Electronic Supplementary Information(ESI)

Slow magnetic relaxation and water oxidation activity of dinuclear $Co^{II}Co^{III}$ and unique triangular $Co^{II}Co^{II}Co^{III}$ mixed-valence complexes

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Shape analysis : Continuous Shape Measurement (CShM)[a] of Co^{II} and Co^{III} coordination sphere using SHAPE v2.1.

Table S1 Results of Continuous Shape Measurement Analysis for the Co(II) & Co(III) coordination Spheres[a] of complex **1**.

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--------------------------------------------------------------------------------
S H A P E   v2.1         Continuous Shape Measures calculation
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                Contact:  llunell@ub.edu
--------------------------------------------------------------------------------
CoL6 structures


HP-6          1 D6h   Hexagon
PPY-6         2 C5v   Pentagonal pyramid
OC-6          3 Oh    Octahedron
TPR-6         4 D3h   Trigonal prism
JPPY-6        5 C5v   Johnson pentagonal pyramid J2

Structure [ML6 ]HP-6       PPY-6       OC-6       TPR-6      JPPY-6

Co1(III) center ,      31.236,     28.474,    0.205,     15.492,     32.094
……
Co2(II) center, 25.782,      14.801,      4.130,      8.281,      18.272
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Table S2 Results of Continuous Shape Measurement Analysis for the Co(II) and Co(III) coordination Spheres[a] of complex **2**.

Analysis of Co1(III) center:

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--------------------------------------------------------------------------------
S H A P E   v2.1         Continuous Shape Measures calculation
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                Contact:  llunell@ub.edu
--------------------------------------------------------------------------------
CoL6 structures
HP-6          1 D6h   Hexagon
PPY-6         2 C5v   Pentagonal pyramid
OC-6          3 Oh    Octahedron
TPR-6         4 D3h   Trigonal prism
```

JPPY-6 5 C5v Johnson pentagonal pyramid J2

Structure [ML6]**HP-6 PPY-6 OC-6 TPR-6 JPPY-6**
Co1(III) center, 31.912, 28.856, 0.233, 15.662, 32.514

Analysis of Co2(II) center:

S H A P E v2.1 Continuous Shape Measures calculation
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CoL6 structures

HP-6 1 D6h Hexagon
PPY-6 2 C5v Pentagonal pyramid
OC-6 3 Oh Octahedron
TPR-6 4 D3h Trigonal prism
JPPY-6 5 C5v Johnson pentagonal pyramid J2

Structure [ML6]**HP-6 PPY-6 OC-6 TPR-6 JPPY-6**
Co2(II) center , 34.485, 23.582, 2.114, 12.639, 28.317

CoL5 structures

PP-5 1 D5h Pentagon
vOC-5 2 C4v Vacant octahedron
TBPY-5 3 D3h Trigonalbipyramid
SPY-5 4 C4v Spherical square pyramid
JTBPY-5 5 D3h Johnson trigonalbipyramid J12

Structure [ML5]**PP-5 vOC-5 TBPY-5 SPY-5 JTBPY-5**
Co2(II) center , 25.914, 1.102, 7.407, 2.015, 8.917

Analysis of Co3(II) center:

S H A P E v2.1 Continuous Shape Measures calculation
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CoL5 structures

PP-5 1 D5h Pentagon
vOC-5 2 C4v Vacant octahedron
TBPY-5 3 D3h Trigonalbipyramid
SPY-5 4 C4v Spherical square pyramid
JTBPY-5 5 D3h Johnson trigonalbipyramid J12

Structure [ML5]	**PP-5**	**vOC-5**	**TBPY-5**	**SPY-5**	**JTBPY-5**
Co3(II) Center ,	32.034,	5.771,	1.418,	4.063,	4.091

Table S3 BVS Calculation data for cobalt centers in complex **1** and**2**.[a]

Complex **1**			Complex **2**		
	$R_0(Co^{III})$	$R_0(Co^{II})$		$R_0(Co^{III})$	$R_0(Co^{II})$
Co(1)	**3.198**	3.258	Co(1)	**3.263**	3.220
Co(2)	1.672	**1.904**	Co(2)	1.985	**2.071**
			Co(3)	1.872	**1.889**

[a]The underlined value is the closest to the charge for which it was calculated.

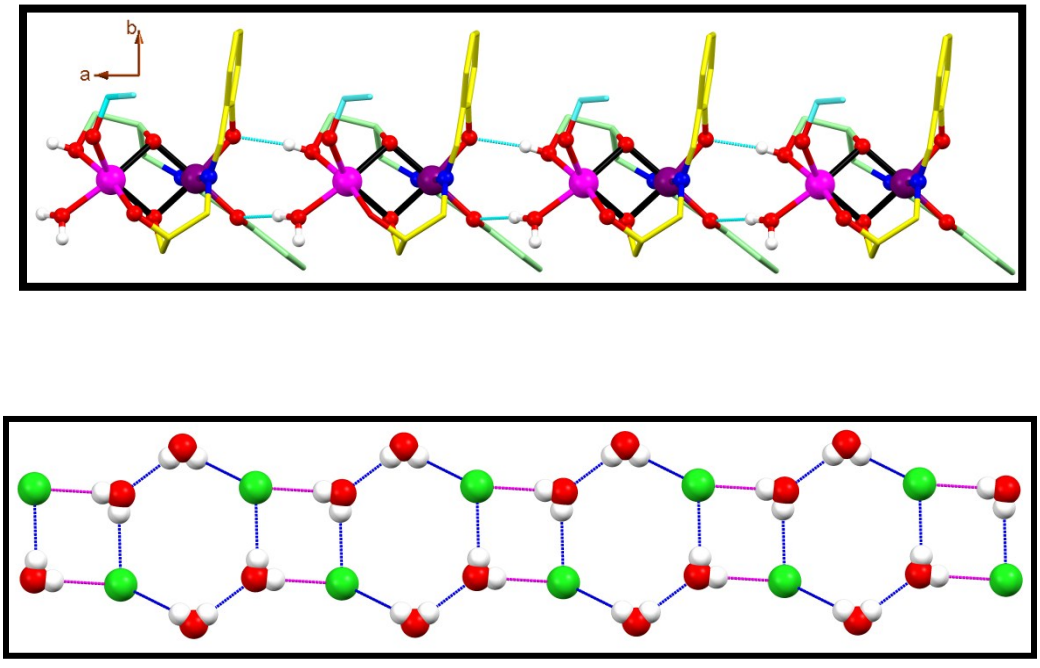

Fig. S1 1D-chain structure formed with intermolecular hydrogen bonds (above). Topology of chloro mediated water ribbon (below).

Table S4 A selection of calculated parameters that defines the *zfs* tensor (D and E/D ratio), spin-spin (D_{SS}) and spin-orbit (D_{SO}) contribution to the axial component of zfs in **1** and **2**. Calculations were carried out on the wavefunction provided by the CASSCF method (see into Experimental Section).

Compound	D^a	$D_{SS}{}^a$	$D_{SO}{}^a$	E/D	$S_{eff} = 1/2^b$		
					g_1	g_2	g_3
1 [$Co^{II}Co^{III}$]	+44.0	+0.6	+43.9	0.185	2.028	3.842	6.245
1 [$Co^{II}Ga^{III}$]	+43.3	+0.6	+43.2	0.188	2.027	3.835	6.240
2 [Co2]	+63.1	–0.6	+63.4	0.208	2.183	4.230	6.130
2 [Co3]	–23.2	+0.5	–23.0	0.084	7.567	0.647	0.600

[c] in cm^{-1}. [b] The directions of the components of the Landé factor (g_i) are not assigned directly in the theoretical calculation, but the positive value of D and the magnitude of the components allows concluding that $g_x = g_2$, $g_y = g_3$ and $g_z = g_1$.

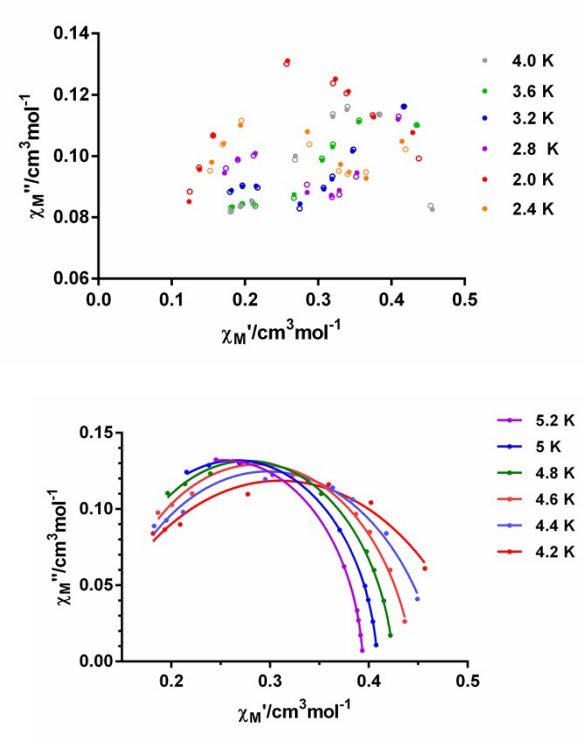

Fig. S2 Cole-Cole plots for temperatures between 2.4–4 K (above) and 4.2–5.2 K (below) of Complex **1**.

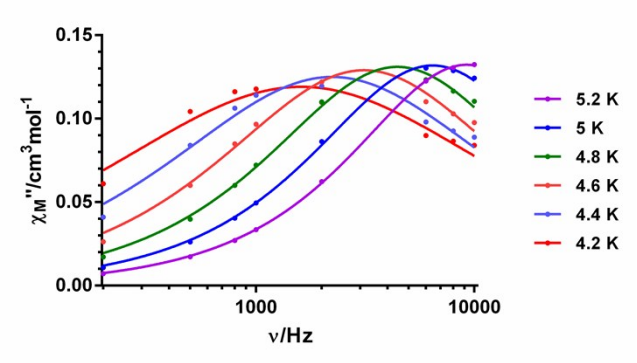

Fig. S3 Frequency dependence of theout-of-phase signal (χ''_M) in the 4.2 K-5.2 K temperature range of **1**. The solids lines correspond to the best-fitting to the Debye model.

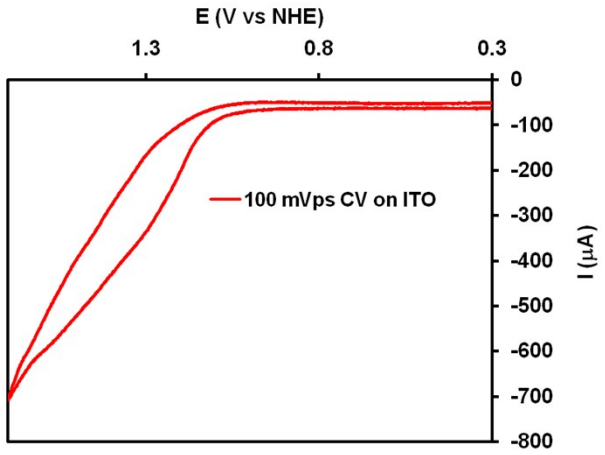

Fig. S4 Cyclic voltammetry of the 0.5 mM of the complex at *pH* 7 phosphate buffer. ITO is used as working electrode, Ag/AgCl as reference electrode and Pt as counter electrode. The potential is adjusted to NHE.

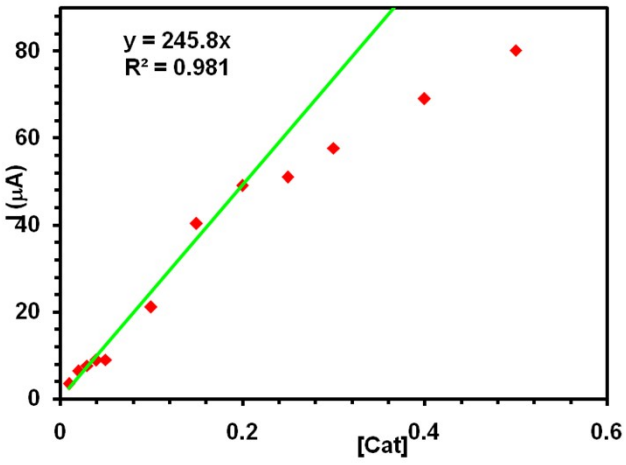

Fig. S5 The plot of catalytic peak current at *pH* 7 with respect to catalyst concentration.

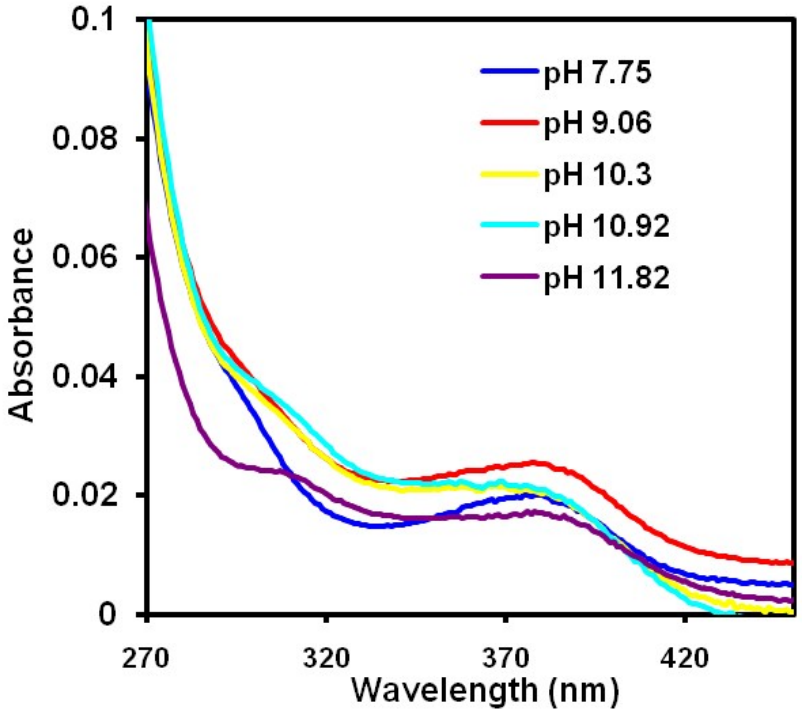

Fig. S6 Absorption spectra of the complex **1** as a function of pH.

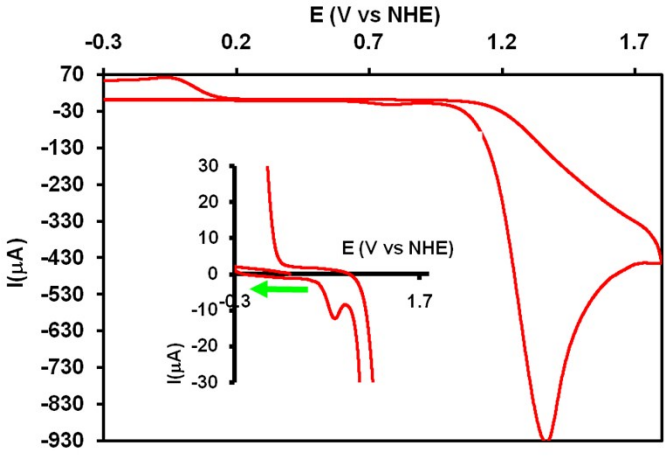

Fig. S7 Cyclic voltammetry of the 0.5 mM of the complex **1** at *pH* 11 phosphate buffer. Inset: The initial cathodic scan under anaerobic conditions is marked in green arrow showing no trace of oxygen reduction. Glassy carbon electrode (GCE) is used as working electrode, Ag/AgCl as reference electrode and Pt as counter electrode. The potential is adjusted to NHE.

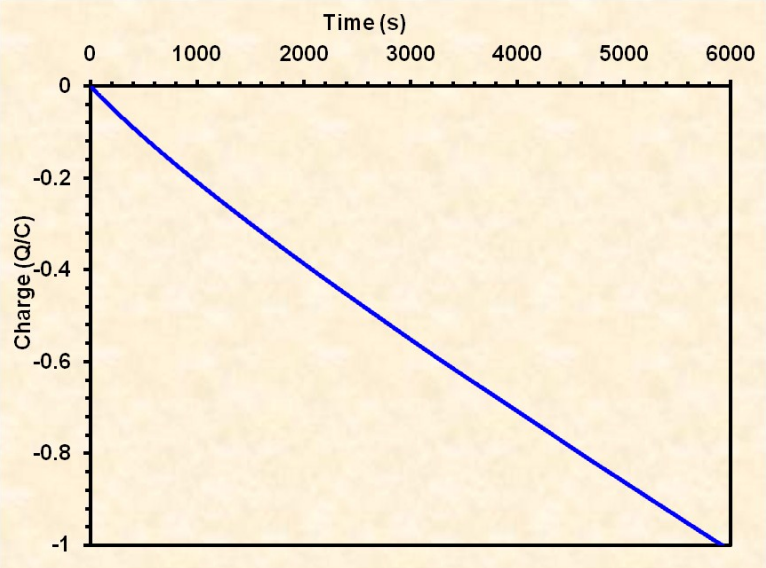

Fig. S8 The charge vs time plot of the 0.5 mM of the catalyst at *pH*7 phosphate buffer. Constant electrode potential = 1.4 V vs NHE. ITO is used as working electrode, Ag/AgCl as reference electrode and Pt as counter electrode.

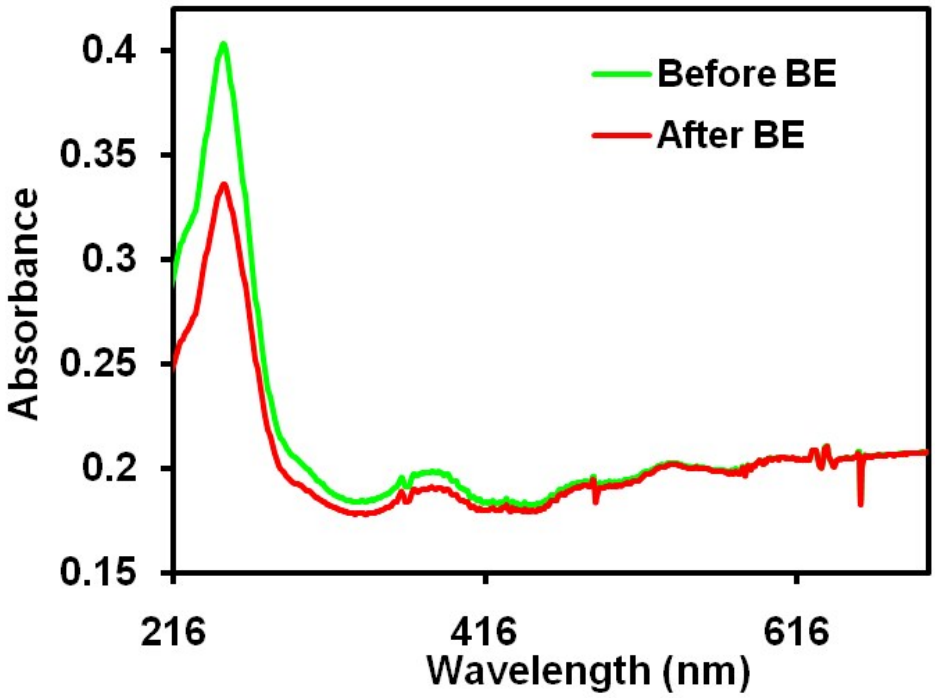

Fig. S9 The absorption spectra of the complex before and after bulk electrolysis (1.4 V *vs* NHE) at *pH*7 phosphate buffer.