A triplet biradical with double bidentate sites based on tert-butyl pyridyl nitroxide as a candidate for strong ferromagnetic couplers

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journal or publication title	New Journal of Chemistry
volume	42
number	22
page range	17874-17878
year	2018
URL	http://id.nii.ac.jp/1438/00008824/

doi: 10.1039/C8NJ04180F

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LETTER

Triplet biradical with double bidentate sites based on *tert*-butyl pyridyl nitroxide as a candidate for strong ferromagnetic couplers

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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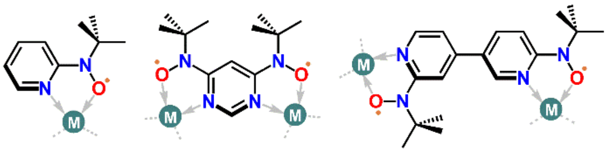
We synthesised a new biradical, 34bpybNO, having two chelating radical sites and demonstrated its crystal structure and ground triplet nature. Frozen-solution magnetic measurement and electron spin resonance results revealed a strong intramolecular ferromagnetic coupling reaching $2J/k_B$ = ~+170 K, which is supported by density functional theory calculations.

Stable organic radicals[1] have blossomed in the field of molecule-based magnets based on metal–radical approach[2] as well as spin labeling,[3] conductive materials,[4] and organic-based radical batteries.[5] In fact, two types of room-temperature magnets embracing organic radical parts have been reported: a TCNE−vanadium complex (TCNE = tetracyanoethylene) by Miller[6] and organic-acceptor–nickel compounds by Hicks[7]. However, materialising room-temperature molecular magnets is still arduous and challenging due to the difficulty of arranging strong magnetic couplings of adjacent spins over the whole compound. One of strategies to overcome such a problem is to develop new radical ligands to be a better magnetic coupler leading to strong exchange couplings comparable to a thermal energy of room temperature.

Among many biradicals (diradicals)[8] showing strong intramolecular ferromagnetic couplings (*e.g.*, $2J/k_B$ > 100 K), there are few successful reports on metal–radical complexes using strong ferromagnetic couplers: bis(nitroxide),[9] bis(dithiadiazolyl),[10] and bis(semiquinone)[11] biradicals. Therefore, it remains challenging to obtain new triplet ligands for affording metal–radical complexes. We have reported 2-pyridyl *tert*-butyl nitroxide (2pyNO in Chart 1) derivatives to show strong metal–radical exchange couplings on the order of room temperature or higher.[12] Thanks to the 5-membered chelation, most of dσ-type metal complexes using 2pyNO families show strong metal–radical couplings often with $2J/k_B$ ~300 K, where the nitroxide moiety and the chelate ring are in a good coplanarity.[13] We are now focusing on the development of multichelating multiradical ligands to act as both a strong magnetic coupler and a paramagnetic building block to metal–organic frameworks. A "*meta*"-pyrimidylidene-bridged biradical, pmbNO (Chart 1),[14] seemed to be also a strong ferromagnetic coupler analogous to *meta*-phenylene-bridged biradical cores developed according to the spin-polarization mechanism.[15] Unfortunately, a weak intramolecular coupling ($2J/k_B$ = +18.5(5) K) of pmbNO was observed in a diluted solution, although the calculated value of +408 K was expected from density functional theory (DFT) calculations.[14] The result is caused by a partial π-conjugation breakdown due to torsion between the pyrimidine ring and *tert*-butyl nitroxide groups.



2pyNO

pmbNO

34bpybNO

Chart 1 Structural formula of 2-pyridyl nitroxides.

As candidates of multichelating multiradical ligands, we have designed new radicals with a bipyridyl skeleton as shown in Fig. 1. They are expected to have the following advantages compared with pmbNO; (i) to become free from the congestion of sterically-hindered *tert*-butyl groups and (ii) to obtain a better stability of radical thanks to the extension of π-conjugated system. Before synthesis, DFT calculations were performed to predict a ground spin state of the three compounds: "*para–para*", "*meta–para*" and "*meta–meta*" bipyridyl-type biradicals (Fig. 1). Triplet and broken-symmetry singlet[16] SCF energies of a geometry-optimized s-*trans*–s-*trans* conformation structure were calculated at the UB3LYP/6–31G(d,p) level[17] in Gaussian 09[18]. The "*meta–para*" compound has the ground triplet state, where the energies of the singlet

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† Electronic Supplementary Information (ESI) available: experimental procedures of syntheses and DFT calculations, NMR spectra, DFT results, magnetic analyses, ESR and UV–vis spectra (Figs. S1–S16). CCDC 1844599. See DOI: 10.1039/x0xx00000x

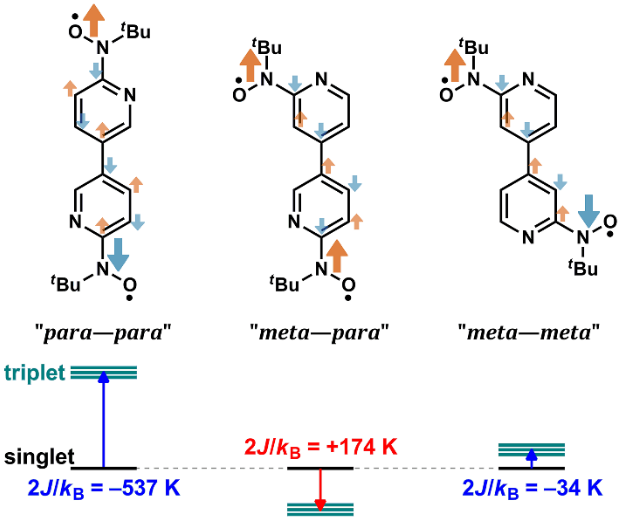
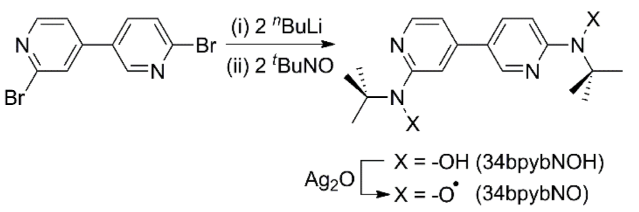


Fig. 1 Schematic presentation of bipyridyl-linked biradicals with the energy levels of their spin states. Arrows on each structural formula denote the spin-polarization mechanism. The singlet–triplet energy gaps are calculated from the DFT MO method (see the text).

and triplet states are E_{BS} = –1069.74554341 a.u. ($\langle S^2\rangle_{BS}$ = 0.1630) and E_T = –1069.74604935 a.u. ($\langle S^2\rangle_T$ = 2.0006), respectively. According to Yamaguchi's equation,[19] $J = (E_{BS} - E_T)/(\langle S^2\rangle_T - \langle S^2\rangle_{BS})$, the exchange coupling parameter (triplet–singlet energy gap) was estimated as $2J_{calc}/k_B$ = +174 K (defined as $H = -2JS_1{\cdot}S_2$). The "*para–para*" and "*meta–meta*" radicals have a ground singlet state (Figs. S6 and S8, ESI†), which therefore are undesired for the present project. Note that the intramolecular coupling of a similar "*meta–meta*" biradical, 2,2'-bipyridyl 6,6'-bis(*tert*-butyl nitroxide), has already reported as $2J/k_B$ = –56(2) K.[20] The DFT-estimated J values for the three candidates are comparable with the experimental results of analogous biphenyl-linked bi- or tri-radicals.[9a,21] Thus, the spin-polarization mechanism (denoted with arrows in Fig. 1) originally developed in hydrocarbon systems also holds for pyridine-containing systems.

Taking into account the DFT results, we focused on preparing a "*meta–para*"-type biradical, 3,4'-bipyridine-6,2'-diyl bis(*tert*-butyl nitroxide) (= 34bpybNO), as shown in Chart 1. The precursor 34bpybNOH was prepared according to a conventional reaction of 2-methyl-2-nitrosopropane with 6,2'-dilithio-3,4'-bipyridyl derived from 6,2'-dibromo-3,4'-bipyridyl[22] (Scheme 1). We found that the yield of the dibromo precursor was improved (41%) by modifying the literature method,[22] where 2-bromo-4-iodopyridine was used as a starting material in place of 2,4-dibromopyridine (see the ESI†). The 34bpybNO biradical was achieved by oxidising the hydroxylamine with excess Ag_2O. Dark red crystals suitable to X-ray structural analysis were isolated by recrystallising from *n*-hexane after purifying through silica-gel column chromatography. The biradical is stable in solution (Figs. S15 and S16, ESI) as well as in crystal at least for a month when stored under ambient conditions, while some 2-pyridyl *tert*-butyl nitroxides are oil and rather unstable.[12b,14]



Scheme 1 Synthesis of 34bpybNO.

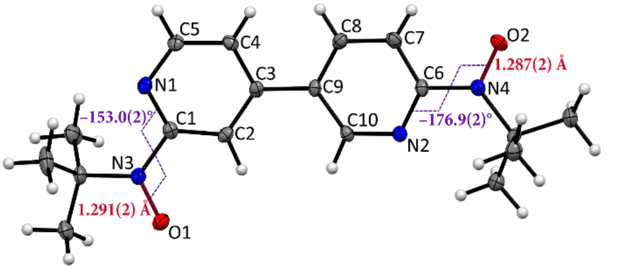


Fig. 2 Molecular structure of 34bpybNO with thermal ellipsoids drawn at the 50% probability. Selected geometrical parameters are: O1–N3, 1.291(2) Å; O2–N4, 1.287(2) Å; O1–N3–C1–N1, –153.0(2)°; O2–N4–C6–N2, –176.9(2)°

The crystal structure of 34bpybNO is shown in Fig. 2.[23] The N–O bond lengths are 1.291(2) and 1.287(2) Å, which are compatible with the values reported for neutral nitroxide groups (1.28–1.32 Å).[12] The distances are apparently shorter than the corresponding bond lengths of hydroxylamines (*ca.* 1.43 Å).[24,25] Both the nitroxide groups adopt the s-*trans* conformation against the pyridine C–N bonds. Note that the C_{py}–N_{rad} bonds can rotate on the occasion of a complexation with metal ions. Compared to the 3-pyridyl moiety, nitroxide on the 4-pyridyl moiety is rather twisted with the torsion angle (O1–N3–C1–N1) of –153.0(2)°.

The ground triplet state of 34bpybNO in the crystal was estimated by using DFT calculations. The SCF energies with the geometry frozen were calculated to give E_{BS} = –1069.51259174 a.u. ($\langle S^2\rangle_{BS}$ = 0.1226) and E_T = –1069.51287112 a.u. ($\langle S^2\rangle_T$ = 2.0003). The exchange coupling parameter was estimated as $2J_{calc}/k_B$ = +94.0 K for the biradical spins in 34bpybNO. The obtained value is somewhat smaller than that of 34bpybNO after the geometrical optimization. The difference is due to N_{py}–C_{py}–N_{rad}–O_{rad} torsion angles, which are given as 178.4 and –179.7° for the 4-pyridyl and 3-pyridyl moieties (Table 1), respectively, related to overlapping between the nitroxide π* and pyridine π orbitals. More coplanar structure of nitroxide–bipyridyl backbone affords a good extended spin orbital on the whole molecule, leading to a large J value.

Magnetic measurements were performed for a crystalline specimen of 34bpybNO on a SQUID magnetometer. The temperature dependence of $\chi_{mol}T$ is shown in Fig. 3a. The $\chi_{mol}T$ value (per biradical molecule) at 300 K is 0.743 cm^3 K mol^{-1},

Table 1 Intramolecular exchange couplings of biradical and torsion angles between nitroxide and pyridine moieties

	$2J_{\mathrm{exp}}\,k_{\mathrm{B}}^{-1}$ (K)	$2J_{\mathrm{calc}}\,k_{\mathrm{B}}^{-1}$ (K)	O1–N3–C1–N1 (°)	O2–N4–C6–N2 (°)
In crystal	+101(10)	+94	−153.02(2)	−176.9(2)
In solution	+166(3)	+174[a]	+178.4[a]	−179.7[a]

[a] The DFT calculation values for the optimized structure as an isolated system in vacuum.

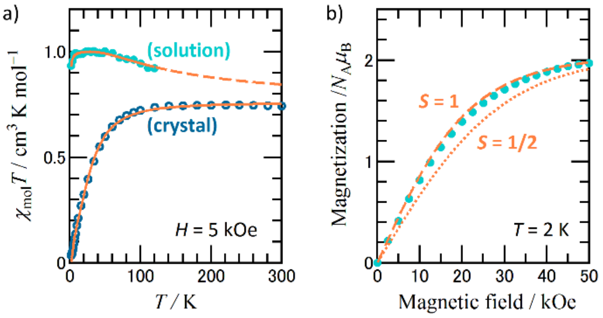


Figure 3 (a) Temperature dependence of $\chi_{\mathrm{mol}}T$ at 5 kOe for 34bpybNO in a crystalline solid state (open circles) and in a frozen solution (filled circles) of 1/1 toluene-methanol. Solid lines stand for the theoretical curves with the parameters estimated (see the text). (b) Field dependence of magnetization (open squares) at 2 K for 34bpybNO in a frozen solution of 1/1 toluene-methanol. Dotted and dashed lines stand for the theoretical curves of the Brillouin functions with S = 1/2 and 1, respectively.

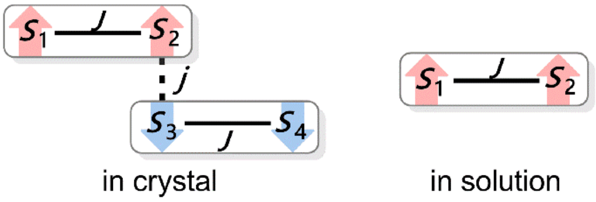


Figure 4 Exchange coupling models applied in magnetic analyses of 34bpybNO in crystal (left) and in solution (right). The ground spin states are drawn with arrows.

being approximately equal to the spin-only value of 0.75 cm^3 K mol^{-1} for two S = 1/2 spins. This result guarantees the purity (> 98%) as a biradical. On cooling, the $\chi_{\mathrm{mol}}T$ value monotonically decreased down to almost zero at 2 K, indicating a dominant antiferromagnetic interaction. The intermolecular exchange coupling is expected to be originated in a π–π dimer contacting between respective C2 and C4 pairs (C2···C4 distance: 3.416(3) Å) with large spin densities, which is in accordance with the McConnell I mechanism[26,27] and is supported by DFT results. Although there are some intermolecular contacts shorter than the sum of van der Waals radii, they are less likely to serve principal pathways, considering its small overlap of singly-occupied molecular orbitals (see the ESI for details).

The magnetic analysis was performed using a four-spin model,[28,29] $H = -2J(S_1 \cdot S_2 + S_3 \cdot S_4) - 2jS_2 \cdot S_3$ (Fig. 4), with respect to the dimerised biradical structure. The curve fittings to the experimental data yield $2J/k_{\mathrm{B}}$ = +101(10) K, $2j/k_{\mathrm{B}}$ = −84(5) K, and θ = −4.4(8) K with the fixed g value of 2.0059 (from the ESR result, see below), where θ is a Weiss mean field parameter as an interdimer magnetic interaction.[29] The exchange coupling values, 2J and 2j, are in good agreement with the values (+94.0 and −43.0 K) from the DFT calculations. With a similar biradical disposition, tris(*tert*-butyl nitroxide) radical containing the cross-linker of the biphenyl-3,4′-diyl moiety were reported.[9a,21a] The exchange coupling between the nitroxide radical spins through the 3,4′-biphenyl linker was estimated as +67(5) K. This value is comparable with that of the present work.

To unveil further the intrinsic ground triplet state of 34bpybNO, we performed magnetic measurement in a frozen MeOH/toluene (1:1) solution (*ca.* 13 mM) from 2 to 120 K at 5 reached the spin-only value expected for S = 1 (1.0 cm^3 K mol^{-1}) kOe. On cooling, the $\chi_{\mathrm{mol}}T$ value gradually increased and then around 50 K, which is apparent evidence for the presence of an intramolecular ferromagnetic coupling. Magnetic properties were analysed by using the Bleaney–Bowers equation, $\chi_{\mathrm{mol}} = 2N_{\mathrm{A}}g^2\mu_{\mathrm{B}}^2/[k_{\mathrm{B}}(T - \theta)\cdot\{3 + \exp(-2J/k_{\mathrm{B}}T)\}]$, for the singlet–triplet model,[30] where a Weiss temperature θ is introduced as a mean-field intermolecular interaction. The parameters were successfully optimized as $2J/k_{\mathrm{B}}$ = +166(3) K and θ = −0.166(8) K using the g value of 2.0059 determined by electron spin resonance (ESR) spectroscopy. The optimized value is excellently consistent with the DFT results. The decrement around the lowest temperature is attributable to a weak dipole–dipole antiferromagnetic interaction. Figure 3b shows the magnetization curve at 2 K for the frozen solution. The obtained data is closely superimposed on the Brillouin function, $B_S(H)$, for S = 1, where $B_S(H) = A\coth(Ax) - B\coth(Bx)$, $A = (2S + 1)/(2S)$, $B = 1/(2S)$ and $x = gS\mu_{\mathrm{B}}H/k_{\mathrm{B}}T$. The result reflects the ground triplet nature of 34bpybNO.

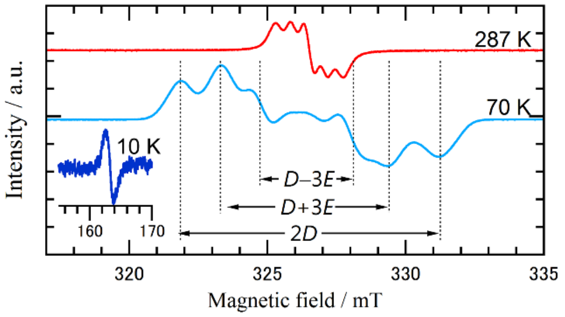


Figure 5 X-band ESR spectra of 34bpybNO in a frozen MeOH/toluene solution (*ca.* 1 × 10^{-4} M) at 287 and 70 K. Widths denoted by an arrow indicate the splits of a fine structure derived mainly from zero-field splitting. Inset shows the half-field absorption at 10 K.

Such a triplet nature can be confirmed by means of the X-band ESR measurements for a degassed toluene solution. As shown in Fig. 5, ESR spectra at 287 K showed an unresolved hyperfine splitting at g = 2.0059 even in a dilute (*ca.* 1 × 10^{-4} M) and deaerated solution. This broadening is derived from an intramolecular exchange coupling among the unpaired electrons, which is typical behaviour for bis(nitroxide) compounds.[31] At 70 K, a fine structure of the triplet state was observed. The zero-field splitting (ZFS) parameters were estimated as $|D|/g\mu_{\mathrm{B}}$ = 4.7 mT and $|E|/g\mu_{\mathrm{B}}$ = 0.44 mT. From the point-dipole approximation,[32] the spin–spin distance is estimated to be 8.4 Å, which is almost consistent with the optimized geometry of 34bpybNO in the DFT calculation (*cf.*, the distance of intramolecular N_{rad}–N_{rad} is 8.69 Å). Furthermore, we found a weak half-field signal assigned to the forbidden transition of $|\Delta m_S| = 2$. The signal gradually intensified with decreasing temperature (Fig. S13, ESI). The temperature dependence of the forbidden transition band clearly indicates the ground triplet state of 34bpybNO.

In summary, we succeeded in preparing a new nitroxide-based biradical having double bidentate chelating sites. The DFT calculations suggest that exchange couplings between two nitroxide spins strongly depend on the positions of radical moieties on the bipyridyl skeleton, and only the "*meta–para*" isomer was expected to have a strong ferromagnetic coupling. Actually, the ground triplet state of 34bpybNO was elucidated by SQUID and ESR results, supported by DFT calculations, where the $2J/k_B$ value reaches 170 K. This study provides a clear guideline for molecular designing of metal–biradical complexes towards high-temperature magnets. Although the exchange coupling between the radical spins correlates with the O_{NO}–N_{NO}–C_{2py}–N_{2py} torsion angles, chelating with a metal ion often improves a planarity of nitroxide–pyridine conjugation.[13a] Complexation with magnetic metal ions using the present ligand is in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank Dr. S. Takizawa and Prof. S. Murata (The University of Tokyo) for their support on UV–vis spectroscopy. This work was financially supported by JSPS KAKENHI Grant Numbers JP15K17841 and JP18K05057, and the research grant of Japan Association for Chemical Innovation.

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