

## Electronic Supporting Information

# ADSORPTION AND LUMINESCENCE PROPERTIES OF FIRST 2D-CADMIUM MOF AND GISMONDINE-LIKE ZINC COORDINATION NETWORK BASED ON N-(2-TETRAZOLETHYL)-4'-GLYCINE LINKER

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### 1. Crystal Data

Table S1. Selected Distances (Å) for compound **1** and **2**

<b>1</b>		<b>2</b>	
Cd1-N1A	2.288(2)	Zn1-O11A	1.980(2)
Cd1-N2A	2.296(2)	Zn1-N4A	2.039(2)
Cd1-O11A	2.2990(19)	Zn1-N1A	2.074(2)
Cd1-N8A	2.324(2)	Zn1-N8A	2.099(3)
Cd1-O12A	2.373(2)	Zn1-O12A	2.185(2)

Table S2 Selected Bond Angles (Å) for compound **1** and **2**

<b>1</b>			<b>2</b>		
N1A Cd1 N2A	111.61(8)	O11A Zn1 N4A	105.04(9)		
N1A Cd1 O11A	158.19(8)	O11A Zn1 N1A	105.47(9)		
N2A Cd1 O11A	89.11(7)	N4A Zn1 N1A	96.30(10)		
N1A Cd1 N8A	85.50(8)	O11A Zn1 N8A	122.53(9)		
N2A Cd1 N8A	158.66(8)	N4A Zn1 N8A	128.68(9)		
O11A Cd1 N8A	72.81(8)	N1A Zn1 N8A	89.11(9)		
N1A Cd1 O12A	84.33(7)	O11A Zn1 O12A	88.75(9)		
N2A Cd1 O12A	81.26(7)	N4A Zn1 O12A	87.35(9)		
O11A Cd1 O12A	106.32(7)	N1A Zn1 O12A	163.73(9)		
N8A Cd1 O12A	114.19(7)	N8A Zn1 O12A	76.37(8)		
N1A Cd1 O1W	80.40(7)				
N2A Cd1 O1W	84.38(7)				
O11A Cd1 O1W	95.58(7)				
N8A Cd1 O1W	86.18(7)				

## 2. Coordination Environments of Metal Ions.

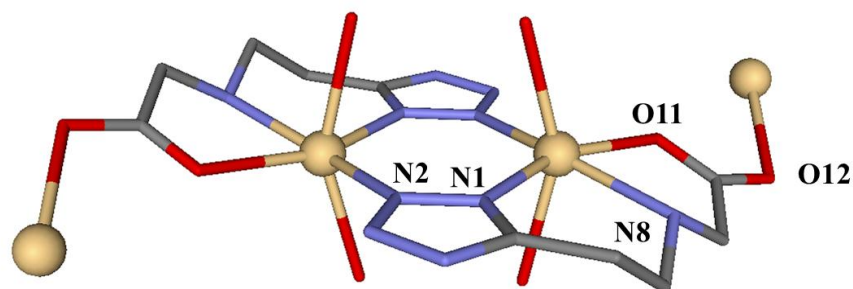


Figure S1. View of the metal environment and coordination mode of the (TeGly)<sup>2-</sup> ligand for **1**.

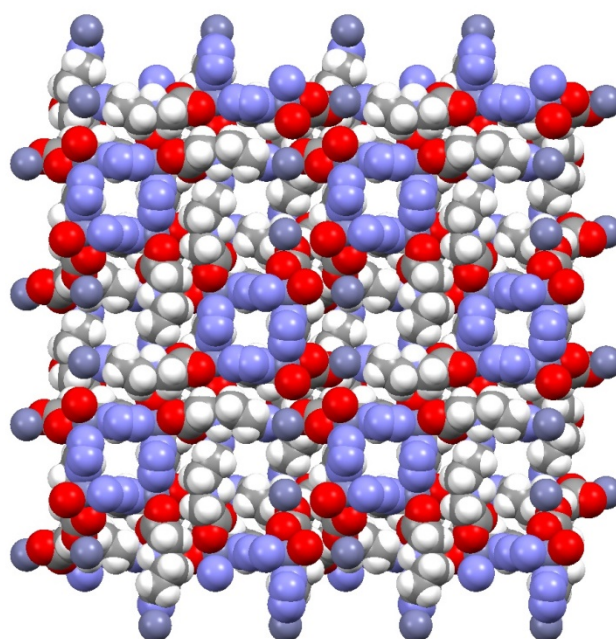


Figure S2. View of the three-dimensional spacefilling for **2**.

## 3. Gas Adsorption Simulations and Computational Structural Characterization

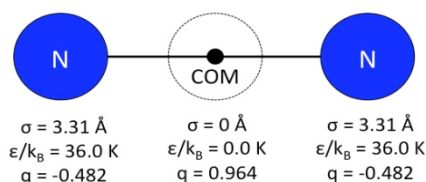
The adsorption of gases was investigated using grand canonical Monte Carlo (GCMC) simulations, performed with the in-house multi-purpose code RASPA.<sup>[1]</sup> We used a rigid atomistic model for **2**, in which the framework atoms were kept fixed at their crystallographic positions. Solid-fluid and fluid-fluid interactions were calculated using a Lennard-Jones (LJ) + Coulomb potential. LJ parameters for the framework atoms were taken from the Universal Force Field (UFF)<sup>[2]</sup> and the fluid LJ parameters from the corresponding force fields (*vide infra*). Lorentz-Berthelot mixing rules were used for all cross terms, and LJ interactions beyond 12 Å were neglected. Coulombic interactions were modelled by placing partial charges on the framework atoms. The partial charges were calculated using an extended charge equilibration method,<sup>[3]</sup> and the long-range electrostatic interactions were calculated using the Ewald summation method.  $6 \cdot 10^4$  Monte Carlo equilibration cycles were performed plus  $4 \cdot 10^4$  production cycles

to calculate the ensemble averages. In one cycle, an average of  $N$  moves were performed, where  $N$  is the number of molecules in the system (which fluctuates in GCMC). Monte Carlo moves used with equal probability were translation, rotation, insertion, deletion, and random reinsertion of an existing molecule at a new position. To calculate the gas-phase fugacity, we used the Peng-Robinson (PR) equation of state (EOS)<sup>[4]</sup>.

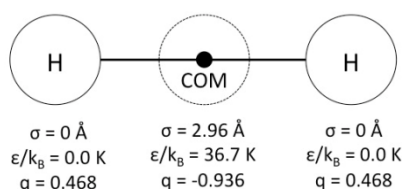
Table S3. Lennard-Jones parameters for framework atoms and the gas molecules.

	$\sigma$ [Å]	$\epsilon/k$ [K]	$q$ [e]
C	3.431	52.838	
N	3.261	34.722	
O	3.119	30.192	
H	2.571	22.142	
Cu	3.114	62.397	

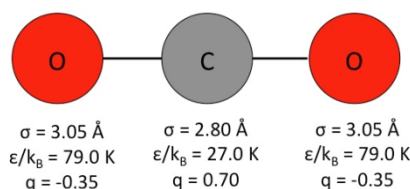
**Nitrogen molecule parameters:** Partial charges and LJ parameters were assigned to nitrogen molecules using the TraPPE force field. This force field was originally fitted to reproduce the vapor-liquid coexistence of nitrogen. In this force field, nitrogen molecules are modeled using a three-site rigid model (N-N = 1.10 Å), with partial charges and LJ parameters assigned according to the scheme below, which reproduces the experimental quadrupole moment of nitrogen molecules:



**Hydrogen molecule parameters:** Partial charges and LJ parameters were assigned to hydrogen molecules using the model of Levesque et al.<sup>7</sup> In this model, hydrogen molecules are modeled using a three-site rigid model (H-H = 0.74 Å), with partial charges and LJ parameters assigned according to the scheme below, which reproduces the experimental quadrupole moment of hydrogen molecules:



**Carbon dioxide molecule parameters:** Partial charges and LJ parameters were assigned to carbon dioxide molecules using the TraPPE force field.<sup>6</sup> In this force field, CO<sub>2</sub> molecules are modeled using a linear three-site rigid model (C-O = 1.16 Å), with partial charges and LJ parameters assigned according to the scheme below:



The pore volume, used to compute excess adsorption from the simulated absolute adsorption, was obtained using a Widom particle insertion method, by probing the structure with a helium molecule at room temperature, recording a large number of random points not overlapping the van der Waals volume of the framework.<sup>[5]</sup> The pore size distributions was calculated using the method of Gelb and Gubbins,<sup>[6]</sup> where the largest sphere that can fit in a random point within a structure without overlapping the van der Waals surface of the framework is recorded for a large number of random points.

#### 4. Gas Adsorption Measurements

N<sub>2</sub> adsorption isotherms were collected at 77 K on an AutoSorb equipment (Quantachrome Instruments). A sample of about 20 mg was previously evacuated under high vacuum ( $<10^{-7}$  bar) for two hours at 353 K. The N<sub>2</sub> isotherm revealed no gas uptake.

High-pressure adsorption isotherms of CO<sub>2</sub> at 273 K were determined using a bench-scale volumetric adsorption instrument equipped with two Baratron absolute pressure transducers (MKS type 627B). Their pressure range span from 0 to 1.33 bar and from 0 to 33.33 bar, respectively. The reading accuracy was 0.05% of the usable measurement range. Prior to all the measurements, samples were degassed at 425 K for 12 h. All gases used were of 99.999% purity. Helium was used for the dead volume determination. H<sub>2</sub> isotherm was obtained in a Hiden Analytical Intelligent Gravimetric Analyser. Approximately 30 mg of the sample was previously evacuated under vacuum ( $10^{-6}$  bar) and 353 K for two hours. Buoyancy effects were corrected as a function of temperature.

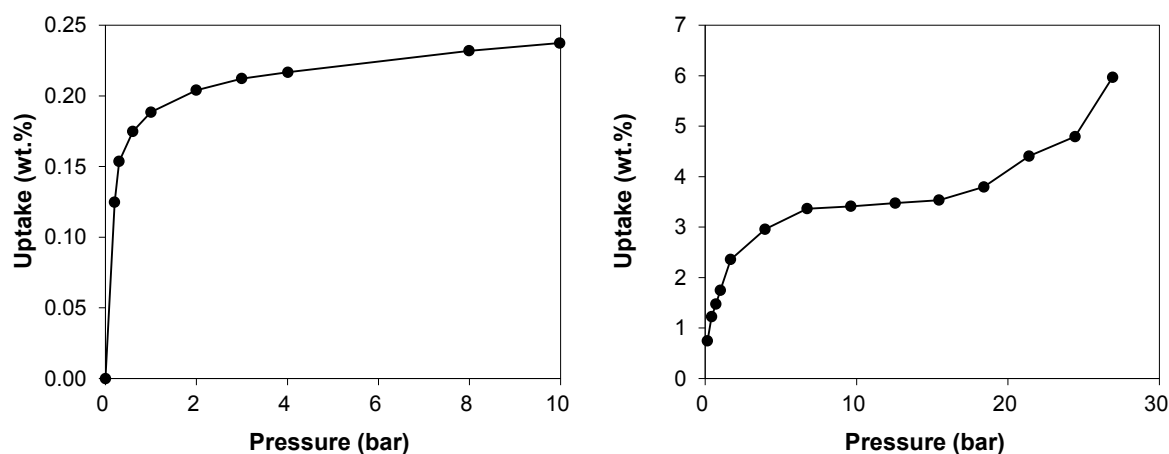


Figure S3. Experimental adsorption isotherms on **2**: H<sub>2</sub> at 77 K (left), and CO<sub>2</sub> at 273 K (right).

## 5. Luminescence Properties

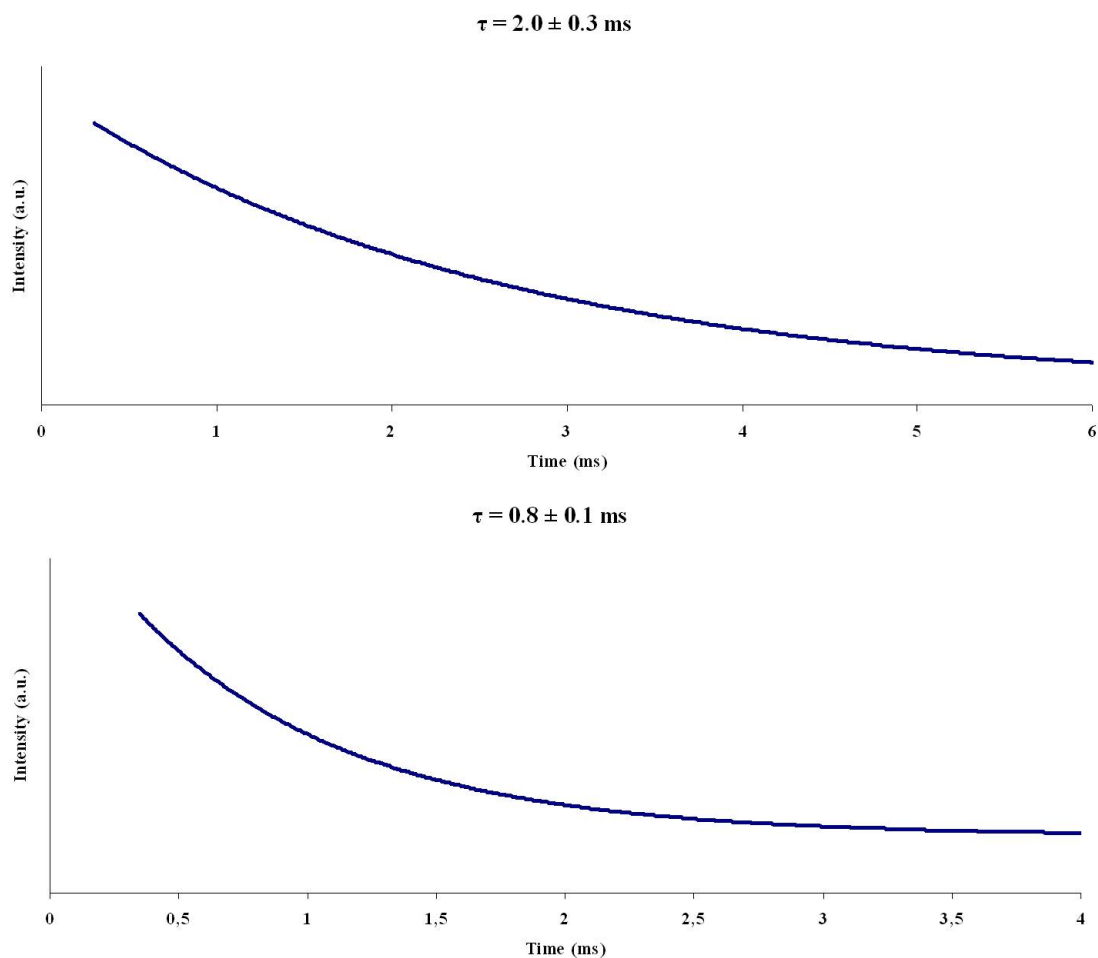


Figure S4. Luminescence decay curves of the compounds **1** and **2**.

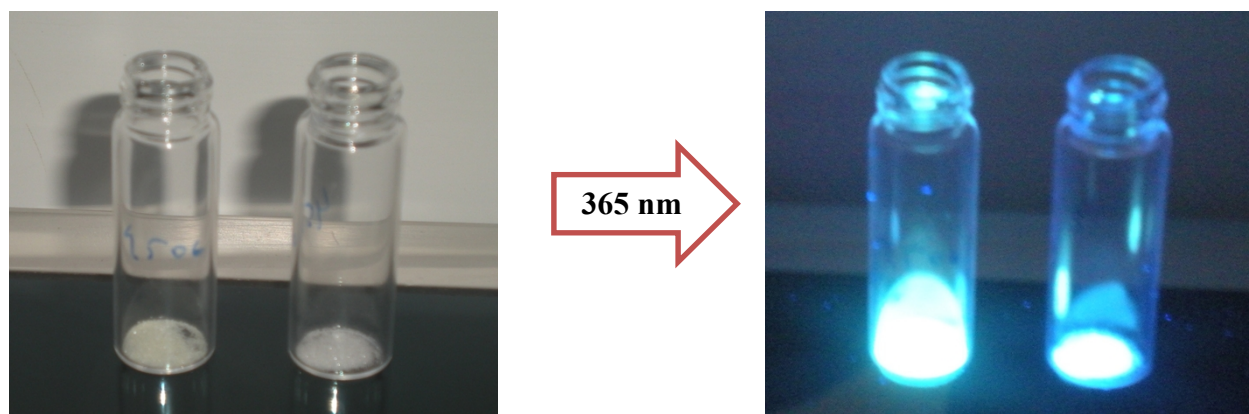


Figure S5. Emission of compound **1** and **2** under 365 nm.

## 6. Topological Simplification.

The structure of compound **2** was topologically simplified by defining the zinc atoms as nodes and the N-(2-tetrazolethyl)-4'-glycine molecules as linkers of the network. Topological analysis was carried out with TOPOS 4.0,<sup>[7]</sup> and the results indicated that the network is uninodal, four-connected, with point symbol (4<sup>3</sup>.6<sup>2</sup>.8), corresponding to the **gis** type.

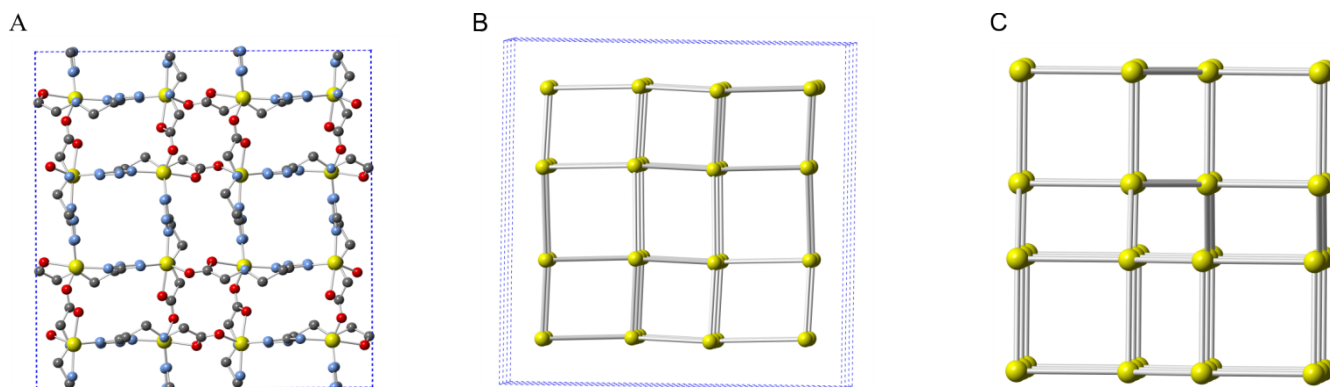


Figure S6. A: Representation of compound **2**. B: Equivalent view of the topologically simplified network, where the nodes occupy the position of the Zn atoms. C: Representation of the **gis** structure type in its maximum symmetry embedding.

## 7. LeBail refinements.

The powders were gently ground in an agate mortar and then deposited with care in the hollow of an aluminum holder equipped with a zero background plate. Diffraction data were collected on a  $\theta$ : $\theta$  Bruker AXS D8 vertical scan diffractometer equipped with primary and secondary Soller slits, a secondary beam curved graphite monochromator and pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. Optics used are the following: divergence  $0.5^\circ$ , antiscatter  $0.5^\circ$ , receiving 0.2 mm. A long scan was performed with  $5 < 2\theta < 25^\circ$  with  $t = 0.5$  s and  $\Delta 2\theta = 0.02^\circ$ . LeBail refinement (Figure 7) was performed verifying the purity of the sample and obtaining the unit cell parameters for compound **1**, monoclinic system,  $C2/c$ ,  $a = 18.749$ ,  $b = 7.556$ ,  $c = 14.267$ ,  $\beta = 119.89$ ,  $V = 1755 \text{ \AA}^3$ . For compound **2**, tetragonal system,  $I41/a$ ,  $a = 21.725$ ,  $c = 6.909$ ,  $V = 3261 \text{ \AA}^3$ .

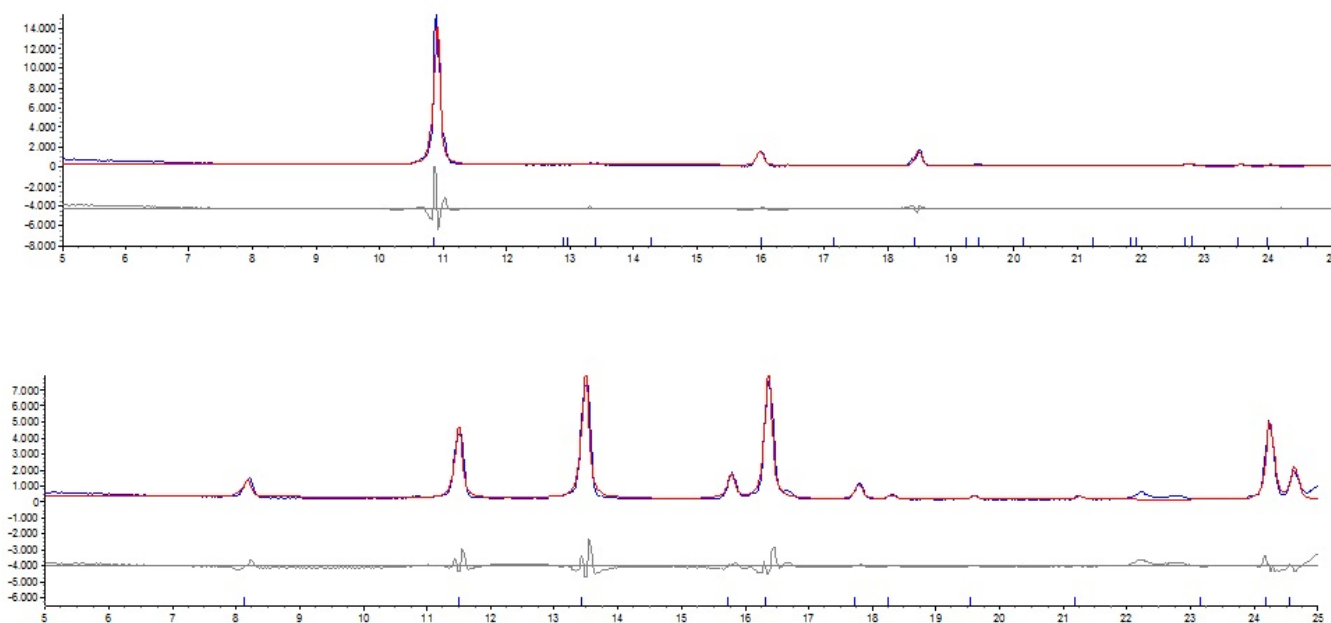


Figure 7. LeBail refinements for compounds **1** (top) and **2** (bottom) as appreciable from experimental (blue), calculated (red), and difference (grey) diffraction patterns.

## 8. TG spectra.

Compound **1** loses its coordinated water molecules at 210 °C and then **1** and **2** decompose at circa 350 and 400 °C, respectively, as measured by TGA.

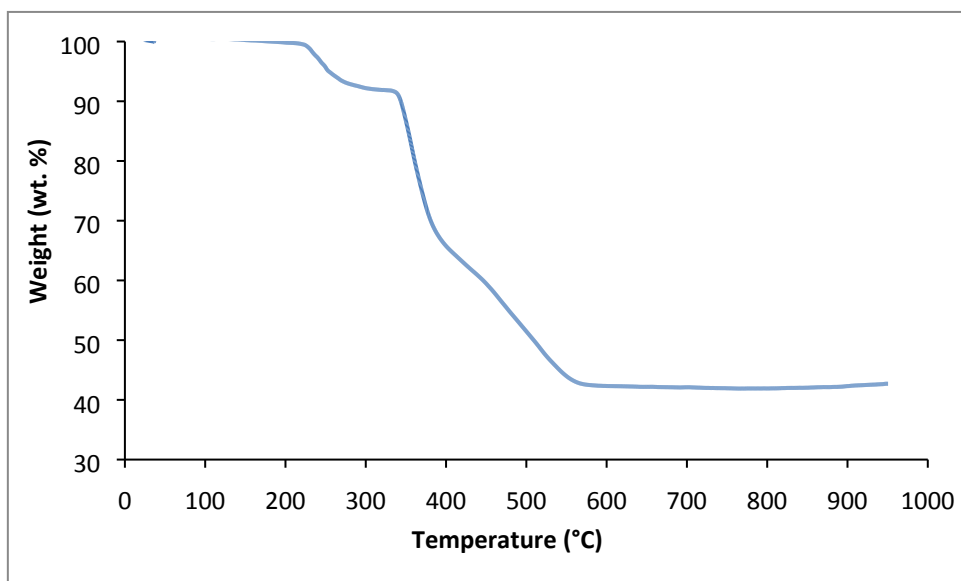


Figure 8. TG spectra for compound **1**.

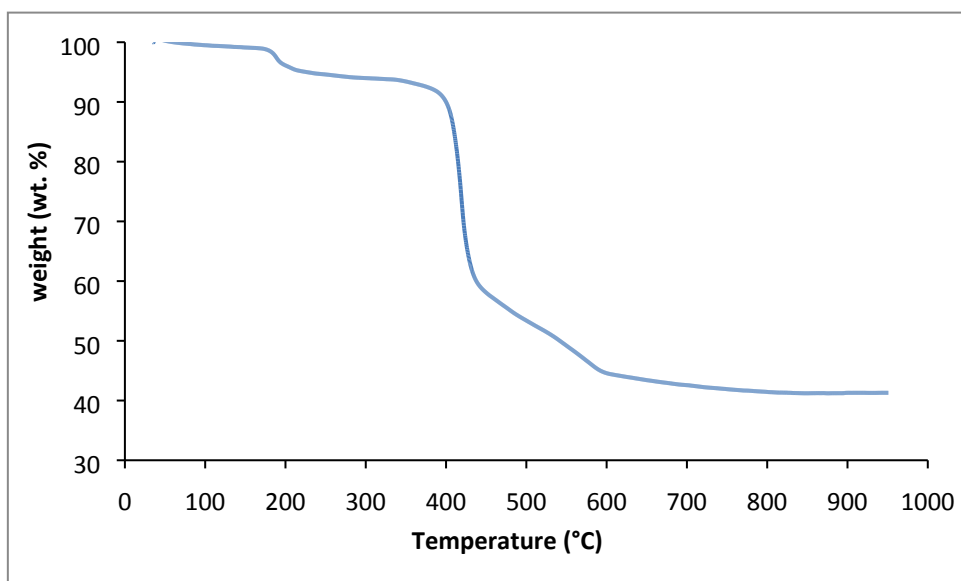


Figure 9. TG spectra for compound **2**.

## References:

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[2] A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. G. III and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024-10035

[3] C.E. Wilmer, K.C. Kim and R.Q. Snurr. *J. Phys. Chem. Lett.*, 2012, **3**, 2506–2511.

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<sup>[5]</sup> (a) A. Leach, *Molecular modelling : principles and applications*, Pearson Prentice Hall, 2001.; (b) A. L. Myers and P. A. Monson, *Langmuir*, 2002, **18**, 10261-10273.

[6] L. D. Gelb and K. E. Gubbins, *Langmuir*, 1998, **15**, 305-308.