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Graphical Abstract

Ground triplet pyrimidine-4,6-diyl bis(*tert*-butyl nitroxide) as a paramagnetic building block for metal-organic frameworks

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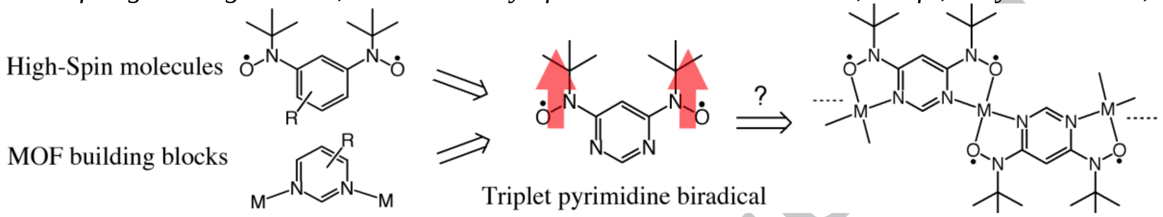

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Ground triplet pyrimidine-4,6-diyl bis(*tert*-butyl nitroxide) as a paramagnetic building block for metal-organic frameworks

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ABSTRACT

We synthesized pyrimidine-4,6-diyl bis(*tert*-butyl nitroxide) (pmbNO), and characterized as a biradical by means of ESR spectroscopy. The zero-field splitting parameters were $|D|/hc$ = 2.52×10^{-2} cm^{-1} and $|E|/hc$ = 2.34×10^{-3} cm^{-1} in frozen toluene at 100 K. Magnetic study clarified the presence of intramolecular ferromagnetic coupling with $2J/k_B$ = +18.5(5) K in frozen toluene-ethanol. DFT calculation supports the ground triplet state of pmbNO. The reaction of pmbNO with $Cu(hfac)_2$ gave $[Cu_3(pmbNO)_2(hfac)_4]$, and the structure was determined by X-ray crystallographic analysis. Though the ligand was reduced to be an anion radical, pmbNO is confirmed to work as a rigid bridge, and the nitroxide oxygen atoms can ligate the metal ions.

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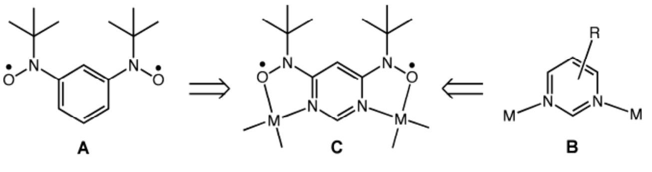
There have been numerous reports on ferromagnetic interactions in genuine organic radical compounds in pursuit of magnetism-based functional materials.[1] For further development of switching, sensing, memory, display and other devices, metal-organic solids are of increasing interest for high-T_C materials and multi-functionality.[2] As an available prescription for high-spin organic compounds, the *meta*-phenylene bridge is well-known to be a robust ferromagnetic coupler, as supported by the extensive studies on high-spin polycarbenes, -nitrenes, and -radicals[3] (including di- and trinitroxide radicals[4]). Spin-transition behavior in biphenyl-3,5-diyl bis(*tert*-butyl nitroxide) derivatives has been reported,[5] where a *meta*-phenylene-bridged biradical core is utilized as a stable triplet building block (Scheme 1, **A**).

Pyrimidines seem to be another promising candidate for a ferromagnetic coupler,[6] as expected from the analogy of *meta*-phenylenes and the spin-polarization mechanism.[3] Actually, pyrimidines have a highly directive nature of the coordination bonds (Scheme 1, **B**), attracting much attention to researchers in supramolecular chemistry including metal-organic frameworks (MOFs), porous materials[7] and molecular grids.[8] Though the role of couplers has been proven to depend on the coordination structures and the σ/π nature of the transition-metal spins,[9] there have been many reports where pyrimidines serve as a ferromagnetic coupler.[6,10]

Nitroxide groups can ligate various metal ions.[11] Combining the two above strategies (Scheme 1, **C**), now we propose a target compound, pyrimidine-4,6-diyl bis(*tert*-butyl nitroxide) ~~(abbrevia~~ted as pmbNO hereafter; see Scheme 2), as a potential paramagnetic building block for multifunctional materials in MOFs. Furthermore, pmbNO may afford strong exchange coupling at the metal-organic bond, because several Cu^{2+} and Ni^{2+} chelates with *tert*-butyl 2-pyridyl nitroxide derivatives showed strong metal-radical exchange interaction as large as the order of room temperature.[12,13] Thus, we have started the preparation and characterization of pmbNO and applied pmbNO to a prototype Cu-organic solid. The motivation of this study is to clarify (1) whether pmbNO possesses a ground high-spin state and (2) works as a rigid bridge.



Scheme 1. Molecular design strategy.

Before preparation of pmbNO, the molecular design should be assessed by the theoretical treatment. The ground spin-multiplicity of *meta*-phenylene-bridged oligo-/polyradicals can be predicted by several ways,[14,15] and the spin-polarization theory is the most versatile when the spin sources are diphenylcarbenes and triphenylmethyls.[3] The polarized spin densities on the carbon $2p_z$ orbitals are alternating in an up-down-up-down-… manner. However, in the present compound, the heteroatoms (nitrogen) are present at the spin center and in the aromatic ring, and the

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singly-occupied molecular orbitals (SOMOs) are somewhat perturbed from those of the hydrocarbons.

We performed the density-functional theory (DFT) molecular orbital (MO) calculation for pmbNO in Gaussian03.[16] The SCF energies of the singlet and triplet states were calculated at the UB3LYP/6-311+G(d,p)//UB3LYP/6-31G(d) level.[17] We obtained E_{BS} = –838.887669739 a.u. with $<S^2>_{BS}$ = 0.0692 and E_T = –838.888916939 a.u. with $<S^2>_T$ = 2.0005, where BS stands for the broken symmetry singlet state[18] and T for the triplet state. The spin density map of the singlet and triplet states is shown in Fig. 1, which approximately demonstrates the two SOMOs. The coupling parameter is estimated according to Yamaguchi's equation:[19] $J = (E_{BS} - E_T)/(<S^2>_T - <S^2>_{BS})$, thus giving $2J/k_B$ = +408 K for pmbNO; namely, the pmbNO is a ground triplet molecule. The optimized molecular structure was highly planar. It is well-known that the ferromagnetic coupling in such *meta*-phenylene biradicals is sensitively reduced upon the π-conjugation breakdown.[20] The calculated J value may be overestimated against the experimental results.

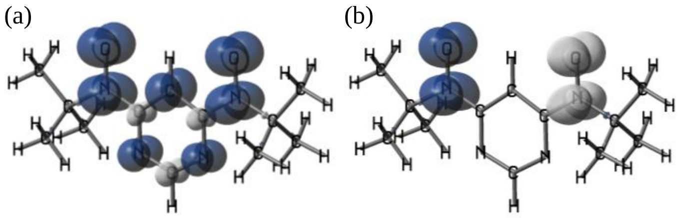
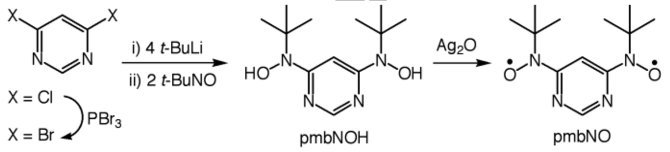


Figure 1. DFT calculation results of spin density for (a) the ground triplet and (b) the excited singlet pmbNO. Light and dark lobes stand for positive and negative spin densities, respectively.

When the radical centers are nitroxides, the spin is similarly polarized throughout the adjacent benzene ring, and the spin multiplicity can be qualitatively evaluated as if the N-O group were a methyl or carbene.[4,21,22] Several experiments support that the spin-polarization scheme is valid for pyridine and azaaromatics.[22,23] As Fig. 1a displays, the spin-polarization mechanism seems to hold also for the pyrimidine ring.



Scheme 2. Synthesis of pmbNO.

Synthetic route to pmbNO is shown in Scheme 2. A precursor 4,6-dibromopyrimidine was prepared according to the procedure reported by Schomaker and Delia,[24] and *N-tert*-butylhydroxylamino groups were introduced at the 4- and 6-positions by way of the conventional organolithium method,[13] giving pmbNOH.[25] The oxidation of pmbNOH in the presence of excess Ag_2O gave pmbNO as dark greenish brown oil.[26] Purification through column chromatography (silica or alumina) was unsuccessful. *tert*-Butyl pyridyl nitroxides are known to be unisolable,[12c,27] and it is acceptable that the isolation of pmbNO would be difficult.

The X-band ESR spectrum of pmbNO showed a broad line with $\Delta B_{p\text{-}p}$ = 2.4 mT (the peak-to-peak linewidth) at g = 2.0070 (in toluene at room temperature), being typical of exchange-coupled bisnitroxide compounds.[5] A fine structure was found in a frozen solution (Fig. 2). A half-field signal also appeared, which can be assigned to the transition of $|\Delta m_s| = 2$. The zero-field splitting parameters $|D|$ and $|E|$ were determined from simulation,[28] giving $|D|/hc = 2.52\times10^{-2}$ cm^{-1} and $|E|/hc = 2.34\times10^{-3}$ cm^{-1} with g_x = 2.0085, g_y = 2.0035, and g_z = 2.0059. The spin-spin distance is estimated to be r = 4.68 Å from the point-dipole approximation.[29] This distance suggests that the C(pyrimidine)–N(nitroxide) single bonds would have an anti,anti-configuration with respect to the pyrimidine N and nitroxide O atoms. It is supported by the geometry optimization in the MO calculation (Fig. 1).

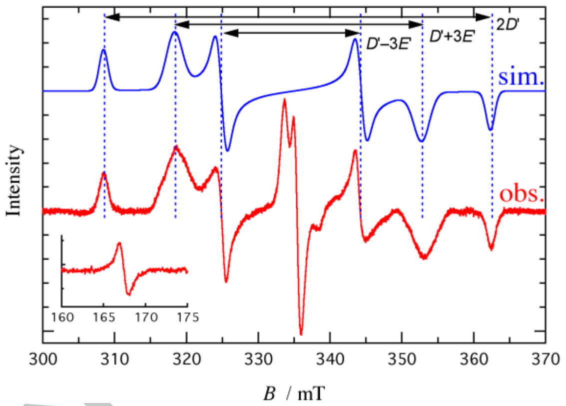


Figure 2. X-Band ESR spectra in a frozen solution of pmbNO (toluene, 100 K, c = ca. 5×10^{-4} mol/L). A central signal at 335 mT is attributed to doublet impurity. A simulated spectrum is also shown. Inset shows the half-field absorption.

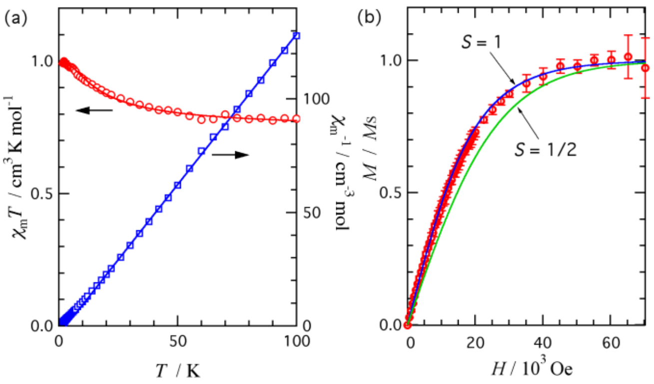


Figure 3. (a) Temperature-dependence of $\chi_m T$ at 5000 Oe and (b) field-dependence of magnetization at 1.8 K for pmbNO in a frozen solution of 1/1 toluene-ethanol. Solid lines are theoretical fits to the Bleaney-Bowers equation for $\chi_m T$ and the Curie-Weiss analysis for χ_m^{-1} in (a). Two solid lines stand for the Brillouin functions with S = 1/2 and 1 in (b). See the text for the equations and parameters.

The ground spin multiplicity of pmbNO was studied by means of magnetometry, but the intermolecular interaction disturbed the analysis of intramolecular one like other organic radical solids.[5,11e] To elucidate the ground spin state of an isolated pmbNO molecule, we measured the magnetic properties in a 1/1 toluene-ethanol solution on a SQUID magnetometer. The solution was diluted to be 5.0×10^{-3} mol/L. As Fig. 3a shows, the $\chi_m T$ value increased on cooling. The data were analyzed on the empirical Curie-Weiss equation ($\chi_m = C/(T - \theta)$; C and θ stand for the Curie and Weiss constants, respectively). Owing to the inaccuracy in sampling the diluted solution, the plots were normalized from a concentration scaling factor to fix C = 0.755 cm^3 K mol^{-1}, which is a theoretical value of two doublets with g = 2.007. Note that it hardly affects the estimation of the intramolecular exchange coupling.[30] The Weiss constant was

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optimized to be +2.8(1) K. The positive θ implies the presence of ferromagnetic coupling. The magnetic coupling parameter was estimated from the Bleaney-Bowers equation (Eq. 1)[31] based on the singlet-triplet model, where the energy gap is defined to be $2J$ (the spin-Hamiltonian $H = -2JS_1 \bullet S_2$). The parameter was optimized as $2J/k_B = +18.5(5)$ K with the triplet ground state. The calculated curve well reproduced the experimental data.

$$\chi_m = \frac{2N_A g^2 \mu_B^2}{k_B T}\frac{1}{3+\exp(-2J/k_B T)} \qquad \text{(Eq.1)}$$

Fig. 3b shows the magnetization curve. The data obeyed the $S = 1$ Brillouin function (Eq. 2)[32] rather than the two times $S = 1/2$ functions, indicating that the specimen practically is a triplet molecule at 1.8 K. This finding is consistent with the $\chi_m(T)$ result.

$$B_J(x) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{1}{2S}x\right) \qquad \text{(Eq.2)}$$

Finally, attempts to prepare various complexes using pmbNO are stated. We have eventually isolated a 2/3 copper-pmbNO adduct from the complexation with $[Cu(hfac)_2]$[26] (hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate). The X-ray crystallographic study clarified the formula of $[Cu_3(pmbNO)_2(hfac)_4]\bullet(C_6H_{14})_x$ (Fig. 4). Considerable disorder of crystal solvent molecules (hexane) gave an unsatisfactory final R factor (R_1 ($I>2\sigma(I)$) = 0.084) even at 90 K, but the molecular structure is unequivocally determined, where the pmbNO works as a bridging ligand. In contrast to the pristine pmbNO, the pmbNO moiety in the complex has a syn,syn-configuration owing to the five-membered chelate structure. The $Cu_3(pmbNO)_2$ core is highly planar. The oxygen atoms (O1 and O2) ligate the metal ions, and the pyrimidine ring plays the role of a μ_2-bridge having strongly 120°-directing nature, as expected from Scheme 1.

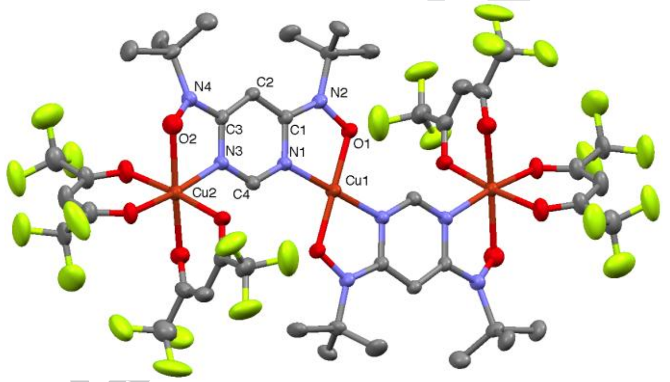

Figure 4. Molecular structure of $[Cu_3(pmbNO)_2(hfac)_4]$. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

The valence of the Cu ions is suggested to be +2 from the coordination structures (square plane on Cu1 and octahedron on Cu2), and that of the pmbNO moiety to be –1. The O1-N2 distance was 1.362(8) Å, much longer than the typical nitroxide O-N distances, 1.28–1.32 Å.[13a] On the other hand, the O2-N4 distance was 1.293(7) Å, which is normal for a nitroxide group. This finding indicates the localization of the spin and anion in $pmbNO^-$. Reduction mechanism of biradical pmbNO is unclear at present, but disproportionation of two radicals to a pair of reduced and oxidized forms in the presence of a catalytic acid is assumed.[33] The present complex can be regarded as a trapping product with a decomposed intermediate.[34]

In summary, we successfully prepared and characterized pmbNO. It is an oily product unfortunately, but the ESR and SQUID results afforded the evidence of a triplet biradical. The preliminary complexation gave $[Cu_3(pmbNO)_2(hfac)_4]$, where the oxygen atoms can ligate the metal ions and at the same time pyrimidine plays the role of a directive μ_2-bridge. Applying pmbNO as a building block to magnet-based functional materials and MOFs is feasible. However, it is also suggested that stabilizing substituents would be better introduced to pmbNO.

Acknowledgment

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Supplementary data

CCDC 927181 contains the supplementary crystallographic data for $[Cu_3(pmbNO)_2(hfac)_4]\bullet(C_6H_{14})_x$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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25. Preparation of pmbNOH. A hexane solution (25.4 mL; 1.58 mol/L) of *t*-BuLi (40.1 mmol) was dropwise to an ether solution (150 mL) containing 4,6-dibromopyrimidine (1.17 g; 10.0 mmol) by a syringe at –90 °C. The mixture was stirred at –90 °C for 1 h. Subsequently, an ether solution (50 mL) involving 2-methyl-2-nitrosopropane (2.10 g; 24.0 mmol) was added from a dropping funnel at –90 °C. The mixture was further stirred for 30 min. The mixture was gradually warmed up to –30 °C, quenched with excess aq. NH_4Cl, and neutralized with aq. $NaHCO_3$. After the organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure, the products were separated on a silica-gel chromatography eluted with 1/1 CH_2Cl_2-ether. Concentration of the eluent under reduced pressure gave pmbNOH as a colorless solid (0.498 g; 1.96 mmol; 20%). M.p. 156–160 °C (decomp.). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.99 (s, 2H), 8.12 (s, 1H), 6.71 (s, 1H), 1.39 (s, 18H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.0, 154.6, 92.0, 61.7, 28.3. MS (time-of-flight (TOF) with positive-mode electrospray ionization (ESI$^+$) in MeOH) *m*/z 277.18 [(M+Na)$^+$]. IR (neat, attenuated total reflection (ATR)) 506, 724, 853, 984, 1025, 1257, 1333, 1360, 1389, 1417, 1462, 1521, 1586, 2928, 2971, 3412 cm^{-1}. Anal. Calcd.: C, 56.67; H, 8.72; N, 22.03% for $C_{12}H_{22}N_4O_2$. Found: C, 56.57; H, 8.84; N, 21.92%.
26. Preparation of pmbNO and $[Cu_3(pmbNO)_2(hfac)_4]$. To a CH_2Cl_2 solution (20 mL) containing pmbNOH (25 mg; 0.10 mmol) was added excess Ag_2O (ca. 1 mmol) with being stirred at room temperature. The mixture was stirred for further 20 min. Filtration followed by concentration under reduced pressure gave an oily product (pmbNO). The IR spectrum supports the absence of the hydroxyl group. IR (neat, ATR) 729, 860, 985, 1191, 1223, 1246, 1344, 1365, 1444, 1481, 1555, 2935, 2984 cm^{-1}. The MS spectrum indicates the loss of two H atoms from the precursor. MS (ESI$^+$-TOF in MeOH) *m*/z 275.16 [(M+Na)$^+$]. At this stage pmbNO could be characterized by means of ESR spectroscopy and SQUID magnetometry (see the main text). The resultant pmbNO was dissolved again in CH_2Cl_2 (20 mL) and covered with a hexane solution (5 mL) of anhydrous $[Cu(hfac)_2]$ (95 mg). After slow diffusion of the solutions, reddish brown plates of $[Cu_3(pmbNO)_2(hfac)_4]\bullet(C_6H_{14})$ (10 mg; 12%) were grown and separated on a filter.
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30. The ESR results suggest that the specimen involves monoradical impurity, which may contribute to both $\chi_m(T)$ and $M(H)$. Fortunately, the quantitative analysis on the $\chi_m(T)$ experiment clarified that the pmbNO purity was high enough in this specimen, because the $\chi_m T$ value approached to 1.0 cm^3 K mol^{-1} on cooling, satisfying the theoretical triplet value expected. The saturation behavior in the $M(H)$ measurement indicates the low concentration of S = 1/2 impurity. In several measurements, the purity factor varied around 90% with sample dependence. The estimation of J may involve ≤4% error from this approximation.
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34. Polycrystalline $[Cu_3(pmbNO)_2(hfac)_4]\bullet(C_6H_{14})_x$ decayed under air owing to loss of the solvent molecules. Preliminary magnetic measurements on the powder specimen exhibited weak antiferromagnetic coupling, as indicated by θ = ca. –3 K.

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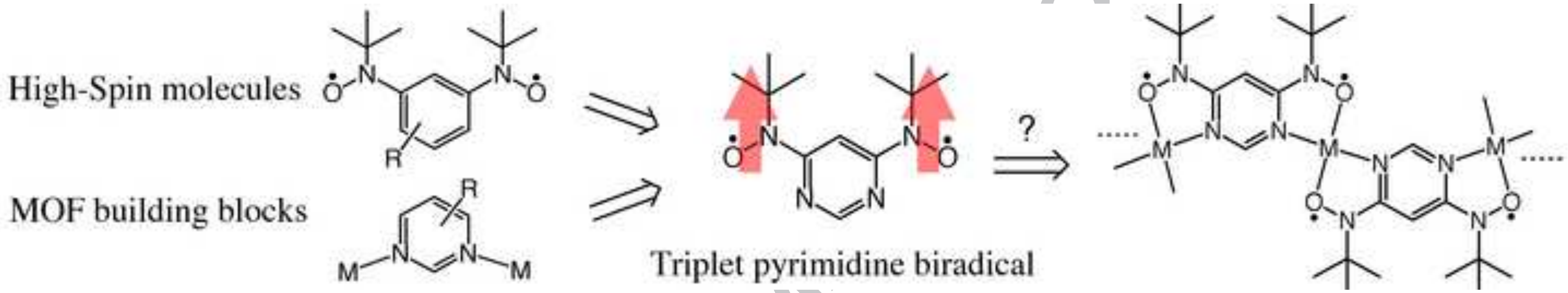

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