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Electronic Supplementary Information

Arylhydrazones of Barbituric Acid: synthesis, coordination ability and catalytic activity of their Co^{II}, $Co^{II/III}$ and Cu^{II} complexes toward peroxidative oxidation of alkanes

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1. ESI-MS analysis

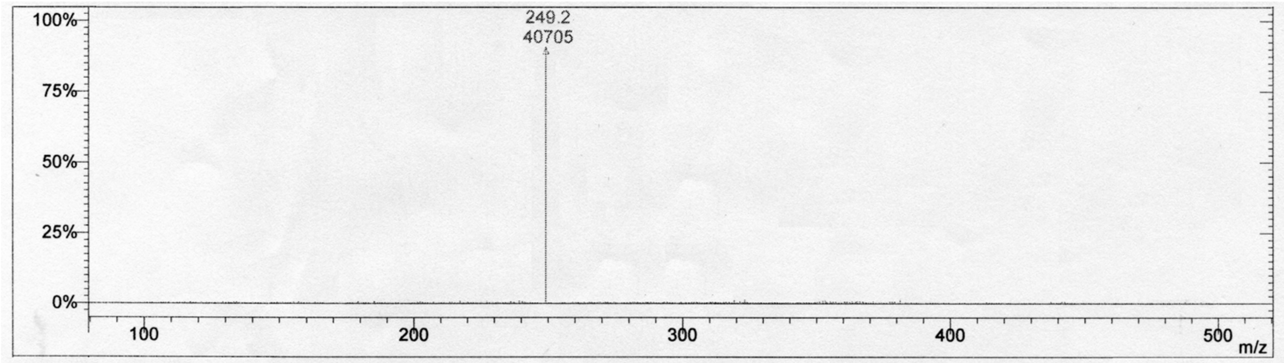


Figure 1S. ESI-MS spectra of H_4L^1.

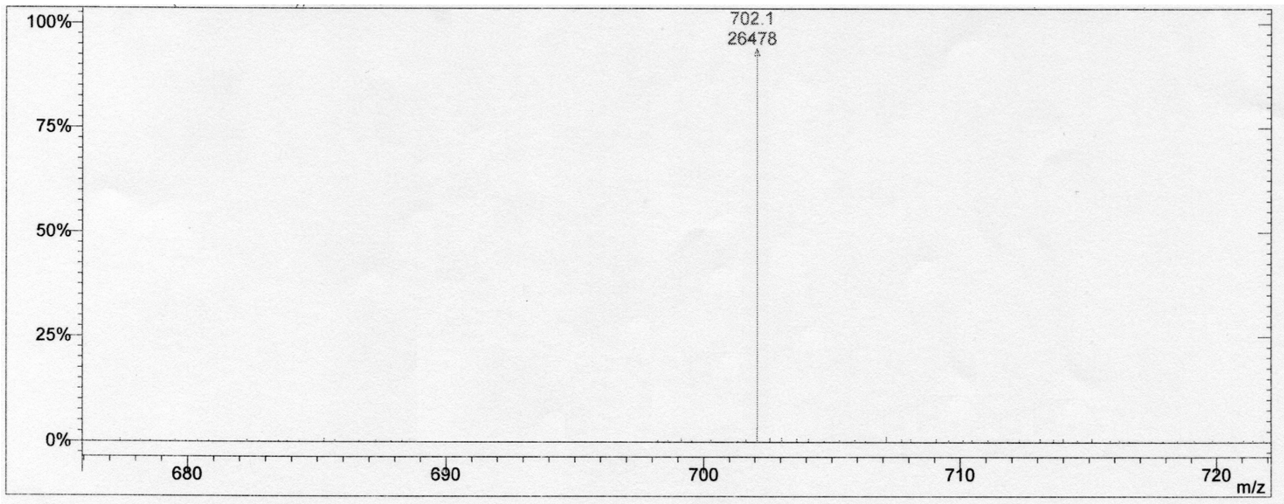


Figure 2S. ESI-MS spectra of **1**.

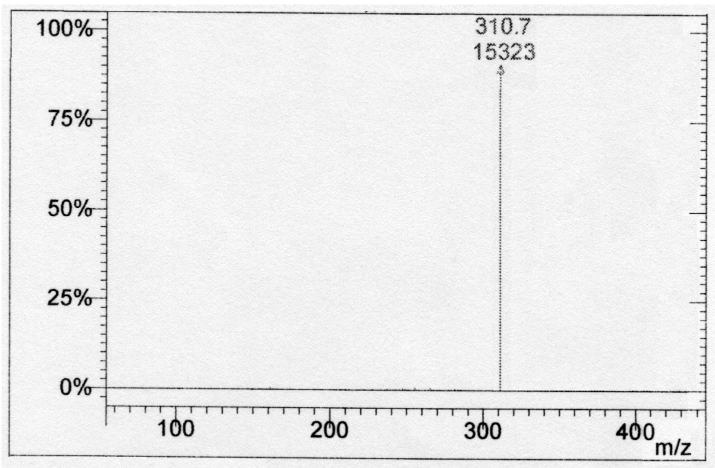


Figure 3S. ESI-MS spectra of **2**.

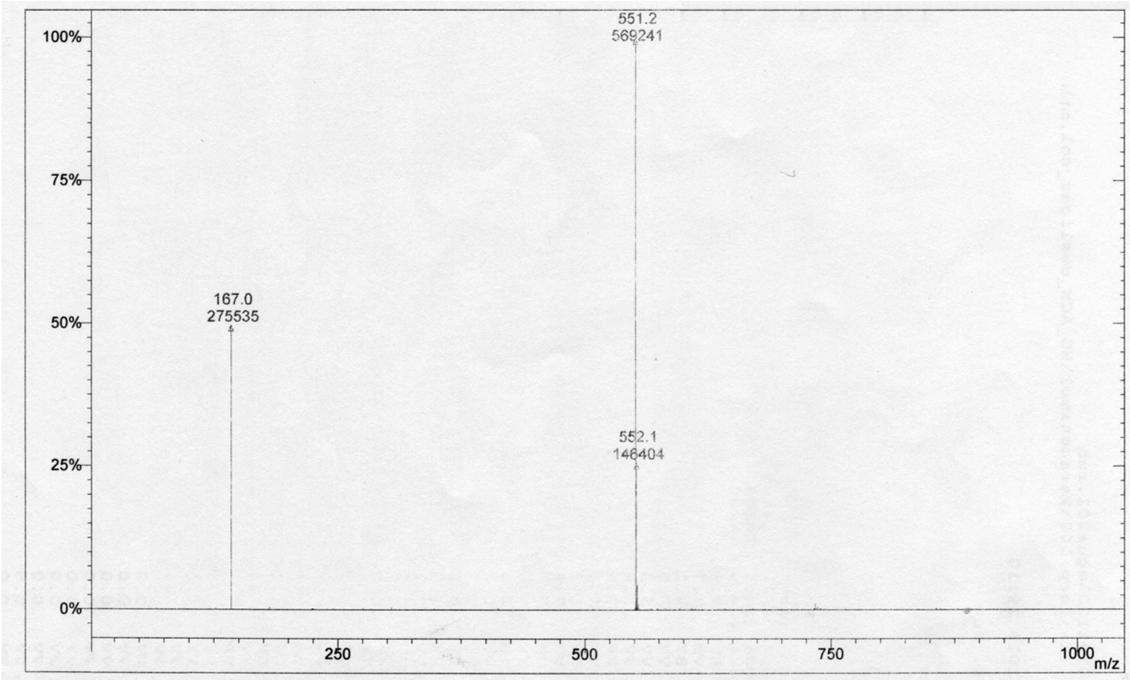


Figure 4S. ESI-MS spectra of **3**.

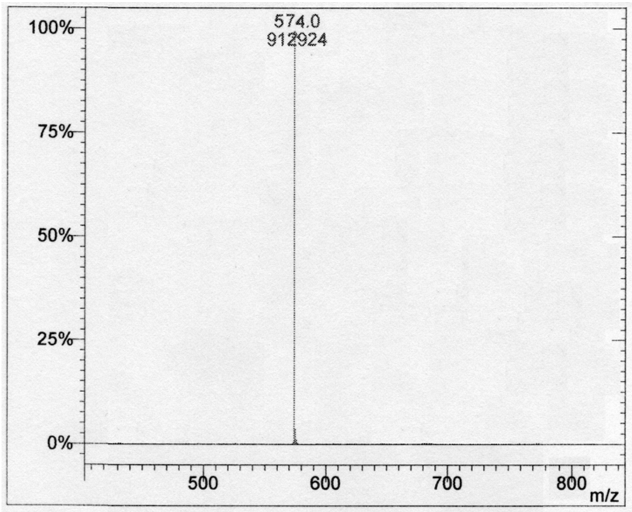


Figure 5S. ESI-MS spectra of **4**.

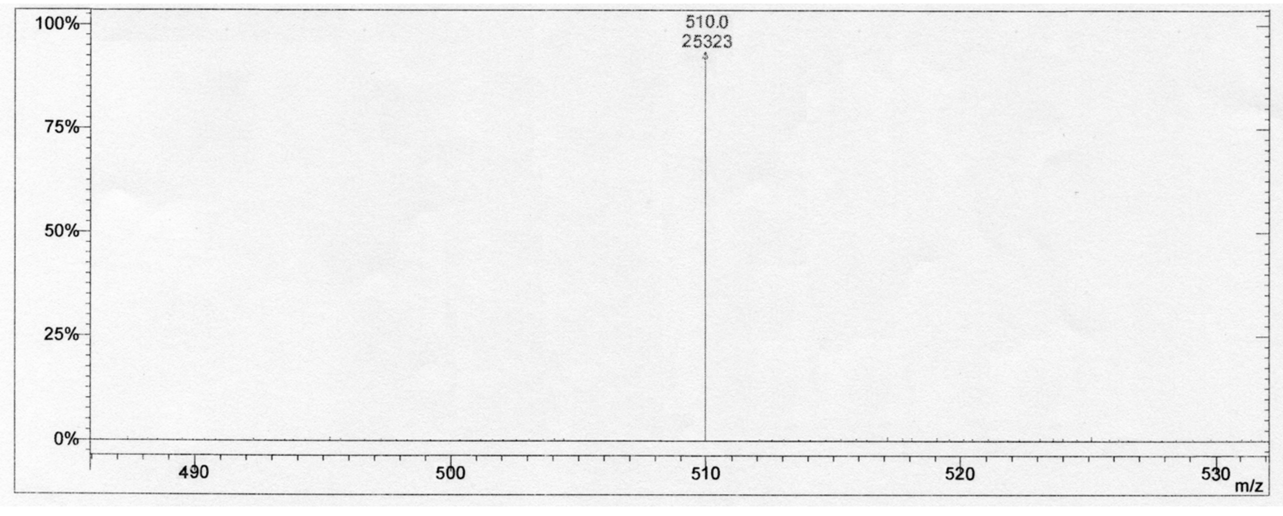


Figure 6S. ESI-MS spectra of **5**.

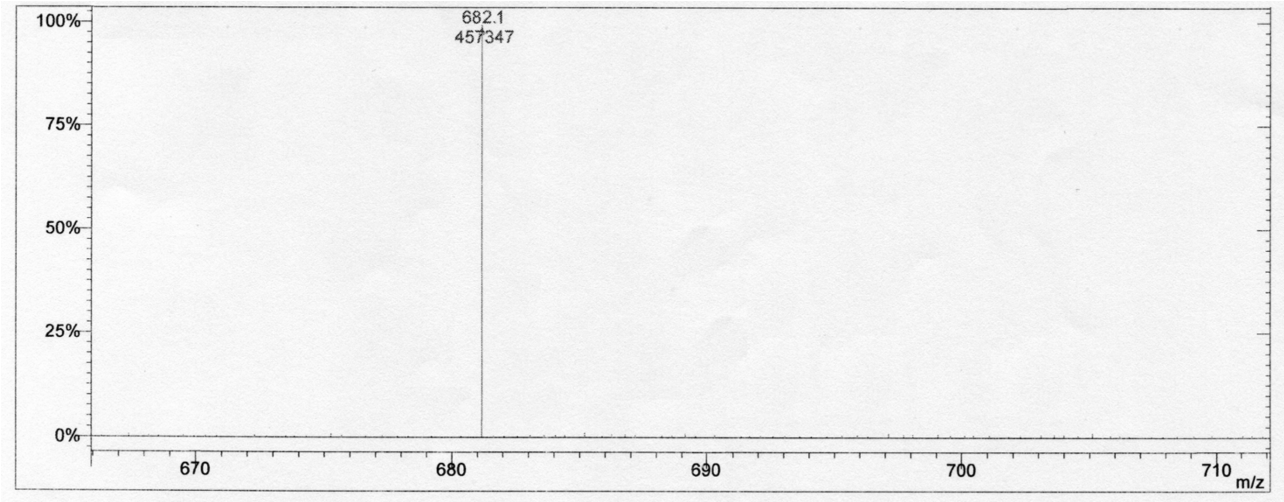


Figure 7S. ESI-MS spectra of **6**.

3. UV-vis spectroscopy

Table 1S. Electronic absorption spectral data of $\mathbf{H_4L^1}$ and **1**−**6**.

Compound	λ_{max} (nm)	ε (L mol^{-1}cm^{-1})
$\mathbf{H_4L^1}$	412	27200
	268	6310
1	389	35000
	234	17200
2	482	16100
	367	9940
	270	11200
3	426	42400
	268	51800
4	395	13600
	262	12200
5	389	14500
	269	4840
6	385	42300
	261	13800

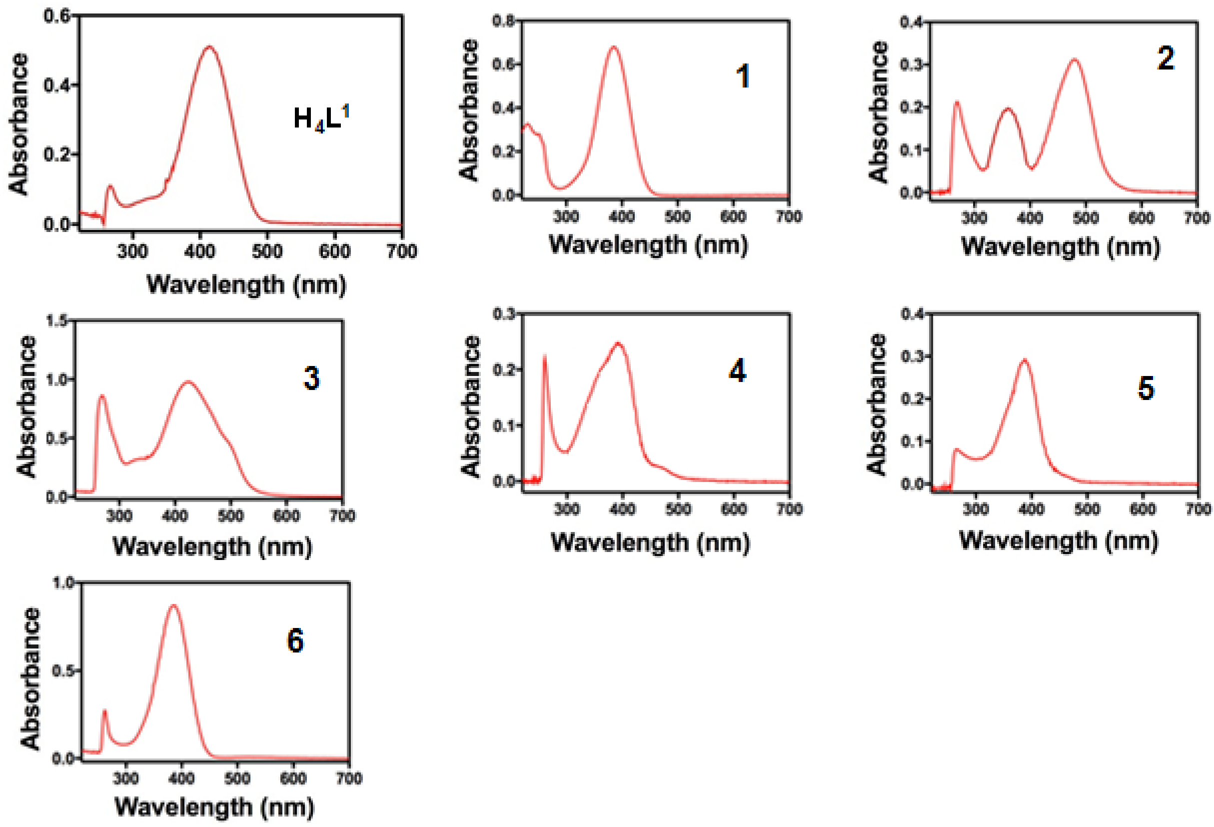


Figure 8S. Absorption UV-vis spectra of **H_4L^1** and **1-6** in water.

3. X-ray analysis

Table 2S. Crystal data, experimental parameters and selected details of the refinement calculations of compounds **1−4**.

Compound	1	2	3	4
Empirical formula	$C_{20}H_{26}N_8Na_2O_{18}S_2$	$C_{13}H_{18}CuN_6O_8$	$C_{40}H_{52}Co_3N_{16}O_{30}$	$C_{19}H_{18}CoN_{10}O_6S$
Formula weight	776.59	449.87	1413.76	573.42
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	*P* -1	*P* -1	*P* -1	*P* 21/c
a (Å)	8.2720(9)	7.7709(9)	10.8762(18)	18.9274(10)
b (Å)	10.0598(8)	9.7428(14)	12.0409(17)	8.6362(5)
c (Å)	10.6312(8)	12.4498(15)	12.2165(19)	16.9906(10)
α (deg)	63.001(4)	80.753(6)	79.360(8)	90
β (deg)	74.356(5)	73.757(6)	65.192(8)	105.753(2)
γ (deg)	76.484(5)	75.927(7)	68.570(8)	90
Z	1	2	1	4
V (Å^3)	752.64(12)	873.4(2)	1350.9(4)	2673.0(3)
T (K)	150	296	150	296
ρcalc (g/cm^3)	1.713	1.711	1.738	1.425
μ(Mo Kα) (mm^{-1})	0.303	1.309	1.022	0.773
Rfl collected/unique/obs		6216/1751/1442	13738/13738/8108	29502/4798/2949
$R1^a$ ($I \geq 2\sigma$)	0.0396	0.0448	0.1054	0.0852
wR2^b ($I \geq 2\sigma$)	0.1008	0.1140	0.3017	0.2114
GOF on F^2	0.955	1.002	1.015	1.059

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = [\sum[w(Fo^2 - Fc^2)2]/\sum[w(Fo^2)^2]]^{1/2}$.

Table 3S. Crystal data, experimental parameters and selected details of the refinement calculations of compounds **5** and **6**.

Compound	**5**	**6**
Empirical formula	$C_{16}H_{16}CuN_8O_7S$	$C_{20}H_{42}CoN_8O_{26}S_2$
Formula weight	527.97	933.66
Crystal system	Monoclinic	Monoclinic
Space group	*P* 21/n	*P* 21/c
a (Å)	8.6884(17)	15.8042(6)
b (Å)	11.586(2)	6.5960(2)
c (Å)	20.943(4)	18.5585(6)
α (deg)	90	90
β (deg)	97.642(7)	96.609(1)
γ (deg)	90	90
Z	4	2
V (Å^3)	2089.4(7)	1921.77(11)
T (K)	296	296
ρcalc (Mg/m^3)	1.678	1.614
μ(Mo Kα) (mm^{-1})	1.204	0.659
Rfl collected/unique/obs	20644/3840/3004	43754/3893/3326
$R1^a$ ($I \geq 2\sigma$)	0.0555	0.0491
wR2^b ($I \geq 2\sigma$)	0.1486	0.1237
GOF on F^2	1.067	1.072

[a] $RI = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = [\sum[w(Fo^2 - Fc^2)2]/\sum[w(Fo^2)^2]]^{1/2}$.

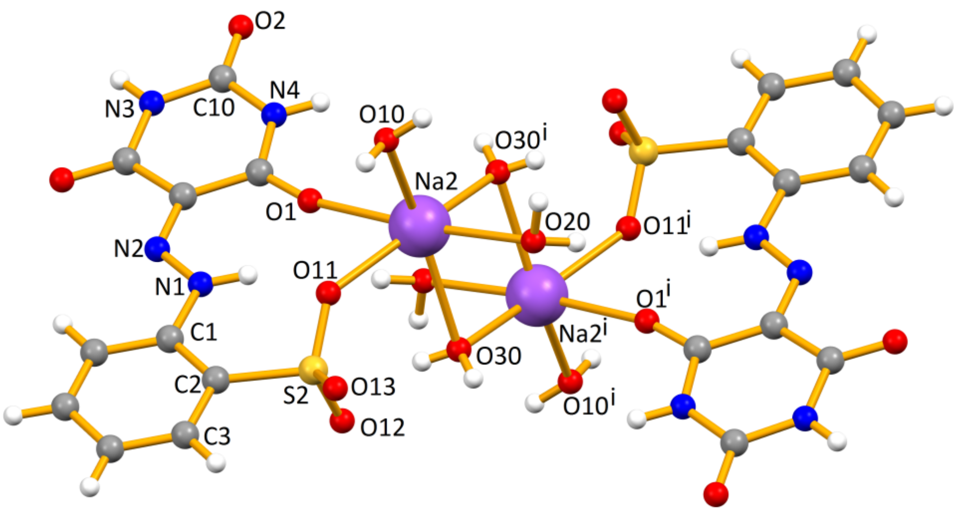
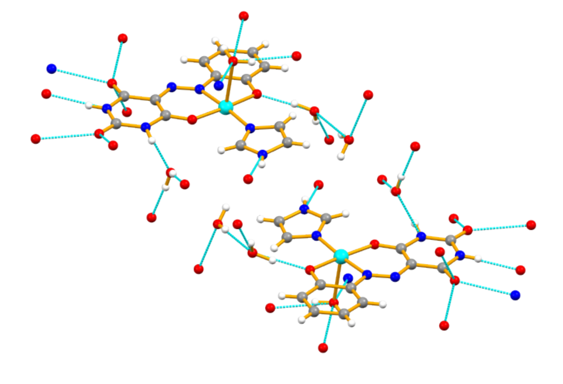


Figure 9S. X-ray structure **1** (78% completeness) with atom numbering scheme. Symmetry operation to generate equivalent atoms: *i*) -x,-y,1-z.



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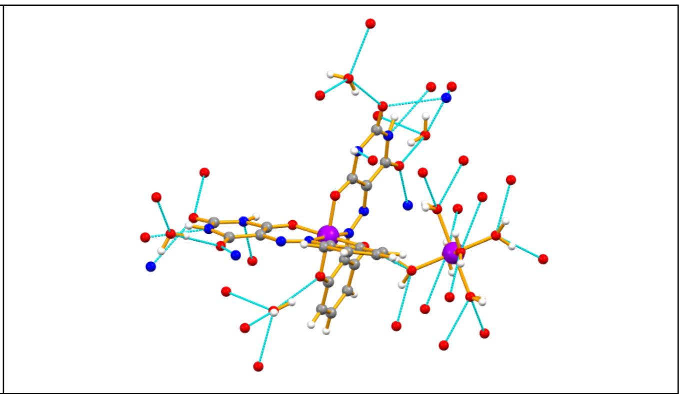

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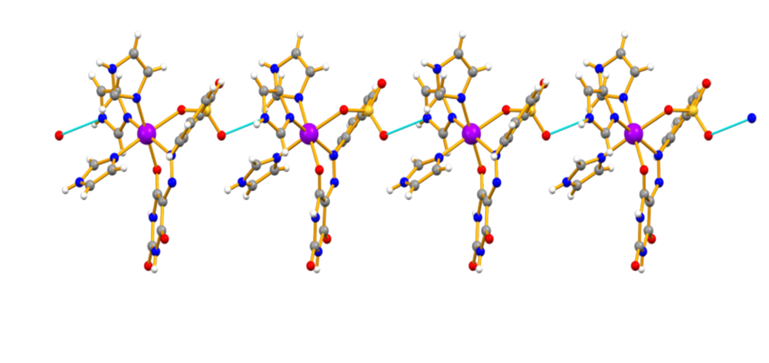

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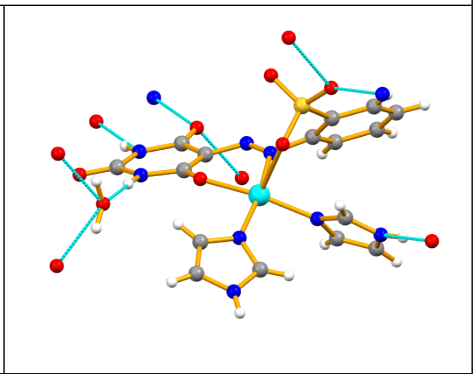

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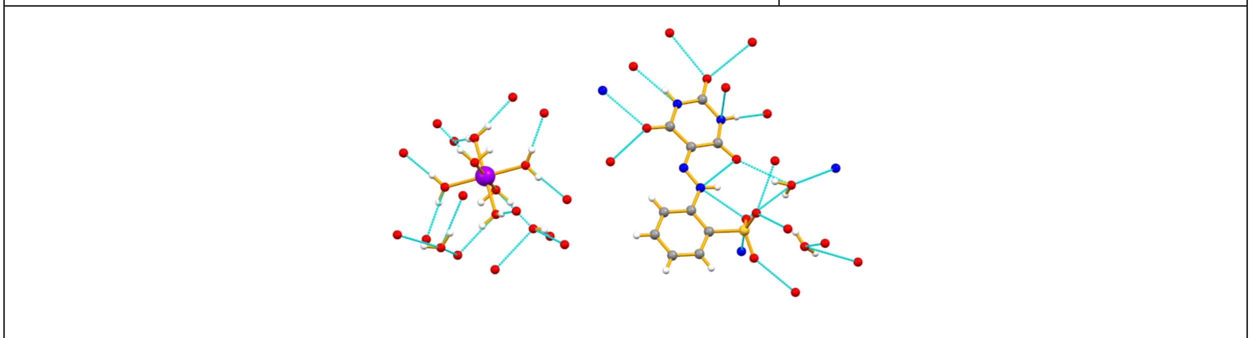

6

Figure 10S. Hydrogen bond interactions (in dashed blue lines; see also Table 3S) in **2**−**6**. Only in **4** these contacts lead to infinite 1D chains; in all the other compounds such interactions give rise to 3D frameworks.

Table 4S. Hydrogen bond interactions (Å, º) in complexes **2–6**.

D–H···A	*d*(H···A)	*d*(D···A)	∠(D–H···A)	Symmetry operation
2				
O1W···H1W1···O3	2.12(6)	2.997(7)	167(5)	*intra*
O1W···H1W2···O1	1.79(6)	2.759(7)	174(6)	*1-x,1-y,-z*
N4···H2N···O2W	1.86(7)	2.776(8)	158(6)	*intra*
O4W···H4W1···O3	2.17(6)	2.820(6)	128(5)	*-x,1-y,-z*
N3···H3N···O3	2.01(7)	2.845(7)	175(7)	*-x,1-y,-z*
O4W···H4W2···O4	2.07(7)	2.906(7)	166(6)	*x,1+y,z*
O2W···H2W1···O3W	1.89(7)	2.717(10)	173(7)	*1-x,-y,1-z*
O2W···H2W2···O4	2.06(7)	2.776(6)	167(9)	*-x,-y,1-z*
N6···H6N···O4W	2.03(7)	2.897(8)	163(7)	*-x,1-y,1-z*
O3W···H3W1···O1W	2.02	2.823(8)	153	*x,y,1+z*
3				
N3···H3N···O8	2.15(11)	2.968(15)	149(9)	*x,1+y,z*
N4···H4N···O7	2.00(12)	2.772(14)	143(10)	*1-x,-y,-z*
N7···H7N···O3	2.43(11)	2.744(12)	101(9)	*1-x,-y,1-z*
N8···H8N···O4	2.03(8)	2.887(12)	156(10)	*x,-1+y,z*
O1W···H11W···O7	2.20	3.063(17)	168	*1-x,-1-y,-z*
O2W···H12W···O4	2.05	2.860(14)	155	*intra*
O3W···H13W···O1	1.93(12)	2.764(15)	153(10)	*intra*
O4W···H14W···O3	2.00(13)	2.818(16)	151(11)	*intra*
O1W···H21W···O7	1.93	2.791(15)	170	*intra*
O3W···H23W···O2W	2.10(13)	2.828(18)	137(8)	*1-x,-y,-z*
O4W···H24W···O11	2.17(11)	2.63(2)	110(6)	*1-x,1-y,1-z*
O10···H110 ..O5	1.79(8)	2.660(13)	163(9)	*intra*
O12···H112···O8	2.08	2.90(2)	163	*-1+x,1+y,z*
O10···H210···O3W	1.92(11)	2.740(16)	152(11)	*-x,-y,1-z*
O11···H211···O1W	2.02	2.67(2)	128	*1-x,-y,-z*
O12···H212···O2W	2.15	2.84(2)	131	*1-x,1-y,-z*
4				
N12···H12···O12	2.44	3.162(9	142	*1-x,-1/2+y,1/2-z*
N12···H12···O12	2.47	3.105(9)	132	*x,1/2-y,-1/2+z*
N22···H22···O13	2.14	2.912(8)	149	*x,3/2-y,-1/2+z*
5				
O1W···H1W1···O13	2.11(5)	2.925(7)	152(4)	*1/2-x,1/2+y,1/2-z*
O1W···H1W2···O2	1.99(6)	2.790(6)	150(5)	*-1+x,y,z*
N3···H3···O2	1.97	2.817(5)	168	*2-x,-y,1-z*
N4···H4···O1W	1.98	2.837(6)	175	*intra*
N22···H22···O13	2.19	2.961(7)	150	*1-x,-y,-z*
6				
O1W···H1W1···O2W	2.32(2)	3.085(6)	153(3)	*intra*
O1W···H1W2···O2	2.24(3)	2.994(4)	147(3)	*1/2-x,3/2+y,3/2-z*
N3···H3N···O1	1.98(3)	2.689(3)	134(3)	*intra*
N3···H3N···O11	2.14(3)	2.795(3)	129(3)	*intra*
O2W···H2W2···O1	2.17(3)	2.979(5)	154(3)	*intra*
O2W···H2W2···O11	2.44(3)	2.946(4)	118(3)	*intra*
O3W···H3W1···O12	2.05(4)	2.754(3)	158(4)	*1-x,1-y,1-z*
N5···H5N···O2W	1.94(2)	2.813(4)	169(3)	*1/2-x,-1/2+y,3/2-z*
O3W···H3W2···O4W	1.88(4)	2.685(4)	159(4)	*1-x,1-y,-z*
N6······H6N···O3	1.96(3)	2.848(3)	168(3)	*1-x,-1-y,1-z*
O4W···H4W1···O3	1.94(3)	2.762(3)	152(3)	*3/2-x,1/2+y,1/2-z*
O4W --H4W2 ..O2	2.04(3)	2.920(4)	168(2)	*1/2+x,-1/2-y,-1/2+z*
O21 --H21A ..O3W	1.73	2.652(4)	169	*intra*
O22 --H22A ..O3W	1.90(3)	2.775(3)	170(3)	*1-x,1-y,-z*
O22 --H22B ..O1W	1.89(3)	2.781(4)	175(3)	*1-x,1-y,1-z*
O23 --H23A ..O12	1.93(3)	2.789(3)	167(3)	*x,y,-1+z*
O23 --H23B ..O13	1.85(3)	2.717(3)	174(3)	*x,-1+y,-1+z*

4. Electrochemistry

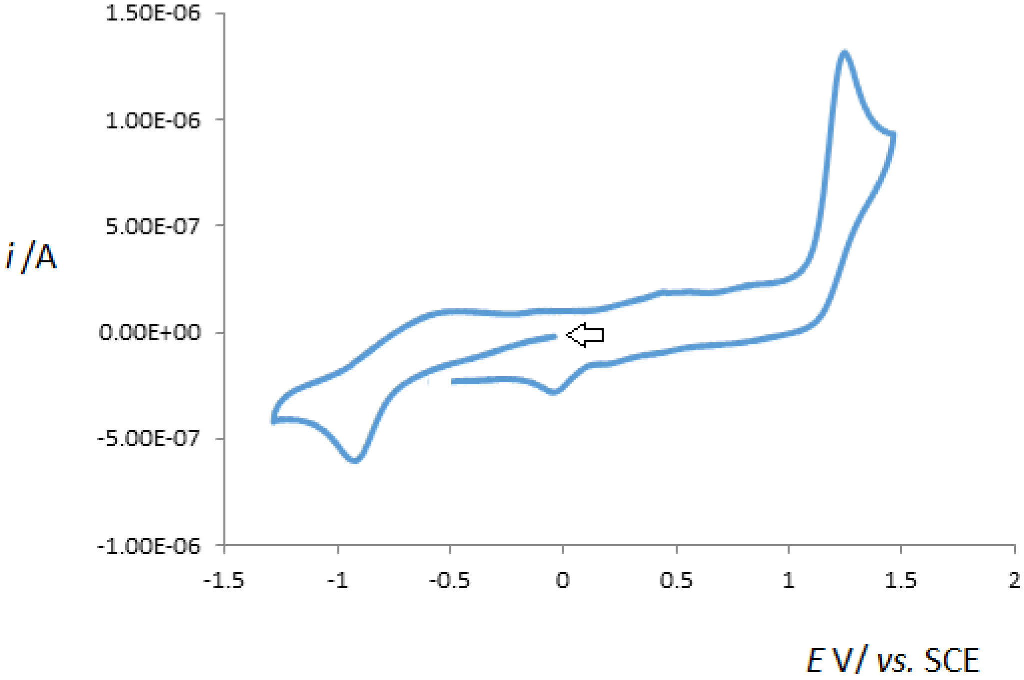

Figure 11S. Cyclic voltammogram, initiated by the cathodic sweep, of $\mathbf{H_4L^1}$ in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/NCMe solution, at a Pt disc working electrode (d = 0.5 mm), run at a scan rate of 200 mVs^{-1}.

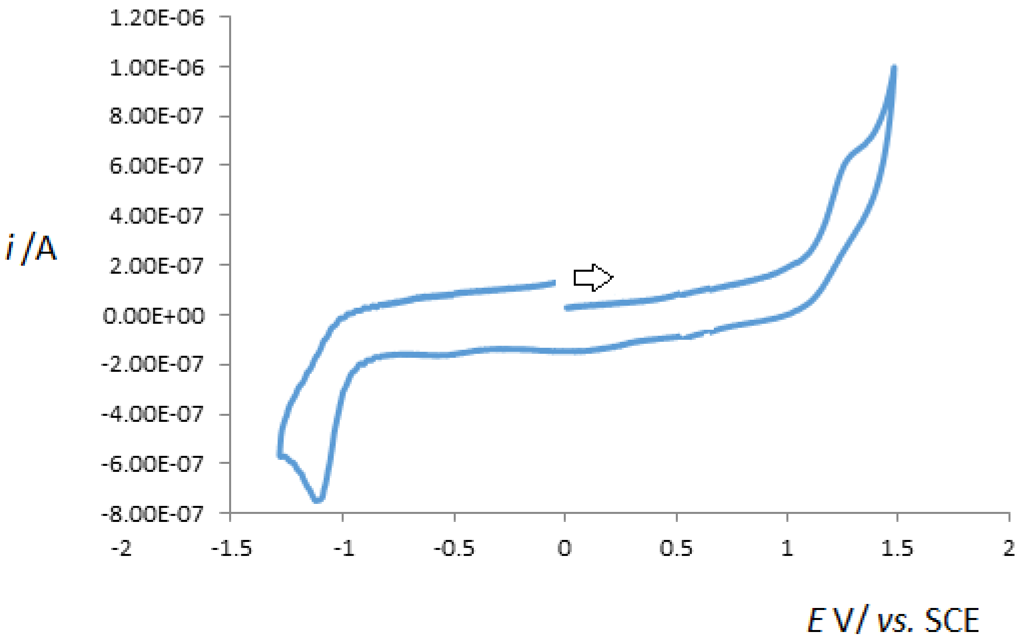

Figure 12S. Cyclic voltammogram, initiated by the anodic sweep, of **1** in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/NCMe solution, at a Pt disc working electrode (d = 0.5 mm), run at a scan rate of 200 mVs^{-1}.

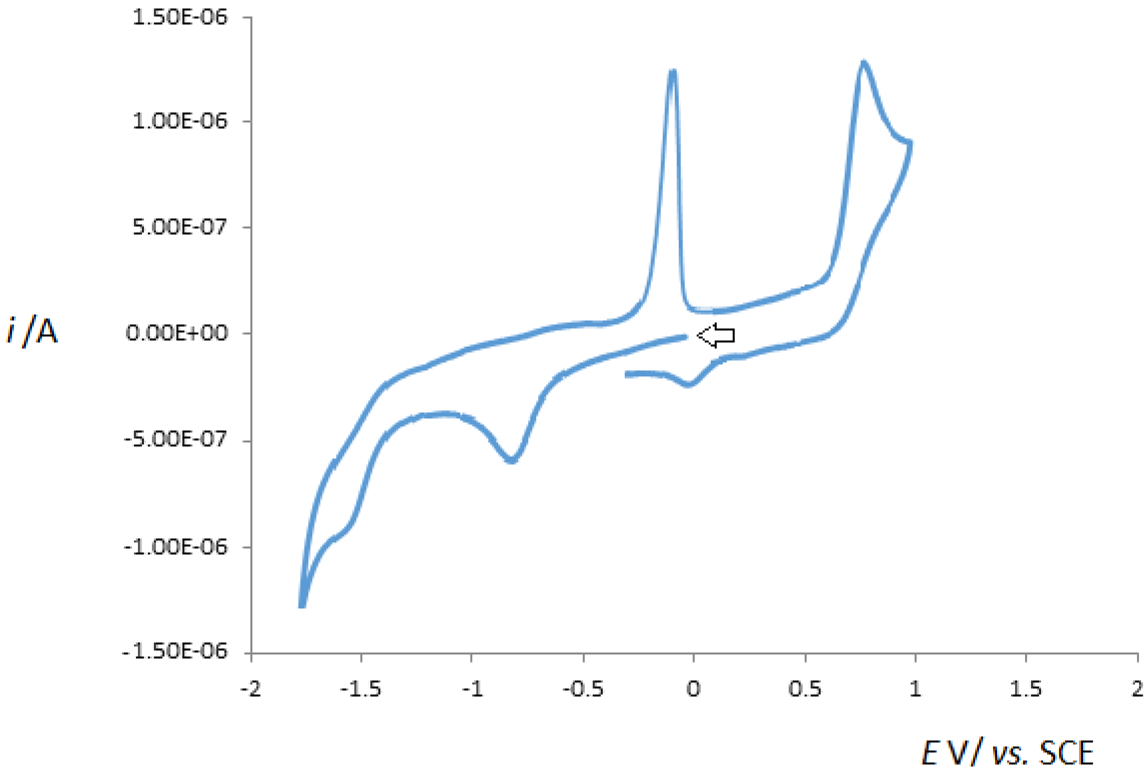

Figure 13S. Cyclic voltammogram, initiated by the cathodic sweep, of **2** in a 0.2 M $[^nBu_4N][BF_4]$/NCMe solution, at a Pt disc working electrode (d = 0.5 mm), run at a scan rate of 200 mVs^{-1}.

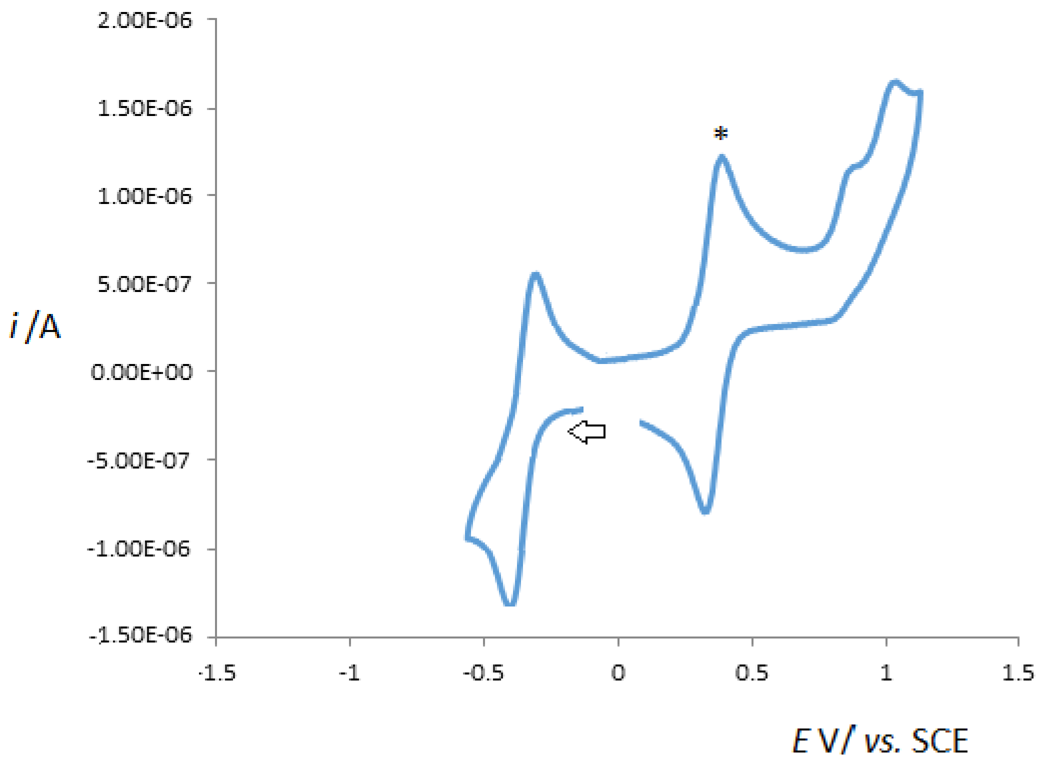

Figure 14S. Cyclic voltammogram, initiated by the cathodic sweep, of **3** in a 0.2 M $[^nBu_4N][BF_4]$/NCMe solution, at a Pt disc working electrode (d = 0.5 mm), run at a scan rate of 200 mVs^{-1}. * $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$.