Electronic Supplementary Information for:

Experimental and Theoretical Study of Photoluminescence and Magnetic Properties of Metal-Organic Polymers Based on a Squarate and Tetrazolate Moieties Containing Linker

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S1. Crystallographic tables

Table S1. Selected Distances (Å) for compound **1** and **3**

1		**3**	
Zn1	O2W 2.064(2)	Co1	O2W 2.073(2)
Zn1	N1 2.098(3)	Co1	N1 2.105(3)
Zn1	N4 2.101(3)	Co1	O1 2.104(2)
Zn1	O1 2.142(2)	Co1	N4 2.108(3)
Zn1	O1W 2.152(2)	Co1	O1W 2.115(3)
Zn1	O3W 2.211(2)	Co1	O3W 2.178(3)

Table S2. Selected Bond Angles (Å) for compound 1 and 3

1		3	
O2W	Zn1 N1 165.47(10)	O2W	Co1 N1 168.06(10)
O2W	Zn1 N4 93.13(10)	O2W	Co1 O1 86.09(9)
N1	Zn1 N4 101.27(10)	N1	Co1 O1 91.51(10)
O2W	Zn1 O1 85.66(9)	O2W	Co1 N4 90.91(10)
N1	Zn1 O1 90.76(9)	N1	Co1 N4 100.98(10)
N4	Zn1 O1 96.51(9)	O1	Co1 N4 95.97(10)
O2W	Zn1 O1W 91.79(9)	O2W	Co1 O1W 91.48(10)
N1	Zn1 O1W 90.74(10)	N1	Co1 O1W 90.41(10)
N4	Zn1 O1W 87.61(10)	O1	Co1 O1W 176.33(9)
O1	Zn1 O1W 175.26(9)	N4	Co1 O1W 88.73(10)
O2W	Zn1 O3W 78.96(10)	O2W	Co1 O3W 80.28(10)
N1	Zn1 O3W 87.14(10)	N1	Co1 O3W 88.14(10)
N4	Zn1 O3W 167.69(10)	O1	Co1 O3W 92.36(9)
O1	Zn1 O3W 92.30(9)	N4	Co1 O3W 167.45(10)
O1W	Zn1 O3W 83.26(9)	O1W	Co1 O3W 84.58(10)

S2. LeBail Refinement for 2

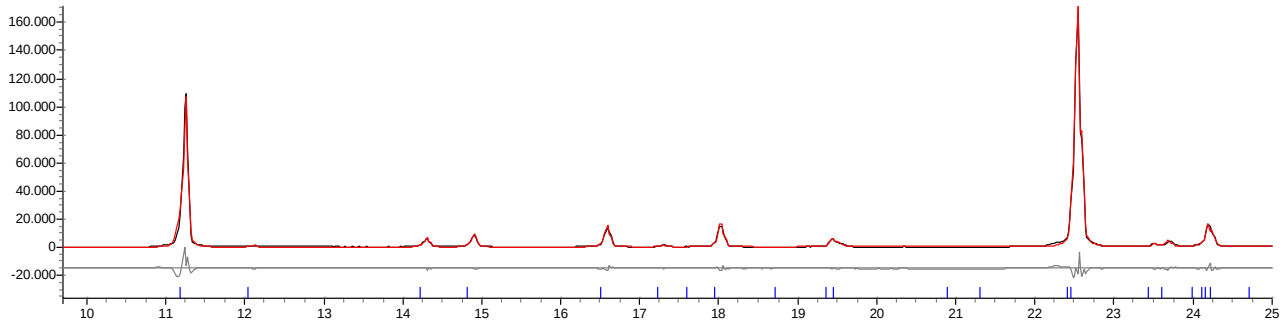

Figure S1. Lebail Refinement for 2: a = 8.1921, b =10.0543, c = 11.1973, β =106.139, sample displacement = 0.184mm.

S3. H-bond network in compounds 1-3

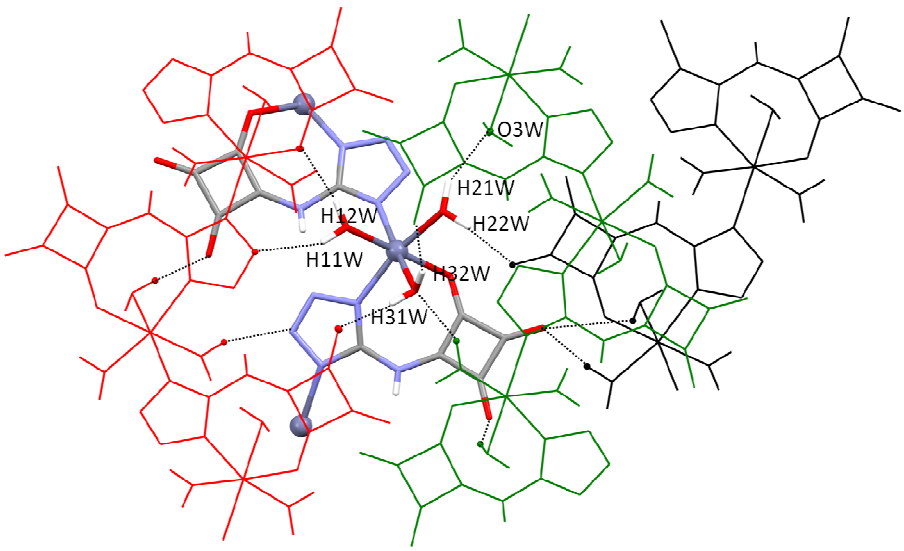

Figure S2. A view of the hydrogen bond network established by a central octahedral metal [M(TnHsq)(H_2O)$_3$] complex (atom type coloring capped stick) to three contiguous chains (red, green and black lines). A hydrogen bonding network links a central octahedral metal complex (atom type colouring) to 3 contiguous chains (coloured black, green and red, respectively) as follows: donor H atoms of the three coordinating water molecules (H11W, H12W, H21W, H22W, H31W and H32W) establish 6 H bonds with oxygen and nitrogen atoms belonging to the

$(TnHsq)^{2-}$ ligand, as well as the O3W atom of a water molecule of three neighbouring chains.

S4. Luminescence Calculations and decay curves

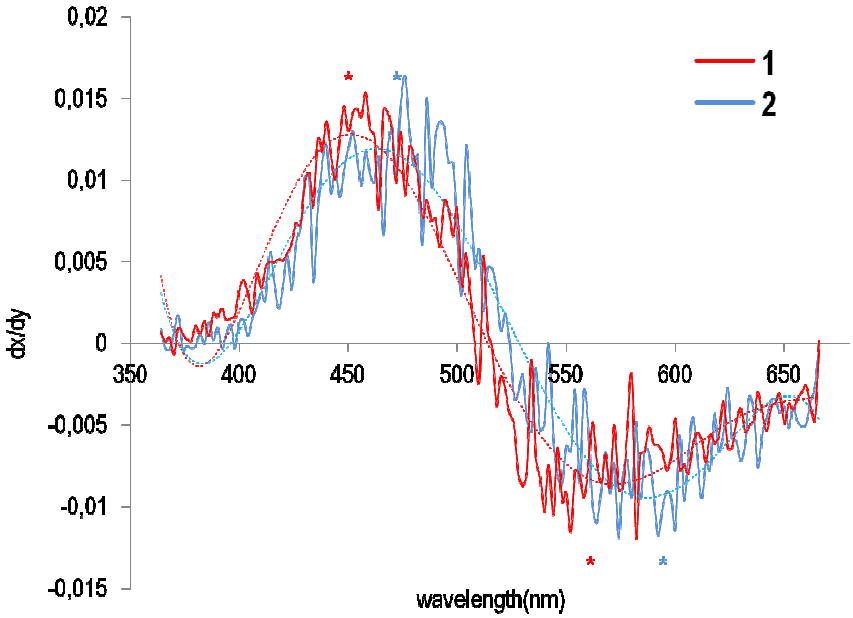

Figure S3. First derivatives of the experimentally obtained emission data for compound **1** (red) and compound **2** (blue). Highlighted with a * are the two relative extreme points observed, which are related to the shoulders sensed on the experimental emission band in Figure 3.

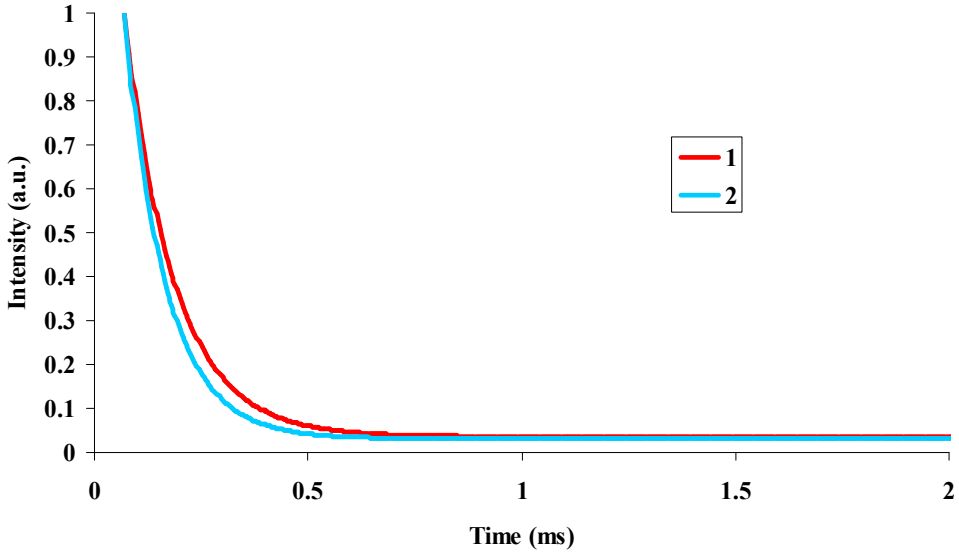

Figure S4. Luminescence decay curves of the compounds **1** (red) and **2** (blue).

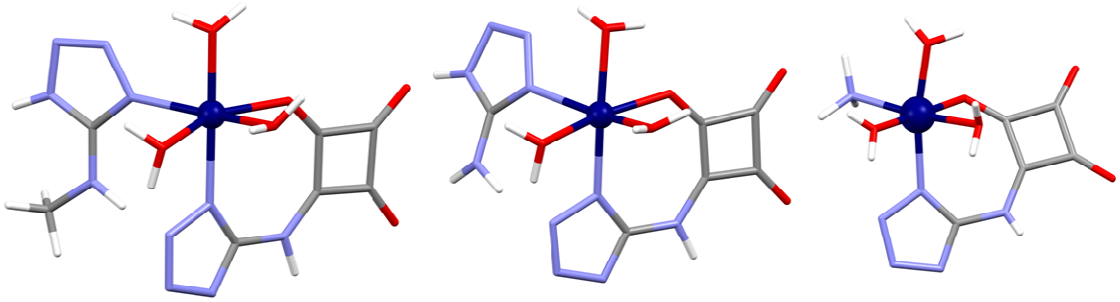

Figure S5. Stick representation of models 1, 2 and 3, used to characterize computationally the excitation and emission spectra of compound **1**. The bridgding $(TnHsq)^{2-}$ ligand is modelled by means of either a N1-proponated C2 methyl-capped tetrazolate derivative (model 1, left), a N5-diproponated tetrazolate derivative (model 2, middle) or an ammonia molecule (model 3, right). Models 1 and 2 yielded appropriate geometries and energetic results, whereas model 3 was shown to be inappropriate due to the loss of the octahedral environment around the metal upon structure optimization. Model 1 was chosen for further analysis throughout the study.

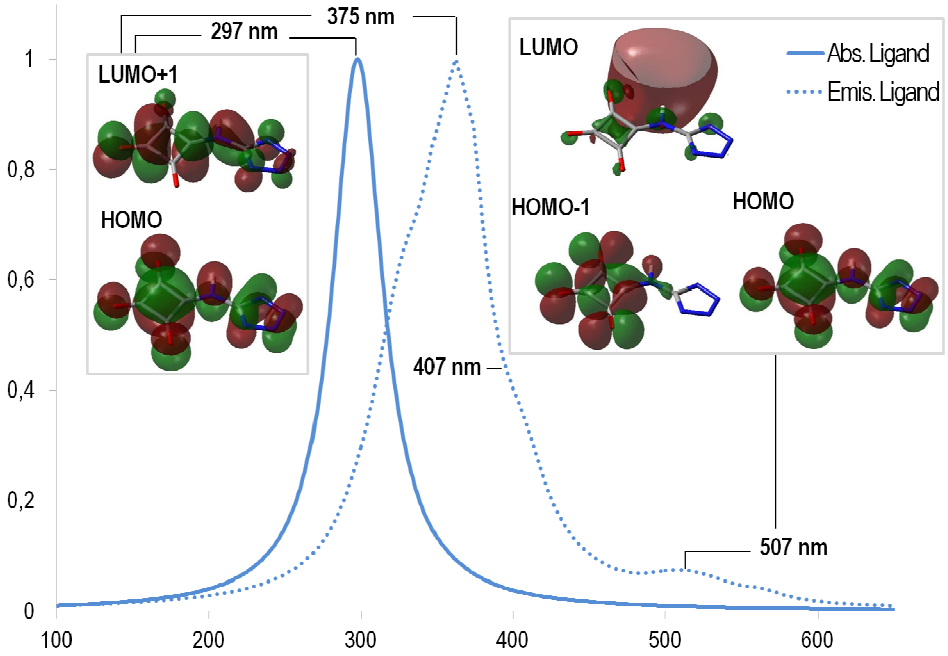

Figure S6. Normalized theoretical absorption (solid line) and emission (dashed line) spectra of free $(TnHsq)^{2-}$ ligand, and isocontour plot representation of the molecular orbitals involved.

	Max. λ (nm)	Calculated Transitions	Osc. Strength
$TnHsq^{2-}$			
Calculated Abs	297.4	H-1←L+2 (11%); H←L+1(79%); H-1←L(3%)	0.428
Calculated Emis	375	H-1←L (32%); H←L(13%); H←L+1(52%)	0.2073
	407	H-1←L (28%); H←L(24%); H←L+1(46%)	0.038
	507	H-1←L (35%); H←L(62%)	0.0187
Model 1			
Calculated Abs.	337	H-1→L+1 (84%); H-1→L+2(7%); H→L+1(8%)	0.0015
	371	H-1→L (90%); H→L(10%)	0.0011

Table S3. Calculated absorption and emission information for the free $(TnHsq)^{2-}$ligand and absorption information for model 1.

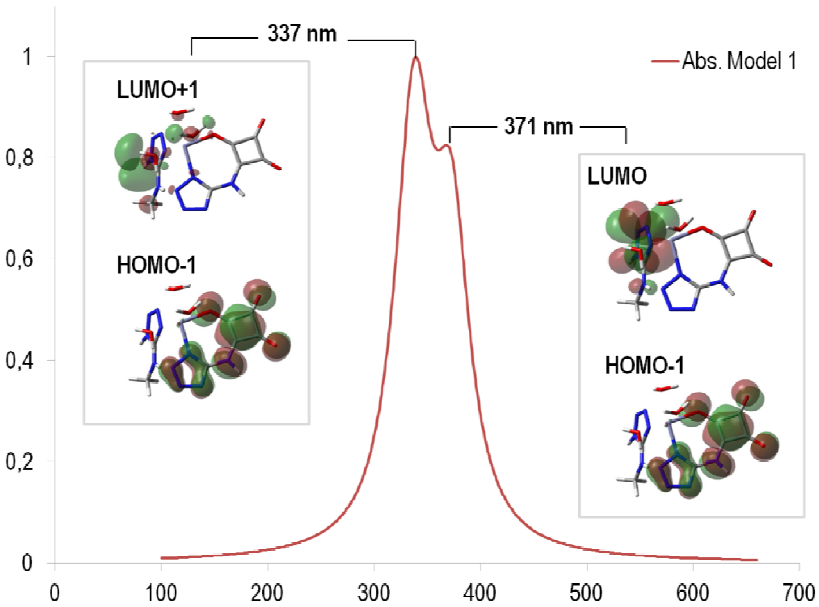

Figure S7. Normalized calculated excitation spectra of model 1, and representation of molecular orbitals involved in the observed electronic transitions.

S5. IR Spectra.

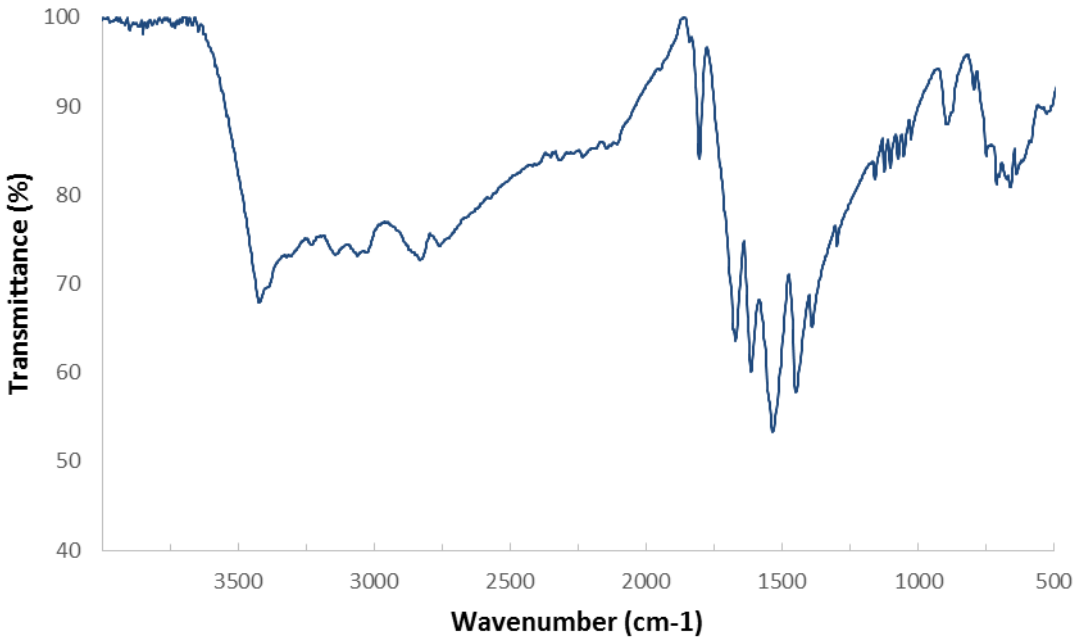

Figure S8. IR spectrum of compound **1** in KBr. FT-IR (KBr pellet): 3422 (s), 3142 (m), 2831 (w), 1805 (s), 1671 (s), 1613 (s), 1537 (s), 1448 (s), 1391 (s), 1159 (w), 1073 (w), 894 (m), 750 (w), 712 (w), 660 (w) cm-1

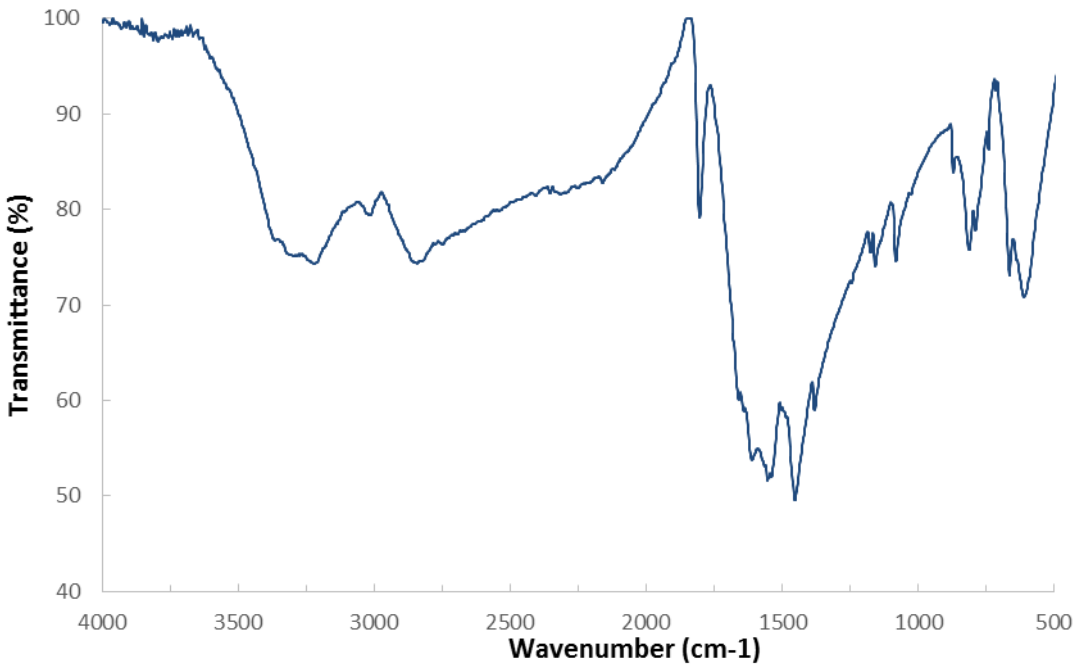

Figure S9. IR spectrum of compound **2** in KBr. FT-IR (KBr pellet): 3221 (m), 3016 (w), 2842 (m), 1803 (m), 1612 (s), 1554 (s), 1453 (s), 1381 (s), 1082 (m), 813 (m), 665 (m), 611 (m) cm-1

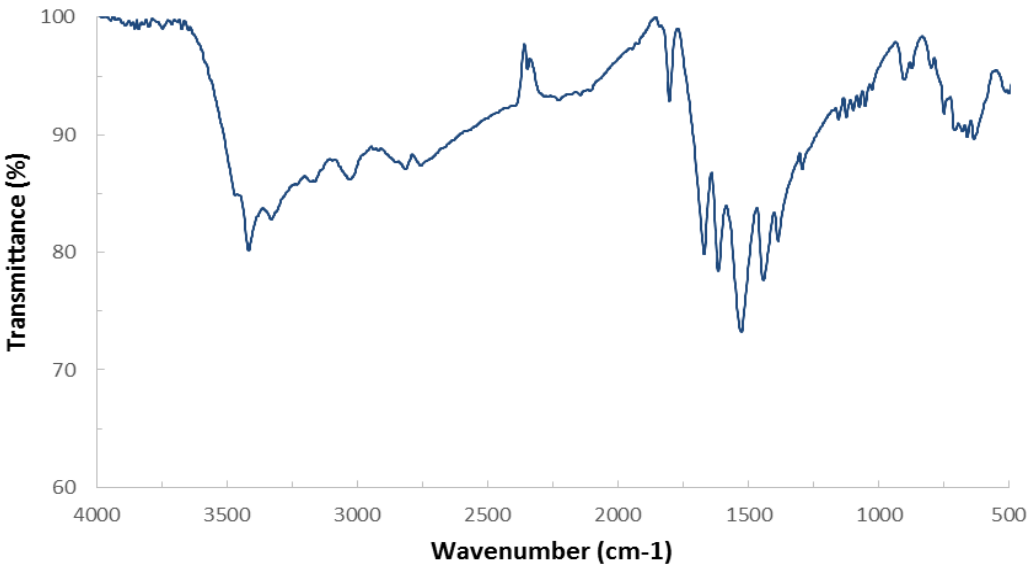

Figure S10. IR spectrum of compound **3** in KBr. FT-IR (KBr pellet): 3416 (s), 3163 (m), 3030 (m), 1803 (w), 1699 (s), (1615 (s), 1527 (s), 1442 (s), 1386 (s), 1098 (w), 903 (w), 750 (w), 660 (w) cm-1

S6. Powder XR Diffraction.

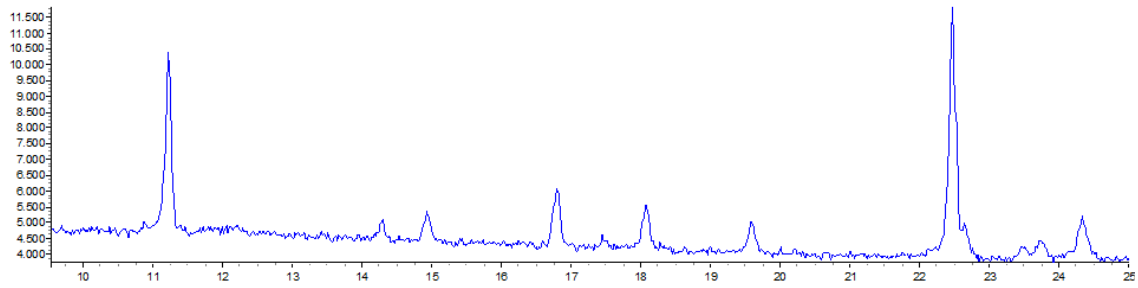

Figure S11. PXRD of compound **1**.

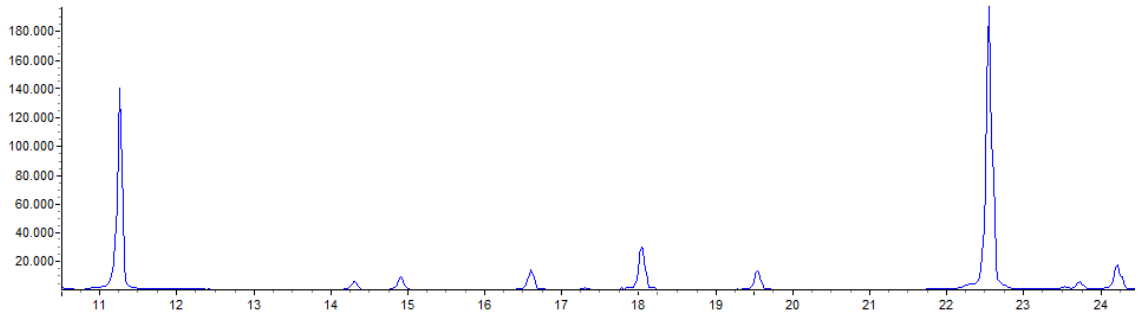

Figure S12. PXRD of compound **3**.

S7. TG and DSC Measurements for 1.

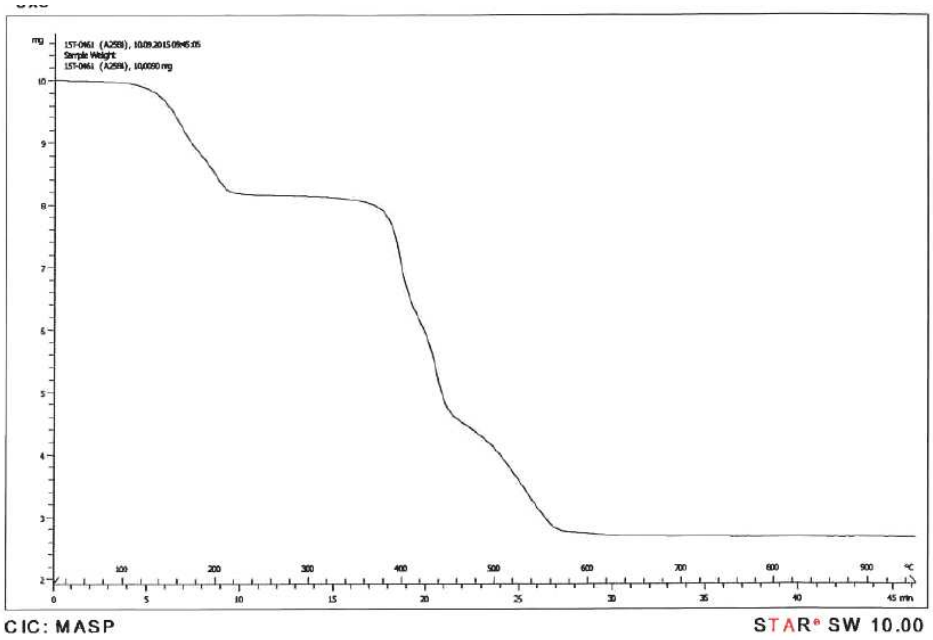

Figure S13. TG Spectrum of **1**.

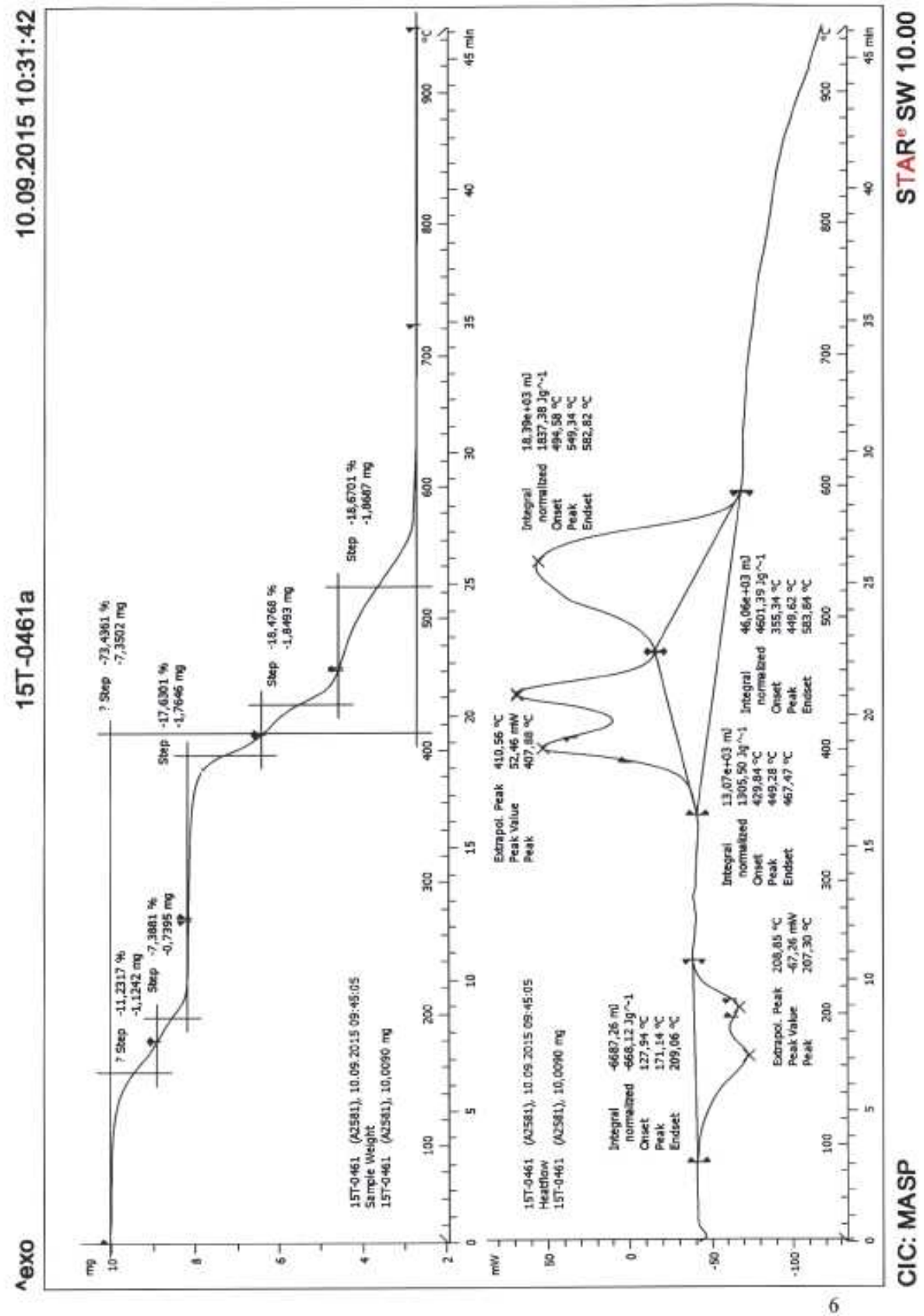

Figure S14.DSC Spectrum of **1**.