

# Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Designed room-temperature triplet ligand from pyridine-2,6-diyl bis(*tert*-butyl nitroxide)

Hinako Kawakami, Asato Tonegawa, Takayuki Ishida\*

Received (in XXX, XXX) Xth XXXXXXXX 201X, Accepted Xth XXXXXXXX 201X

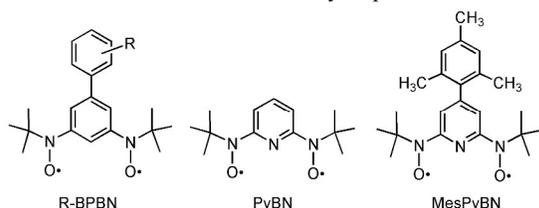
First published on the web Xth XXXXXXXX 201X

DOI: 10.1039/b000000x

The magnetic study on newly developed 4-mesitylpyridine-2,6-diyl bis(*tert*-butyl nitroxide) shows that almost all population has a ground triplet state at room temperature, and the ability of complex formation as a tridentate triplet ligand was proven with a diamagnetic yttrium(III) ion.

The metal-radical approach has intensively been applied to development of molecular magnets.<sup>1</sup> Various 2-pyridyl-based paramagnetic ligands containing nitronyl and imino nitroxides,<sup>2</sup> verdazyl,<sup>3</sup> thiazyls,<sup>4</sup> and oxazolidinoyl<sup>5</sup> groups have been available to construct chelate rings where a radical centre directly participates in coordination bonds. We have proposed 2-azaaromatic *tert*-butyl nitroxide family as a promising building block for paramagnetic chelates, because the localized electron spin at a nitroxide group leads to strong magnetic coupling.<sup>6</sup> Recent challenges involve rare-earth metal complexes.<sup>7</sup> Magnetic interaction is proportional to the magnitude of the spin, but the ligands are always only doublet at room temperature. This work presents a stable triplet ligand with a practically 100% population at room temperature and may open a new high-spin molecule science toward electro- and spintronics operative at ambient conditions.

As for the ligand design, the nitroxide chromophore is suitable for intra-ligand magnetic coupling; namely, the low-lying ferromagnetic state has been well established in many *m*-phenylene-bridged biradicals.<sup>8</sup> For an instance, the **BPBN** family (Scheme 1) can afford room-temperature triplet materials, owing to the intramolecular exchange coupling of the order of >300 K.<sup>9</sup> It seems to be quite natural for us to design **PyBN** as a tridentate ligand. However, heteroatom effects from a pyridine group instead of a benzene ring on the ground state multiplicity have not yet been understood well. Furthermore, heteroaromatic rings are known to have a weaker stabilizing effect than a phenyl ring,<sup>11</sup> and actually the preparation of the mother **PyBN** skeleton was unsuccessful.<sup>12</sup> Peripheral bulky substituents would stabilize **PyBN**.<sup>9,13</sup> We moved to synthesize **MesPyBN**, which possess a mesityl group at the pyridine ring at the 4-position. Eventually, this derivatization was found to drastically improve the stability.



Scheme 1. Structural formulas.

Furthermore, complex formation with tridentate **MesPyBN** and a diamagnetic yttrium(III) ion was successful.

Precursory 4-mesityl-2,6-dibromopyridine was prepared from 2,6-dibromo-4-iodopyridine<sup>14</sup> and mesityl boronic acid by the Suzuki coupling reaction.<sup>15</sup> The bromine atoms were substituted with *N-tert*-butylhydroxylamino groups by conventional organolithium method.<sup>6,9</sup> The oxidation of the above bishydroxylamine with excess Ag<sub>2</sub>O gave **MesPyBN** as a red crystalline product.† The product could be purified by passing through a basic-alumina short column followed by recrystallization from hexane. The crystalline solid can be stored in a refrigerator under nitrogen for at least two years. The X-band EPR spectra of **MesPyBN** showed a broad single line with  $\Delta B_{pp} = \text{ca. } 1.8 \text{ mT}$  at  $g = 2.0058$  (in toluene, room temperature), being typical of strongly exchange-coupled bisnitroxides.<sup>9</sup>

The molecular structures of **MesPyBN** was confirmed by means of X-ray crystallographic analysis (Table 1).‡ The N1-O1 and N2-O2 distances are 1.289(3) and 1.286(3) Å, respectively (Fig. 1a), supporting the absence of any charge in the N-O group.<sup>6b</sup> The molecules exhibit an almost planar Py(NO•)<sub>2</sub> skeleton and all *anti* configurations with respect to the py-N(O) bonds. The two aromatic rings are considerably twisted by the dihedral angles of 58.7(1)°.

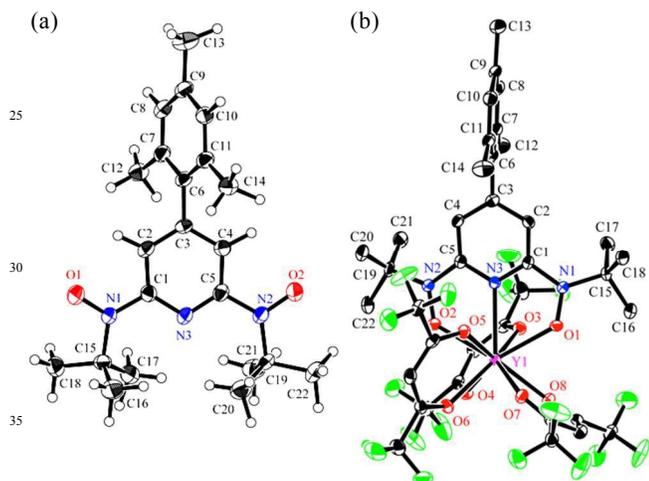
Table 1. Selected crystallographic data for **MesPyBN** and **Y-MesPyBN**.

	<b>MesPyBN</b>	<b>Y-MesPyBN</b>
Chemical Formula	C <sub>22</sub> H <sub>31</sub> N <sub>3</sub> O <sub>2</sub>	C <sub>37</sub> H <sub>34</sub> F <sub>18</sub> N <sub>3</sub> O <sub>8</sub> Y
Formula Weight	369.51	1079.57
Crystal Habit	red platelet	orange block
Crystal System	monoclinic	monoclinic
Space Group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / Å	10.089(6)	11.7495(9)
<i>b</i> / Å	9.896(5)	29.1245(18)
<i>c</i> / Å	21.005(13)	12.9481(10)
$\beta$ / deg	97.91(5)	91.279(5)
<i>V</i> / Å <sup>3</sup>	2077(2)	4429.7(6)
<i>Z</i>	4	4
<i>d</i> <sub>calc</sub> / g cm <sup>-3</sup>	1.181	1.619
$\mu$ (MoK $\alpha$ ) / mm <sup>-1</sup>	0.076	1.446
Unique data	4451	10146
<i>R</i> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0510	0.0515
<i>R</i> <sub>w</sub> <sup>b</sup> (all)	0.0483	0.0629
Goodness-of-fit	0.948	1.063
<i>T</i> / K	90	100

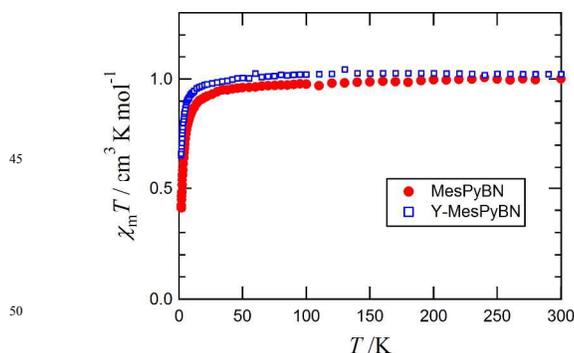
$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

The ground spin state of **MesPyBN** was studied using a SQUID magnetometer. As Fig. 2 shows, the  $\chi_m T$  value increased on elevating temperature and reached a plateau. The spin-only  $\chi_m T$  value for triplet species is  $1.0 \text{ cm}^3 \text{ K mol}^{-1}$  (i.e., the Curie constant,  $C$ ) and that of two doublets is  $0.75 \text{ cm}^3 \text{ K mol}^{-1}$ . The observed  $\chi_m T$  values at 300 K were  $1.00 \text{ cm}^3 \text{ K mol}^{-1}$ . This  $\chi_m T$  profile implies that almost all population have a ground triplet state at room temperature. The Curie-Weiss analysis ( $\chi_m = C/(T - \theta)$ ) gave  $C = 1.006(1) \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -2.2(1) \text{ K}$  for **MesPyBN**. The ground high-spin state is rationally explained in terms of spin-polarization,<sup>16</sup> which fortunately holds for azaaromatic systems as well as hydrocarbon aromatics.<sup>10,13,17</sup>

From the crystallographic study of **MesPyBN**, the nearest intermolecular radical-radical distance is  $4.766(5) \text{ \AA}$  ( $\text{N1} \cdots \text{N2}^i$  and  $\text{N2} \cdots \text{N1}^i$ ) in an antiparallel positioned dimer (the symmetry operation code of  $i$ :  $-x+1, -y, -z+1$ ). This geometry seems to be responsible for the intermolecular antiferromagnetic coupling, as indicated with the  $\chi_m T$  drop in a low temperature region and negative Weiss temperature ( $\theta$ ).



**Fig. 1.** X-Ray crystal structures of (a) **MesPyBN** and (b) **Y-MesPyBN**. Thermal ellipsoids are drawn at the 50% probability level for non-hydrogen atoms. The hydrogen atoms were omitted in (b).



**Fig. 2.** Temperature-dependence of the product  $\chi_m T$  of **MesPyBN** and **Y-MesPyBN** measured at 5000 Oe.

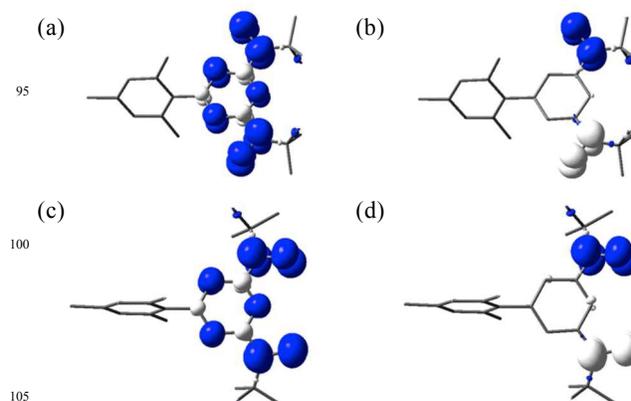
We found that complexation of **MesPyBN** and  $\text{Y}(\text{hfac})_3$  gave a well-shaped crystalline product,  $[\text{Y}(\text{hfac})_3(\text{MesPyBN})]$  (**Y-MesPyBN**),<sup>†</sup> where  $\text{Y}(\text{hfac})_3$  stands for 1,1,1,5,5,5-hexafluoropentane-2,4-dione. The molecular structure was

characterized by means of crystallographic study (Table 1).<sup>‡</sup> The coordination sphere belongs to a capped square antiprism with the pyridine N atom as a cap (Fig. 1b). The conformations around the  $\text{Py-N}(\text{O})$  bonds are changed to *syn* to form five-membered chelate rings. The  $\text{Y1-O1}$  and  $\text{Y1-O2}$  distances are  $2.3937(18)$  and  $2.4249(18) \text{ \AA}$ , respectively. The two aromatic rings are twisted by  $82.6(1)^\circ$ .

As Fig. 2 shows, the  $\chi_m T$  value of **Y-MesPyBN** increased on elevating temperature. The  $\text{Y}^{3+}$  ion is diamagnetic, so that the magnetic properties should be attributed to the organic magnetism. The observed  $\chi_m T$  value is  $1.02 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K. The Curie-Weiss analysis gave  $C = 1.028(1) \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -0.92(8) \text{ K}$ . The ground triplet state maintained, and furthermore the ferromagnetic exchange interaction was still as large as the order of 300 K after the complexation.

The shortest intermolecular distance in the crystal of **Y-MesPyBN** is found to be  $3.468(4) \text{ \AA}$  between  $\text{C9} \cdots \text{C9}^{\text{ii}}$  (the symmetry operation code of  $\text{ii}$ :  $-x+1, -y, -z$ ). The mesityl groups are arranged parallel with an inversion symmetry, and considerably short interplanar separation is given. Though the distance is short, the very small spin density at  $\text{C9}$  (see below) leads to intermolecular interaction as weak as  $\theta = -0.92(8) \text{ K}$ .

Density functional theory (DFT) MO calculation was performed. The SCF energies of the singlet and triplet states were calculated at the UB3LYP/6-311+G(2d,p) level<sup>18</sup> in Gaussian03.<sup>19</sup> The geometry was frozen as determined by the crystallography. The triplet state was found to be ground for **MesPyBN** (Figs. 3a and 3b), and the spin-polarization is realized in the spin density surface on the triplet state. The exchange parameter was calculated according to Yamaguchi's equation,  $J = (E_{\text{BS}} - E_{\text{T}})/(\langle S^2 \rangle_{\text{T}} - \langle S^2 \rangle_{\text{BS}})$ ,<sup>20</sup> with the spin-Hamiltonian  $H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$ , where BS stands for the broken symmetry singlet state<sup>21</sup> and T for the triplet state. The singlet-triplet energy gap was estimated as  $2J/k_{\text{B}} = +710 \text{ K}$ .<sup>§</sup>



**Fig. 3.** DFT MO calculation results showing spin density surfaces for (a) triplet and (b) singlet **MesPyBN** and (c) triplet and (d) singlet **MesPyBN** moieties in **Y-MesPyBN**. Blue and white lobes stand for positive and negative spin densities, respectively.

Similarly, DFT MO calculation was performed on the same level for the **MesPyBN** portion in **Y-MesPyBN** (Figs. 3c and 3d). The triplet state is ground with  $2J/k_{\text{B}} = +488 \text{ K}$ .<sup>§</sup> This  $J$  value is large enough but smaller than that of the free ligand, possibly owing to through-space  $\text{O1} \cdots \text{N3} \cdots \text{O2}$  interaction. These calculation results confirm that **MesPyBN** is a robust

stable triplet molecule, regardless of the conformation.

In summary, we have developed **MesPyBN** with an extremely low-lying ground triplet state and clarified the ability of complex formation. From viewing the ionic radius (0.90 Å for  $Y^{3+}$  vs 0.94 Å for  $Gd^{3+}$  for example<sup>22</sup>), heterospin systems having 4f ions will be good candidates for strongly exchange coupled magnetic solids.

This work was partly supported by KAKENHI (Grant Number JSPS/15H03793).

## Notes and references

<sup>a</sup> Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan. Fax: 81 42 443 5501; Tel: 81 42 443 5490; E-mail: takayuki.ishida@uec.ac.jp

† **Preparation of 2,6-dibromo-4-mesitylpyridine.** A mixture of 2,6-dibromo-4-iodopyridine<sup>14</sup> (1.81 g, 5.0 mmol), mesityl boronic acid (1.64 g, 10 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.20 g, 2%), Na<sub>2</sub>CO<sub>3</sub> (1.58 g, 15 mmol), THF (40 mL), and water (30 mL) was heated at 75°C under nitrogen for 6 days. After aqueous workup, the products were separated on a silica gel column chromatography (2/1 CH<sub>2</sub>Cl<sub>2</sub>-hexane), to give 0.64 g of 2,6-dibromo-4-mesitylpyridine (1.8 mmol, 36%) as a colorless solid. M.p. 87–90°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 (s, 2H), 6.94 (s, 2H), 2.32 (s, 3H), 2.01 (s, 6H). MS (ESI) *m/z* 353.99, 355.99, 357.99 (M+H<sup>+</sup>).

**Preparation of MesPyBN.** To an dry ether solution (20 mL) of 2,6-dibromo-4-mesitylpyridine (0.71 g, 2.0 mmol) was added a pentane solution of *t*-BuLi (10 mmol) at –75 °C under nitrogen. After stirring for 1 h, an ether solution (10 mL) of *t*-BuNO (0.44 g, 5.0 mmol) was added. The mixture was further stirred for 3 h and gradually warmed up to r.t. The mixture was quenched with aqueous NH<sub>4</sub>Cl and then neutralized with Na<sub>2</sub>CO<sub>3</sub>. After aqueous workup, brown solid was solidified, separated, and washed with hexane, giving 0.31 g of the bishydroxylamine (0.82 mmol, 41%) as a colorless solid. M.p. 167–169 °C. <sup>1</sup>H NMR (500 MHz (CD<sub>3</sub>)<sub>2</sub>SO) δ 8.54 (s, 2H, OH), 6.90 (s, 2H), 6.52 (s, 2H), 2.24 (s, 3H), 1.94 (s, 6H). <sup>13</sup>C NMR (128 MHz, CDCl<sub>3</sub>): δ 159.7, 151.8, 137.6, 136.7, 135.2, 128.3, 113.4, 62.1, 26.8, 21.1, 20.5. MS (ESI) *m/z* 372.32 (M+H<sup>+</sup>). IR (neat, attenuated total reflection (ATR)) 3205 (OH), 2967, 1551, 1382, 1197, 821 cm<sup>-1</sup>. To a CH<sub>2</sub>Cl<sub>2</sub> solution (10 mL) involving the bishydroxylamine (0.20 g, 0.53 mmol) was added Ag<sub>2</sub>O (0.89 g, 5.24 mmol). The mixture was stirred for 15 min. The red product was isolated by alumina column chromatography (1/1 ether-hexane). Recrystallization from hexane gave **MesPyBN** as 0.19 g of red crystals (0.49 mmol; 97%). M.p. 87–90°C. MS (ESI) *m/z* 398.23 (M+Na<sup>+</sup>). IR (neat, ATR) 2964, 1569, 1357, 1189, 832, 759 cm<sup>-1</sup>. Anal. Calcd.: C, 71.51; H, 8.46; N, 11.37% for C<sub>22</sub>H<sub>31</sub>N<sub>3</sub>O<sub>2</sub>. Found: C, 71.54; H, 8.75; N, 11.28%.

**Preparation of Y-MesPyBN.** After a heptane solution (45 mL) of [Y(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] (74.0 mg, 0.10 mmol) was boiled and concentrated to 10 mL, a CH<sub>2</sub>Cl<sub>2</sub> solution (4 mL) of **MesPyBN** (37.0 mg, 0.10 mmol) was added to it while hot. The mixture was allowed to stand in a refrigerator. Orange prisms of **Y-MesPyBN** were precipitated and separated. The yield was 78.3 mg (0.072 mmol, 72%). M.p. 136–138°C. IR (neat, ATR) 1651, 1493, 1250, 1189, 1135, 659 cm<sup>-1</sup>. Anal. Calcd.: C, 41.16; H, 3.17; N, 3.89% for C<sub>37</sub>H<sub>34</sub>F<sub>18</sub>N<sub>3</sub>O<sub>8</sub>Y. Found: C, 41.22; H, 3.12; N, 3.94 %.

‡ The diffraction data were collected on a RIGAKU Saturn70 CCD diffractometer with graphite monochromated MoK $\alpha$  radiation. The structure was directly solved by a heavy atom method and expanded using Fourier techniques in the CRYSTALSTRUCTURE 4.0 program package. The thermal displacement factors of non-hydrogen atoms were anisotropically refined, and those of hydrogen atoms were isotropically optimized by using a riding model after the hydrogen atoms were placed at calculated positions. CCDC 1432390 and 1432391 contain the experimental details and supplementary crystallographic data for **MesPyBN** and **Y-MesPyBN**, respectively. See DOI:10.1039/b000000/x/.

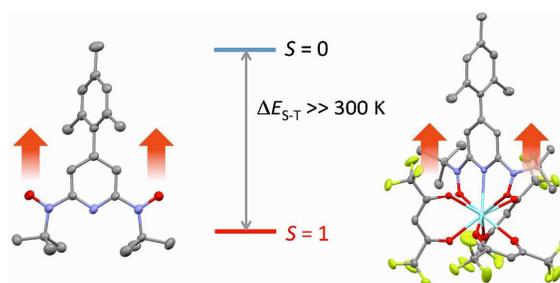
§ DFT calculation results. **MesPyBN**:  $E_{BS} = -1171.75533684$  a.u. with  $\langle S^2 \rangle_{BS} = 0.0754$  and  $E_T = -1171.75751376$  a.u. with  $\langle S^2 \rangle_T = 2.0004$ . **MesPyBN** in **Y-MesPyBN**:  $E_{BS} = -1171.49011465$  a.u. with  $\langle S^2 \rangle_{BS} = 0.0794$  and  $E_T = -1171.49159918$  a.u. with  $\langle S^2 \rangle_T = 2.0003$ .

- (a) S. Demir, I.-R. Jeon, J.R. Long and T.D. Harris, *Coord. Chem. Rev.*, 2015, **289–290**, 149; (b) A.I.O. Suarez, V. Lyaskovskyy, J.N.H. Reek, J.I. van der Vlugt and B. de Bruin, *Angew. Chem. Int. Ed.*, 2013, **52**, 12510; (c) K.E. Vostrikova, *Coord. Chem. Rev.*, 2008, **252**, 1409; (d) R.G. Hicks, *Org. Biomol. Chem.*, 2007, **5**, 1321; (e) A. Caneschi, D. Gatteschi and R. Sessoli, *Acc. Chem. Res.*, 1989, **22**, 392.
- (a) A. Lannes, M. Intissar, Y. Suffren, C. Reber and D. Luneau, *Inorg. Chem.*, 2014, **53**, 9548; (b) D. Luneau, P. Rey, J. Laugier, P. Fries, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Am. Chem. Soc.*, 1991, **113**, 1245; (c) K. Mitsumoto, T. Shiga, M. Nakano, M. Nihei, H. Nishikawa and H. Oshio, *Eur. J. Inorg. Chem.*, 2008, 4851.
- (a) J.B. Gilroy, B.D. Koivisto, R. McDonald, M.J. Ferguson and R.G. Hicks, *J. Mater. Chem.*, 2006, **16**, 2618; (b) D.J.R. Brook, C.J. Richardson, B.C. Haller, M. Hundley and G.T. Yee, *Chem. Commun.*, 2010, **46**, 6590; (c) J.-B. Rota, L. Norel, C. Train, N.B. Amor, D. Maynau and V. Robert, *J. Am. Chem. Soc.*, 2008, **130**, 10380.
- (a) K. E. Preuss, *Dalton Trans.*, 2007, 2357; (b) N.G.R. Hearn, K.E. Preuss, J.F. Richardson and S. Bin-Salamon, *J. Am. Chem. Soc.*, 2004, **126**, 9942; (c) J. Wu, D.J. MacDonald, R. Clerac, I.-R. Jeon, M. Jennings, A.J. Lough, J. Britten, C. Robertson, P.A. Dube and K.E. Preuss, *Inorg. Chem.*, 2012, **51**, 3827.
- I.A. Gass, S. Tewary, A. Nafady, N.F. Chilton, C.J. Gartshore, M. Asadi, D.W. Lupton, B. Moubaraki, A.M. Bond, J.F. Boas, S.-X. Guo, G. Rajaraman and K. S. Murray, *Inorg. Chem.*, 2013, **52**, 7557.
- (a) K. Osanai, A. Okazawa, T. Nogami and T. Ishida, *J. Am. Chem. Soc.*, 2006, **128**, 14008; (b) A. Okazawa, Y. Nagaichi, T. Nogami and T. Ishida, *Inorg. Chem.*, 2008, **47**, 8859; (c) A. Okazawa, T. Nogami and T. Ishida, *Polyhedron*, 2009, **28**, 1917; (d) A. Okazawa, D. Hashizume and T. Ishida, *J. Am. Chem. Soc.*, 2010, **132**, 11516.
- (a) T. Ishida, R. Murakami, T. Kanetomo and H. Nojiri, *Polyhedron*, 2013, **66**, 183; (b) R. Murakami, T. Ishida, S. Yoshii and H. Nojiri, *Dalton Trans.*, 2013, **42**, 13968; (c) T. Kanetomo and T. Ishida, *Inorg. Chem.*, 2014, **53**, 10794; (d) T. Kanetomo, S. Yoshii, H. Nojiri and T. Ishida, *Inorg. Chem. Front.*, 2015, **2**, 860.
- (a) K. Mukai, H. Nagai and K. Ishizu, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2381; (b) T. Ishida and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 4238; (c) Y. Kanzaki, D. Shiomi, K. Sato and T. Takui, *J. Phys. Chem. B*, 2012, **116**, 1053.
- (a) H. Nishimaki, S. Mashiyama, M. Yasui, T. Nogami and T. Ishida, *Chem. Mater.*, 2006, **18**, 3602; (b) H. Nishimaki and T. Ishida, *J. Am. Chem. Soc.*, 2010, **132**, 9598; (c) T. Konno, H. Kudo and T. Ishida, *J. Mater. Chem. C*, 2015, **3**, 7813.
- (a) H. Kumada, A. Sakane, N. Koga and H. Iwamura, *J. Chem. Soc., Dalton Trans.*, 2000, 911; (b) G. Zoppellaro, V. Enkelmann, A. Geies and M. Baumgarten, *Org. Lett.*, 2004, **6**, 4929.
- (a) A. Okazawa, T. Nogami and T. Ishida, *Chem. Mater.*, 2007, **19**, 2733; (b) J. F. Keana, *Chem. Rev.*, 1978, **78**, 37.
- A. Okazawa, T. Nogami and T. Ishida, *Polyhedron*, 2007, **26**, 1965.
- T. Konno, K. Koide and T. Ishida, *Chem. Commun.*, 2013, **49**, 5156.
- K. Snegoroff, T.T. Nguyen, N. Marquise, Y.S. Halauko, P.J. Harford, T. Roisnel, V. E. Matulis, O. A. Ivashkevich, F. Chevallier, A.E.H. Wheatley, P. C. Gros and F. Mongin, *Chem. Eur. J.*, 2011, **17**, 13284.
- A. Suzuki, *Angew. Chem. Int. Ed.*, 2011, **50**, 6722.
- (a) H. Iwamura, *Adv. Phys. Org. Chem.*, 1991, **26**, 179; (b) A. Rajca, *Chem. Rev.*, 1994, **94**, 871; (c) N. Mataga, *Theor. Chim. Acta*, 1967, **10**, 372; (d) J. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.
- (a) K. Hayakawa, D. Shiomi, T. Ise, K. Sato and T. Takui, *J. Mater. Chem.*, 2006, **16**, 4146; (b) R. Ziessel, G. Ulrich, R.C. Lawson and L. Echegoyen, *J. Mater. Chem.*, 1999, **9**, 1435; (c) T. Shimada, T. Ishida and T. Nogami, *Polyhedron*, 2005, **24**, 2593.
- (a) A.D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, 1998, **37**, 785.
- Gaussian 03*, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- M. Nishino, S. Yamanaka, Y. Yoshioka and K. Yamaguchi, *J. Phys. Chem. A*, 1997, **101**, 705.
- E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.*, 1999, **20**, 1391.
- (a) R.D. Shannon and C.T. Prewitt, *Acta Crystallogr. Sect. B*, 1969, **25**, 925; (b) R.D. Shannon, *Acta Crystallogr. Sect. A*, 1976, **32**, 751.

Designed room-temperature triplet ligand from pyridine-2,6-diyl bis(*tert*-butyl nitroxide)

Hinako Kawakami, Asato Tonegawa, Takayuki Ishida\*

Graphical Abstract (8 cm x 4 cm)



Synopsis (20 words)

Ligating ability of MesPyBN was proven to form Y-MesPyBN, and the low-lying triplet state maintained after complex formation.