Supporting Information

A Co(II) Framework derived from a tris(4-(triazol-1-yl)phenyl)amine Redox-Active linker: electrochemical and magnetic study

Chin-May Ngue,[a,b,c] Ching-Wen Chiu,[b] Gene-Hsiang Lee,[b] Shie-Ming Peng,[a,b] Man-Kit Leung,*[b] Chen-I Yang,*[e] Yen-Hsiang Liu,*[d] Kuang-Lieh Lu*[a]

[a]Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

[b]Department of Chemistry, National Taiwan University, Taipei 107, Taiwan

[c]Nano Science and Technology Program, Taiwan International Graduate Program, Institute of Physics, Academia Sinica and National Taiwan University

[d]Department of Chemistry, Fu Jen Catholic University, New Taipei City 242, Taiwan

[e]Department of Chemistry, Tunghai University, Taichung 407, Taiwan

Crystallographic Measurements

A block shaped, red coloured crystal of **1** suitable for crystallographic measurement was mounted on the tip of a glass fiber with dimensions of 0.169 x 0.151 x 0.137 mm^3 and placed on the goniometer head for indexing and intensity data collection using a Nonius Kappa CCD diffractometer equipped with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected at 150 K. Data reduction included correction for absorption corrections by the MULTISCAN method using Bruker *SAINT*[1] and *SADABS*.[2] The structure was solved by direct methods and refined against F^2 by the full-matrix least-squares technique using the SHELX-97 software packages.[3] All non-hydrogen atoms were refined anisotropically. The C-bound H atoms were placed in the calculated positions and refined by the riding-model approximation. Further details of the crystallographic data are shown in Table S1.

References

1. *SAINT*, Bruker (2003), Bruker AXS Inc., Madison Wisconsin, USA.

2. SADABS, Bruker (2002), Bruker AXS Inc., Madison Wisconsin, USA.

3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr*., 2008, **64**, 112.

Table S1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{51}H_{41}Co_2N_{15}O_{11}S_4$
F_w	1286.09
Temperature, K	150(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	12.7016(5)
b, Å	20.9067(10)
c, Å	20.8591(11)
β, $^\circ$	96.5309(16)
V, Å^3	5503.2(4)
Z	4
λ, Å	0.71073
D_{calc}, g/cm^3	1.552
μ, mm^{-1}	0.829
$F(000)$	2632
Crystal size, mm^3	0.169 × 0.151 × 0.137
Reflections collected	44603
R_{int}	0.0234
Refinement method	Full–matrix least–squares on F^2
Data/restrains/parameters	12599/6/759
Goodness of fit	1.084
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0402, wR2 = 0.1096
R indices (all data)	R1 = 0.0482, wR2 = 0.1169

$^*R_1 = \Sigma||F_0|-|F_c|| \ / \ \Sigma|F_0|$; $^*wR_2 = [\Sigma w(F_0{}^2-F_c{}^2)^2 \ / \ \Sigma w(F_0{}^2)^2]^{1/2}$

Table S2. Bond lengths [Å], angles [°], and dihedral angle [°] for **1**.

_____

bond lengths

Co(1)–O(2)	2.0553(17)	Co(2)–O(7)	2.0518(16)
Co(1)–O(8)	2.0697(18)	Co(2)–O(3)	2.0733(16)
Co(1)–O(6)	2.0770(17)	Co(2)–O(1)	2.0886(17)
Co(1)–O(4)	2.0868(17)	Co(2)–N(4)	2.1206(19)
Co(1)–N(1)	2.114(2)	Co(2)–N(7)	2.146(2)
Co(1)–O(1)	2.1415(17)		

bond angles

O(2)–Co(1)–O(8)	176.56(7)	O(3)–Co(2)–O(1)	93.07(7)
O(2)–Co(1)–O(6)	89.97(7)	O(7)–Co(2)–N(4)	176.11(7)
O(8)–Co(1)–O(6)	88.72(8)	O(1)–Co(2)–N(4)	85.40(7)
O(2)–Co(1)–O(4)	90.09(7)	O(7)–Co(2)–N(7)	87.22(7)
O(8)–Co(1)–O(4)	90.90(8)	N(4)–Co(2)–N(7)	90.54(8)
O(4)–Co(1)–N(1)	86.91(8)	O(1)–Co(2)–O(10)	84.71(8)
O(2)–Co(1)–O(1)	91.37(7)	N(4)–Co(2)–O(10)	90.13(8)
O(6)–Co(1)–O(1)	96.91(7)	N(7)–Co(2)–O(10)	84.53(8)
O(4)–Co(1)–O(1)	88.78(7)	O(7)–Co(2)–O(3)	96.13(7)

dihedral angles

O(2)–Co(1)–O(10)–Co(2)	50.91	N(1)–Co(1)–O(1)–Co(2)	142.98
O(4)–Co(1)–O(1)–Co(2)	140.97	O(10)–Co(2)–O(1)–Co(1)	130.07
O(6)–Co(1)–O(1)–Co(2)	39.23	N(4)–Co(2)–O(1)–Co(1)	139.37
O(8)–Co(1)–O(1)–Co(2)	128.18	N(7)–Co(2)–O(1)–Co(1)	150.98

Symmetry transformations used to generate equivalent atoms:
#1 x + 1/2, −y + 1/2, z + 1/2; #2 x − 1/2, −y + 1/2, z − 1/2; #3 x − 1/2, −y + 1/2, z + 1/2; #4 x, y + 1, z; #5 x + 1/2, −y + 1/2, z − 1/2; #6 x, y − 1, z.
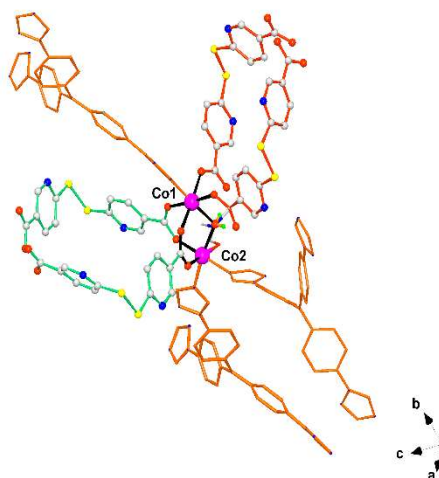
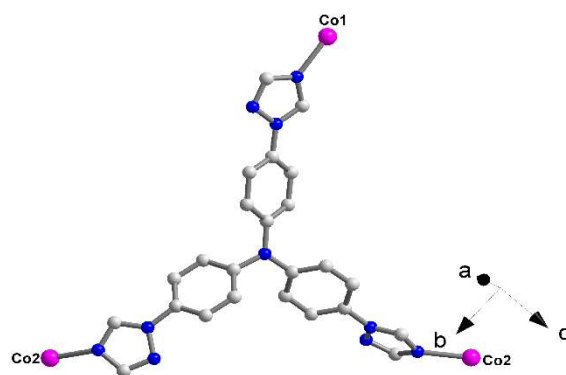Fig. S1 Coordination environment of **1**.

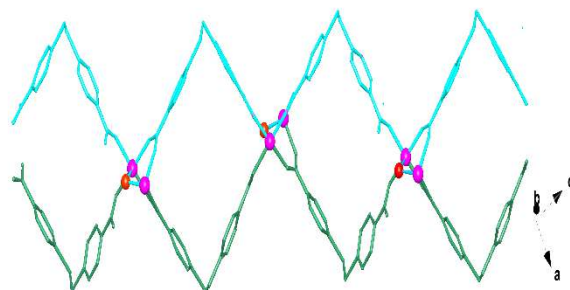Fig. S2 The coordination mode of the TTPA ligand in compound **1**.

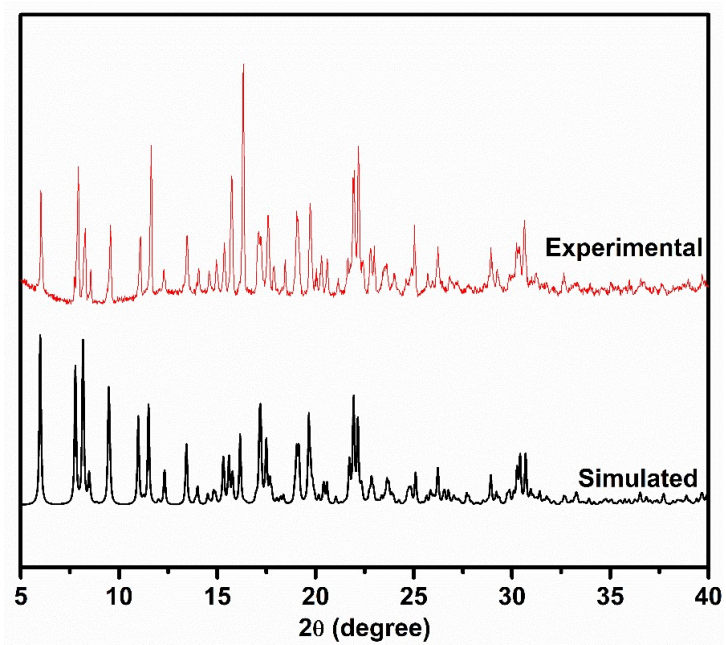Fig. S3 DTDN^{2-} ligands displaying P and M forms.

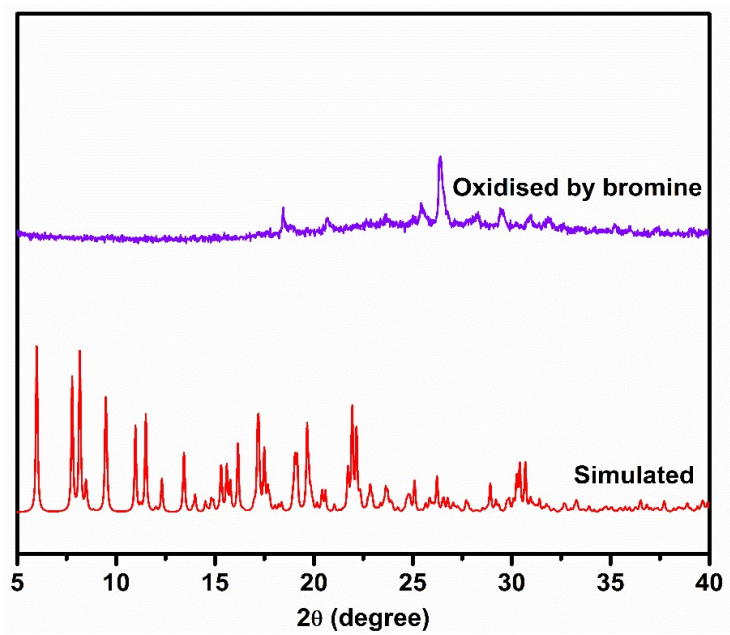Fig. S4 Simulated and experimental PXRD patterns of **1**.

Fig. S5 PXRD pattern of the oxidised sample of **1**.

Solid–State Spectroelectrochemistry

10 mg of **1** was ground into fine particles, and 2 mL of THF was then added to form a paste. An indium tin oxide (ITO) glass (6 cm x 0.9 cm) was pretreated by washing with ethanol, acetone and purged with nitrogen. The sample was coated on the ITO glass by repeated 4 spin coatings (3100 rpm for 30 s). The coated ITO sample was placed inside a 50 °C oven for 15 min. The spectrum of the coated sample was obtained using a Jasco V-570 UV/vis/NIR spectrometer to confirm that its absorption peaks are identical to those of the original framework. The electrochemical set up employed a three-electrode system, ITO as the working electrode, Pt mesh as the counter electrode and Ag/Ag$^+$ as the reference electrode in a 0.1 M n-Bu$_4$NPF$_6$ propionitrile electrolyte. The above described electrode was placed inside a 1 cm quartz cell, with the coated ITO sample and Pt mesh facing opposite in the cell. To minimize the risk of short-circuits, the compartment was separated by a tailor made Teflon block. A blank ITO with electrolyte was measured as background. The samples were scanned continuously with increments in potential using a Hokuto Denko potentiostat until a change of the spectrum was detected.

Oxidation of the framework

Bromine oxidation of **1**. Compound **1** was placed inside a small vial. The vial was then placed in a beaker containing 3 to 5 drops of bromine with a watch glass on top. Bromine vapour was allowed to diffuse into the framework for 30 minutes.
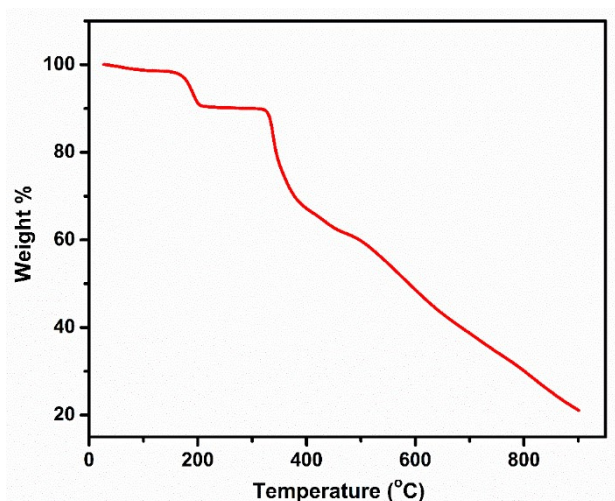

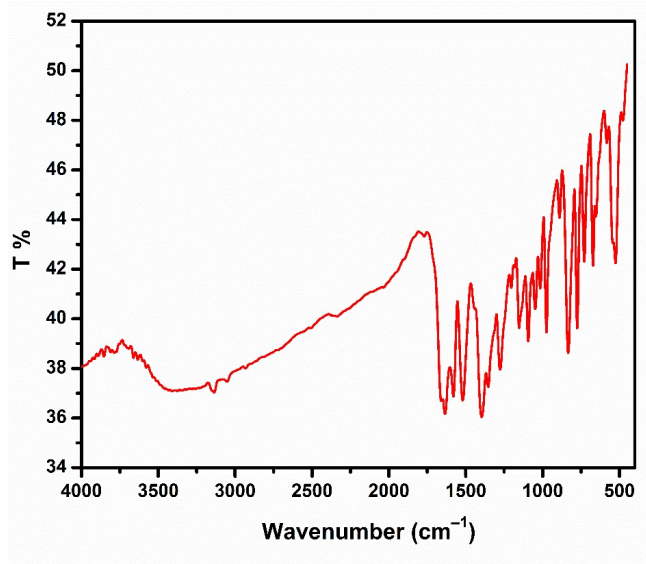Fig. S6 Thermal gravimetric analysis (TGA) pattern of **1**.

Fig. S7 IR spectrum of **1**.

IR (KBr, cm^{-1}): 3134sh (stretching of triarylamine), 1634s (stretching of carbonyl), 1581s (stretching of aromatic C=C), 1520s (bending of triarylamine), 1274m (stretching of C–O), 832s (bending of aromatic ring).
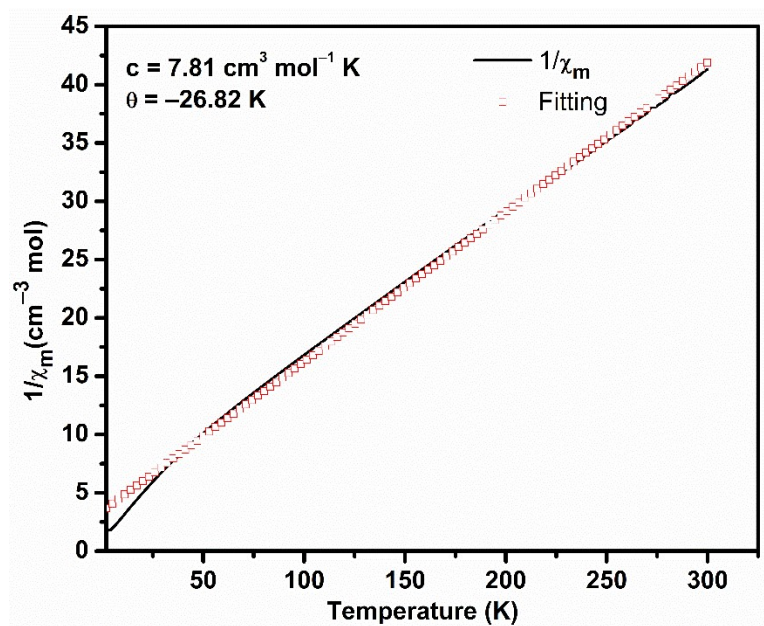

c = 7.81 cm^3 mol^{-1} K
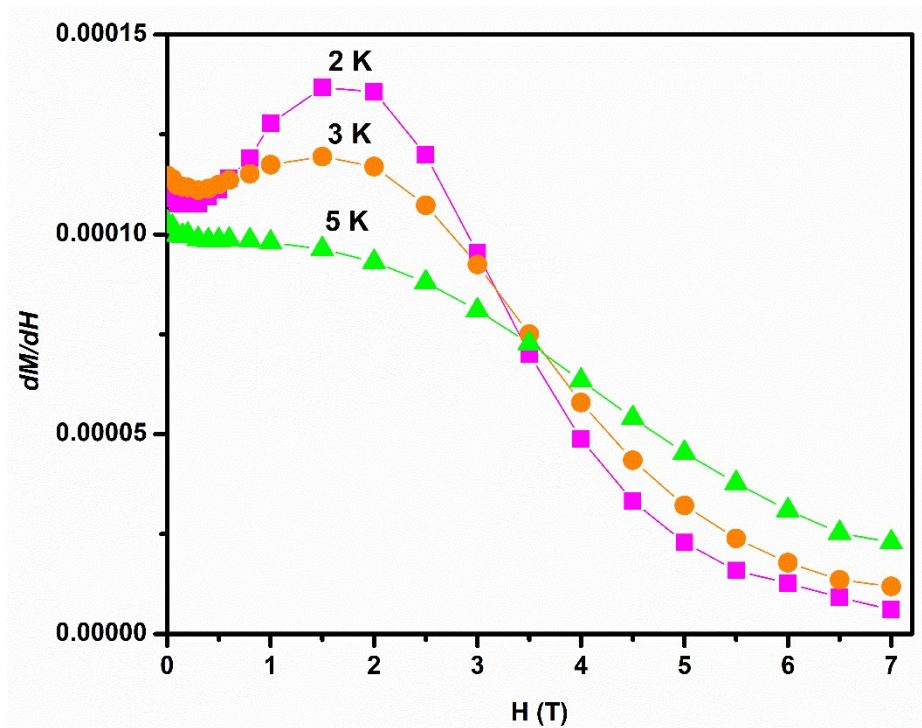θ = −26.82 K

Fig. S8 Plot of $1/\chi_M$ vs. T for compound **1**.

Fig. S9 First derivative plot of *dM/dH* for compound **1** at 2, 3, and 5 K.