Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Cu(II) Complex with Nitronyl Nitroxide Whose Paramagnetism is Suppressed by Temperature Decrease and/or Pressure Increase

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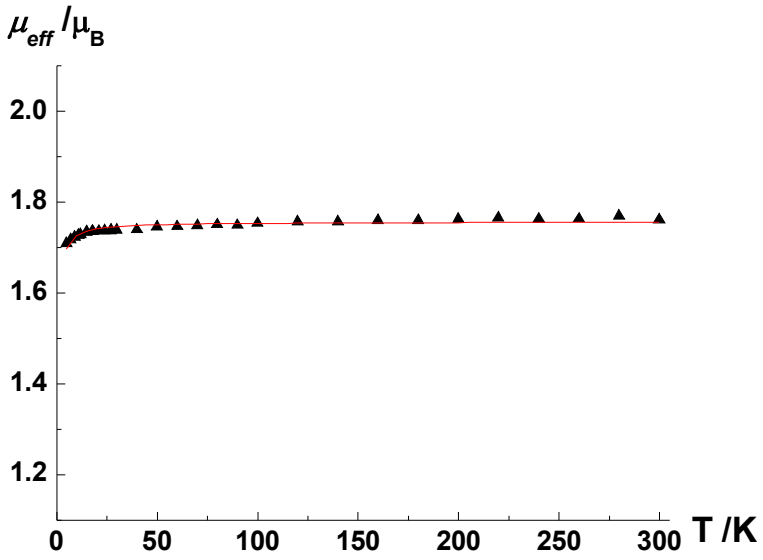

Fig. S1. Experimental dependences $\mu_{eff}(T)$ for the L^{Et}.

The μ_{eff} value for L^{Et} is 1.76 μ_B at 300 K (Fig. S1) and agrees good with theoretical spin-only value 1.73 μ_B for one paramagnetic center with spins S = 1/2 with g = 2. The μ_{eff} is practically constant in the temperature range 300-15 K, that points to absence of noticeable exchange interactions between spins of radicals. The Curie-Weiss law describes good the μ_{eff}(T) dependence with the best fit parameters C and Θ are 0.385 K·cm^3/mol and –0.4 K. The Curie constant C is in good agreement with theoretical spin-only one 0.375 K·cm^3/mol for monoradical. The small negative value of Weiss constant Θ points to a presence of very weak intermolecular exchange interactions antiferromagnetic in character.

Table S1. Experimental details, selected bond lengths (Å) and angles for L^{Et}, $[Cu(hfac)_2L^{Et}]$ "head-to-tail" and "head-to-head" modifications.

Parameter	L^{Et}	$[Cu(hfac)_2L^{Et}]$				
		"head-to-tail"				"head-to-head"
T, K	295	295	240	150	110	295
Space group, Z	$P2_1/c$, 8	$P2_1/n$, 4				P-1, 2
a, b, c, Å	18.0709(5) 11.8731(4) 16.6240(5)	13.113(6) 15.597(7) 16.766(8)	13.0582(5) 15.5436(5) 16.7528(6)	12.9049(6) 15.4562(7) 16.6873(8)	13.481(2) 14.380(2) 16.521(3)	11.4229(9) 11.4410(9) 14.0936(11)
α, ° β, ° γ, °	115.7250(10)	111.173(19)	111.039(3)	110.803(2)	111.680(7)	105.066(5) 95.834(5) 109.950(6)
V, Å^3	3213.29(17)	3198(3)	3173.7(2)	3111.5(3)	2976.1(8)	1634.7(2)
D_c, g cm^{-3}	1.254	1.622	1.635	1.667	1.743	1.587
μ/cm^{-1}	0.686	0.799	0.805	0.821	0.858	0.781
θ_{max}, deg.	66.987	28.334	28.17	28.155	27.194	28.008
I_{hkl} (meas/uniq) R_{int}	22304/5165 0.0267	20570/7920 0.0416	27859 /7691 0.0502	27313/7556 0.0421	15295/5608 0.1339	26753 / 7807 0.0539
I_{hkl} (I>2σ$_I$) / N	4232 / 471	43931/ 523	4955 / 523	5419 / 522	3007 / 469	2827 / 546
GooF	1.074	1.004	0.948	1.039	1.043	0.920
R_1 / wR_2 (I>2σ$_I$)	0.0554 / 0.1617	0.0495 / 0.1164	0.0414 / 0.1065	0.0408 / 0.1061	0.0680 / 0.1558	0.0549 / 0.1385
R_1 / wR_2 (all data)	0.0645 / 0.1710	0.1081 / 0.1391	0.0691 / 0.1164	0.0610 / 0.1130	0.1474 / 0.1989	0.1822 / 0.1855
Cu-O, Å		2.451(2)	2.4377(16)	2.4085(14)	2.002(4)	2.406(3)
Cu-O_{hfac}, Å		1.950(2), 1.953(2), 1.959(2), 1.955(2)	1.9563(16), 1.9574(14), 1.9605(15), 1.9611(15)	1.9540(14), 1.9600(14), 1.9606(14), 1.9634(14)	2.263(4), 1.985(4), 1.988(4), 2.213(4)	1.933(3), 1.963(3) 1.939(3), 1.951(3)
Cu-N, Å		2.333(2)	2.3254(18)	2.3194(17)	2.034(5)	2.523(4)
∠Cu-O-N, °		139.0(2)	138.56(14)	138.31(13)	128.6(3)	127.9(2)
N-O_{Cu}, Å		1.292(3)	1.291(2)	1.292(2)	1.308(6)	1.298(3)
N-O, Å	1.276(2)-1.284(2)	1.269(3)	1.270(2)	1.276(2)	1.280(6)	1.277(4)
∠{ONCNO}-Pz, °	2.7, 5.5	1.1	0.2	1.5	4.6	11.7
∠{N-Et}-Pz, °	86.3, 60.3	30.6	30.5	34.0	13.0	36.0

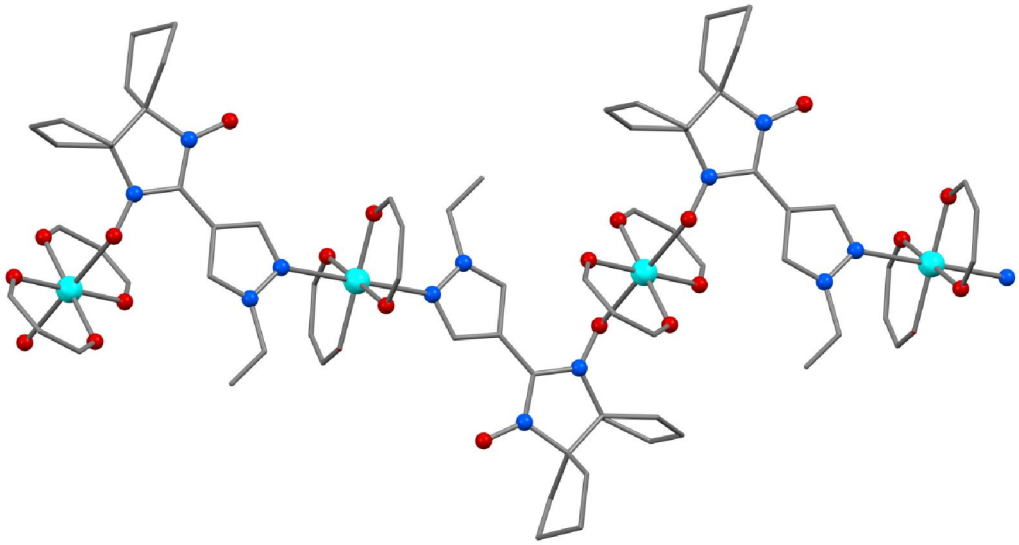

Fig. S2. Structure of [Cu(hfac)$_2$L^{Et}]-II "head-to-head" chain.

Applying external pressure leads pronounce color change of solid [Cu(hfac)$_2$L^{Et}]-I (Fig. S3). An increase in pressure of the polycrystalline sample of [Cu(hfac)$_2$L^{Et}]-I preliminarily placed into the diamond anvil pressure cell caused to a drastic change of its color from blue to dark brown. (See also corresponding figure in the graphical abstract).

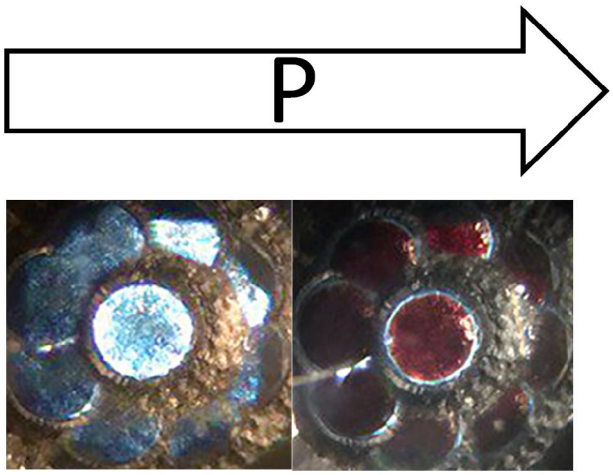

Fig. S3. Pressure induced color change of [Cu(hfac)$_2$L^{Et}]-I.