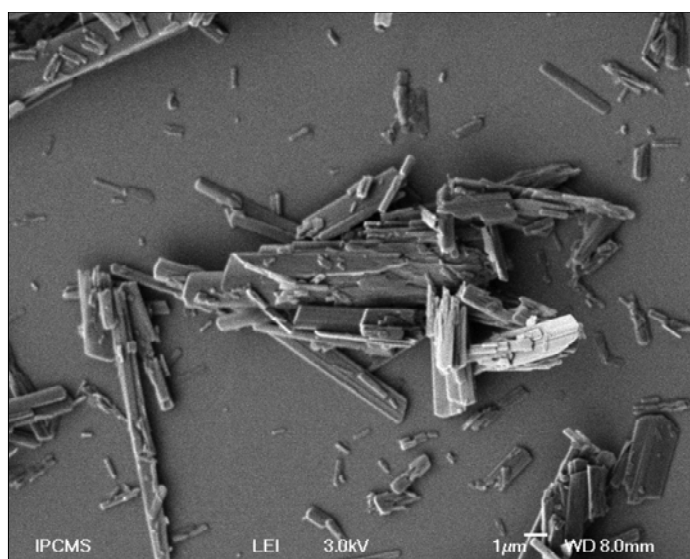


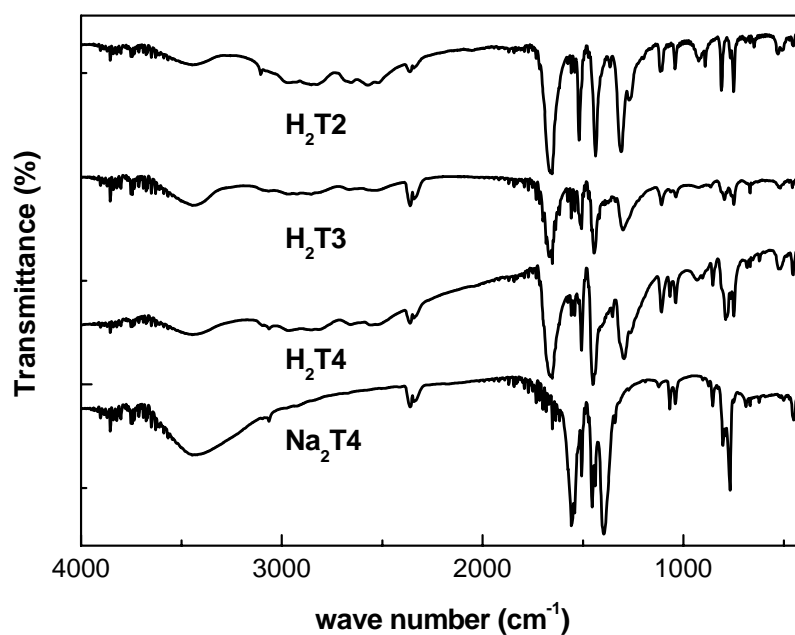
Fig. S2 PXRD pattern of the anion exchange reaction product of  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{CO}_2)\cdot\text{H}_2\text{O}$  with  $\text{H}_2\text{T2}$ , **2a**, after 27 h reaction and **2** obtained after re-dispersion in water.



**Fig. S3** PXR D pattern of **10**. **(a)** as synthesized, **(b)** after 16 h hydrothermal treatment **(c)** after additional 60 h treatment.



**Fig. S4** SEM picture of Co-T1 (**1**) coated on silicon.

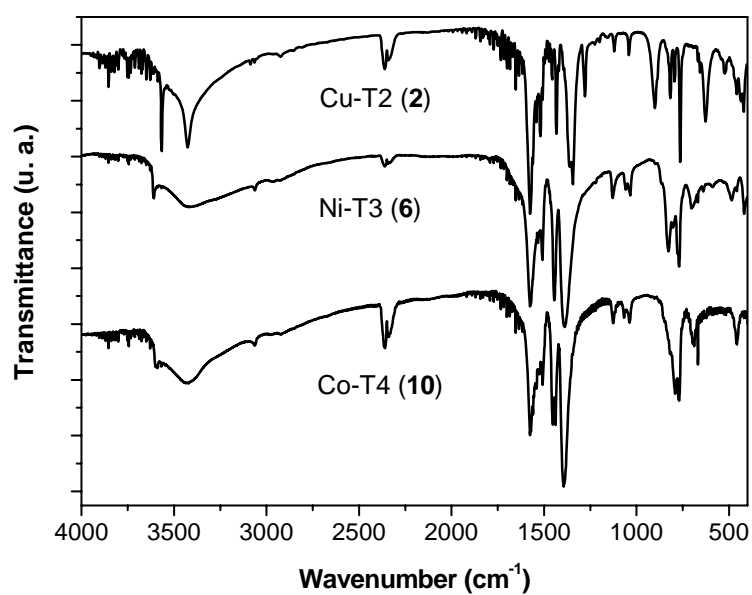


**Fig. S5** Infrared spectra of the free oligothiophenedicarboxylic acids ( $H_2T_2$ ,  $H_2T_3$  and  $H_2T_4$ ) and the quaterthiophenedicarboxylate sodium salt ( $Na_2T_4$ ).

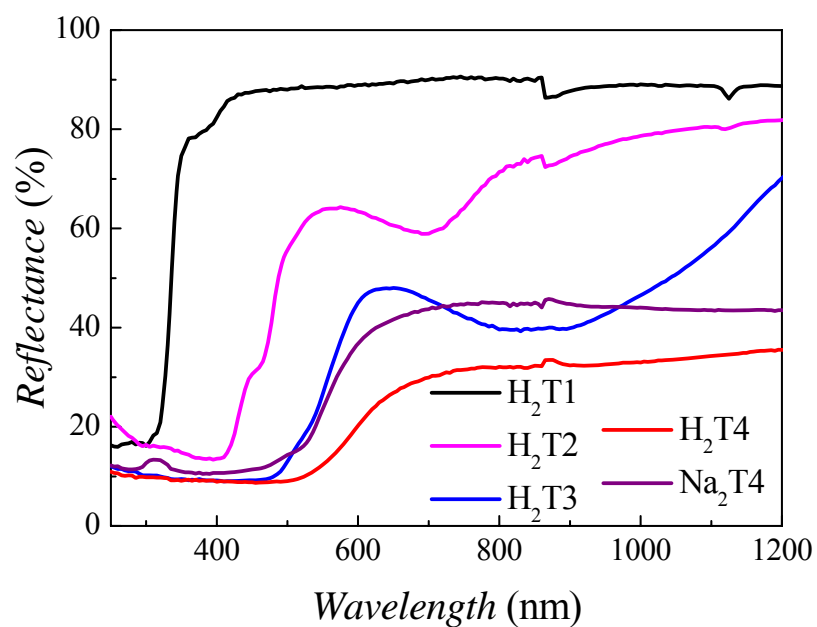
**Table S1** Infrared bands the free oligothiophenedicarboxylic acids ( $H_2T_2$ ,  $H_2T_3$  and  $H_2T_4$ ) and the quaterthiophenedicarboxylate sodium salt ( $Na_2T_4$ ) ( $cm^{-1}$ ).

	$H_2T_2$	$H_2T_3$	$H_2T_4$	$Na_2T_4$
$\nu(C_{\beta}-H)$	3105	-	3065	3065
$\nu_{as}COO$	1660	1665	1660	1555
$\nu_{as}C_{\alpha}=C_{\beta}$	1520	1510	1505	1505
$\nu_sC_{\alpha}=C_{\beta}$	1435	1445	1450	1455, 1440
$\nu C_{\beta}-C_{\beta}$	1365	1340	1355	1340
$\nu_sCOO$	1310	1300	1295	1395
$\delta(C_{\beta}-H)$	1265	-	1260	-
$C_{\alpha}-C_{\alpha}$ intercycles	1110	1110	1110	-
$\delta(C_{\beta}-H)$	1040	1065, 1040	1065, 1040	1065, 1040
$\nu_{as}C_{\alpha}-S$	890	865	850	870
$\gamma C_{\beta}-H$	810	790	790	800
$\nu_sC_{\alpha}-S$	750	750	750	770

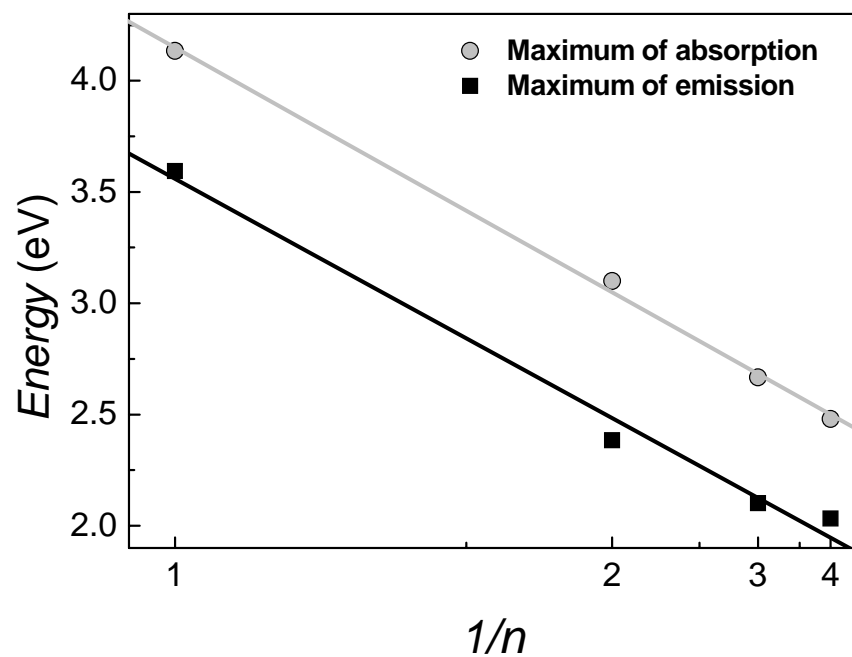
$\nu$ : elongation;  $\delta$ : deformation in-plane,  $\gamma$ : deformation out of plane, s: symmetrical; as: antisymmetrical.



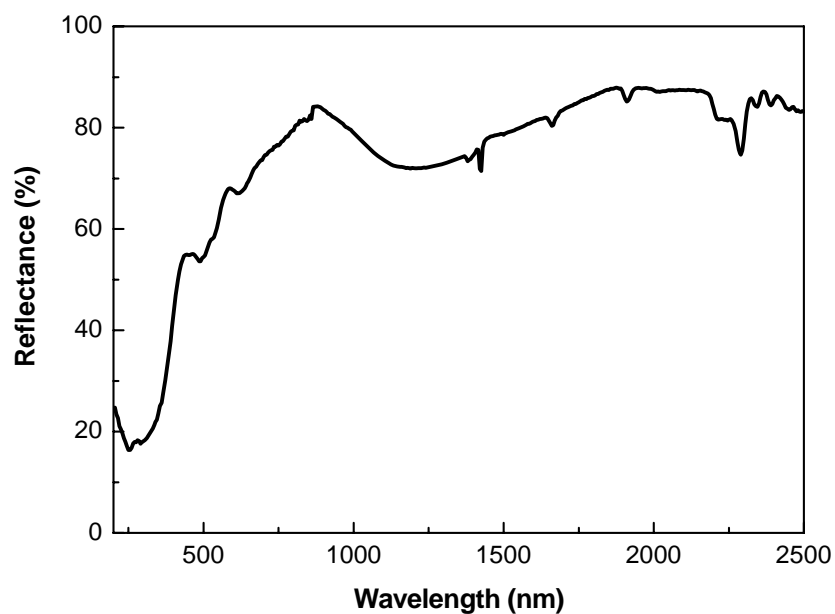
**Fig. S6** FTIR spectra of the hybrid compounds **2**, **6** and **10**.



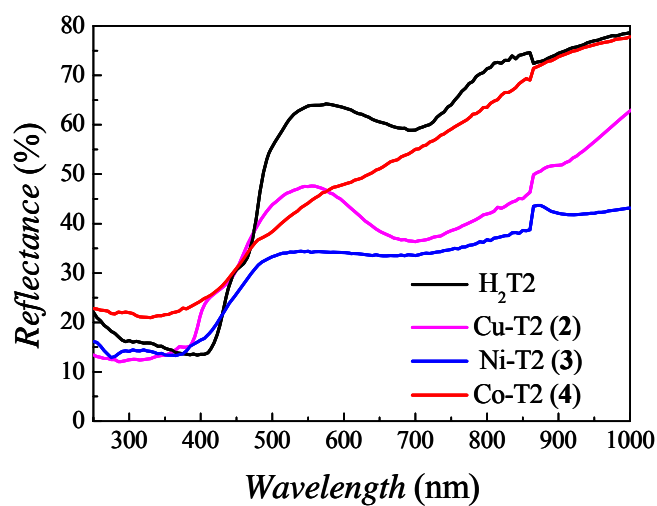
**Fig. S7** Solid state absorption spectra of the oligothiophenedicarboxylic acids and of the sodium quaterthiophenedicarboxylate.



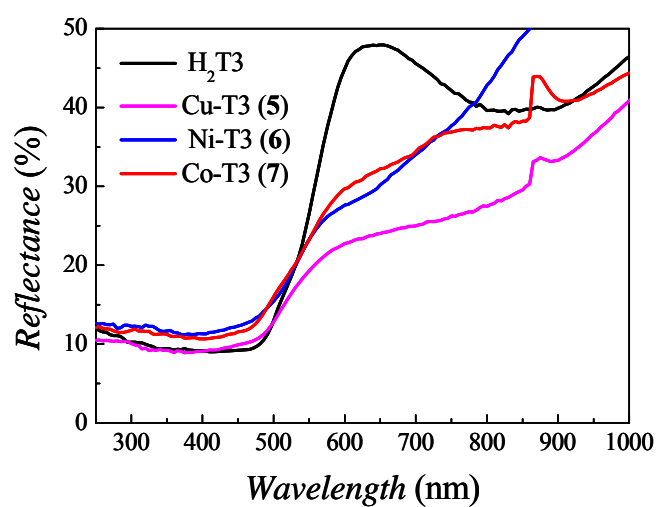
**Fig. S8** Variation of the maximum of absorption and emission as a function of the number of thiophene cycles  $n$  in the oligothiophenedicarboxylic acids in the solid state.



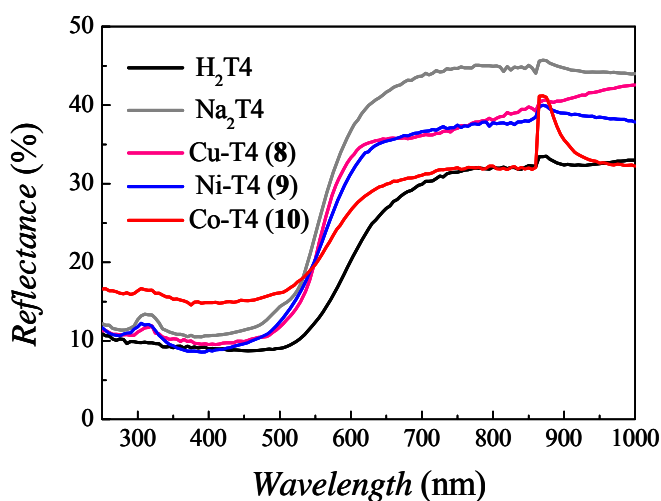
**Fig. S9** Solid state absorption spectrum of Co-T1 (**1**).



a



b



c

**Fig. S10** UV-vis absorption spectra of the hybrid compounds compared with that of the acids alone : a) the T2, b) the T3 and c) the T4 compounds.



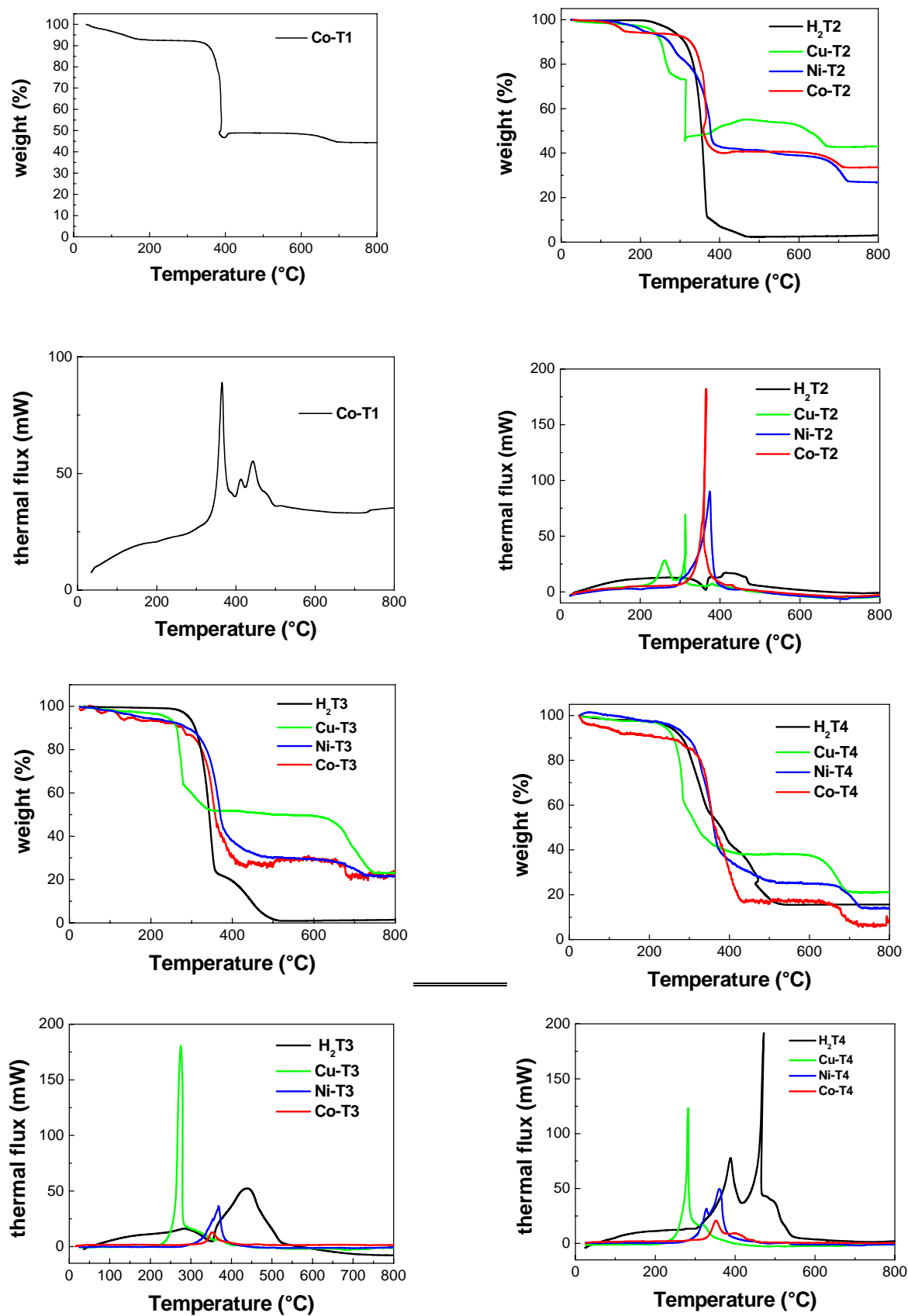
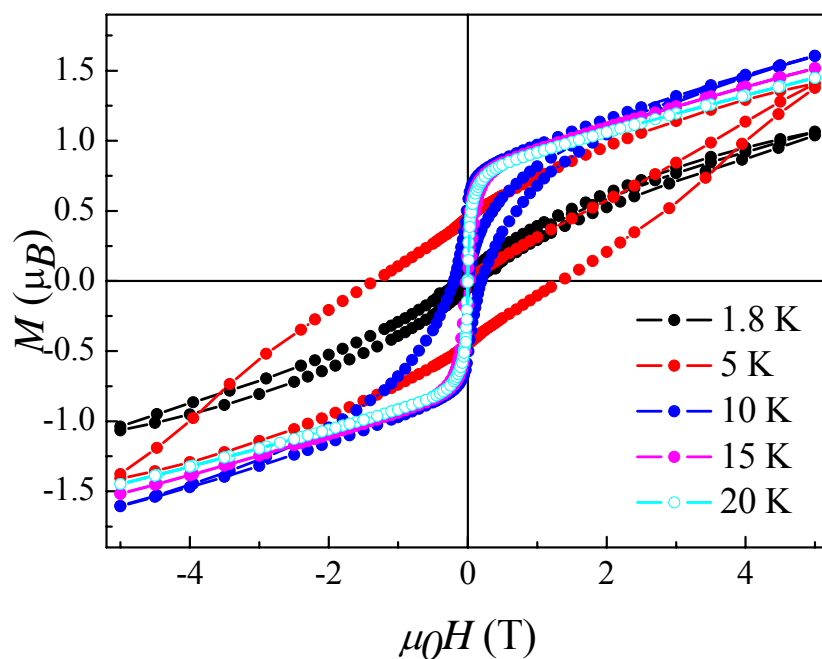
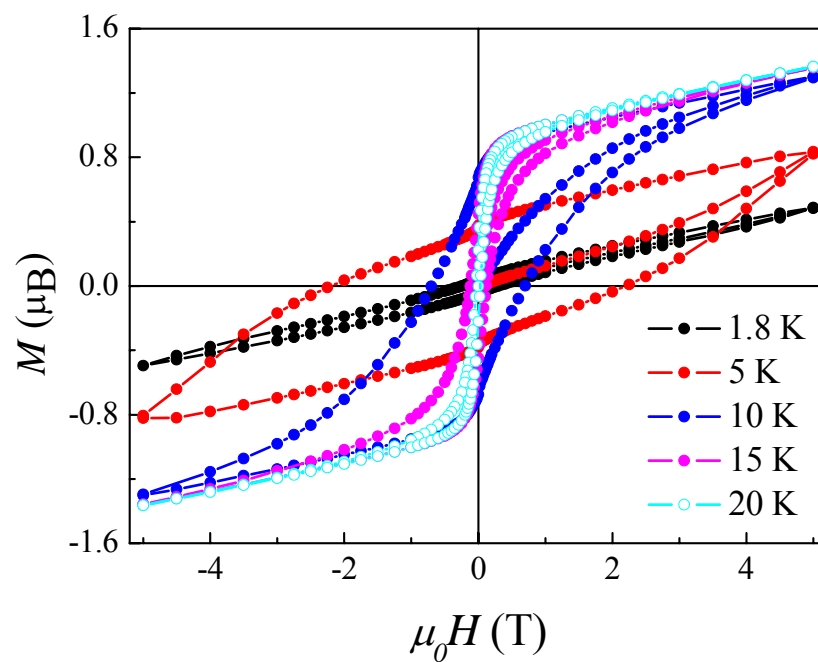


Fig S11 Thermogravimetric and thermodifferential analyses of the hybrid materials and the free acids.



**Fig. S12** Magnetization versus field hysteresis loops of Co-T3 (**7**) at  $T = 1.8, 5, 10, 15$  and  $20$  K.



**Fig. S13** Magnetization versus field hysteresis loops of Co-T4 (**10**) at  $T = 1.8, 5, 10, 15$  and  $20$  K.