Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supporting Information

Diazine based ligand supported Co^{II}_3 and Co^{II}_4 coordination complexes: role of the anions

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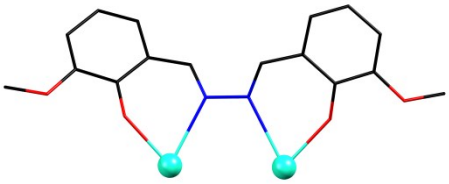
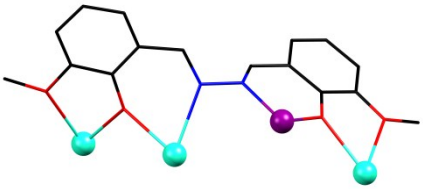
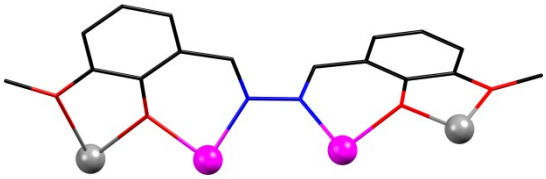
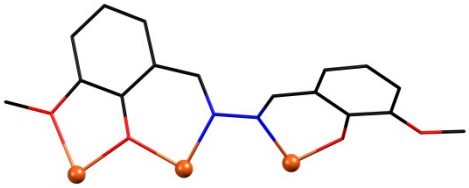
Coordination Mode	Metallic core	Magnetic property	Reference
	Dy_4O_6	SMM	*Angew. Chem. Int. Ed.* 2009, **48**, 9489 – 9492
	$Dy_{10}Co_2$ wheel	SMM	*Chem. Commun.*, 2011, **47**, 8659–8661
	$3d_2–4f_2$	F(Co_2–Ln_2) AF(Ni_2–Ln_2) AF(Cu_2–Ln_2) SMM($Zn2_2$–Dy_2)	*Dalton Trans.*, 2015, **44**, 11935–11942
	Cu_3	Not performed	*Eur. J. Inorg. Chem.*, 2014, 345–351

Abbreviation, F: ferromagnetic, AF: antiferromagnetic, SMM: single molecule magnet
Colour code, cyan: Dy, violet: Co, pink− 3d metal, gray− 4f metal, orange−Cu

Scheme S1: Coordination mode of ligand H_2hydva in coordination complex found in literature

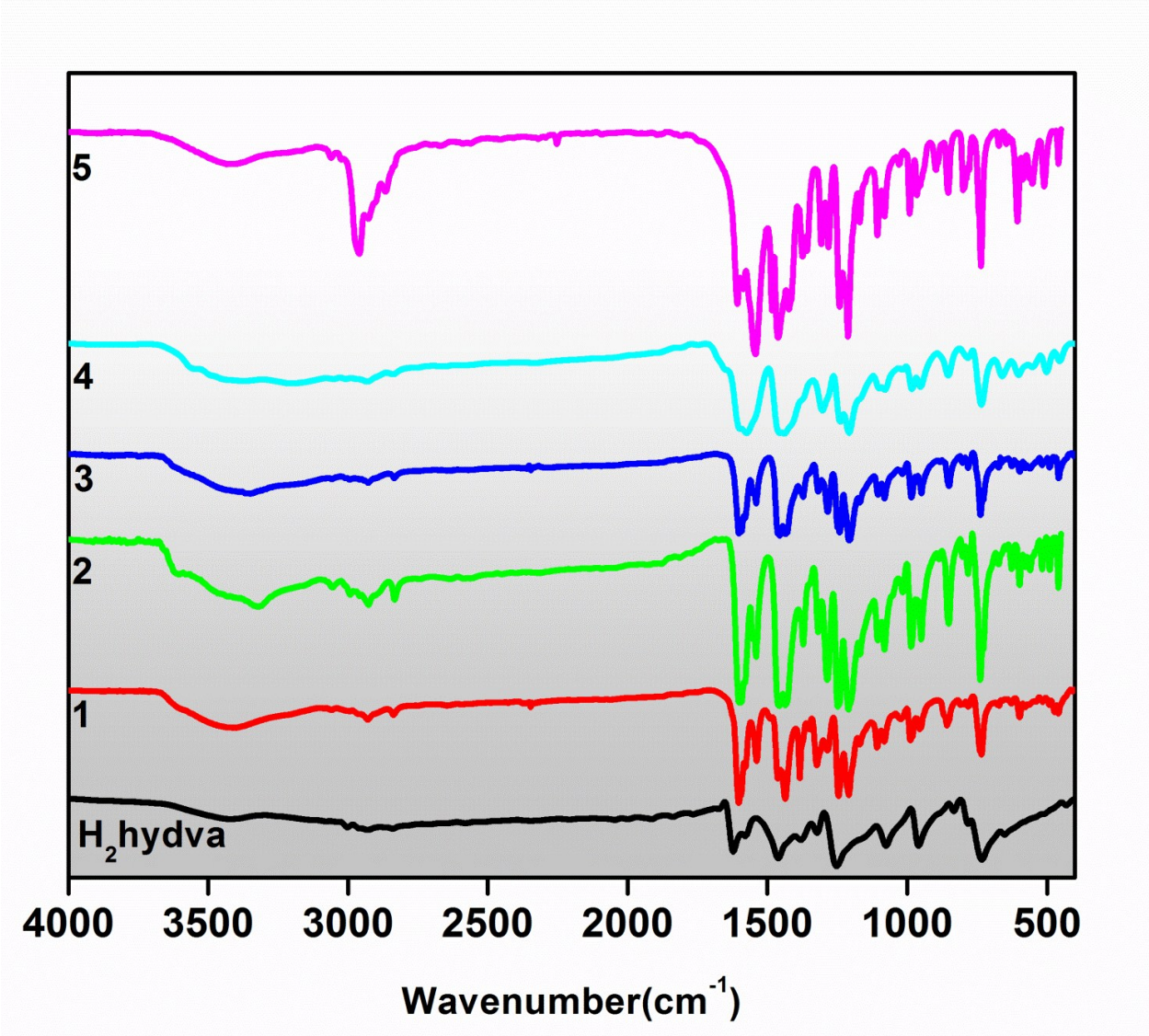


Figure S1: FT−IR spectra of H_2hydva and complex **1**−5 recorded in KBr disk in the spectral region 400−4000 cm^{-1} in Perkin Elmer Spectrum 100 spectrometer.

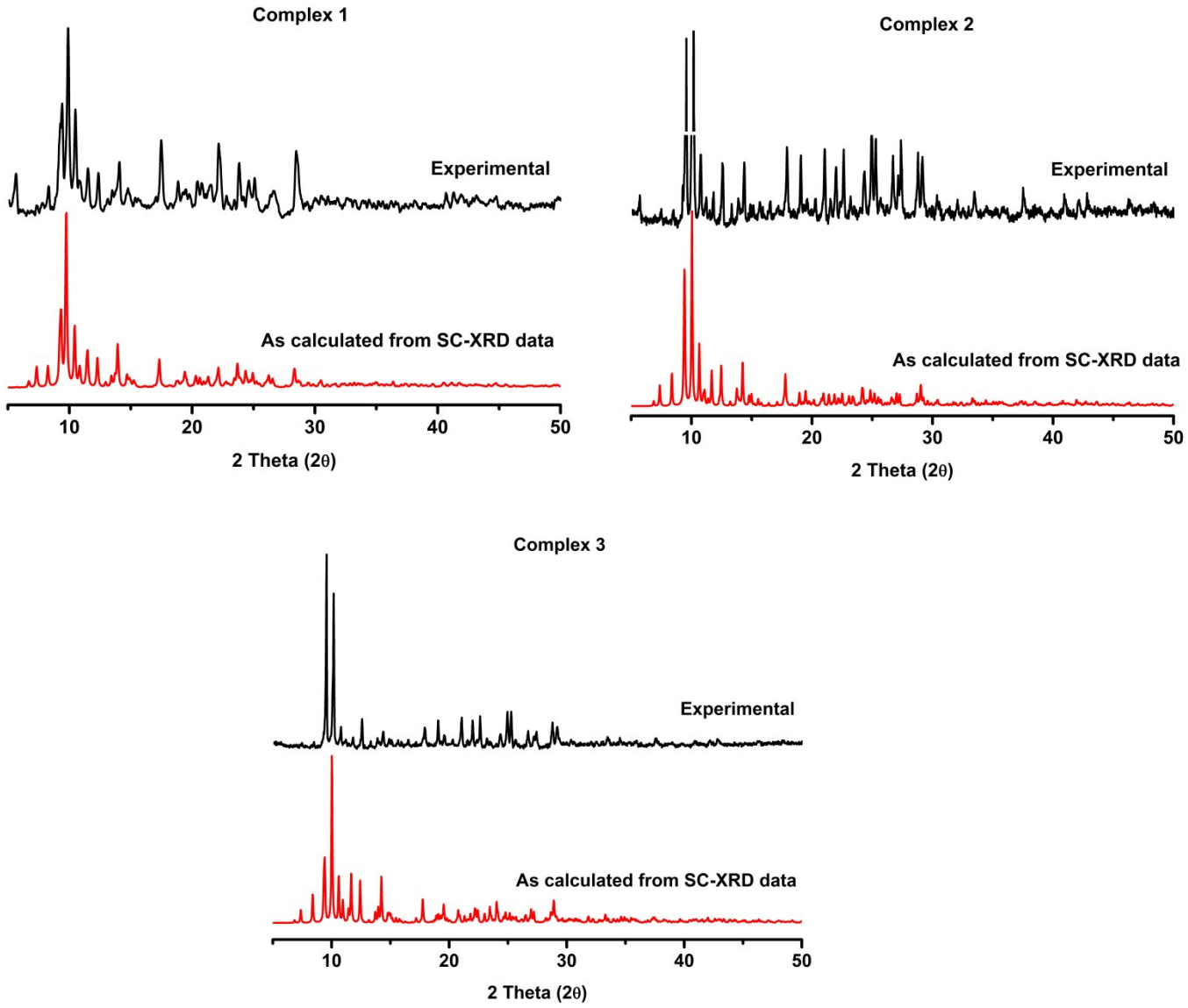


Figure S2: Powder X−ray diffraction (PXRD) patterns of the synthesized tetranuclear complexes **1−3** in comparison with the calculated data obtained from Single crystal X−ray diffraction.

The PXRD analysis of the samples was performed using powder X'Pert, Panalytical diffractometer at room temperature using Cu−Kα (= 1.5418 Å) as the X−ray source and at a generator voltage of 40 kV and a current of 30 mA.. Calculated data was generated from Mercury 3.9 software.

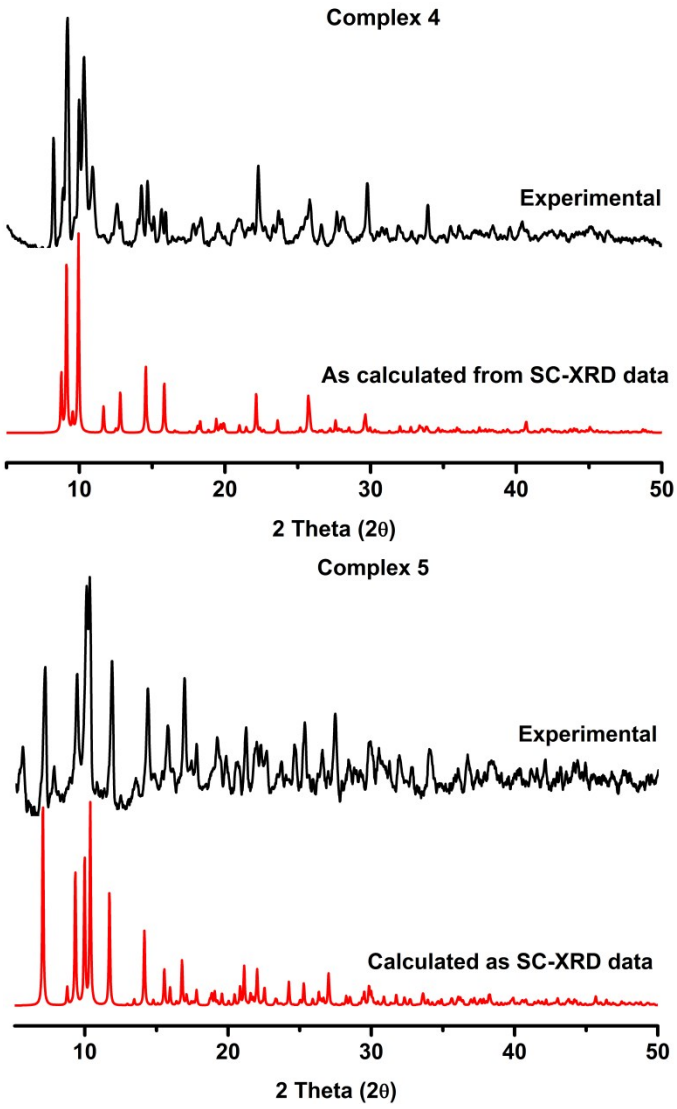


Figure S3: Powder X− ray diffraction (PXRD) patterns of the synthesized trinuclear complexes **4−5** in comparison with the calculated data obtained from Single crystal X−ray diffraction.

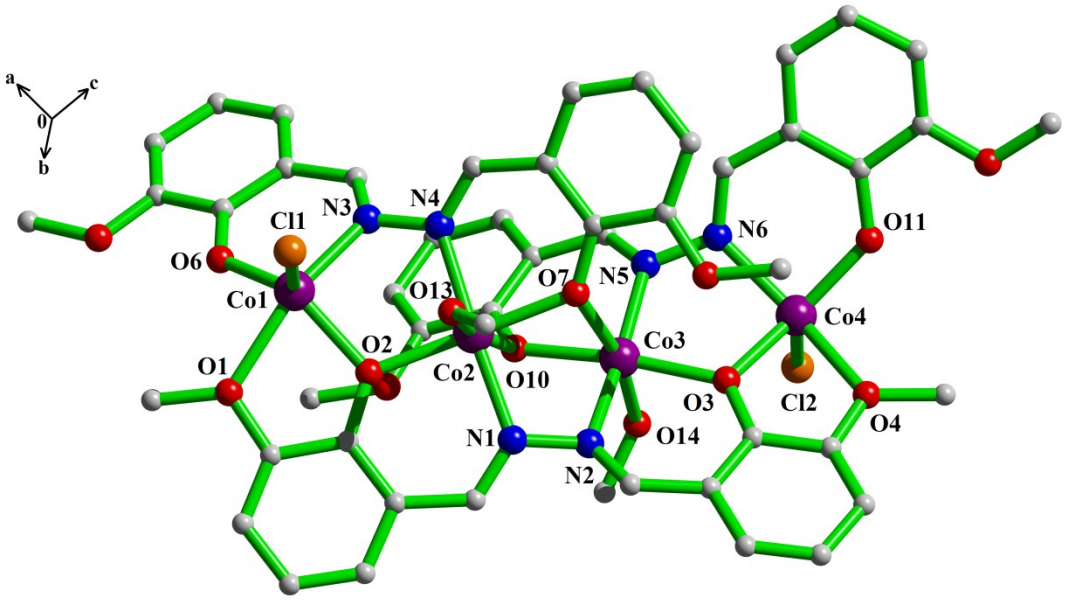


Figure S4: Crystal structure of complex **2** along with the partial atom numbering scheme. All the hydrogen atoms are omitted for clarity.

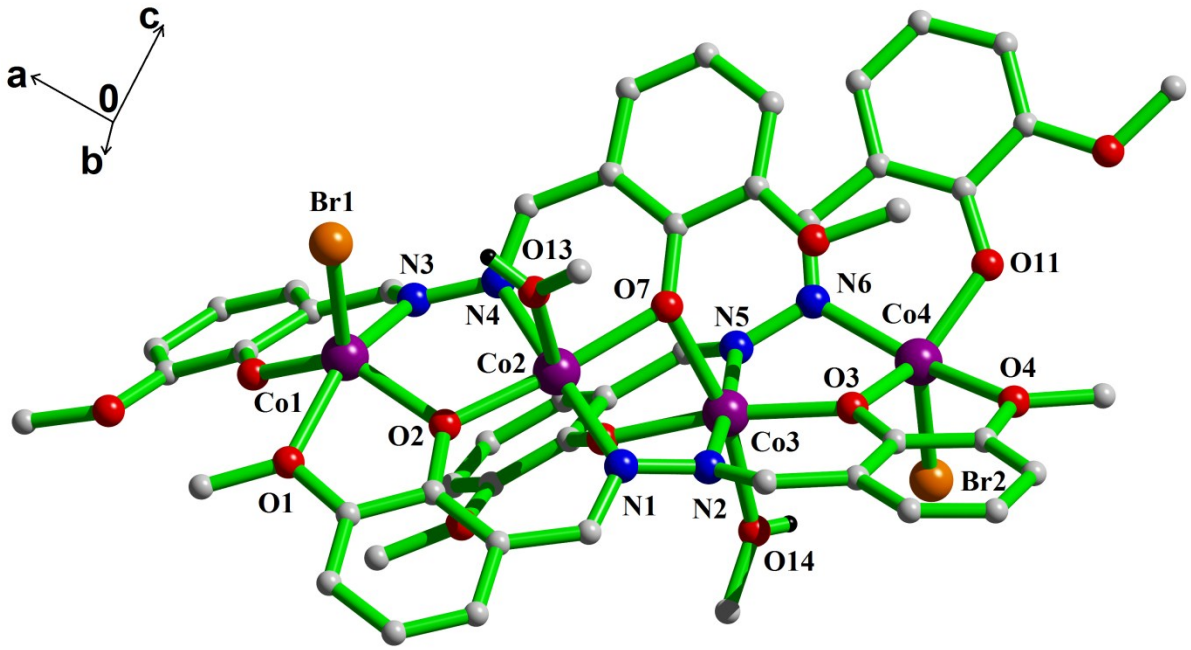


Figure S5: Crystal structure of complex **3** along with the partial atom numbering scheme. All the hydrogen atoms are omitted for clarity.

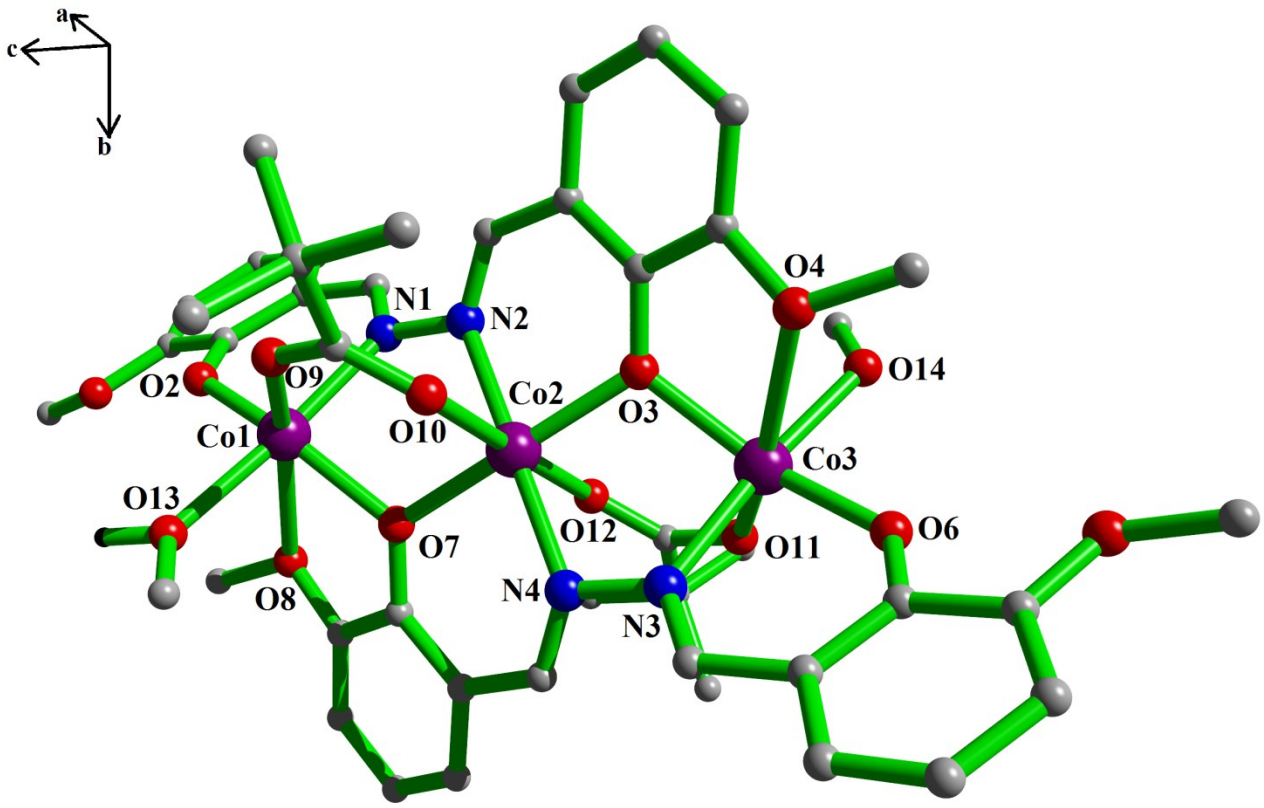


Figure S6: Crystal structure of complex **5** along with the partial atom numbering scheme. All the hydrogen atoms and water of crystallizations are omitted for clarity.

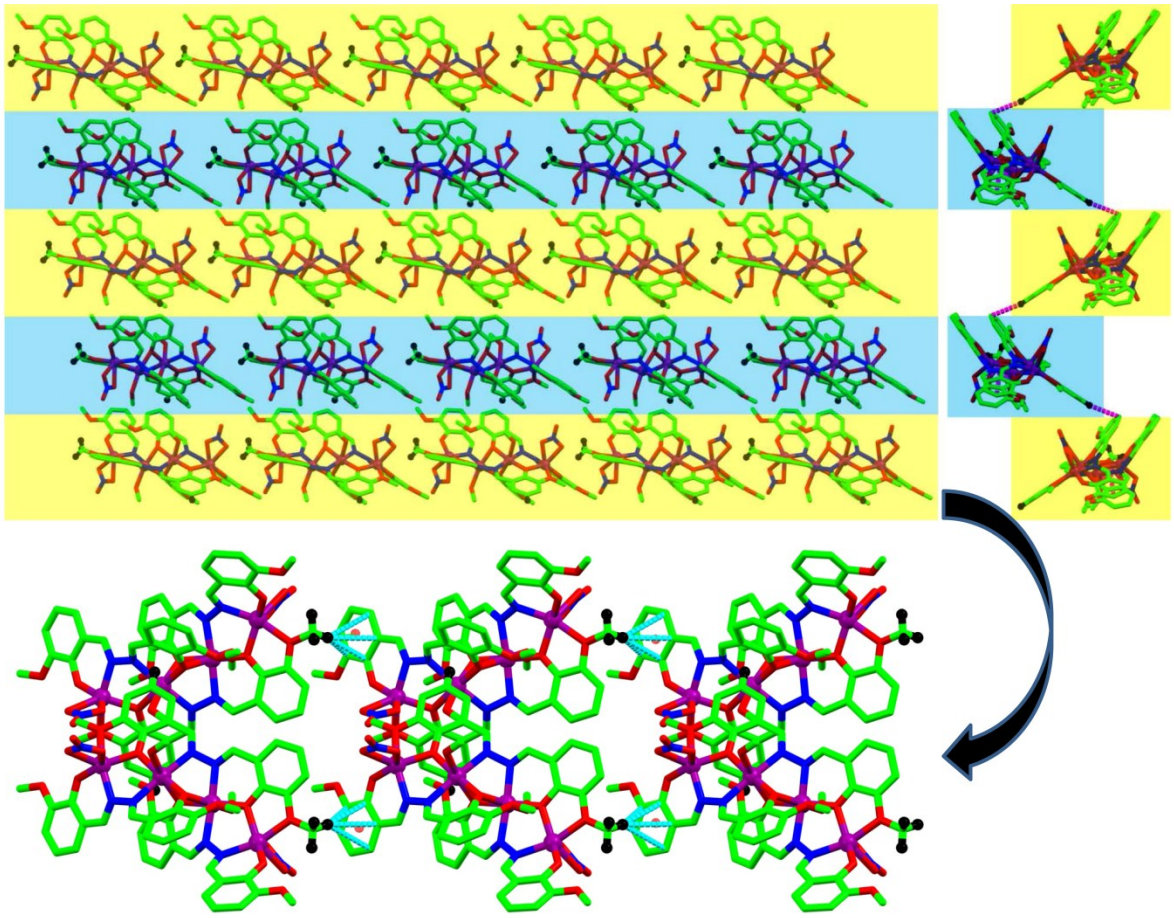


Figure S7: 2−D supramolecular architecture formed by complex **1** in the *ac* plane (Top left). The zig− zag nature of 1−D chain propagated along crystallographic axis *a* connected through C−H···π interaction (top right). The zoom view of each of the 1−D chain stabilized by inter molecular C−H···π interaction between the–CH_3 of –OMe group and the adjacent phenyl ring along crystallographic axis *c* (bottom).

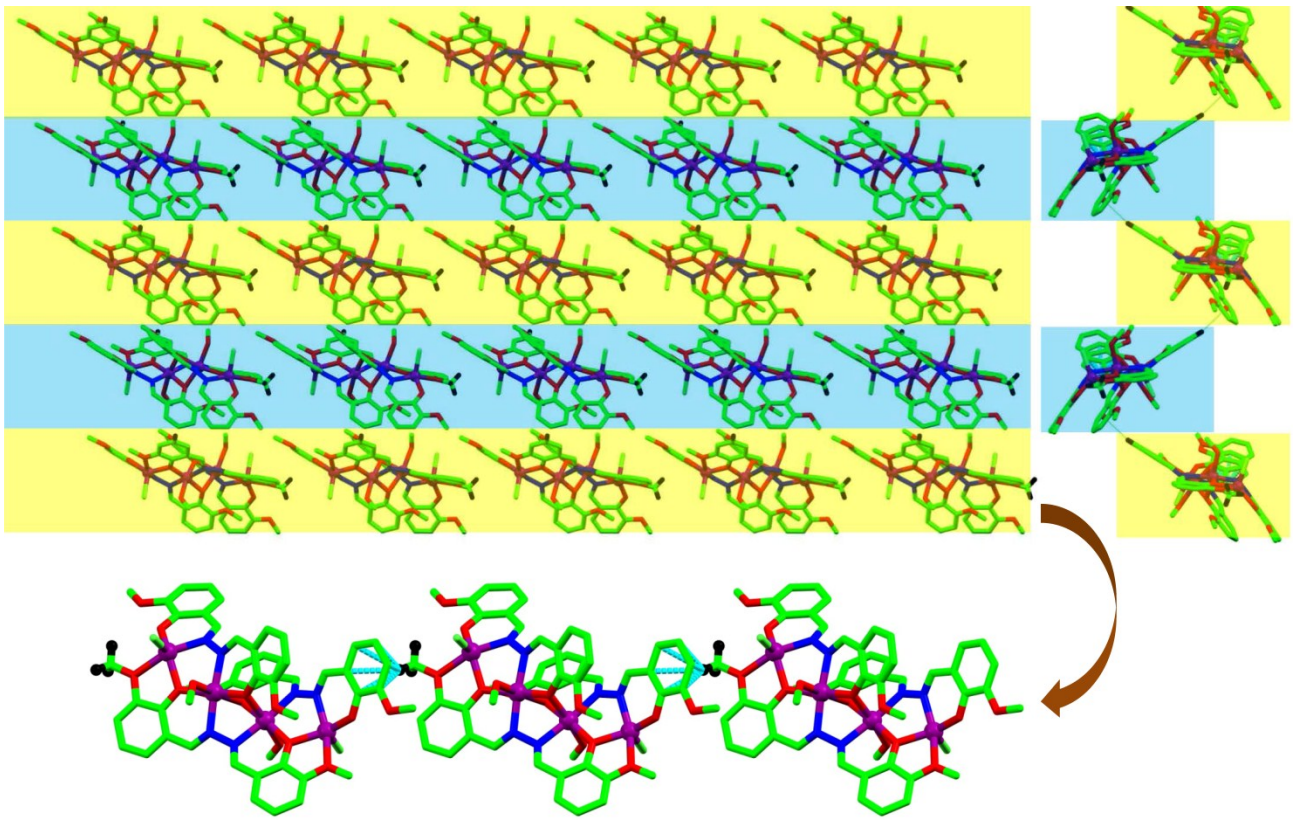


Figure S8: 2−D supramolecular architecture formed by complex **2** in *ac* plane (Top left). The zig− zag nature of 1−D chain propagated along crystallographic axis *a* connected through C−H···π interaction (top right). The zoom view of each of the 1−D chain stabilized by inter molecular C−H···π interaction between the $–CH_3$ of –OMe group and the adjacent phenyl ring along crystallographic axis *c* (bottom).

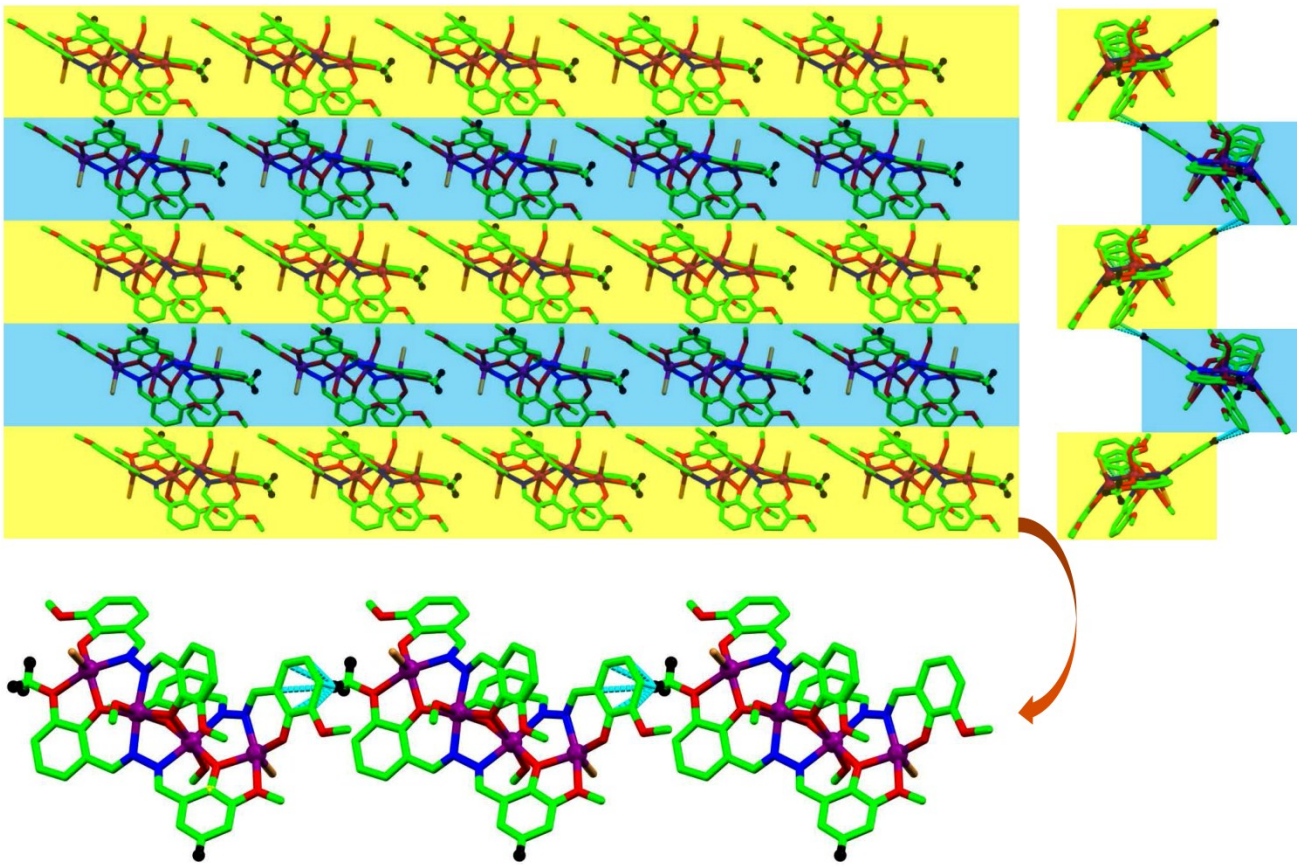


Figure S9: 2−D supramolecular architecture formed by complex **3** in *ac* plane (Top left). The zig− zag nature of 1−D chain propagated along crystallographic axis *a* connected through C−H···π interaction (top right). The zoom view of each of the 1−D chain stabilized by inter molecular C−H···π interaction between the $–CH_3$ of –OMe group and the adjacent phenyl ring along crystallographic axis *c* (bottom).

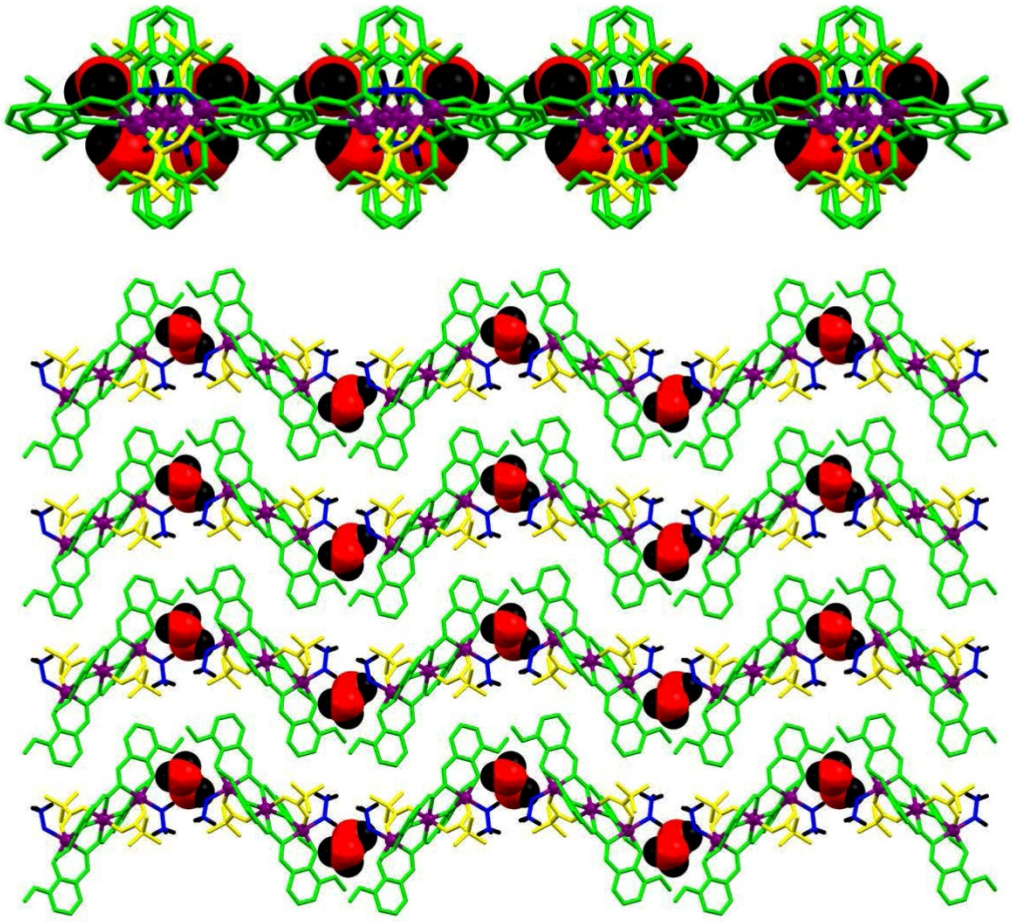


Figure S10: 2D supramolecular assembly formed in complex **5** by the combination of intermolecular H−bond with host water (shown in spacefill model) molecule and C−H···π interaction viewed along *c* (top) and *b* (bottom).

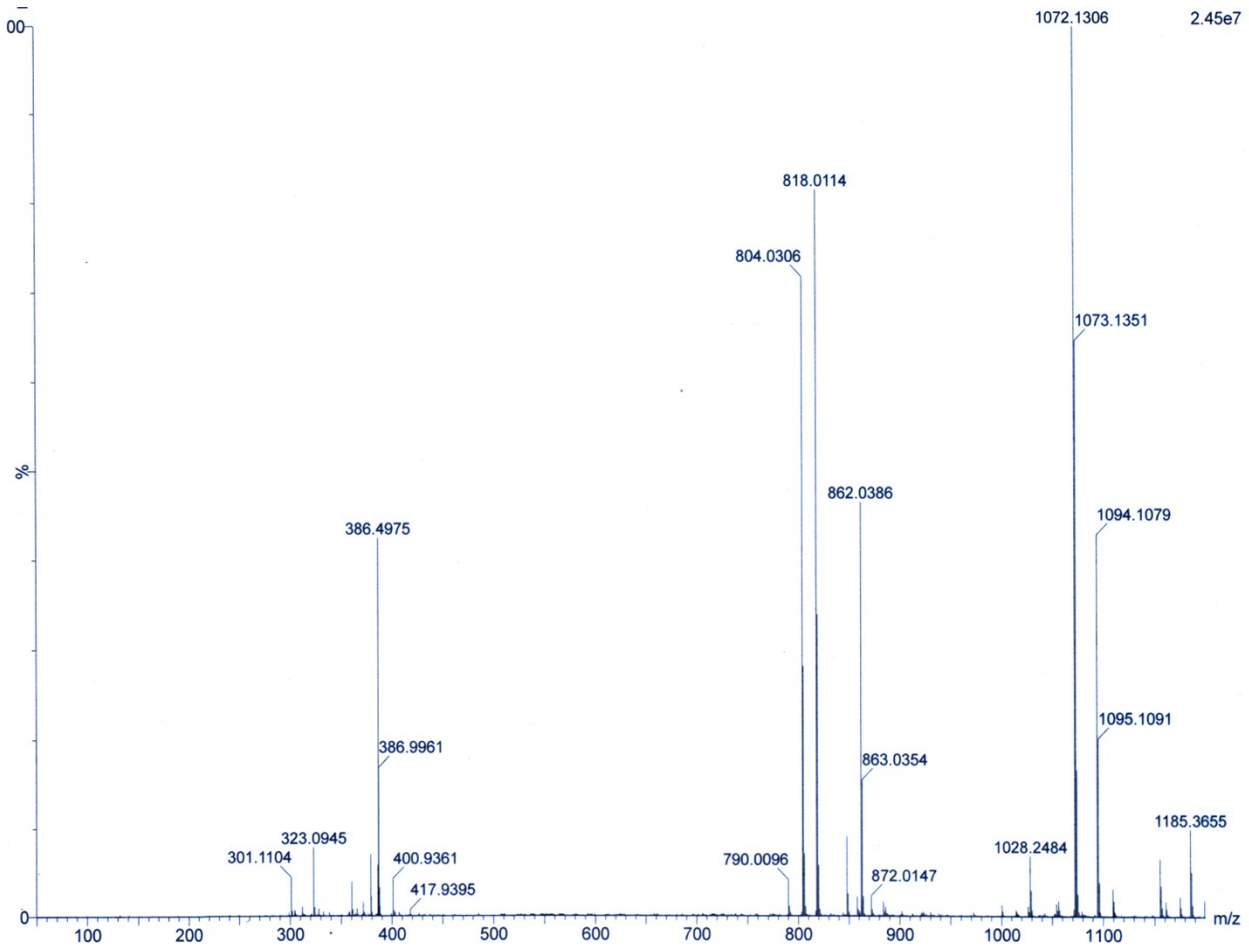


Figure S11: ESI−MS spectrum of complex **1** in methanol.

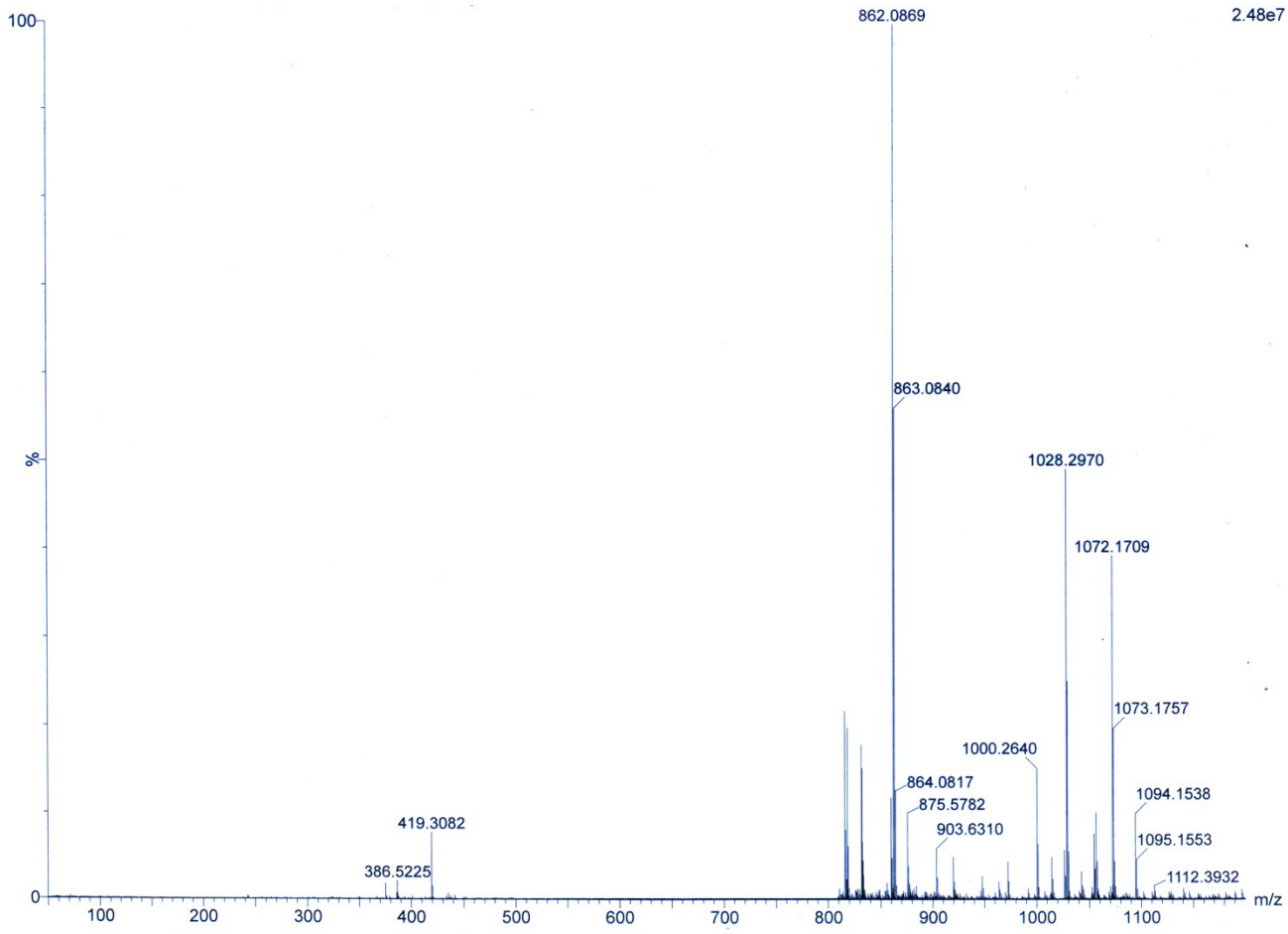


Figure S12: ESI−MS spectrum of complex **2** in methanol.

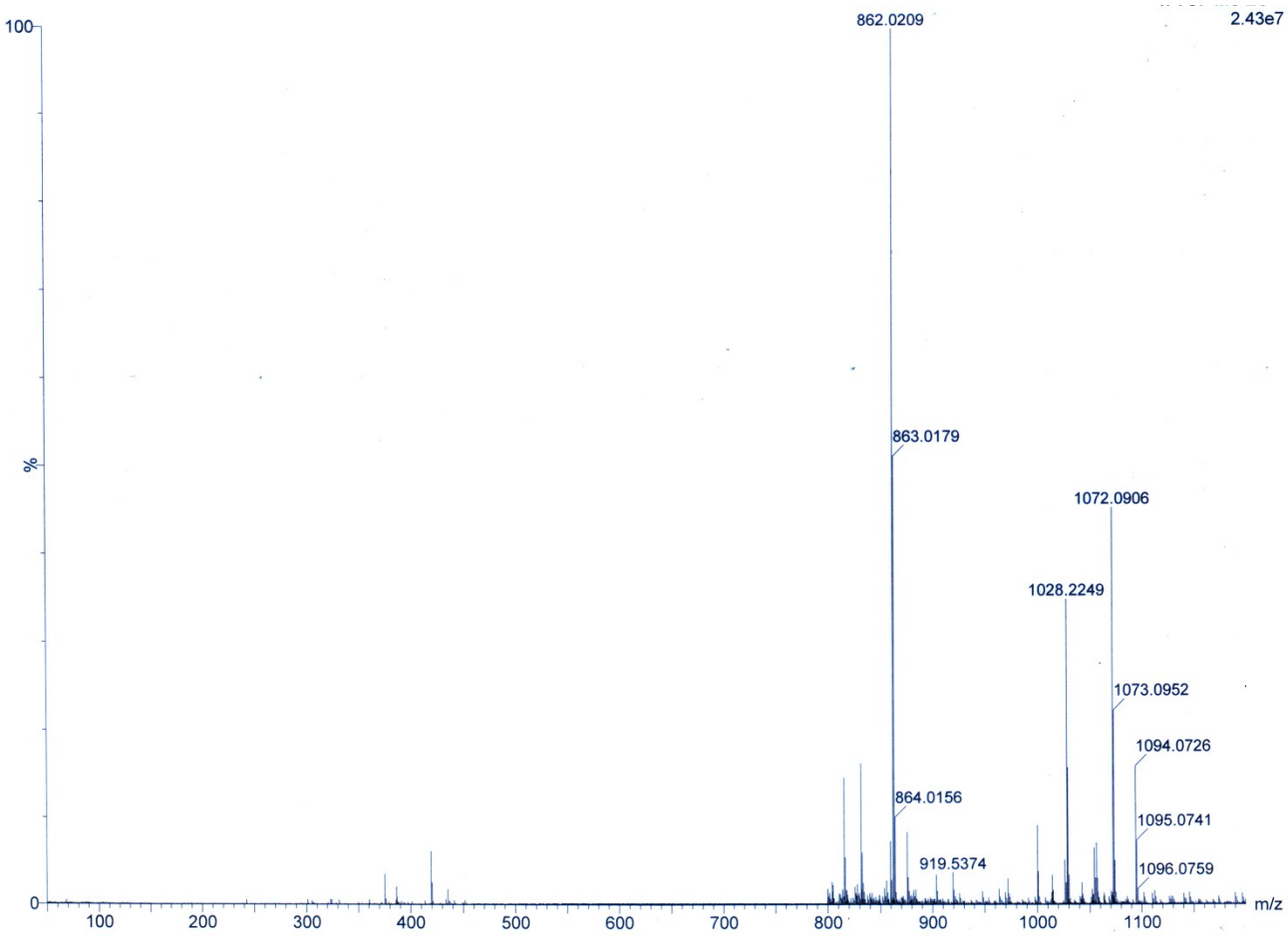


Figure S13: ESI−MS spectrum of complex **3** in methanol.

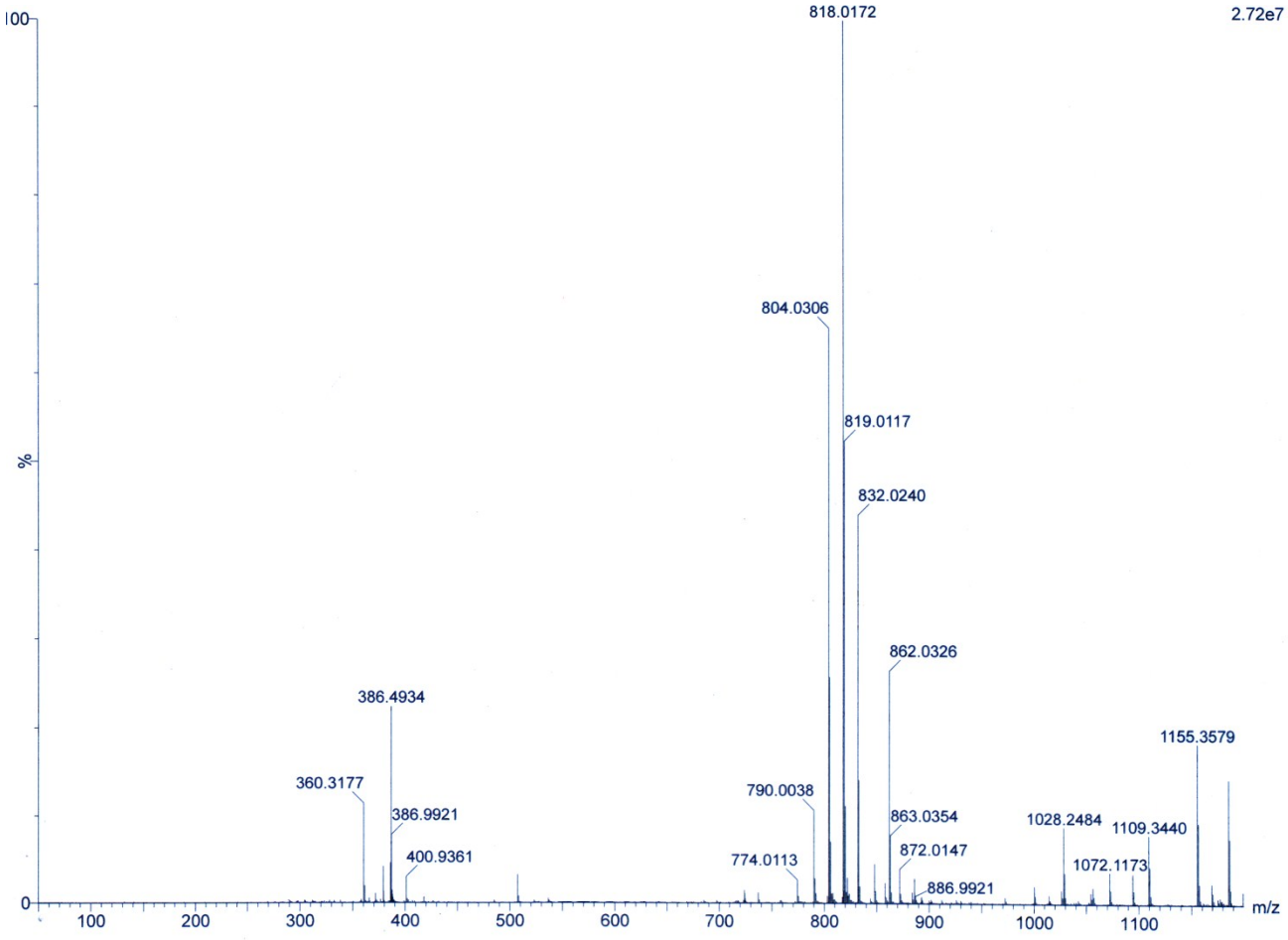


Figure S14: ESI−MS spectrum of complex **4** in methanol.

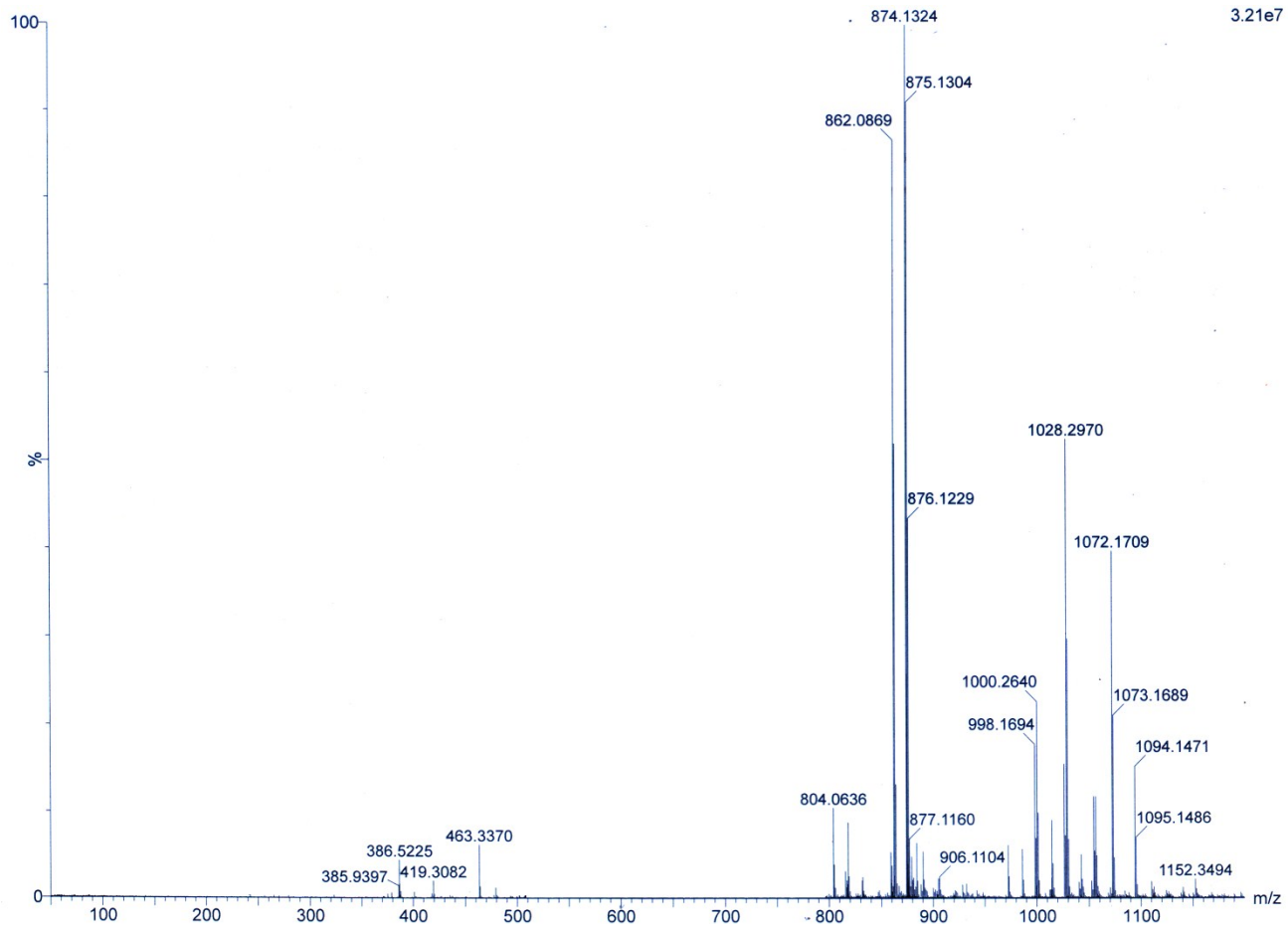


Figure S15: ESI−MS spectrum of complex **5** in methanol.

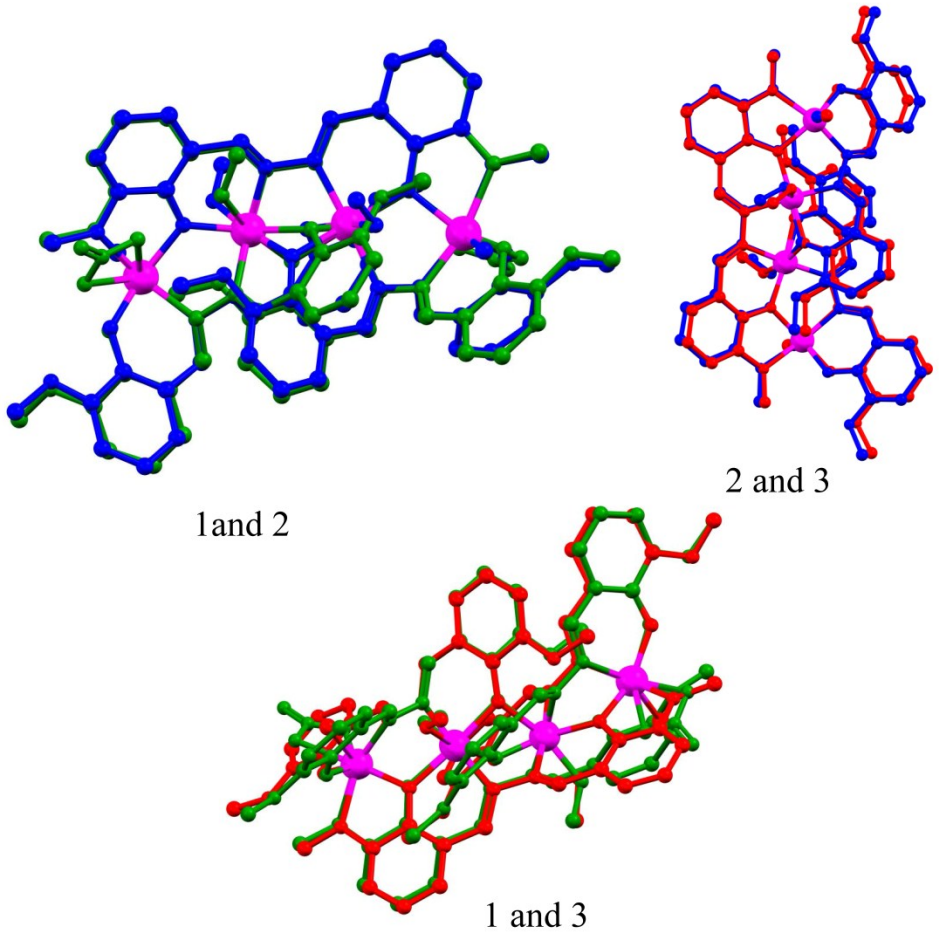


Figure S16: Structure overlay of complex **1**(green), **2**(blue) and **3**(red) in pair generated from mercury 3.8 CSD licensed version. RMSD value: 0.0347(**1** and **2**), 0.0234(**2** and **3**), 0.0581(**1** and **3**).

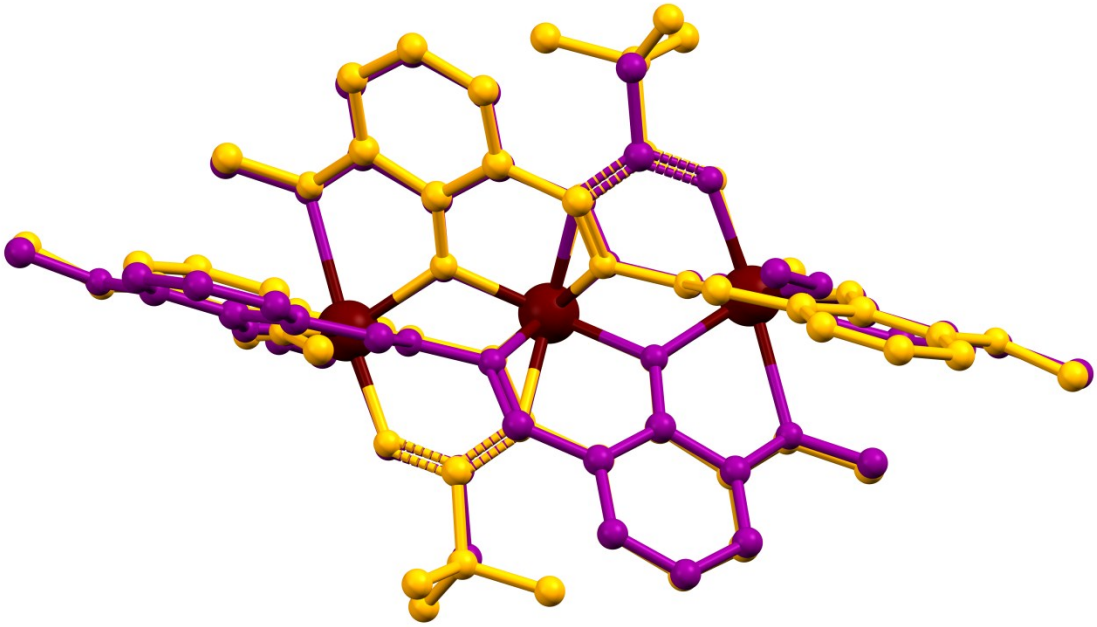


Figure S17: Structure overlay of complex **4**(violet) and **5**(yellow) generated from mercury 3.8 CSD licensed version. RMSD value: 0.0426.

Table S1: Crystal parameters for complex **1−5**

	1	**2**	**3**	**4**	**5**
CCDC No	1826188	1826189	1826190	1826192	1826193
Chem. formula	$C_{50}H_{50}Co_4N_8O_{20}$	$C_{50}H_{50}Cl_2Co_4N_6O_{14}$	$C_{50}H_{50}Br_2Co_4N_6O_{14}$	$C_{38}H_{42}Co_3N_4O_{14}$	$C_{44}H_{58}Co_3N_4O_{16}$
Formula weight	1318.70	1265.58	1354.48	955.55	1075.74
Crystcolor, habit	red/block	red/block	red/block	red/block	red/block
Temp (K)	298(2)	298(2)	296(2)	298(2)	298(2)
λ[a]/ Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P-1$	$Pca2_1$
Unit cell dimensions					
a (Å)	15.6970(8)	15.7486(6)	15.667(3)	10.499(6)	11.3899(5)
b(Å)	19.1711(10)	18.8273(7)	18.919(4)	10.701(6)	17.0364(7)
c(Å)	18.4094(10)	17.8550(7)	17.862(4)	10.8086(6)	24.9905(11)
α (deg)	90.00	90.00	90.00	63.723(2)	90.00
β (deg)	99.743(2)	99.5610(10)	99.176(4)	84.122(2)	90.00
γ (deg)	90.00	90.00	90.00	73.876(2)	90.00
Volume (Å^3), Z	5460.0(5)	5220.5(3)	5226.5(18)	1045.78(10)	4849.2(4)
Density (mg m^{-3})	1.604	1.610	1.721	1.517	1.474
Absol. coef (mm^{-1})	1.279	1.423	2.848	1.246	1.086
F(000)	2696	2584.0	2728	491	2236
Crystal size (mm)	0.22×0.25×0.28	0.30×0.26×0.22	0.26×0.22×0.18	0.22×0.18×0.15	0.22×0.18×0.14
θ range (deg)	2.84−28.3	2.2−28.4	1.3−25.5	3.4−28.3	2.3−27.1
Limiting indices	−20≤h≤20 −25≤k≤25 −24≤l≤24	−21≤h≤21 −25≤k≤25 −23≤l≤23	−18≤h≤18 −22≤k≤22 −21≤l≤21	−14≤h≤14 −14≤k≤14 −14≤l≤14	−14≤h≤14 −21≤k≤21 −31≤l≤31
Reflections collected	88121	81441	38277	10216	67756
Unique reflections [R_{int}]	13570(0.043)	13055(0.0380)	9752(0.1142)	3694(0.0333)	10587(0.047)
Completeness to θ	99.7(28.3)	99.7%(28.37)	98.2%(25.53)	95.8%(25.0)	99.7(27.12)
Data/restraints/p	13570/6/ 765	13017/2/701	9580/1/701	3538/0/276	10587/2/625

arameters					
GOOF on F^2	1.041	1.085	0.996	1.212	1.105
Final R indices [I > 2σ(I)]	0.0411[b], (0.0955[c])	0.0490[b], (0.0985)[c]	0.0477[b], (0.0947[c])	0.0486[b], (0.1153[c])	0.0461[b], (0.1250[c])
R indices (all data)	0.0664[b], (0.1720[c])	0.0706[b], (0.1139 [c])	0.0947[b], (0.1400 [c])	0.0611[b], (0.1153 [c])	0.0600[b], (0.1429[c])
Largest residual peaks (e $Å^{-3}$)	0.527	0.81	0.73	1.37	0.767
[a]Graphite monochromator, [b]$R_1 = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$. [c]$wR_2 = \{\Sigma[w(\|F_o\|^2 - \|F_c\|^2)^2]/\Sigma[w(\|F_o\|^2)^2]\}^{1/2}$					

Table S2: Selected Geometrical Parameters (Distances/Å and Angles/deg) for **1**

Co1−O1	2.154(2)	Co1−O2	2.038(2)	Co1−O6	1.940(2)
Co1−O15	2.230(3)	Co1−O16	2.286(5)	Co1−N3	2.046(2)
Co2−O2	2.025(2)	Co2−O7	2.040(2)	Co2−O10	2.144(2)
Co2−O13	2.160(2)	Co2−N1	2.068(2)	Co2−N4	2.058(2)
Co3−O3	2.027(2)	Co3−O7	2.108(2)	Co3−O10	2.039(2)
Co3−O14	2.166(3)	Co3−N2	2.067(2)	Co3−N5	2.071(3)
Co4−O3	2.016(2)	Co4−O4	2.181(2)	Co4−O11	1.913(2)
Co4−O18	2.137(9)	Co4−N6	2.034(2)	Co4−O19	2.540(1)

Co1−O2−Co2	113.50(8)	Co2−O7−Co3	92.46(7)
Co3−O10−Co2	91.43(7)	Co4−O3−Co3	112.69(9)
C8−N1−N2−C9	55.3(3)		

C24−N3−N4−C25	58.4(3)
C40−N5−N6−C41	58.6(3)

Table S3: Selected Geometrical Parameters (Distances/Å and Angles/deg) for **2**

Co1−Cl1	2.01(4)	Co2−O13	2.173(4)	Co3−N5	2.059(2)
Co1−O1	2.200(3)	Co2−N1	2.077(2)	Co4−Cl2	2.38(4)
Co1−O2	2.011(2)	Co2−N4	2.075(2)	Co4−O3	2.031(2)
Co1−O6	1.906(3)	Co3−O3	2.018(2)	Co4−O4	2.173(3)
Co1−N3	2.029(3)	Co3−O7	2.145(2)	Co4−O11	1.941(2)
Co2−O2	2.021(3)	Co3−O10	2.025(2)	Co4−N6	2.032(2)
Co2−O7	2.017(2)	Co3−O14	2.172(3)		
Co2−O10	2.096(2)	Co3−N2	2.069(2)		

O2−Co1−O6	136.01(12)	O1−Co1−N3	156.96(11)
Co1−O2−Co2	111.68(11)	Co2−O7−Co3	91.53(10)
Co2−O10−Co3	92.78(8)	Co3−O3−Co4	112.13(9)
O2−Co2−O7	170.19(9)	O3−Co3−O10	170.30(9)
O3−Co4−O11	138.14(9)		

C8−N1−N2−C9	56.2(4)
C24−N3−N4−C25	58.4(4)
C40−N5−N6−C4	58.3(4)

Table S4: Selected Geometrical Parameters (Distances/Å and Angles/deg) for **3**

Co1− Br1	2.471(4)	Co2−O2	2.011(3)	Co3−O3	2.008(3)
Co1−O1	2.192(4)	Co2−O7	2.018(3)	Co3−O7	2.125(3)
Co1−O2	1.997(3)	Co2−O10	2.082(3)	Co3−O10	2.023(3)
Co1−O6	1.894(3)	Co2−O13	2.154(6)	Co3−O14	2.152(4)
Co1−N3	2.013(4)	Co2−N1	2.067(4)	Co3−N2	2.059(4)
		Co2−N4	2.055(4)	Co3−N5	2.046(4)
Co4−O3	2.023(3)				
Co4−O4	2.151(3)				
Co4−O11	1.920(3)				
Co4−N6	2.026(3)				
Co4−Br2	2.37(3)				

O2 −Co1−O6	136.27(15)	Co1−O2 −Co2	111.84(15)
Co2−O7 −Co3	91.54(13)	Co2−O10−Co3	92.67(12)
Co3−O3 −Co4	112.49(14)	O2 −Co2−O7	169.86(13)
O3 −Co3−O10	170.13(13)	O3 −Co4−O11	139.60(15)

C8−N1−N2−C9	56.6(5)
C24−N3−N4−C25	58.8(6)
C40−N5−N6−C4	59.3(5)

Table S5: Selected Geometrical Parameters (Distances/Å and Angles/deg) for **4**

Co1−O5	2.076(3)	Co1−O7	2.153(3)
Co1−N1	2.116(3)	Co1−O3$^{\#}$	2.030(3)
Co2−O3	2.015(3)	Co2−O6	2.119(3)
Co2−N2	2.096(3)	Co2−O3$^{\#}$	2.015(3)
Co2−O6$^{\#}$	2.119(3)	Co2−N2$^{\#}$	2.096(3)

Co1$^{\#}$−O3−Co2	111.60(15)
C8−N1−N2−C9	50.4(6)

Table S6: Selected Geometrical Parameters (Distances/Å and Angles/deg) for **5**.

Co1−O2	1.974(6)	Co1−O9	2.005(5)	Co1−O7	2.011(5)
Co1−N1	2.130(5)	Co1−O13	2.134(8)	Co1−O13	2.134(8)
Co2−O7	2.005(5)	Co2−O3	2.015(5)	Co2−N4	2.105(6)
Co2−N2	2.106(6)	Co2−O12	2.150(5)	Co2−O10	2.130(4)
Co3−N3	2.126(5)	Co3−O6	1.957(5)	Co3−O3	2.006(5)
Co3−O11	2.031(5)	Co3−O14	2.117(7)		

O2−Co1−O7	149. 5(2)	O3−Co3−O6	149.1(2)
Co2−O7−Co1	110.4(2)	Co2−O3−Co3	110.8(2)
O10−Co2−O12	178.7(2)	O3−Co2−O7	178.9(2)

C8−N1−N2−C9	51.0(8)
C24−N3−N4−C25	52.6(8)

Table S7: Continuous Shape Measures (CShMs) of Co(II) ions in $[Co_4(hydva)_3(NO_3)_2(MeOH)_2]$ (**1**) relative to the ideal 6−vertex[1,2] polyhedra. The lowest CShMs value, and thus the closest geometry is highlighted in green.

	1, Co1	**1**, Co2	**1**, Co3	**1**, Co4	**Symmetry**	**Ideal shape**
HP−6	36.712	29.048	29.124	35.124	D_{6h}	Hexagon
PPY−6	16.540	23.746	24.113	16.099	C_{5v}	Pentagonal pyramid
OC−6	8.649	0.981	0.913	9.940	O_h	Octahedron
TPR−6	4.867	12.679	12.450	4.603	D_{3h}	Trigonal prism
JPPY−6	20.586	27.228	27.736	20.576	C_{5v}	Johnson pentagonal pyramid J2

Table S8: Continuous Shape Measures (CShMs) of Co(II) ions in $[Co_4(hydva)_3(Cl)_2(MeOH)_2]$ (**2**) relative to the ideal 5−vertex[3] (Co1, Co4) and 6−vertex[2] (Co2, Co3) polyhedra.[1] The lowest CShMsvalue, and thus the closest geometry is highlighted in green.

	2, Co1	**2**, Co4	**Symmetry**	**Ideal shape**
PP−5	30.866	32.272	D_{5h}	Pentagon
vOC−5	4.233	3.831	C_{4v}	Vacant octahedron
TBPY−5	3.114	2.960	D_{3h}	Trigonal bipyramid
SPY−5	1.415	1.164	C_{4v}	Square pyramid
JTBPY−5	5.760	5.860	D_{3h}	Johnson trigonal bipyramid J12

	2, Co2	**2**, Co3	**Symmetry**	**Ideal shape**
HP−6	28.554	28.974	D_{6h}	Hexagon
PPY−6	24.436	23.460	C_{5v}	Pentagonal pyramid
OC−6	0.869	1.073	O_h	Octahedron
TPR−6	12.988	12.228	D_{3h}	Trigonal prism
JPPY−6	27.946	26.926	C_{5v}	Johnson pentagonal pyramid J2

Table S9: Continuous Shape Measures (CShMs) of Co(II) ions in $[Co_4(hydva)_3(Br)_2(MeOH)_2]$ (**3**) relative to the ideal 5−vertex[3] (Co1, Co4) and 6−vertex[2] (Co2, Co3) polyhedra.[1] The lowest CShMsvalue, and thus the closest geometry is highlighted in green.

	3, Co1	**3**, Co4	**Symmetry**	**Ideal shape**
PP−5	31.727	33.279	D_{5h}	Pentagon
vOC−5	4.757	4.254	C_{4v}	Vacant octahedron
TBPY−5	3.254	3.214	D_{3h}	Trigonal bipyramid
SPY−5	1.630	1.340	C_{4v}	Square pyramid
JTBPY−5	6.259	6.446	D_{3h}	Johnson trigonal bipyramid J12

	3, Co2	**3**, Co3	**Symmetry**	**Ideal shape**
HP−6	28.832	29.283	D_{6h}	Hexagon
PPY−6	24.509	23.720	C_{5v}	Pentagonal pyramid
OC−6	0.856	1.008	O_h	Octahedron
TPR−6	13.231	12.412	D_{3h}	Trigonal prism
JPPY−6	28.089	27.219	C_{5v}	Johnson pentagonal pyramid J2

Table S10: Continuous Shape Measures (CShMs) of Co(II) ions in $[Co_3(hydva)_2(OAc)_2(MeOH)_2]$ (**4**) relative to the ideal 6−vertex polyhedra.[1, 2] The lowest CShMsvalue, and thus the closest geometry is highlighted in green.

	1, Co1	**1**, Co2	**1**, Co1'	**Symmetry**	**Ideal shape**
HP−6	32.406	29.768	32.404	D_{6h}	Hexagon
PPY−6	17.780	28.429	17.780	C_{5v}	Pentagonal pyramid
OC−6	4.177	0.249	4.176	O_h	Octahedron
TPR−6	6.534	16.088	6.534	D_{3h}	Trigonal prism
JPPY−6	21.13	31.088	21.13	C_{5v}	Johnson pentagonal pyramid J2

Table S11: Continuous Shape Measures (CShMs) of Co(II) ions in $[Co_3(hydva)_2(Piv)_2(MeOH)_2]$ (**5**) relative to the ideal 6−vertex[2] (Co1,Co2,Co3) polyhedra.[1] The lowest CShMs value, and thus the closest geometry is highlighted in orange.

	6, Co1	**6**, Co2	**6**, Co3	**Symmetry**	**Ideal shape**
HP−6	31.315	31.545	30.978	D_{6h}	Hexagon
PPY−6	18.798	16.089	18.583	C_{5v}	Pentagonal pyramid
OC−6	3.272	0.249	3.471	O_h	Octahedron
TPR−6	8.421	28.429	7.97	D_{3h}	Trigonal prism
JPPY−6	22.085	29.768	21.722	C_{5v}	Johnson pentagonal pyramid J2

Complex	Atom	$R_0(Co^{II})$	$R_0(Co^{III})$	Assignment
1	Co1	2.001	1.775	Co^{II}
	Co2	2.137	1.911	Co^{II}
	Co3	2.145	1.918	Co^{II}
	Co4	1.956	1.872	Co^{II}
2	Co1	2.129	1.97	Co^{II}
	Co2	2.166	1.936	Co^{II}
	Co3	2.148	1.936	Co^{II}
	Co4	2.073	1.921	Co^{II}
3	Co1	2.031	1.88	Co^{II}
	Co2	2.239	2.008	Co^{II}
	Co3	2.223	1.988	Co^{II}
	Co4	1.892	2.091	Co^{II}
4	Co1/1#	1.981	1.755	Co^{II}
	Co2	2.161	1.93	Co^{II}
5	Co1	2.045	1.811	Co^{II}
	Co2	2.123	1.896	Co^{II}
	Co3	1.98	1.858	Co^{II}

Table S12: BVS value calculated for cobalt centre between oxidation state +2 and +3*

* Theoretical value was taken from 'http:www.iucr.org__dataassetsfile0007126574bvparm2016.cif' retrieved on 13.7.2017.

Table S13: BVS value calculated for oxygen atom of the coordinated methanol molecule to Co(II) centre to determine the protonation level

Complex	Atom	BVS value[a]	Assignment[b]
1	O13	1.419	Singly protonated
	O14	1.492	
2	O13	1.933	Singly protonated
	O14	1.298	
3	O13	1.804	Singly protonated
	O14	1.417	
4	O7	1.196	Singly protonated
5	O13	1.308	Singly protonated
	O14	1.393	

[a]Singly protonated concerened atom refers to neutral methanol molecule

[b]BVS value of ~1.8−2.0, 1.0−1.3 and 0.2−0.4 calculated for oxygen typically corresponds to non−, singly−, doubly− protonated oxygen. The values may vary due to the extensive H−bonding and uncertainties in bond distancedarises from disorder.

PLATON/SQUEEZE output results of complex 4

```
# SQUEEZE RESULTS (Version = 211017)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1  0.000  0.500  0.000        85        6 ' '
_platon_squeeze_void_probe_radius              1.20
_platon_squeeze_details                        ?
TITL 4.res in P-1
CELL   10.4995   10.7010   10.8086     63.72     84.12     73.88
SPGR P-1
# Solvent Accessible Volume =        85
# Electrons Found in S.A.V. =        5
# Note: Atoms in Void are Labelled as Cxxx and Qxxx for all Others
Q101 0.500 0.500 0.500 !       1.94 eA-3
```

Q102 0.752 0.654 0.434 ! 1.89 eA-3
Q103 1.013 0.795 0.376 ! 1.48 eA-3
C104 0.246 0.467 0.029 ! 0.69 eA-3
C105 0.153 0.411 0.030 ! 0.52 eA-3

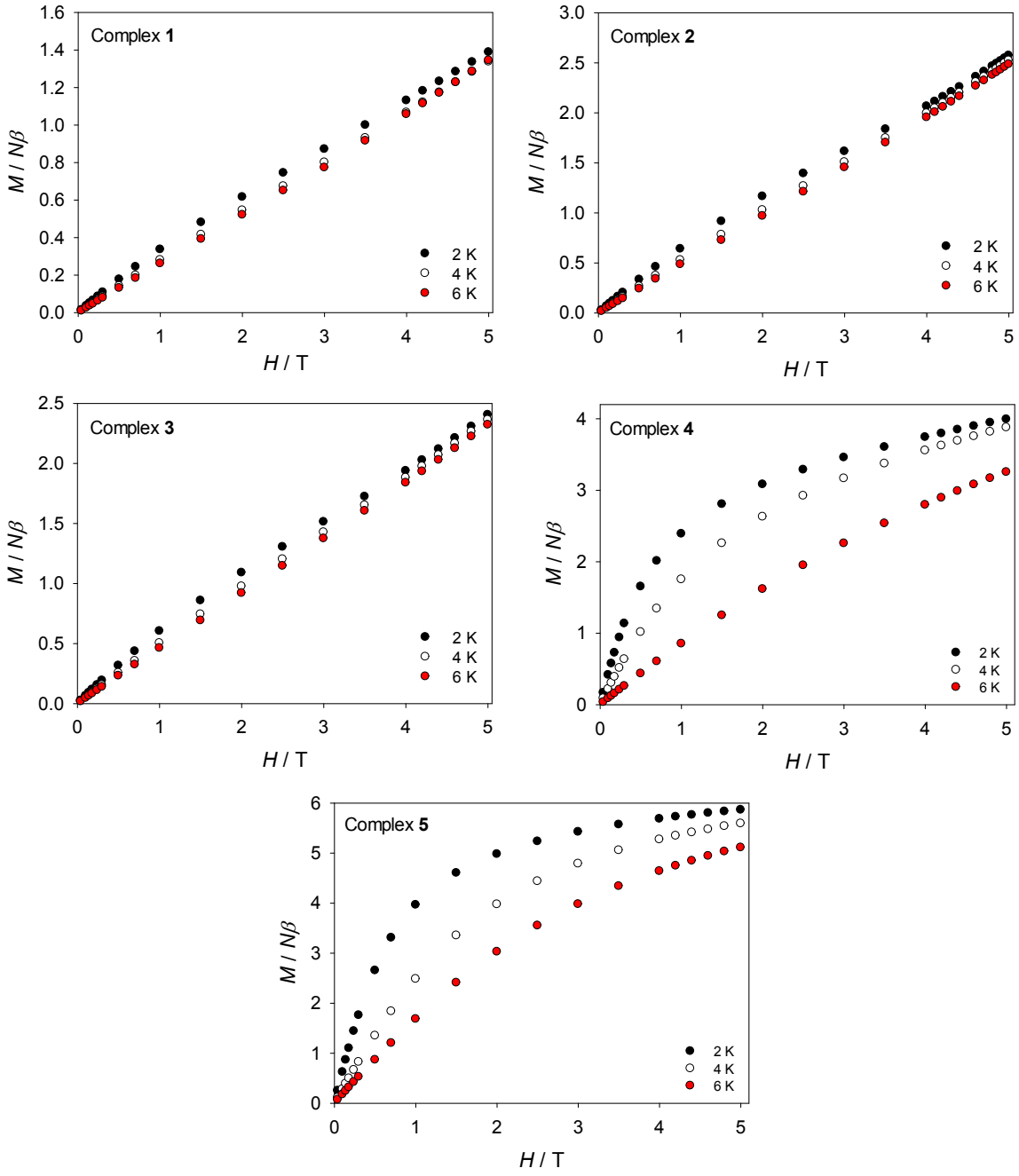


Figure S18: *M*/*Nβvs*. *H* at 2, 4, 6 K for **1**–**5**.

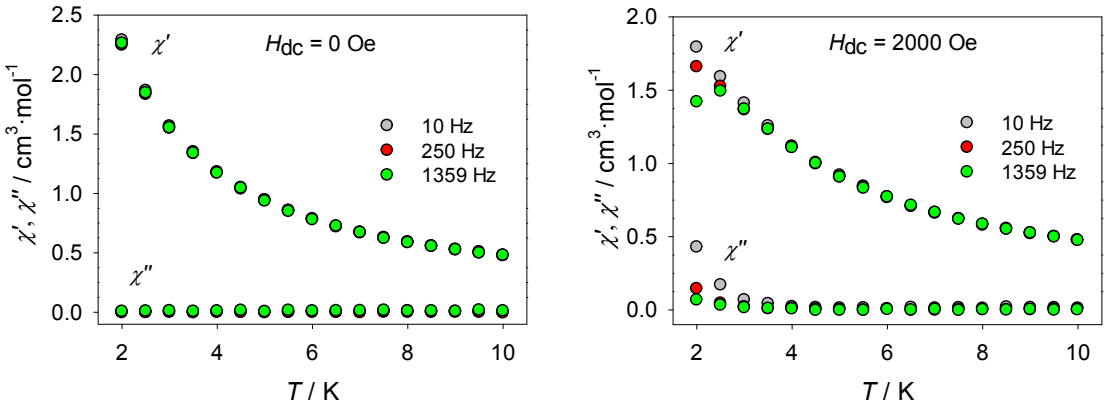


Figure S19: Ac magnetic susceptibility of **4** as a function of the temperature (T = 2 − 10 K) at zero field (left), and in an external field of H_{dc} = 2000 Oe (right) at selected frequencies (υ = 10, 250, 1358 Hz).

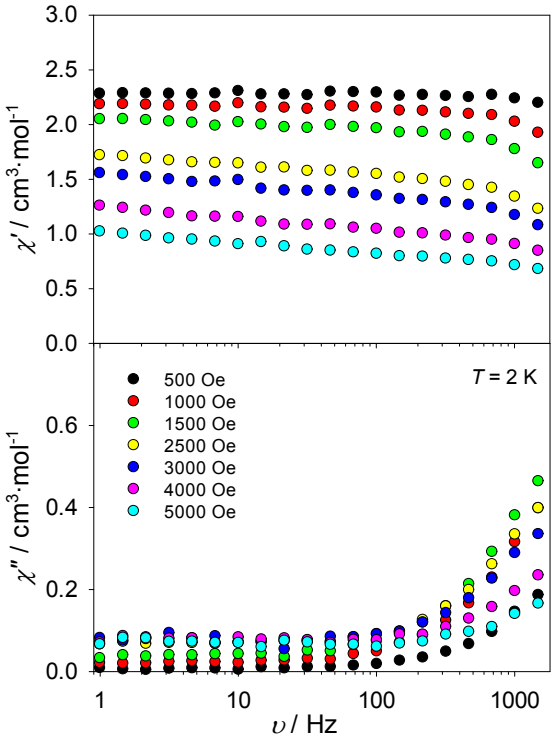


Figure S20: Ac magnetic susceptibility of **4** at T = 2 K in applied fields over 500−5000 Oe

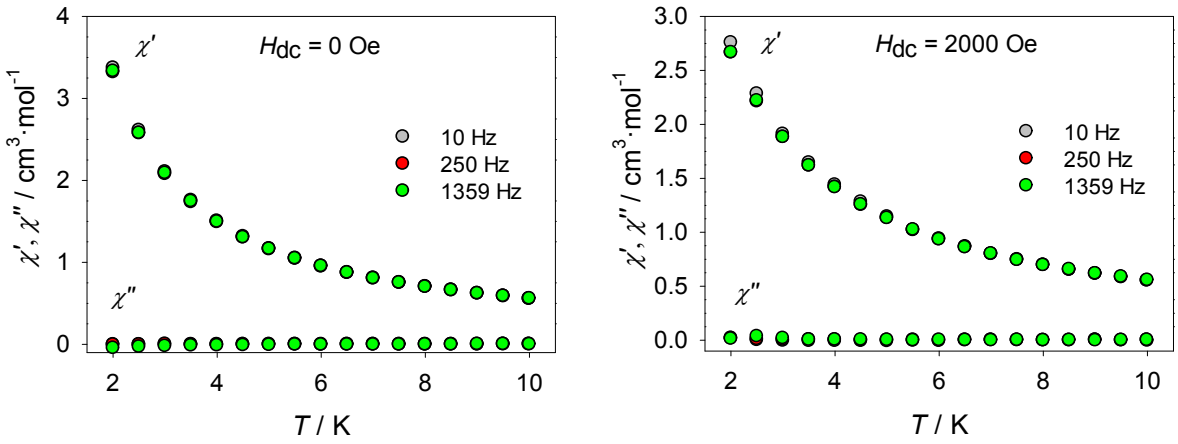


Figure S21: Ac magnetic susceptibility of **5** as a function of the temperature (T = 2 − 10 K) at zero field (left), and in an external field of H_{dc} = 2000 Oe (right) at selected frequencies (υ = 10, 250, 1358 Hz).

References

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3. S. Alvarez, M. Llunell. *J. Chem. Soc.*, *Dalton Trans.*, 2000, 3288.