Supporting Information

Electronic and spin delocalization in a switchable trinuclear triphenylene trisemiquinone bridged Ni_3 complex

Yiting Wang[1], François Lambert[1], Eric Rivière[1], Régis Guillot[1], Christian Herrero[1], Antoine Tissot[2], Zakaria Halime[1], Talal Mallah[1]*

[1]Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris-Sud, CNRS, Université Paris-Saclay, 91405 Orsay cedex, France
[2]Institut des Matériaux Poreux de Paris, UMR 8004 CNRS, École Normale Supérieure, Ecole Supérieure de Physique et de Chimie Industrielles de Paris, PSL University, 75005 Paris, France

Keywords: triphenylene, trisemiquinone, switchable, Ni, HHTP

I-Synthesis and characterization

$KBH(TP^{Ph,Ph})_3$ (1.89 g, 2.7 mmol) was dissolved in 60 mL $CHCl_3$, and the colorless solution was added into a methanolic solution of $NiCl_2 \cdot 6H_2O$ (0.71 g, 3 mmol) with stirring. A pink precipitate was generated immediately. Two hours later, the solid was filtered, washed with a small amount of $CHCl_3$ and dried under vacuum. The pink solid obtained corresponds to $Ni[BH(TP^{Ph,Ph})_3]Cl$.

HHTP (32.5 mg, 0.01 mmol) was dissolved in a methanolic solution (15 mL) containing 0.6 mL of tetrabutylammonium hydroxide (TBAOH). The obtained dark violet solution was added to a 15 mL CH_2Cl_2 solution of $Ni[BH(TP^{Ph,Ph})_3]Cl$ (229 mg, 0.3 mmol) with stirring. A darkish blue suspension was produced. The reaction was left overnight, and then filtered. A black precipitate was obtained, it was thoroughly washed with methanol. Yield 62%, 156 mg. The solid was redissolved in $CHCl_3$, and the final solution was obtained after chromatography (SiO_2). The solvent was completely removed using a rotatory evaporator. The solid obtained was dissolved in acetone and crystals suitable for X-ray analysis were obtained by slowly evaporating acetone. Elem Anal. for $Ni_3(HHTP)[BH(TP^{Ph,Ph})_3]_3(C_3H_6O)_{0.5}$ Calcd: C, 73.19%; H, 4.53%; N, 9.94%; Found: C, 73.14%; H, 4.35%; N, 10.04%. M_W = 2535.19 g/mol. Single-crystal unit cell: Triclinic, space group, *P*-1. a = 14.2552(18) Å, b = 17.287(2) Å, c = 32.407(4) Å, α = 94.408(4)°, β = 101.051(4)°, γ = 101.473(4)°, V = 7626.4(17) $Å^3$. IR (KBr) ν/cm^{-1}: 3456 (w), 3062 (w), 2617 (w), 1603 (w), 1545 (s), 1502 (s), 1479 (s), 1462 (s), 1364 (m), 1329 (m), 1282 (w), 1232 (w), 1170 (m), 1118 (w), 1064 (m), 1013 (m), 972 (w), 915 (w), 844 (w), 827 (w), 803 (s), 759 (s), 696 (s), 669 (m), 619 (w), 571 (m), 543 (m), 403 (w), 353 (w).

II-Single Crystal X-ray analysis

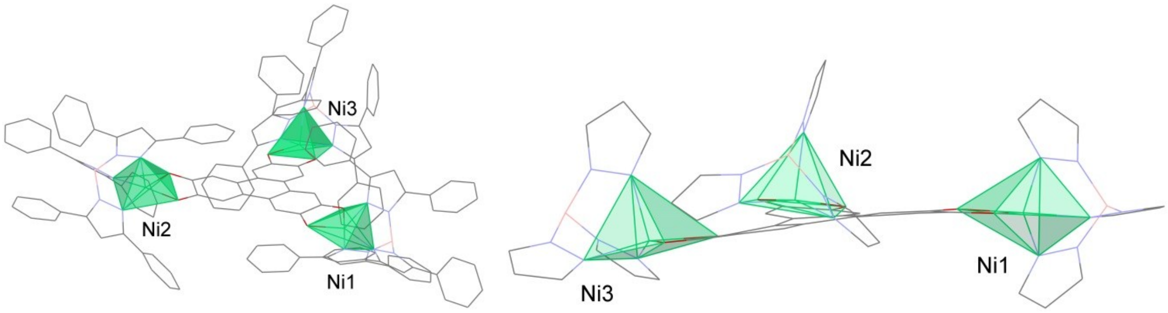

Figure S1. Polyhedral representation of the crystal structure

X-ray diffraction data for compound **1** was collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Mo Kα radiation. Crystal was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value by means of an N-Helix to within an accuracy of ±1K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[2] with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[3]

The crystal data collection and refinement parameters are given in Table S1.

CCDC 1936818 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Table S1. Crystallographic data and structure refinement details.

Compound	**1**
CCDC	1936818
Empirical Formula	$C_{153} H_{108} B_3 N_{18} Ni_3 O_6$, 7($C_3 H_6 O$)
M_r	2909.67
Crystal color	black
Crystal size, mm^3	0.100 x 0.095 x 0.035
Crystal system	triclinic
Space group	*P* -1
a, Å	14.2552(18)
b, Å	17.287(2)
c, Å	32.407(4)

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[1] Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.

[2] Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.,* **2008**, 64, 112-122.

[3] Farrugia, L. J. *J. Appl. Cryst*. **1999**, *32*, 837.

α, °	94.408(4)
β, °	101.051(4)
γ, °	101.473(4)
Cell volume, Å^3	7626.4(17)
Z ; Z’	2 ; 1
T, K	100 (1)
Radiation type ; wavelength Å	MoKα; 0.71073
F_{000}	3046
μ, mm^{-1}	0.435
θ range, °	2.156 - 30.951
Reflection collected	217 860
Reflections unique	47 603
R_{int}	0.3232
GOF	1.015
Refl. obs. ($I>2\sigma(I)$)	16 901
Parameters	1856
wR_2 (all data)	0.3393
R value ($I>2\sigma(I)$)	0.1390
Largest diff. peak and hole (e-.Å^{-3})	1.483 ; -1.004

Table S2. Some selected bonds distances and angles of complex

Complex					
Ni1		Ni2		Ni3	
d_{Ni1-N1}	2.009(5)	d_{Ni2-N7}	2.057(6)	$d_{Ni3-N13}$	2.038(5)
d_{Ni1-N2}	1.987(5)	d_{Ni2-N8}	2.031(7)	$d_{Ni3-N14}$	2.018(5)
d_{Ni1-N3}	2.067(5)	d_{Ni2-N9}	2.040(7)	$d_{Ni3-N15}$	2.028(5)
d_{Ni1-O1}	2.039(4)	d_{Ni2-O3}	1.984(6)	d_{Ni3-O5}	1.971(4)
d_{Ni1-O2}	1.957(5)	d_{Ni2-O4}	2.020(5)	d_{Ni3-O6}	2.022(4)
d_{C3-O1}	1.247(7)	d_{C9-O3}	1.293(9)	d_{C15-O5}	1.291(7)
d_{C4-O2}	1.300(7)	d_{C10-O4}	1.270(8)	d_{C16-O6}	1.278(7)
d_{C3-C4}	1.469(8)	d_{C9-C10}	1.459(10)	$d_{C15-C16}$	1.448(9)
$O1\hat{N}i1O2$	81.94(17)	$O3\hat{N}i2O4$	81.8(2)	$O5\hat{N}i3O6$	81.92(17)

III-Electrochemical Characterization Procedures

Cyclic voltammetry measurements were performed in an electrochemical cell composed of a glassy carbon (3 mm diameter) working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum mesh counter electrode. Dichloromethane (Fisher Chemical 99+%) was distilled over $CaCl_2$ and *tetra*-*N*-butylammonium hexafluorophosphate ($[Bu_4N]PF_6$, Aldrich 99%) was recrystallized in ethanol. Solutions of the complex were prepared at a concentration of 1 mM and $[Bu_4N]PF_6$ was used as supporting electrolyte and its concentration was maintained at a hundred-fold excess compared to the sample. The solutions were purged with inert argon gas and the cyclic voltammograms were measured at a scan rate of 100 mV/s.

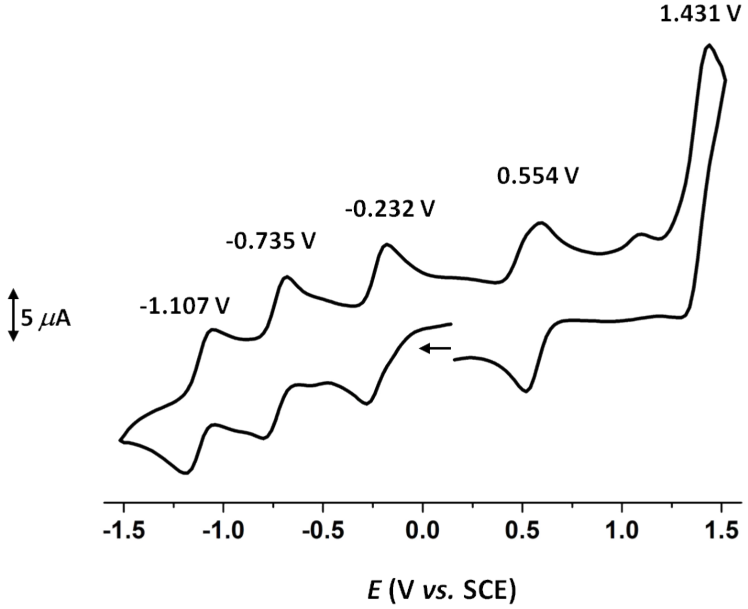

Figure S2. Cyclic voltammograms of 1mM **1** in argon-degassed dichloromethane containing 0.1 M $[Bu_4N]PF_6$ at 25 °C and recorded using a glassy carbon working electrode, a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

Bulk electrolysis for the preparation of the samples for EPR studies was performed in the same conditions as for cyclic voltammetry experiments except for the glassy carbon working electrode that was replaced by 5 mm^3 carbon foam with high effective surface (Alfa Aesar. carbon felt 99.0%). After each electrolysis, samples were transferred using a cannula under argon atmosphere into EPR tubes and then frozen immediately in a liquid nitrogen bath.

IV-Magnetic studies

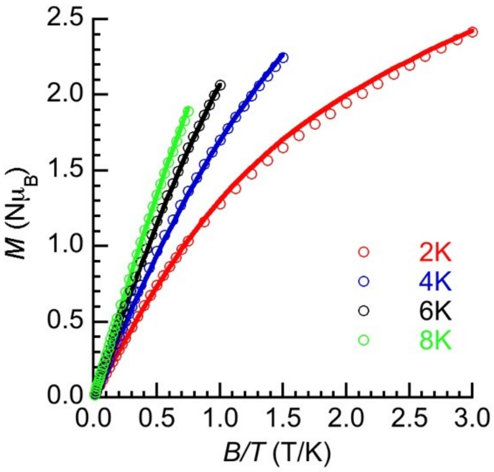

Figure S3. M = f(B/T) for **1**.

The magnetic data were fitted by fixing the rhombic parameters E for the three Ni^{II} to zero. Letting the E values free during the fitting procedure does not lead to a large change in the axial ZFS parameters D; the J values are also not very different. The best fit solution is not unique. Other solutions can be found by interchanging the J values; they however remain in the same range: one strongly antiferromagnetic, one weakly antiferromagnetic and weakly ferromagnetic.

V-Electron Paramagnetic Resonance

X-band EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with a Bruker ER 4116DM X band resonator, an Oxford Instrument continuous flow ESR 900 cryostat, and an Oxford ITC 503 temperature control system.

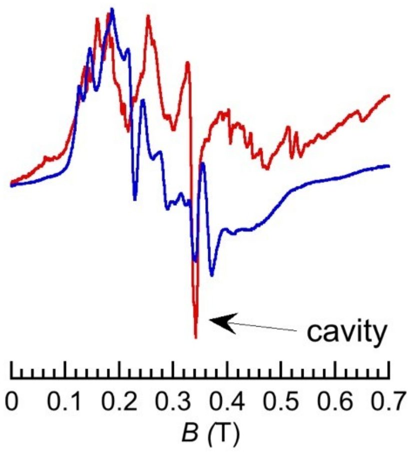

Figure S4. EPR spectra of **1** in dichloromethane solution (blue) and the solid state (red) at T = 5 K (Microwave power = 1 mW, modulation amplitude = 8 Gauss, gain = 50 db, temperature = 5 K).

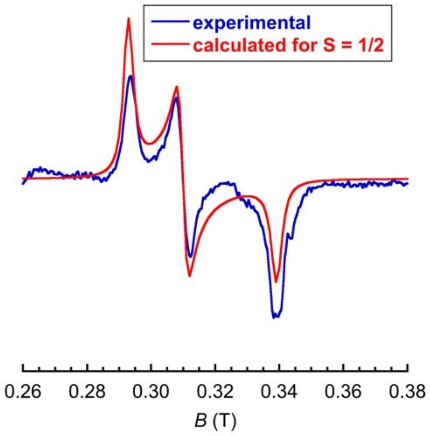

Figure S5. EPR spectra of the two-reduced species (blue) ((microwave power = 1 mW, modulation amplitude = 8 Gauss, gain = 50 db, temperature = 30 K) and simulation (red) considering S = ½ with the following g_{eff} values g_{xeff} = 2.3499, g_{yeff} = 2.2205, g_{xeff} = 2.0293