Electronic Supplementary Information

"The two spin states of an end-on copper(II)-superoxide mimic"

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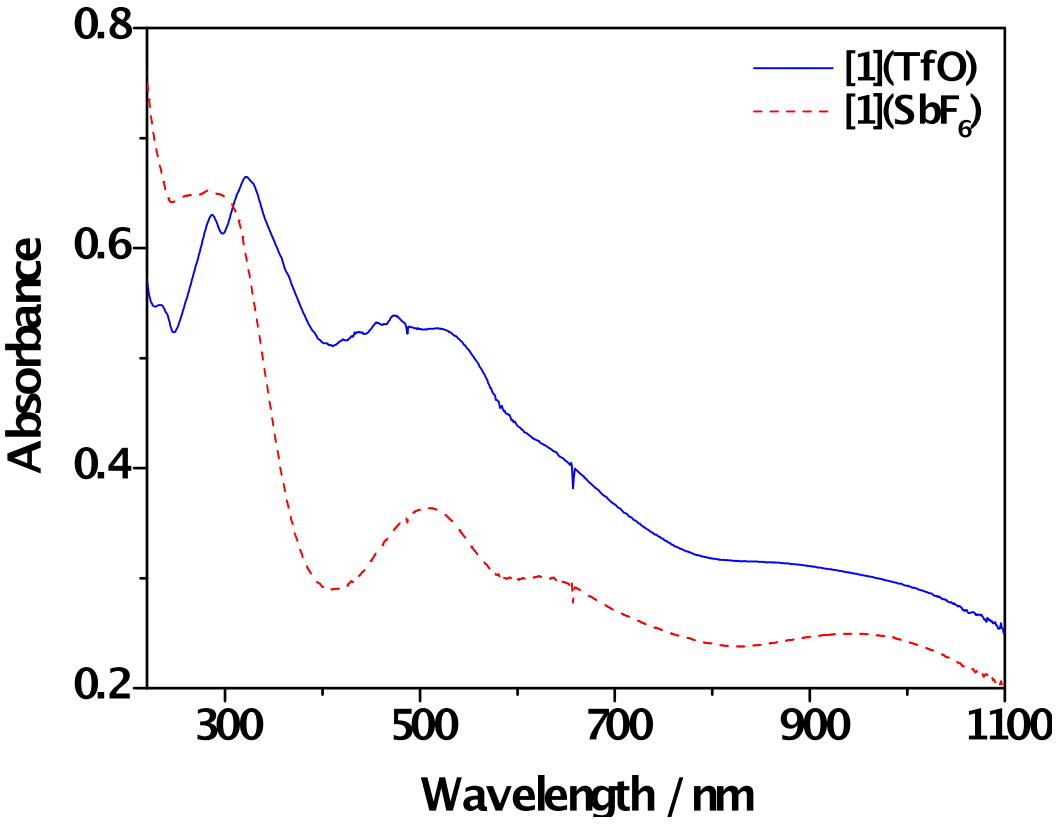
Experimental procedures

All the syntheses of the copper complexes were performed in a dry nitrogen filled glove-box (O_2 < 0.1 ppm, H_2O < 0.1 ppm). Solvents were dried by standard procedures, degassed, and stored over activated molecular sieves (4 Å) in the glove-box. The ligand Me_6tren was prepared following a literature procedure,[1] distilled over CaH_2 under vacuum, and stored under the inert atmosphere of the glove-box. The copper salts $[Cu(MeCN)_4](TfO)$ and $[Cu(MeCN)_4](SbF_6)$ were prepared according to the standard literature procedure using TfOH or $HSbF_6$ (Sigma-Aldrich).[2] Nitrosobenzene (Sigma-Aldrich) was stored in the glove-box at -30 °C.

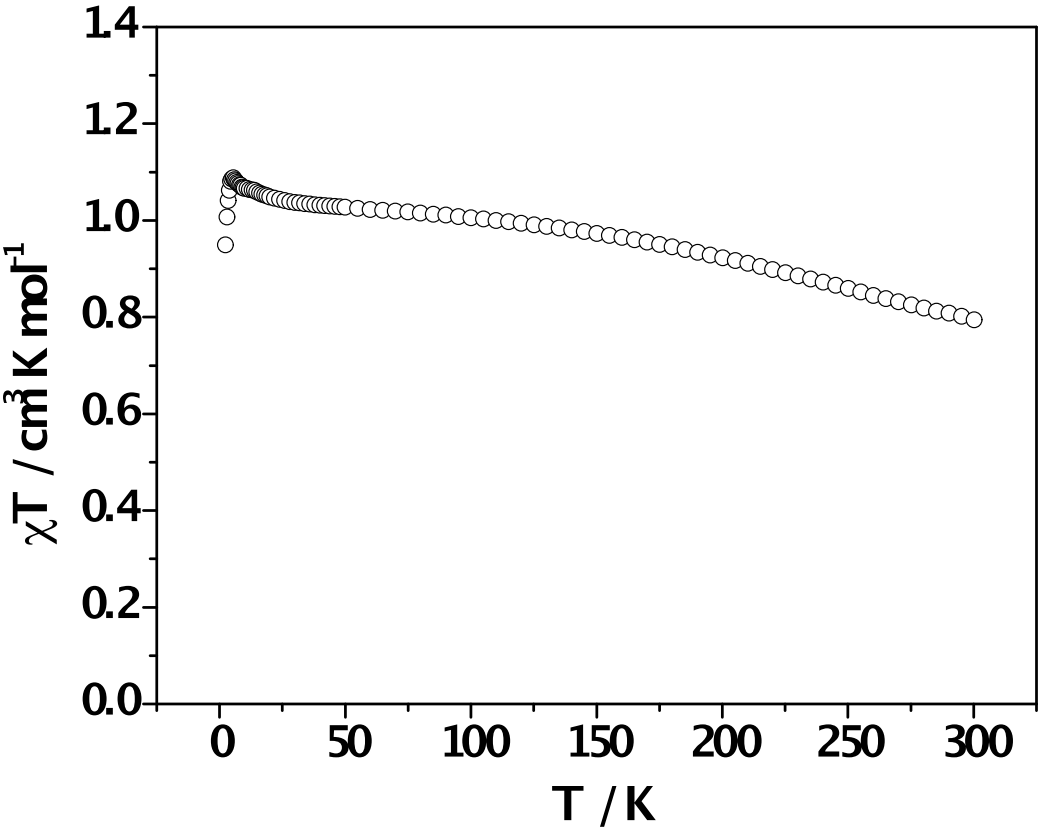
Solid State UV-Vis

UV-visible spectra were recorded on an Agilent 8453 spectrophotometer. The samples were prepared by grinding the compounds in Nujol and placing the suspension between two quartz disks.



Magnetic Behaviour of [1](TfO):

Variable temperature dc magnetic susceptibility measurements were performed on a 50 mg crushed crystalline sample in the temperature range of 2.5–300K and an applied dc field of 1000 Oe. The χT *vs*. *T* plot shown below indicates a room temperature value of 0.79 $cm^3 \cdot K \cdot mol^{-1}$ which is in good agreement with the value for two non-interacting S=1/2 spins (0.75 $cm^3 \cdot K \cdot mol^{-1}$). The χT product increases immediately upon decreasing the temperature indicating strong ferromagnetic coupling within the molecule.



Computational Details

The calculations were performed using the 6-31G(d) basis set and the BP86 functional[3-5] with the Gaussian-09 quantum chemistry package.[6] The crystal structure geometries were used as the initial coordinates for optimization. Atomic coordinates of the optimized geometries:

1. $[(Me_6tren)Cu(PhNO)]^+$, S=0

Atom	X	Y	Z
Cu	0.7142660	-0.0470230	-0.0764740
O	-0.9281390	-0.0755350	-1.0260120
N	-1.8375040	0.8438600	-0.8109080
N	1.3759630	-1.6342900	-1.3573900
N	0.1147930	-0.4457450	1.9089430
N	1.1565150	2.0746190	-0.6159380
N	2.6750100	-0.0424070	0.6324210
C	-3.1037080	0.3368950	-0.4704680
C	-4.0999330	1.3183380	-0.2230490
H	-3.8155530	2.3744690	-0.2838930
C	-5.4093280	0.9328210	0.0767460
H	-6.1735030	1.6943120	0.2648740
C	-5.7463520	-0.4323580	0.1322210
H	-6.7732210	-0.7348260	0.3624920
C	-4.7636480	-1.4127030	-0.1194550
H	-5.0356070	-2.4738040	-0.0891460
C	-3.4521770	-1.0404070	-0.4208660
H	-2.6869800	-1.7900810	-0.6424520
C	3.4919160	-0.9139710	-0.2626360
H	4.4016940	-1.2792290	0.2560320
H	3.8370660	-0.2985740	-1.1099830
C	2.6626010	-2.0975680	-0.7741060
H	3.2569610	-2.6853750	-1.5051620
H	2.4213970	-2.7814160	0.0598890
C	0.4219650	-2.7668730	-1.4693030
H	0.7929470	-3.5413300	-2.1719790
H	-0.5404680	-2.3743230	-1.8322430
H	0.2663500	-3.2273470	-0.4806310
C	1.5752710	-1.0872730	-2.7242280
H	1.9080850	-1.8767540	-3.4299690
H	2.3303900	-0.2852500	-2.7124820
H	0.6206420	-0.6630970	-3.0727600
C	3.1880490	1.3616210	0.6348470
H	4.2968850	1.3785750	0.6317440

H	2.8673400	1.8386860	1.5762210
C	2.6378770	2.1425050	-0.5627450
H	3.0011690	3.1919920	-0.5230100
H	3.0250300	1.7112890	-1.5037990
C	0.6792380	2.4506900	-1.9725470
H	0.9926650	3.4828230	-2.2364430
H	-0.4184950	2.3820430	-1.9852720
H	1.0879470	1.7536720	-2.7202800
C	0.5495580	3.0269450	0.3465440
H	0.7988440	4.0788940	0.0889990
H	0.9078280	2.8296220	1.3708440
H	-0.5436790	2.8946000	0.3170980
C	2.6085500	-0.5981720	2.0165120
H	3.4986160	-0.3053800	2.6099910
H	2.6263880	-1.6988020	1.9450750
C	1.3297080	-0.1336360	2.7191870
H	1.2643840	-0.5896740	3.7293840
H	1.3546520	0.9608070	2.8630830
C	-1.0264320	0.3668930	2.4110340
H	-1.2326690	0.1458840	3.4785050
H	-1.9222580	0.1396650	1.8162030
H	-0.8000430	1.4381230	2.3016330
C	-0.2517310	-1.8800370	2.0691460
H	-0.4946060	-2.1156620	3.1264040
H	0.5787180	-2.5268280	1.7453350
H	-1.1295000	-2.0942650	1.4406400

2. $[(Me_6tren)Cu(PhNO)]^+$, S=1

Atom	X	Y	Z
Cu	-0.7601130	0.0479100	-0.0253180
N	1.9015050	-0.4961240	-0.0769300
N	-0.7529120	-1.5453350	-1.4583200
N	-1.2373150	2.0870510	-0.6036500
N	-0.7952110	-0.5027720	2.0843930
N	-2.8035330	-0.2164060	0.0426530
O	1.0553200	0.5467850	-0.0540050
C	3.2420350	-0.1428690	-0.0464620
C	4.1761900	-1.2190870	-0.0794380
H	3.7936330	-2.2446540	-0.1275500
C	5.5470340	-0.9631940	-0.0511310
H	6.2550420	-1.7986200	-0.0776150

C	6.0233720	0.3618350	0.0111280
H	7.0999260	0.5593530	0.0332380
C	5.1066850	1.4312530	0.0448820
H	5.4758680	2.4620440	0.0935650
C	3.7309200	1.1944290	0.0171400
H	3.0182960	2.0230730	0.0443760
C	-3.4495880	0.9594780	-0.6211680
H	-3.4501770	0.7740400	-1.7081900
H	-4.5099580	1.0522000	-0.3117790
C	-2.6848640	2.2486470	-0.3065350
H	-3.1287980	3.0967050	-0.8690240
H	-2.7797610	2.4961200	0.7655560
C	-0.4427790	3.1211620	0.1072770
H	-0.6881630	4.1392230	-0.2582720
H	0.6250910	2.9155030	-0.0592380
H	-0.6428050	3.0716260	1.1886520
C	-0.9725220	2.2387350	-2.0582300
H	-1.2036180	3.2679840	-2.4035170
H	-1.5846010	1.5298270	-2.6386240
H	0.0901650	2.0214890	-2.2469570
C	-3.2056700	-0.3058580	1.4818900
H	-4.1980420	-0.7893090	1.5836760
H	-3.3115190	0.7225330	1.8647450
C	-2.1559710	-1.0653450	2.3003060
H	-2.4397140	-1.0524860	3.3738410
H	-2.1288740	-2.1260600	1.9941240
C	0.2378140	-1.4885160	2.4983430
H	0.1949780	-1.6777800	3.5906770
H	1.2316590	-1.1037280	2.2251710
H	0.0830940	-2.4380680	1.9642890
C	-0.5937860	0.7244090	2.8976290
H	-0.6155730	0.4952440	3.9834210
H	-1.3804510	1.4650160	2.6813490
H	0.3822520	1.1624290	2.6377530
C	-3.1188190	-1.4815850	-0.6929340
H	-4.1755070	-1.4906670	-1.0268630
H	-2.9991940	-2.3220150	0.0107770
C	-2.1746190	-1.6540000	-1.8874500
H	-2.3748180	-2.6226240	-2.3911980
H	-2.3588420	-0.8634690	-2.6371540
C	-0.2870190	-2.8213210	-0.8504390
H	-0.2703400	-3.6360770	-1.6037190
H	-0.9532940	-3.1221200	-0.0257400

H	0.7265800	-2.6541750	-0.4531540
C	0.1208350	-1.2677900	-2.6300890
H	0.0693830	-2.0930240	-3.3691150
H	1.1558440	-1.1601250	-2.2703160
H	-0.1902540	-0.3302810	-3.1162630

References

1. G. J. P. Britovsek, J. England and A. J. P. White, *Inorg. Chem.*, 2005, **44**, 8125-8134.
2. G. J. Kubas, *Inorg. Synth.*, 1990, **28**, 68-70.
3. A. D. Becke, *J. Chem. Phys.*, 1986, **84**, 4524-4529.
4. J. P. Perdew, Phys. Rev. B: Condens. Matter Mater. Phys., 1986, **33**, 8822.
5. J. P. Perdew, Phys. Rev. B: Condens. Matter Mater. Phys., 1986, **34**, 7406.
6. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.