Electronic Supplementary Information (ESI) available: [Relevant crystallographic data, TG and IR characterization]. See DOI:

DPDS-DPS *in situ* Transformation at Room Temperature via a 1,2-Nucleophilic Addition Mechanism

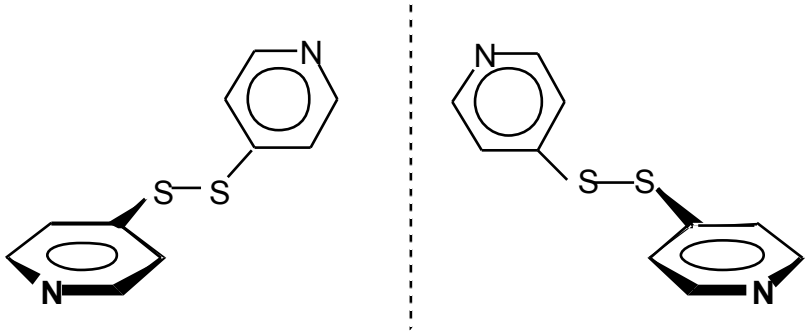
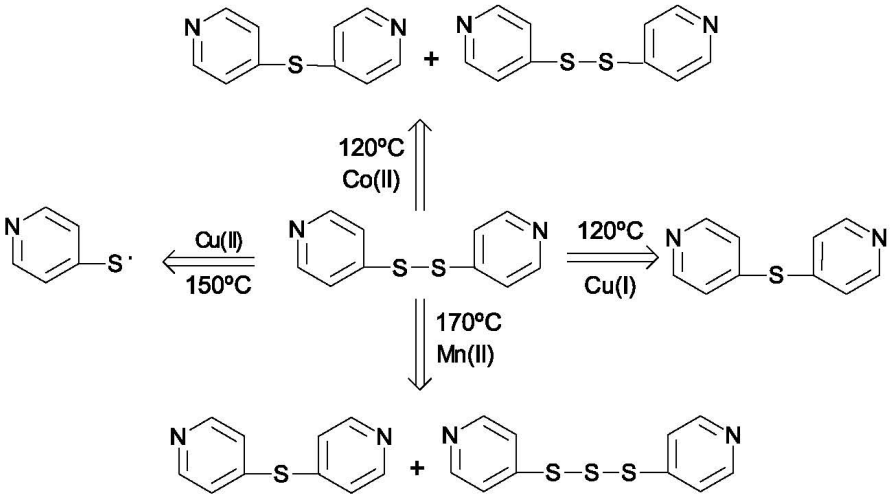


Fig. S1. Optical isomers of DPDS.



Scheme S1. Some different transformations of DPDS ligand.

Table S1. Crystal data and structure refinement for compound $Mn(NCS)_2(DPS)_4$ (**1**)

Empirical formula	$C_{42}H_{32}MnN_{10}S_6$	
Formula weight	924.08	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit Cell Dimensions	a = 9.694(3) Å	α= 87.71(4)°
	b = 11.143(4) Å	β= 76.90(3)°
	c = 11.326(3) Å	γ = 67.65(4)°
Volume	1100.5(6) eÅ^3	
Z	1	
Density (calculated)	1.394 Mg/m^3	
μ	0.628 mm^{-1}	
F(000)	475	
θ range for data collection	1.98° to 26.08°	
Index ranges	-11≤ h ≤11, -13≤ k ≤13, -13≤ ℓ ≤13	
Collected reflections	8602	
Independent reflections	4003 [R(int) = 0.0608]	
Refinement method	Full-matrix on F^2	
Data / restraints / parameters	4003 / 0 / 277	
Goodness-of-fit on F^2	0.787	
R indices	R_1 = 0.0394, wR_2(all data) = 0.0940	
Largest Δρ peak and hole	0.548 and -0.435 eÅ^{-3}	

Table S2. Most important intermolecular H-Bonds (units in Å and º) for compound $Mn(NCS)_2(DPS)_4$ (**1**). Symmetry codes: i) *2-x,1-y,-z*. ii) *2-x,-y,-z*. iii) *-1+x,y,z*.

C6-H6	H6···S1^{i}	C6···S1^{i}	C6-H6···S1^{i}
0.930(5)	3.083(2)	3.687(5)	124.3(2)
C5-H5	H5···S1^{i}	C5···S1^{i}	C5-H5···S1^{i}
0.929(4)	3.012(2)	3.640(5)	126.3(3)
C18-H18	H18···S2^{ii}	C18···S2^{ii}	C18-H18···S2^{ii}
0.929(5)	3.11(1)	4.01(1)	162.0(3)
C15-H15	H15···N5^{i}	C15···N5^{i}	C15-H15···N5^{i}
0.930(5)	2.895(5)	3.708(7)	146.7(3)
C2-H2	H2···N3^{iii}	C2···N3^{iii}	C2-H2···N3^{iii}
0.930(4)	2.875(7)	3.473(8)	123.2(3)
C3-H3	H3···N3^{iii}	C3···N3^{iii}	C3-H3···N3i^{iii}
0.931(5)	2.712(6)	3.379(8)	129.3(3)
C13-H13	H13···N5^{iii}	C13···N5^{iii}	C13-H13···N5i^{iii}
0.930(4)	3.044(4)	3.753(6)	134.3(2)

Table S3. Crystal data and structure refinement for $[Fe(NCS)_2(DPS)_2]\cdot 2H_2O$ (**2**)

Empirical formula	$C_{22}H_{20}FeN_6O_2S_4$	
Formula weight	584.53	
Temperature	293(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	C*2/c*	
Unit cell dimensions	a = 17.001(6) Å	α= 89.99(4)°
	b = 10.288(4) Å	β= 118.53(4)°
	c = 16.629(6) Å	γ = 90.14(4)°
Volume	2555.3(16) $Å^3$	
Z	4	
Density (calculated)	1.519 Mg/m^3	
μ	0.950 mm^{-1}	
F(000)	1200	
θ range for data collection	2.40° to 26.12°.	
Index ranges	$-20 \le h \le 20$, $-12 \le k \le 12$, $-20 \le \ell \le 20$	
Reflections collected	9614	
Independent reflections	2490 [R(int) = 0.2777]	
Refinement method	Full-matrix on F^2	
Data / restraints / parameters	2490 / 3 / 174	
Goodness-of-fit on F^2	0.625	
R indices	R_1 = 0.0446, wR_2(all data) = 0.1051	
Largest Δρ peak and hole	0.298 and -0.621 $eÅ^{-3}$	

Table S4. Most important intermolecular H-Bonds (units in Å and º) for compound $[Fe(NCS)_2(DPS)_2]\cdot 2H_2O$ (**2**). Symmetry codes: i) 1/*2-x*,*1/2+y*,3/2-*z*. ii) ½+*x*,3/2-*y*,1/2+*z*. iii) -*1+x*,*y*,*z*.

O1-H1O1	H1O1···S3'[i]	O1···S3'[i]	O1-H1O1···S3'[i]
0.850(10)	2.7(8)	3.26(7)	130(9)
O1-H2O1	H2O1···S3	O1···S3	O1-H2O1···S3
0.850(5)	1.9(7)	2.52(4)	132(7)
C12-H12	H12···O1[ii]	C12···O1[ii]	C12-H12···O1[ii]
0.930(8)	2.68(4)	3.21(5)	117(1)

Table S5. Crystal data and structure refinement for $Zn(NCO)_2(DPS)$ (**3**)

Empirical formula	$C_{12}H_8N_4O_2SZn$	
Formula weight	337.65	
Temperature	293(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	P*cab*	
Unit cell dimensions	a = 14.545(3) Å	α= 90.00°
	b = 14.834(3) Å	β= 90.00°
	c = 12.805(4) Å	γ = 90.00°
Volume	2762.8(1) $Å^3$	
Z	8	
Density (calculated)	1.624 Mg/m^3	
μ	1.934 mm^{-1}	
F(000)	1360	
θ range for data collection	2.52° to 25.99°	
Index ranges	$-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $0 \leq \ell \leq 15$	
Reflections collected	9399	
Independent reflections	2698	
Refinement method	Full-matrix on F^2	
Data / restraints / parameters	2698/ 0 / 182	
Goodness-of-fit on F^2	0.801	
R indices	$R_1 = 0.0289$, wR_2 (all data) = 0.0679	
Largest Δρ peak and hole	0.199 and -0.304 $eÅ^{-3}$	

Table S6. Most important intermolecular H-Bonds (units in Å and º) for compound $Zn(NCO)_2(DPS)$ (**3**). Symmetry codes: i) 3/*2-x,1/2+y,-z*. ii) ½+*x*,1/2-*y*,*z*. iii) *3/2-x*,1/2+*y*,1-*z*.

C11-H11	H11···O1[i]	C11···O1[i]	C11-H11···O1[i]
0.930(5)	2.389(4)	3.187(7)	143.7(3)
C6-H6	H6···O2[ii]	C6···O2[ii]	C6-H6···O2[ii]
0.930(6)	2.686(6)	3.582(8)	162.0(3)
C10-H10	H10···O2[iii]	C10···O2[iii]	C10-H10···O2[iii]
0.930(6)	2.630(4)	3.365(7)	136.4(3)

Table S7. Crystal data and structure refinement for $[Zn(DPS)_4(H_2O)_2](ClO_4)_2]\cdot H_2O$ (**4**)

Empirical formula	$C_{40}H_{38}C_{12}N_8O_{11}S_4Zn$	
Formula weight	1071.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_12_12$	
Unit cell dimensions	a = 16.529(2) Å	α = 90º
	b = 16.529(2) Å	β = 90º
	c = 16.604(2) Å	γ = 90º
Volume	4536.3(11) $Å^3$	
Z	4	
Density (calculated)	1.569 Mg/m^3	
μ	0.912 mm^{-1}	
F(000)	2200	
θ range for data collection	1.74º to 28.20º	
Index ranges	$-21 \leq h \leq 18$, $-21 \leq k \leq 11$, $-21 \leq \ell \leq 20$	
Reflections collected	28832	
Independent reflections	5315	
Refinement method	Full-matrix on F^2	
Data / restraints / parameters	5315 / 0 / 311	
Goodness-of-fit on F^2	1.021	
R indices	R_1 = 0.0511, wR_2 (all data) = 0.1195	
Largest $\Delta\rho$ peak and hole	1.030 and -0.372 $eÅ^{-3}$	

Table S8. Most important intermolecular (units in Å and º) H-Bonds for compound $[Zn(DPS)_4(H_2O)_2](ClO_4)_2]\cdot H_2O$ (**4**)

O5-H51	H5···N3	O5···N3	O5-H51···N3
0.93(3)	1.92(3)	2.852(4)	176(3)
O1W-H12W	H12W···O5	O1W···O5	O1W-H12W···O5
0.78(5)	2.02(5)	2.781(3)	165(4)
O1W-H11W	H11W···N4	O1W···N4	O1W-H11W···N4
0.79(5)	2.03(5)	2.813(4)	170(5)

Table S9. Details of the coordination environment for compounds **1- 4**.

	(1)	**(2)**	**(3)**	**(4)**
Minimum distance	N1 = 2.158(5)	N2 = 1.902(5)	N3 = 2.099(8)	N2 = 2.138(3)
Maximum distance	N4 = 2.350(4)	N4 = 2.046(5)	N2 = 2.239(8)	N1 = 2.184(3)
ℓ_{av} (Å)	2.2636	1.9769	2.1887	2.1582
Volume (Å^3)	15.4291	3.9123	13.9122	13.3324
D	0.03120	0.03345	0.02745	0.00810
$\langle\lambda\rangle$	1.0027	1.0101	1.0041	1.0037
σ^2 (^{o}^{2})	0.8913	45.3154	8.5863	12.9896

ℓ_{av} is the average bond length; $D = \frac{1}{n}\sum_{i=1}^{n}\frac{|\ell_i - \ell_{av}|}{\ell_{av}}$ is the distortion index on bond lengths[14], where ℓ_i is the distance from the central atom to the i^{th} coordinating atom; $\langle\lambda\rangle = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{\ell_i}{\ell_o}\right)^2$ is the cuadratic elongation[15] where ℓ_o is the center to vertex distance of a regular polyhedron of the same volume; $\sigma^2 = \frac{1}{m-1}\sum_{i=1}^{m}(\phi_i - \phi_o)^2$ is the bond angle variance[15], where m is the number of bond angles, ϕ_i the i^{th} bond angle and ϕ_o the ideal bond angle for a regular polyhedron.

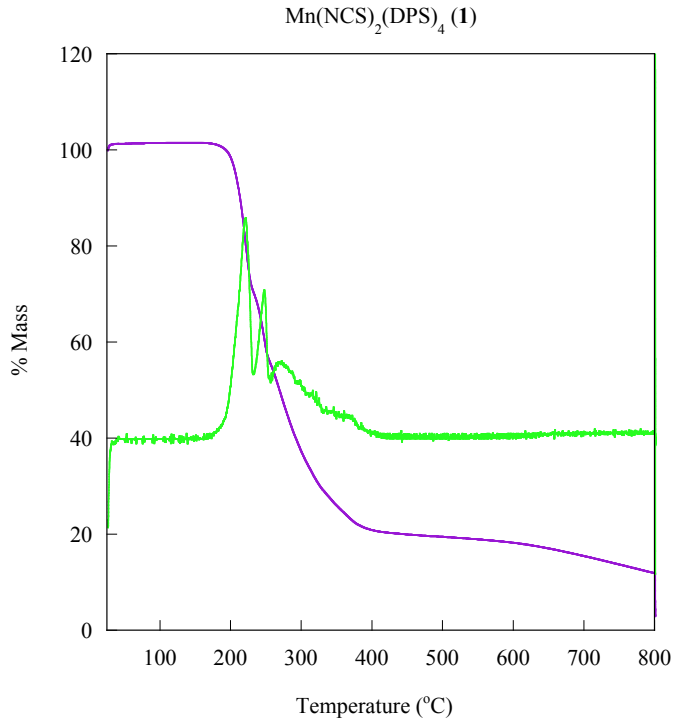


Fig. S2. Graphic of TG and DTG of compound $Mn(NCS)_2(DPS)_4$ (**1**)

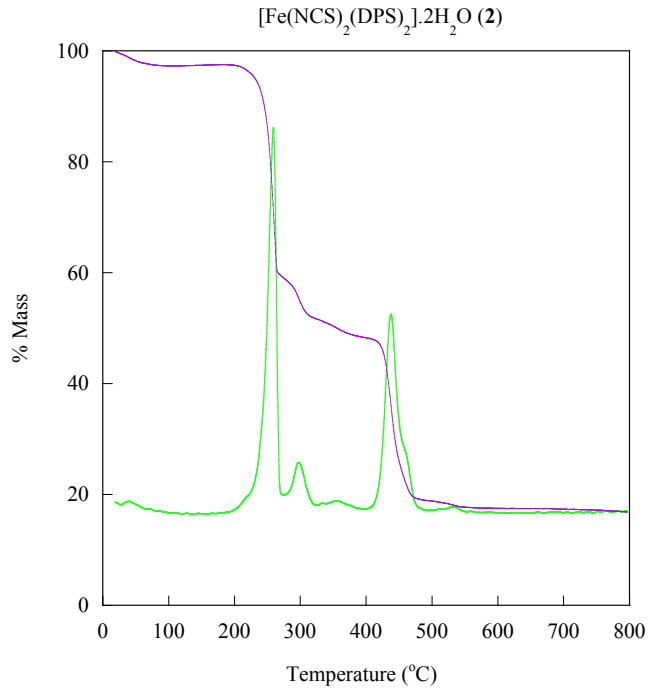


Fig. S3. Graphic of TG and DTG of compound $[Fe(NCS)_2(DPS)_2]\cdot 2H_2O$ (**2**)

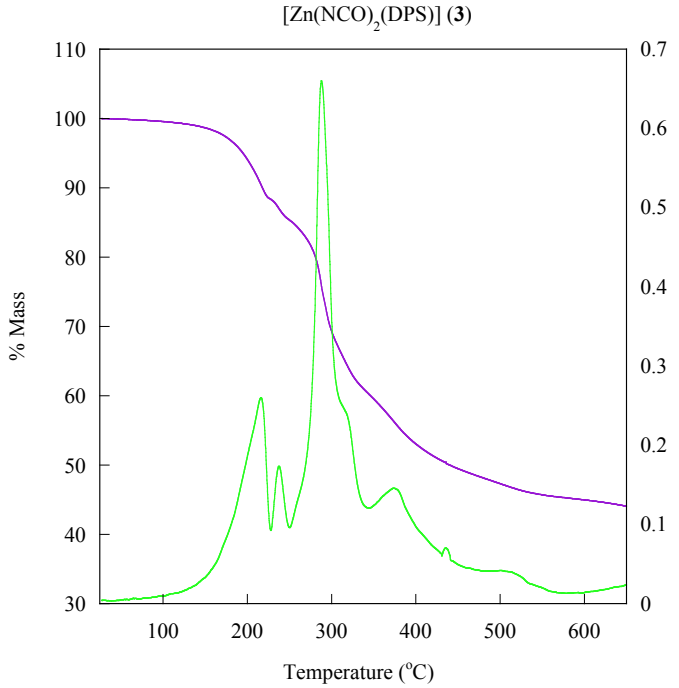


Fig. S4. Graphic of TG and DTG of compound [Zn(NCO)$_2$(DPS)] (**3**)

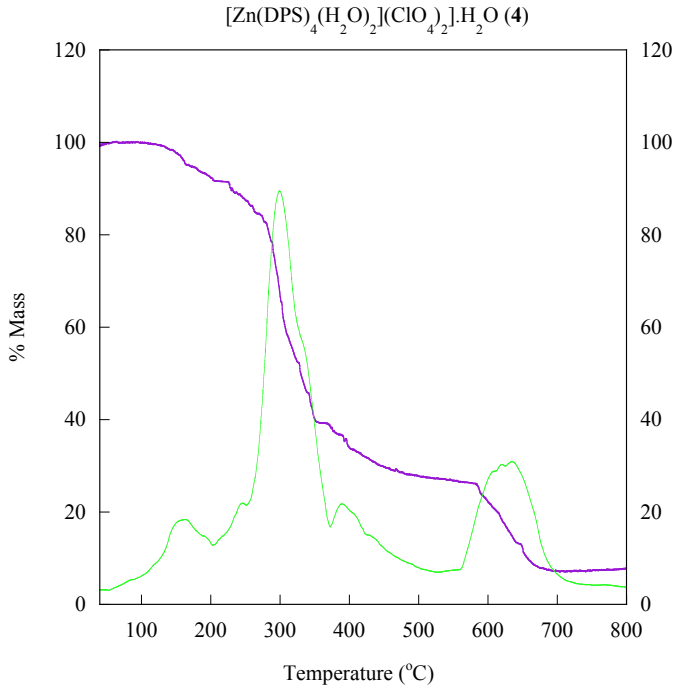


Fig. S5. Graphic of TG and DTG of compound [Zn(DPS)$_4$(H$_2$O)$_2$](ClO$_4$)$_2$]·H$_2$O (**4**)

Table S10. Thermogravimetric analysis for compounds **1-4**. Notice that owing to the complex TG/DTG behaviour showed by compound **3** (see Fig. S4) the interpretation of the decomposition process is merely qualitative

COMPOUND	STEP	T_i(ºC)	T_f(ºC)	%Δm exper.	%Δm theor.	Assignment (per unit formula)
$[Mn(DPS)_4(NCS)_2]$	1	193	479	80.2	81.48	Loss of 4 DPS ligands
	2	479	791	12.27	12.56	Decomposition of NCS group
	TOTAL	193	791	92.47	94.04	
$[Fe(NCS)_2(DPS)_2]\cdot 2H_2O$	1	40	190	4	6.15	Loss of 2 molecules of water
	2	190	421	54.9	64.4	Decomposition of DPS ligands
	3	421	514	24.2	19.9	Pyrolisis of NCS groups
	TOTAL	40	514	83.1	90.45	
$[Zn(NCO)_2(DPS)]$	1	110	278	14.74		Decomposition of DPS ligand
	2	278	323	24.12		
	3	323	572	15.86		Pyrolisis of NCO groups
	TOTAL	110	572	54.72		
$[Zn(DPS)_4(H_2O)_2(ClO_4)_2]\cdot H_2O$	1	67	171	5.23	5.04	Loss of 3 molecules of water
	2	171	570	68.23	68.04	Decomposition of 4 DPS ligands
	3	570	700	19.11	18.56	Pyrolisis of ClO_4 groups
	TOTAL	67	700	92.57	91.64	

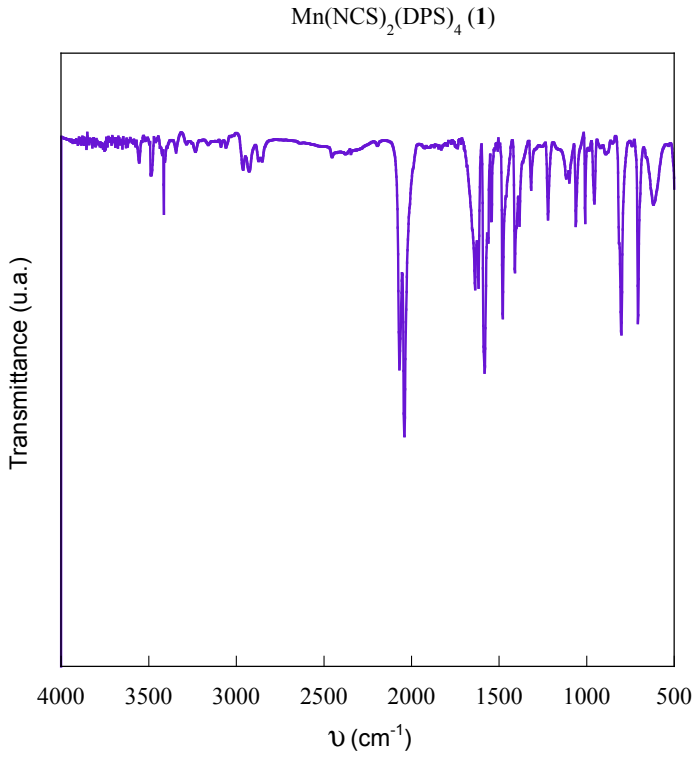


Fig. S6. IR spectra of $Mn(NCS)_2(DPS)_4$ (**1**).

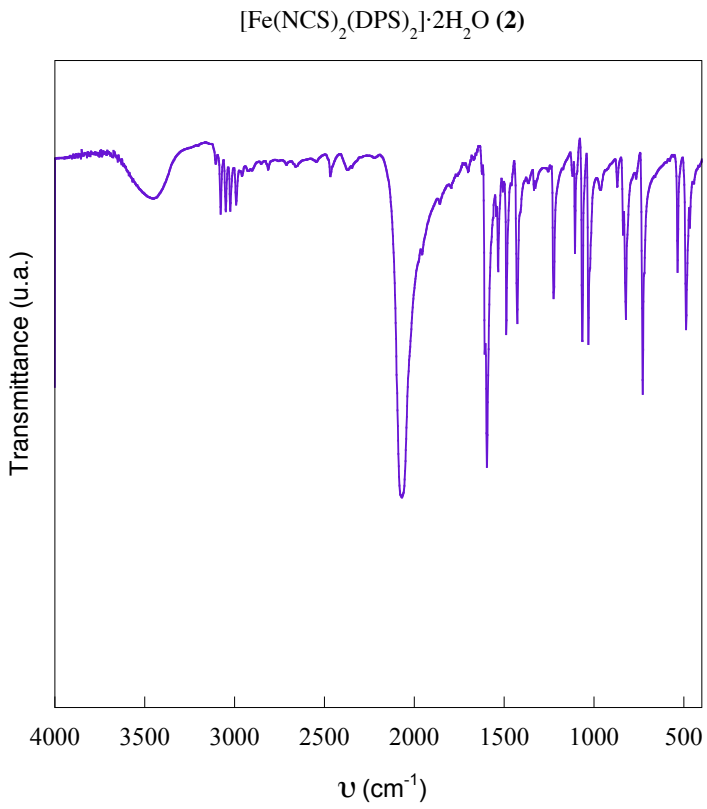


Fig. S7. IR spectra of $[Fe(NCS)_2(DPS)_2]\cdot 2H_2O$ (**2**)

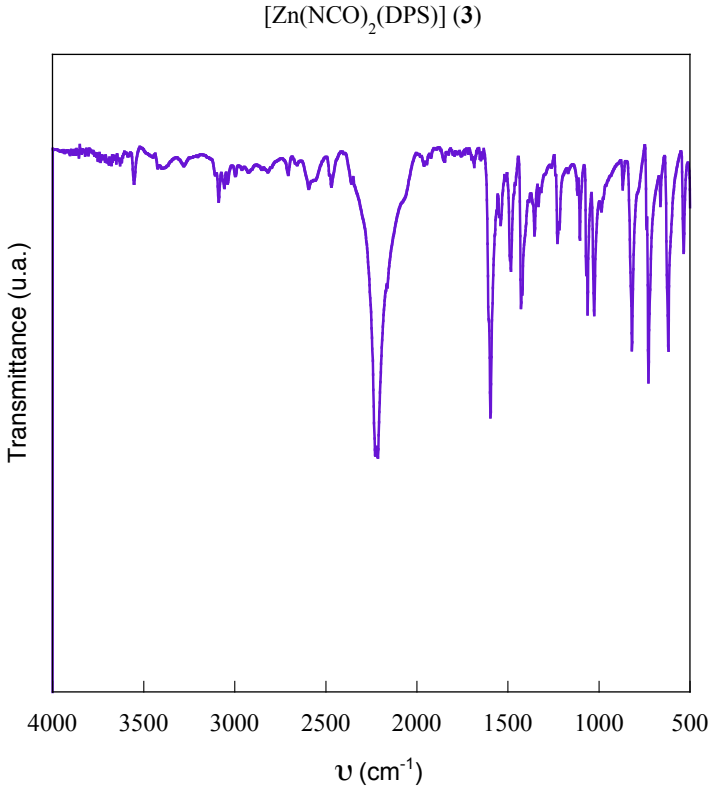


Fig. S8. IR spectra of $[Zn(NCO)_2(DPS)\ ]$ (**3**)

$[Zn(bps)_4(H_2O)_2](ClO_4)_2].H_2O$ (**4**)

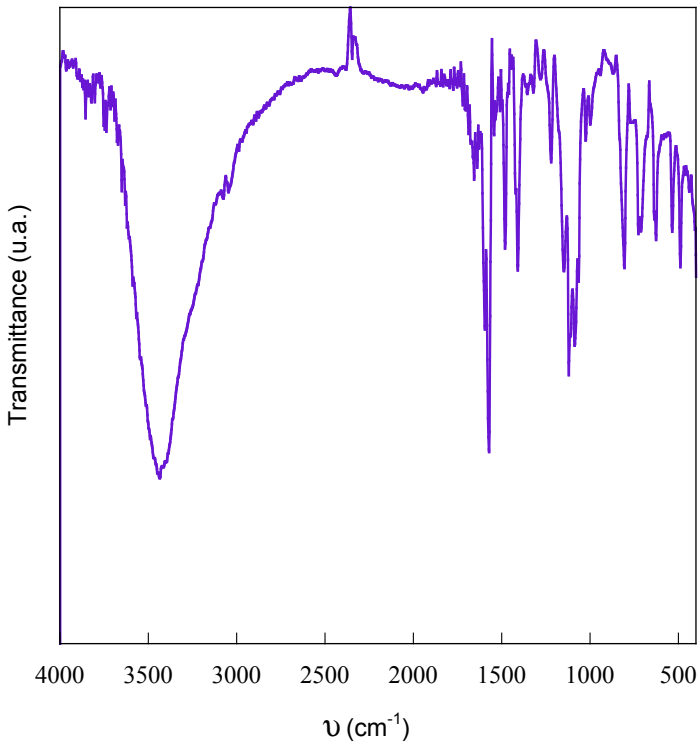


Fig. S9. IR spectra of $[Zn(DPS)_4(H_2O)_2](ClO_4)_2]\cdot H_2O$ (**4**)

Table S11. Interpretation of IR bands in compounds **1-4**. Bands corresponding to DPS are also included for reference.

DPS	**(1)**	**(2)**	**(3)**	**(4)**	**assignment**
		3450		3500	$\nu(O\text{-}H)_{H2O}$
3000	2980	3000	3000-3100	3020	$\nu(C\text{-}H)_{DPS}$
	2095	2064	2212		$\nu_{as}(C\text{-}N)_{NCO/NCS}$
1576	1579	1598	1598	1570	$\nu(C{=}C),\upsilon(C{=}N)_{DPS}$
1413	1481	1420	1429	1480	$\nu(ArC\text{-}C)_{DPS}$
	1229	805	1229		$\nu(C\text{-}O/S)_{NCO/NCS}$
				1093	$\nu_{as}(Cl\text{-}O)_{ClO4}$
1067/991	1063/1005	1095/1058	1065/1029	1062/1070	$\delta_{ep}(ArC\text{-}H)_{DPS}$
700	694	712	732	740	$\nu_{fp}\ (ArC\text{-}S)_{DPS}$
	626	690	620		$\delta(NCO)_{NCO/NCS}$
				630	$\nu_{Fas}(Cl\text{-}O)_{ClO4}$