Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Cycle contraction and symmetrisation in Redox-active ligands: from alloxazine to *iso*imidazolonequinoxaline derivatives, and their electrochemical and coordination studies

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UV CHARACTERIZATION OF **L1** AND **L2** IN SOLUTION

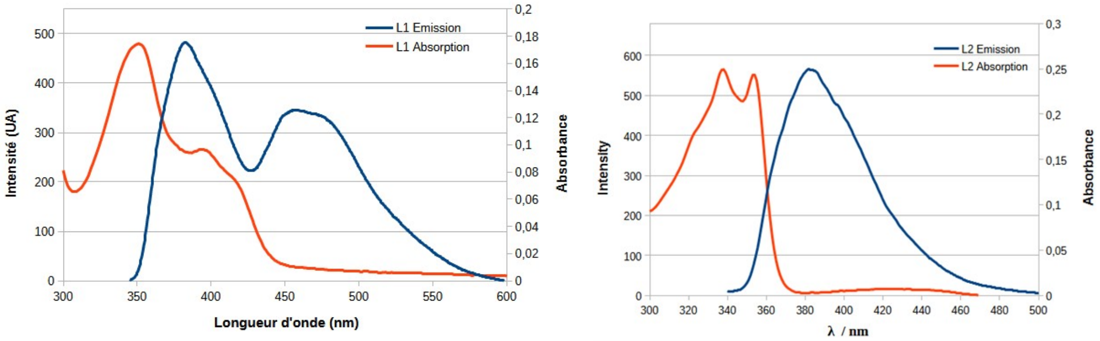
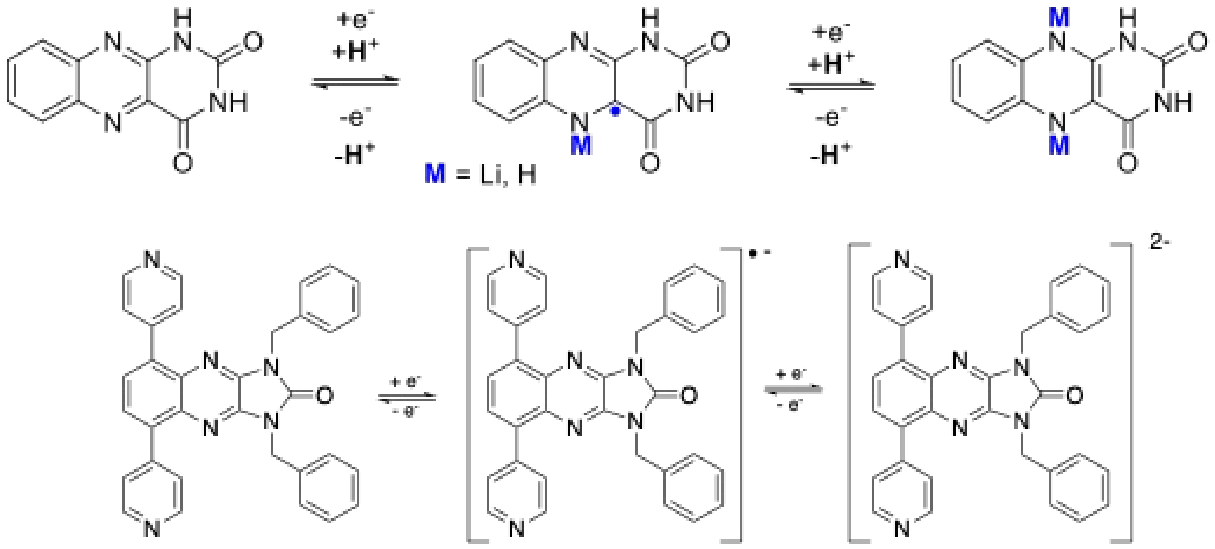


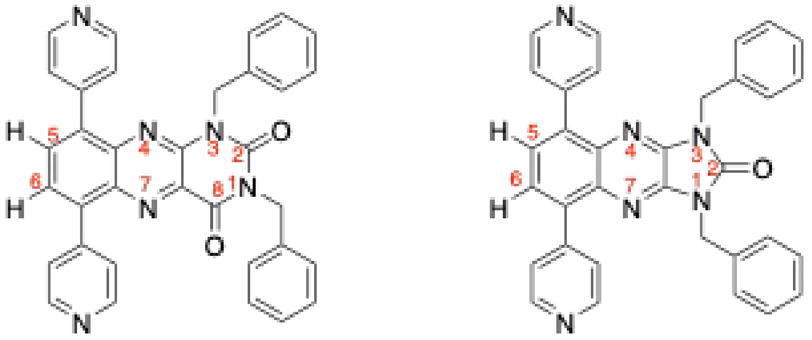
Figure S1. Absorption (10^{-5} M) and emission (5×10^{-6} M) spectra of **L1** (left) and **L2** (right) in CH_2Cl_2 recorded at RT; **L1**, λ_{exc} = 320 nm (left) and **L2**, λ_{exc} = 349 nm(left)

PROPOSED REDOX-BEHAVIOUR OF ELECTROCHEMICAL STUDIES IN THE SOLID-STATE



Scheme S1. Proposed Redox States for 1) ligand **L1**, and 2) the imidazo[4,5-b]quinoxaline derivatives **L2**: Oxidized, Radical, and Reduced

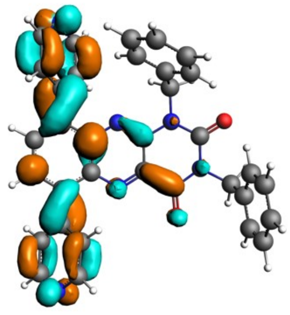
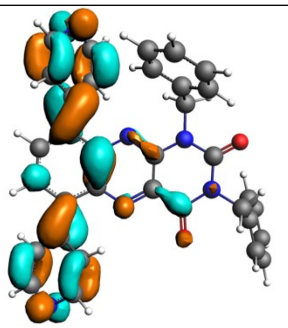
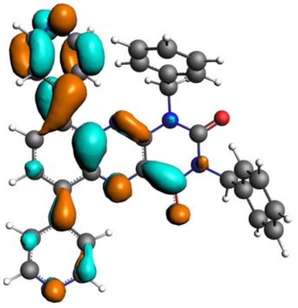
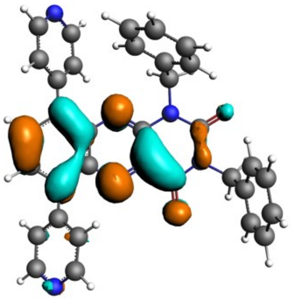
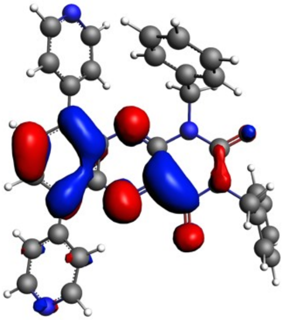
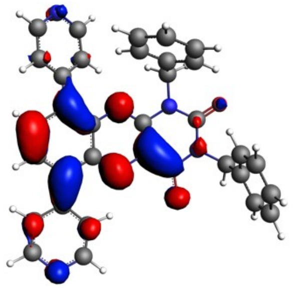
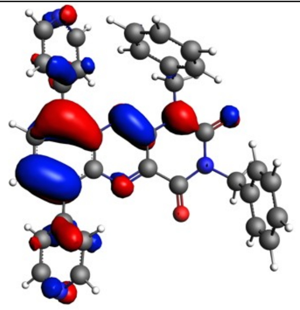
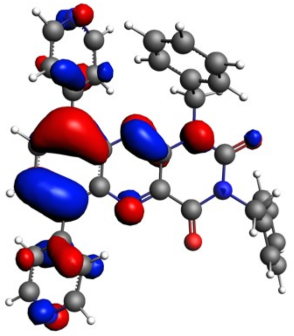
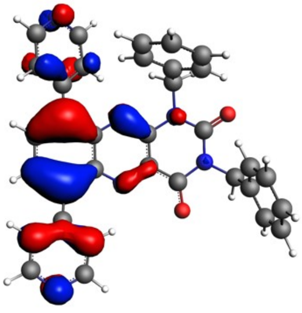
NUMBERING SCHEME FOR **L1** AND **L2**



L1 **L2**

Scheme S2. Numbering scheme for L1 and L2, used for EPR fitting

DFT CALCULATIONS FOR **L1** AND **L2**

	L1 (oxidized)	**L1 radical** **L1$^{\bullet-}$**	**L reduced** **L1^{2-}**
LUMO			
HOMO			
HOMO_1			

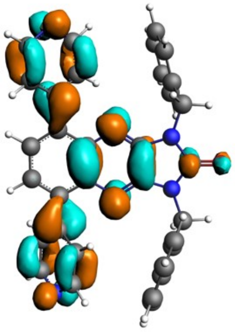
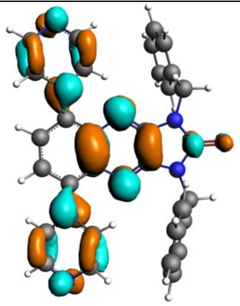
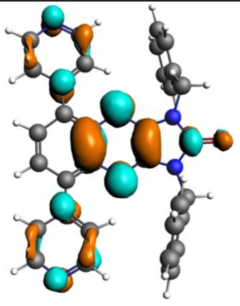
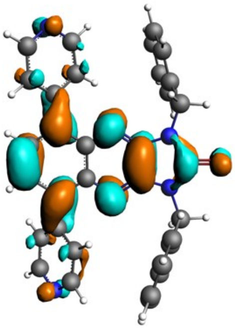
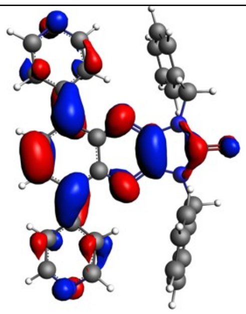
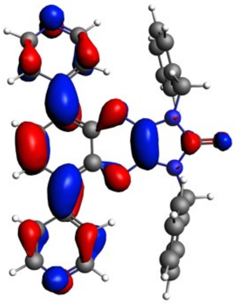
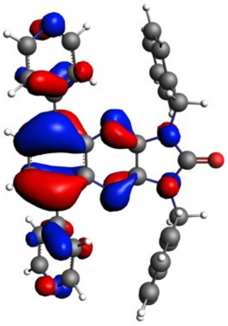
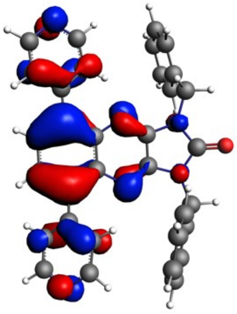
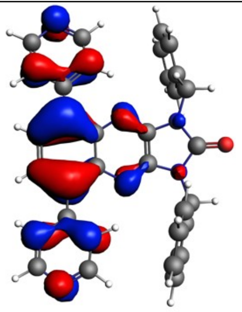
	L2 (oxidized)	**L2 radical** **L2$^{\bullet-}$**	**L2 reduced** **L2^{2-}**
LUMO			
HOMO			
HOMO_1			

Figure S2. LUMO, HOMO and HOMO-1 electron density maps of ligands **L1** and **L2** in their oxidized, radical, and reduced states.

L1	**L1 (oxidized)**	**L1 radical** **L1$^{\bullet-}$**		**L1 reduced** **L1^{2-}**
		Alpha	Beta	
LUMO+2	-1.348	-0.838	-0.791	-0.450
LUMO+1	-1.698	-1.494	-1.267	-1.210
LUMO	-2.920	-3.683	-2.150	-3.118
HOMO	-6.572	-6.053	-5.783	-5.250
HOMO-1	-6.929	-6.493	-6.297	-5.776

L2	**L2 (oxidized)**	**L2 radical** **L2$^{\bullet-}$**		**L2 reduced** **L2^{2-}**
		Alpha	Beta	
LUMO+2	-1.005	-0.786	-0.612	-0.372
LUMO+1	-1.447	-1.275	-0.895	-0.749
LUMO	-2.296	-3.113	-1.900	-2.762
HOMO	-6.413	-5.796	-5.445	-4.982
HOMO-1	-6.576	-6.154	-5.949	-5.694

Table S1. Energy levels (eV) from LUMO+2 to HOMO-1 for **L1** and **L2** in different oxidation state

Representation of **L2-Zn** from the crystallographic data

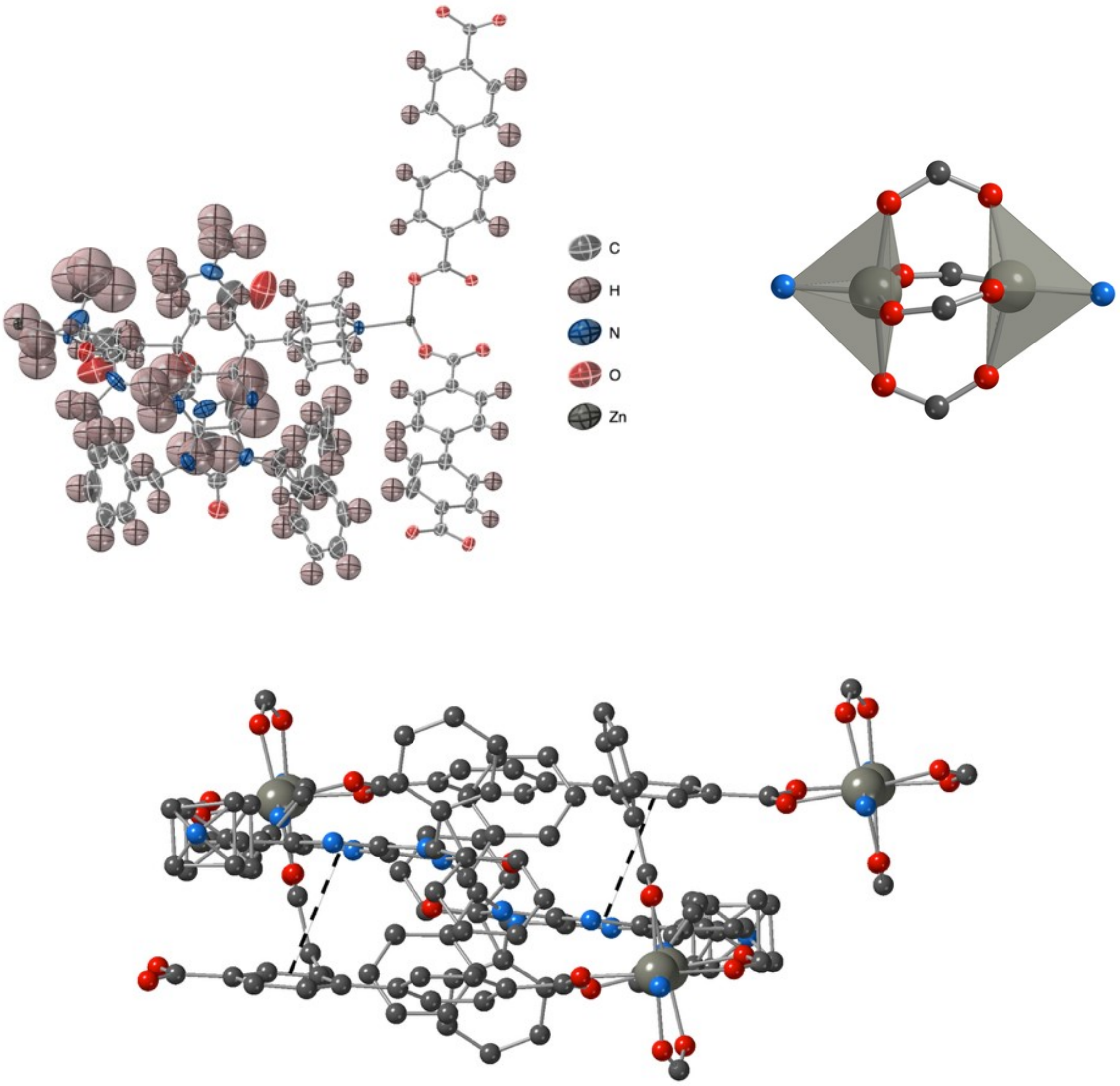


Figure S3: The X-ray crystal structures of **L2-Zn**: the asymmetric unit with thermal ellipsoids are at 50% probability (top left), the environment around the metal centres (top right) and the detailed π-π interactions (represented as dashed lines and H atoms were omitted for clarity) (bottom).

CRYSTALLOGRAPHIC DATA, SELECTED BOND LENGTHS

	L2-Ni	**L2-Zn**
CCDC		**2515971**
Empirical formula	$C_{61}H_{40}N_6Ni_2O_9$, C_3H_7NO, solvent	$C_{61}H_{40}N_6O_9Zn_2$, $2(C_3H_7NO)$, solvent
Formula weight	2309.91	1277.92
Crystal system, space group	Monoclinic, *C*2/c	Monoclinic, *C*2/c
Unit cell dimensions	a = 19.4046(17) Å b = 23.3120(19) Å c = 35.579(3) Å	a = 19.0178(6) Å b = 23.6399(7) Å c = 36.2931(10) Å
	α = 90 deg. β = 90.581(5) deg. γ = 90 deg.	α = 90 deg. β = 92.589(2) deg. γ = 90 deg.
Volume	16094(2) Å^3	16300.0(8) Å^3
Z, Calculated density		8, 1.041 Mg/m^3
Absorption coefficient		1.147 mm^{-1}
F(000)		5280
Crystal size		0.200 x 0.180 x 0.140 mm
Theta range for data collection		2.437 to 66.948 deg.
Limiting indices		-22<=h<=22, -28<=k<=28, -39<=l<=43
Temperature		120(2) K
Wavelength		1.54178 Å
Reflections collected / unique		157280 / 14421 [R(int) = 0.0451]
Completeness to theta =		99.4%
Max. and min. transmission		
Data / restraints / parameters		14421 / 27 / 980
Goodness-of-fit on F^2		1.030
Final R indices [I>2sigma(I)]		R1 = 0.0612, wR2 = 0.1926
R indices (all data)		R1 = 0.0658, wR2 = 0.1972
Largest diff. peak and hole		0.974 and -0.631 e.Å^{-3}

Table S2 : Crystallographic data for **L2-Ni** and **L2-Zn**, measured at 120 K.

	L2-Ni	**L2-Zn**
M–O	1.968(6) 1.980(6) 1.985(6) 1.998(6) 2.011(6) 2.015(6)	2.022(2) 2.028(2) 2.029(2) 2.032(2) 2.037(2) 2.043(2) 2.046(2) 2.052(2)
M–N	2.006(10) 2.007(9)	2.022(2) 2.025(2)
M-M	2.580(2)	2.9186(5)

Table S3 : Selected bonds lengths (Å) around the M(II) ions for **L2-Ni** and **L2-Zn**

	L1-Co
Empirical formula	$C_{50}H_{32}N_6O_{10}Co_2$, $2(C_3H_7NO)$, solvent
Formula weight	1140.87
Crystal system, space group	Orthorhombic *C* mcm
Unit cell dimensions	a = 22.2727(10) Å b = 20.7207(10) Å c = 18.0575(7) Å
	α = 90 deg. β = 90 deg. γ = 90deg.
Volume	8333.6(6) Å^3

Table S4 : Cell parameters determined for **L1-Co**, measured at 120 K..

REPRESENTATION AND DESCRIPTION OF **L1-CO** FROM PRELIMINARILY CRYSTALLOGRAPHIC DATA

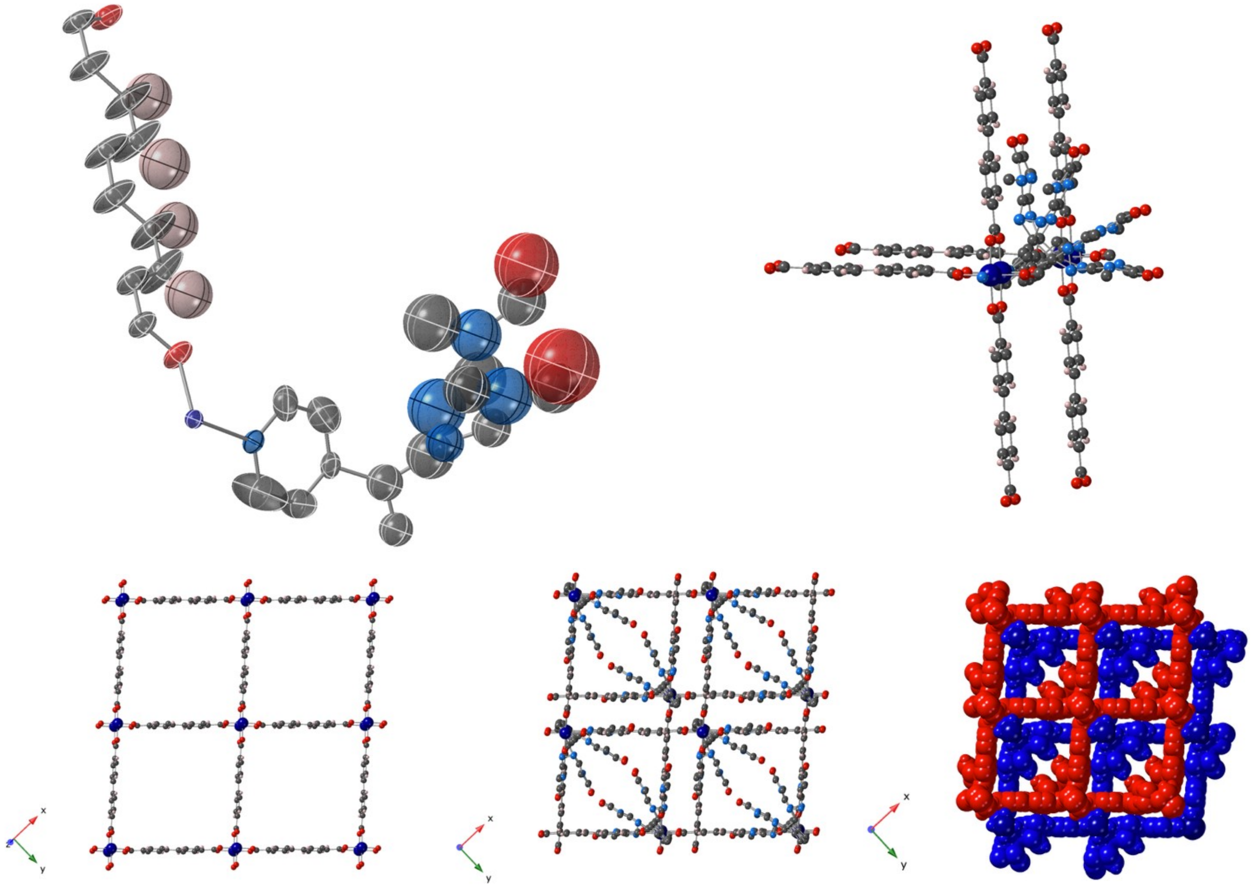


Figure S4: Preliminary data of the X-ray crystal structures of **L1-Co**: the asymmetric unit with thermal ellipsoids are at 50% probability (top left), the disorder on the **L1** ligand (top right) and the pillared 3D network together with space filling representation.

Description of the L1-Co structure :

L1-Co crystallises in the monoclinic *C* mcm space group. The asymmetric unit is composed of one pbdc^{2-} ligand, one ligand **L1**, one M^{2+} cations (see Figure S4). In **L1-Co**, high disorder is observed : on the pyridyl rings, on the benzyl moieties appended to **L1** and also on the alloxazine moiety, which is disordered on four different positions (see Figure S4), and the benzyl rings are also highly disordered and could not be refined. The connectivity in **L1-Co** can be described as the formation of Co$_2$ paddlewheels which are the corner square connecting units surrounded by four disordered pbdc^{2-} ligands, ensuring the 1:1 metal-to-ligand leading to a 2D system pillared by the disordered **L1** ligands, resulting in a pillared 3D network with a metal: pbdc:L2 stochiometric ratio of 2:2:1. The disordered alloxazine moieties are “blocking the pores of the formed coordination compound.

PXRD PATTERNS FOR **L2-M** (M = ZN, NI AND CO) AND **L1-M** (M = ZN, NI, CO AND CU)

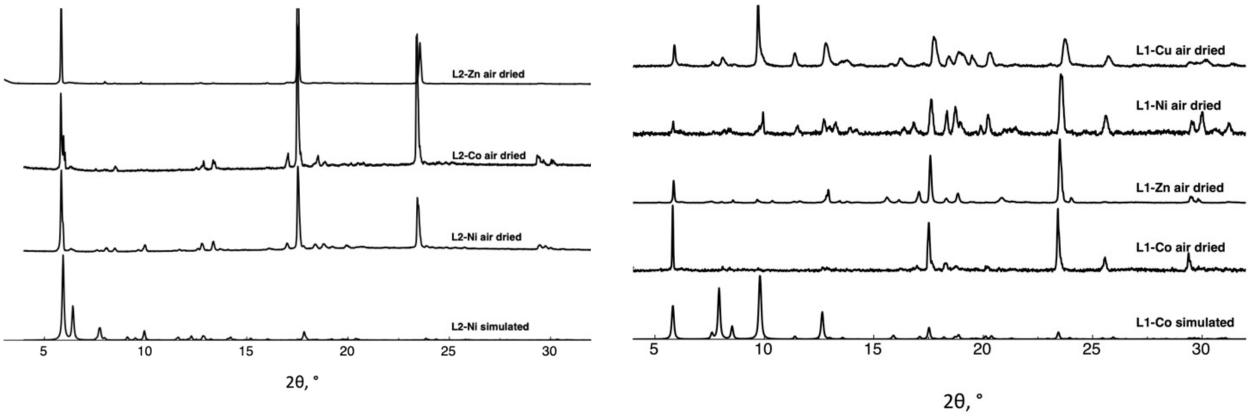


Figure S5: PXRD patterns of the series of the series (left) **L2-M** (M = Zn, Ni and Co) and (right) **L1-M** showing (M = Zn, Ni, Co and Cu) closely matching peak positions, indicating isostructural frameworks. Discrepancies in intensity of peaks are due to preferential orientation of crystals within samples.

TGA for **L1-M** (M = Zn, Ni, Co and Cu) and **L2-M** (M = Zn, Ni and Co)

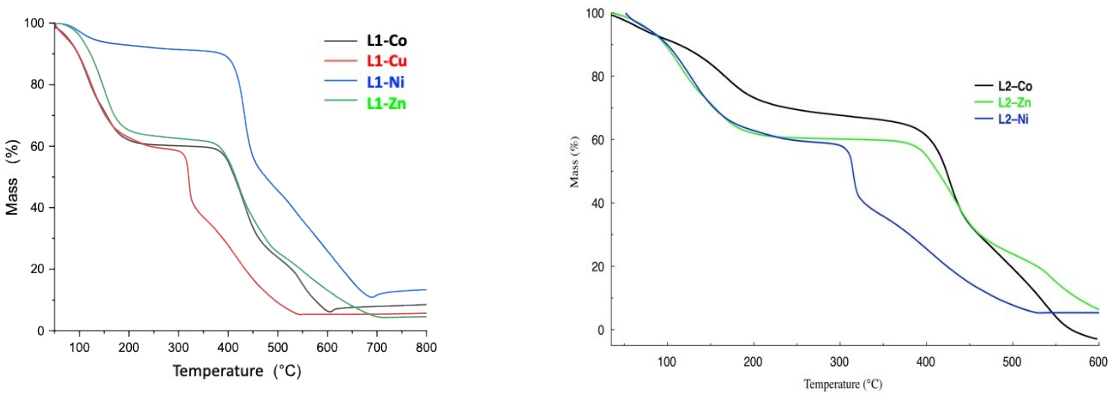


Figure S6. For **L1-M** (M = Co, Cu, Ni and Zn) and **L2-M** (M = Zn, Ni and Co), TGA thermograms

N_2 ADSORPTION FOR **L1-M** (M = CO AND ZN)

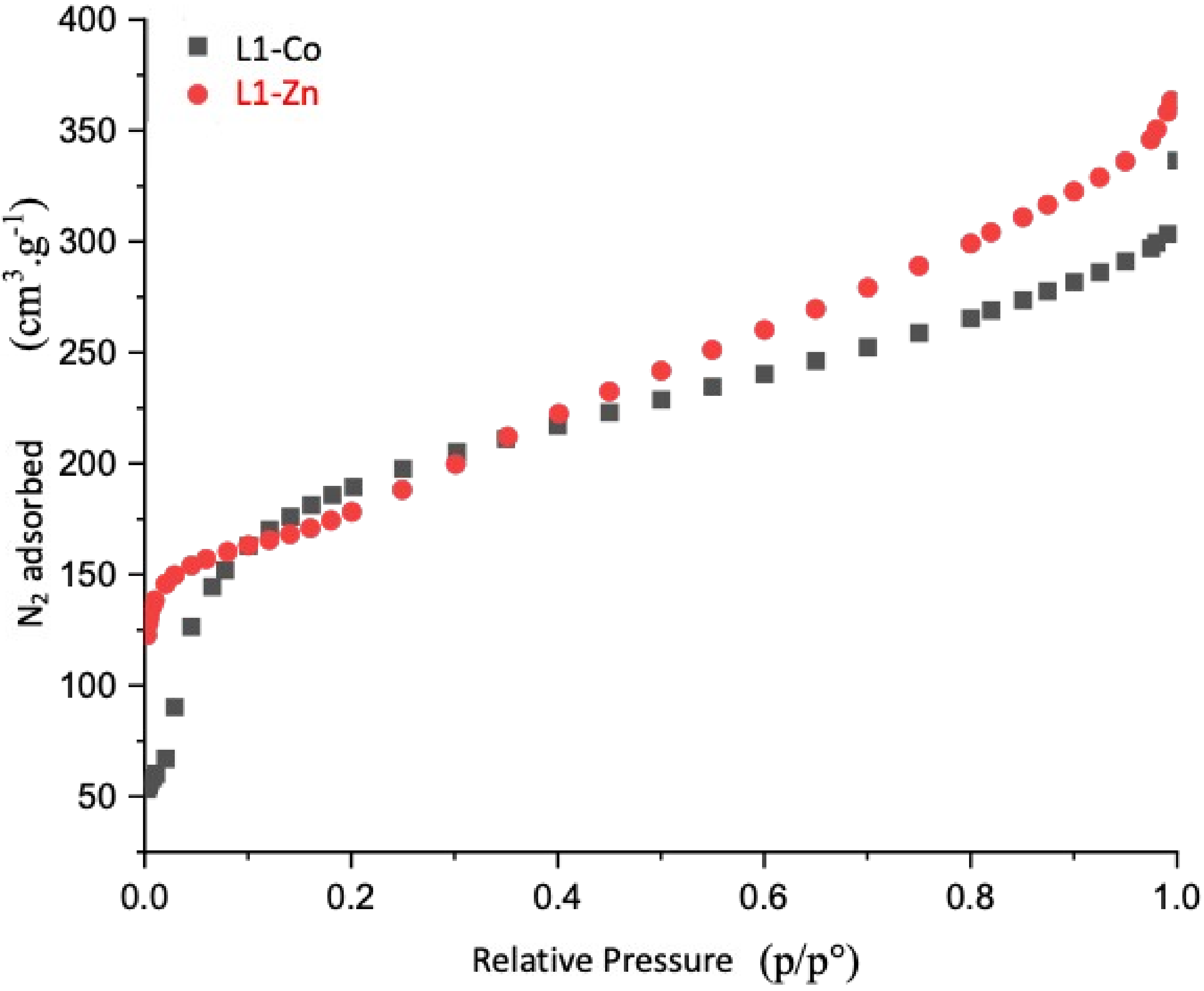


Figure S7. For **L1-M** (M = Co or Zn), adsorption isotherms N_2 at T = 77K.