Stable diarylnitroxide diradical with triplet ground state†

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Nitroxide diradical 2, the first isolated diarylnitroxide diradical, is stable in the solid state at room temperature and it possesses triplet ground state with strong ferromagnetic coupling.

Diarylnitroxide polyradicals with alternating connectivity of nitroxide radicals and the strong ferromagnetic coupling unit such as *m*-phenylene are attractive building blocks for high-spin polyradicals that could be useful in the development of organic magnetic materials.[1–5] However, there are only a few known diarylnitroxide radicals, almost all of them are monoradicals.[6–8] Steric shielding of spin density at the *meta* positions with respect to the nitroxides has shown to be somewhat effective in providing radical stability for the triplet ($S = 1$) ground state diarylnitroxide diradical **1** (Fig. 1), which however, could only be prepared and detected at low temperature.[9] Thus, the design and synthesis of extended high-spin diarylnitroxide polyradicals remain a challenge.
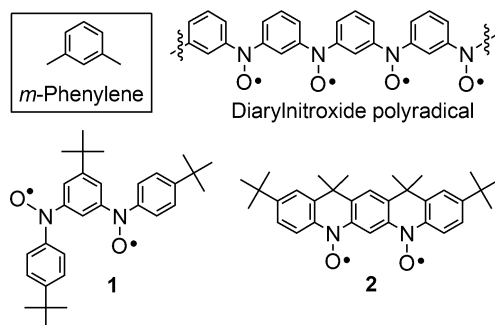

Fig. 1

We now report the synthesis, isolation, and magnetic characterization of stable diarylnitroxide diradical **2** (Fig. 1). To enhance its stability, diradical **2** is designed with sterically shielded *para*-positions of the *m*-phenylene, where significant spin density is expected by delocalization from both nitroxide moieties. The annelated structure of **2** enforces a co-planar conformation for the nitroxide moieties and the *m*-phenylene coupling unit, and thus is expected to provide a relatively large singlet–triplet energy gap (strength of the ferromagnetic coupling). Although diradical **2** shows signs of slow decomposition in concentrated solutions, it is relatively stable in the solid state at ambient conditions. Magnetic data for **2** in the solid state and in solution indicate

that the diradical possesses triplet ($S = 1$) ground state with a large singlet–triplet energy gap. Therefore, the diarylnitroxide diradical **2** demonstrates the effect of sterically hindered but planar structure on the strength of the ferromagnetic coupling and radical stability.[10]

Diamine **3** is prepared as reported previously.[11] We first carried out oxidation of **3** with dimethyldioxirane (DMDO) at low temperatures, in which the frozen reaction mixtures are monitored by EPR spectroscopy (Scheme 1).[9] Treatment of **3** with 4.5 equiv. of DMDO in dichloromethane (DCM) at -78 °C for 2 h, and then at -40 °C for another 2 h, provided EPR spectra with increasing intensity of the side bands flanking strong triplet-like center resonances of nitroxide monoradical. Numerical simulation of the side bands with the parameters for a triplet state ($S = 1$) nitroxide diradical adequately reproduces the experimental spectrum, providing evidence for the presence of **2** (Fig. S1, ESI†). However, the double integration of the EPR spectra suggests that diradical **2** is obtained in low yield ($\sim 10\%$).[12]
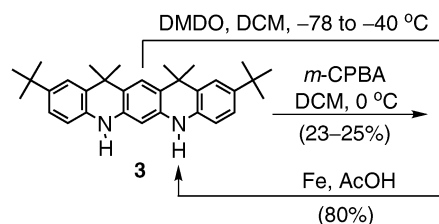

Scheme 1 Synthesis and reduction of diradical **2**.

Oxidations of diamine **3** with *meta*-chloroperbenzoic acid (*m*-CPBA) in DCM at 0 °C, followed by a rapid filtration through deactivated silica gel, gave nitroxide diradical **2** in $\sim 20\%$ yields (Scheme 1). These isolated yields correspond to the product for which EPR spectra show that the diradical is the major component with negligible content of nitroxide monoradical by-product (Fig. S2, ESI†). However, careful measurements of paramagnetic susceptibility (χ) by the NMR-based Evans method in solution and superconducting quantum interference device (SQUID) magnetometry in the solid state suggest the presence of diamagnetic by-products (Fig. S3, ESI†).[13] In other experiments, where further purification is carried out, diradical **2** is obtained (5–10% isolated yields) with negligible paramagnetic and diamagnetic by-products, as illustrated by EPR spectroscopic and magnetic data described below.

Reduction of diradical **2** with iron/acetic acid[14] gave cleanly diamine **3** (Scheme 1). This result coincides with the test reduction of a typical diarylnitroxide radical,

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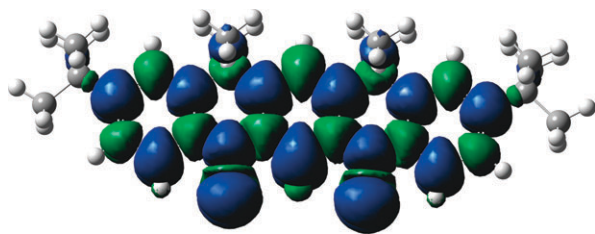
Fig. 2 UB3LYP/6-31G(d) spin densities for the triplet ground state diradical **2**. The blue and green lobes correspond to positive and negative densities, respectively.

4,4′-di-*tert*-butyldiphenylnitroxide radical,[9] in which 4,4′-di-*tert*-butyl-diphenylamine is obtained in nearly quantitative yield, as determined by ^{1}H NMR spectroscopy. These results provide an indirect confirmation for molecular connectivity of diradical **2**.[15]

Structure and properties of diradical **2** are evaluated by DFT calculations. The fully optimized geometry for the lowest triplet state of diradical **2** at the UB3LYP/6-31G(d) level indicates the C_{2v}-symmetric structure with planar π-system, similar to those obtained from the X-ray structure of diamine **3**.[11,16] In planar diradical **2**, a greater fraction of spin density is delocalized to *m*-phenylene (Fig. 2), compared to diradical **1**; *e.g.*, the UB3LYP/6-31G(d) spin densities of $+0.23$ and $+0.19$ at the *ortho* positions with respect to both nitroxides are calculated in **2** and **1**, respectively.[9] Consequently, the singlet–triplet energy gap is somewhat greater for **2** (2.0 kcal mol^{-1}), compared to that for **1** (1.5–1.8 kcal mol^{-1}).[9,17,18]

EPR spectra of **2** in toluene at both 80 and 140 K show six symmetrically disposed intense peaks in the $|\Delta m_s = 1|$ region and an intense transition in the $|\Delta m_s = 2|$ region (Fig. 3).

This spectral pattern corresponds to magnetic dipole–dipole coupling between the two unpaired electrons with the zero-field splitting (zfs) parameters $|D/hc| = 1.223 \times 10^2$ cm^{-1} and $|E/hc| = 1.44 \times 10^{-3}$ cm^{-1}. The middle pair of peaks appears
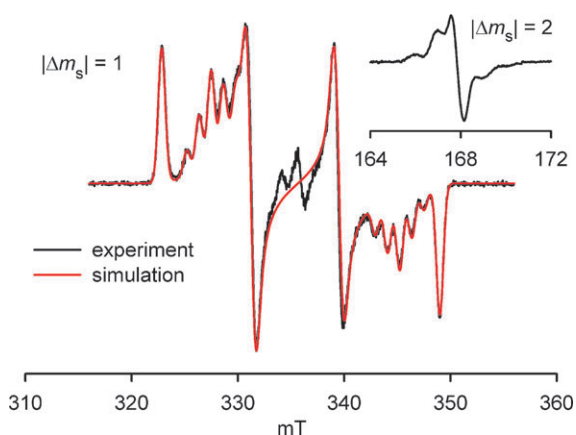
Fig. 3 EPR (X-Band, 9.4246 GHz) spectrum of 1 mM diradical **2** in toluene at $\sim$80 K. The fitting parameters for the spectral simulation (red trace) to the $S = 1$ state are: $|D/hc| = 1.223 \times 10^{-2}$ cm^{-1} ($|D/g\mu_B| = 13.08$ mT), $|E/hc| = 1.44 \times 10^{-3}$ cm^{-1} ($|E/g\mu_B| = 1.56$ mT), $|A_{yy}/2hc| = 1.06 \times 10^{-3}$ cm^{-1} ($|A_{yy}/2g\mu_B| = 1.13$ mT), $g_x = 2.0074$, $g_y = 2.0016$, $g_z = 2.0045$, Gaussian line ($L_x = 0.75$ mT, $L_y = 0.69$ mT, $L_z = 0.65$ mT). The center lines correspond to an $S = 1/2$ (monoradical) by-product.
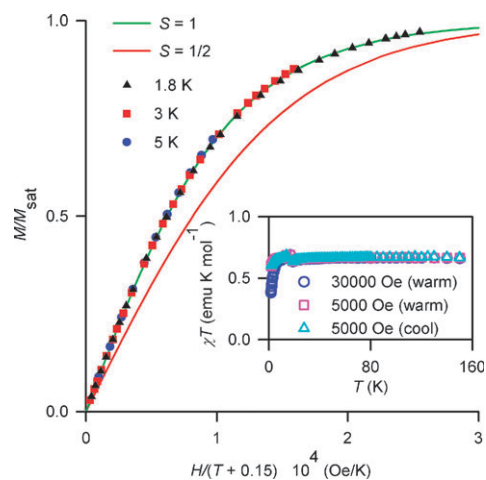
Fig. 4 SQUID magnetometry for $\sim$15 mM diradical **2** in THF. Main plot: M/M_{sat} *vs.* $H/(T - \theta)$, with solid lines showing plots of Brillouin functions with $S = 1/2$ and $S = 1$. Inset plot: χT *vs.* T in cooling and warming modes.

as pentuplets, which may be simulated with the ^{14}N-hyperfine coupling of two nitrogens atoms with spacings of $|A_{yy}/2hc| = 1.06 \times 10^{-3}$ cm^{-1}. This well-resolved ^{14}N-hyperfine coupling implies that the $2p_\pi$ orbital on each nitrogen is approximately parallel to the *y*-axis, corresponding to the direction of the second largest principal value for the magnetic dipole tensor.[19,20] The simulated components of the *g*-tensor at $\sim$80 K may be averaged to an isotropic $g = 2.0045$, which is in good agreement with $g = 2.0051$ for 9,9-dimethyl-9,10-dihydroacridine nitroxide monoradical in benzene at room temperature.[21] These results confirm the structure for diradical **2** and indicate that the nitroxides and *m*-phenylene adopt a coplanar conformation.[20,22]

For $\sim$15 mM diradical **2** in tetrahydrofuran (THF),[23] the magnetization (*M*) *vs.* magnetic field (*H*) data at low temperatures ($T = 1.8, 3, 5$ K) provide excellent fits to the Brillouin functions with a mean-field parameter ($\theta < 0$), *i.e.*, *M* *vs.* $H/(T - \theta)$. Such fits have two variable parameters, *i.e.*, total spin (*S*) and magnetization at saturation (M_{sat}); the mean-field parameter θ is adjusted until the M/M_{sat} *vs.* $H/(T - \theta)$ plots overlap at all temperatures. The value of $S = 0.99 \approx 1.0$, determined from the curvature of the Brillouin plots, indicate the triplet ($S = 1$) ground state for diradical **2** (Fig. 4). The value of $\theta < 0$ and $|\theta| \approx 0.15$ K imply very weak, and almost certainly intermolecular, antiferromagnetic coupling.

M_{sat} measures the number of unpaired electron spins (or spin concentration) in the limit of low temperature and high magnetic field. For an $S = 1$ diradical, M_{sat} should be 1.00 in the units of Bohr magneton (μ_B) per radical site. The value of χT (product of magnetic susceptibility and temperature) and its temperature dependence measure both the ground state and the strength of exchange coupling in **2** (Fig. 4, inset plot). For an $S = 1$ diradical, with strong ferromagnetic coupling, value of χT should be 1.00 emu K mol^{-1} (per mol of diradical). The measured values for **2**, $M_{sat} = 0.66$ μ_B and $\chi T = 0.67$ emu K mol^{-1}, are below the expected values. Unlike the values of *S*, values of M_{sat} and χT

are dependent upon mass of the diradical. Values of both M_{sat} and χT would be lower if nitroxide diradical **2**, which is an electrostatic amorphous powder, is incompletely transferred to the reaction vessel. Most importantly, the measured values of χT (in units of emu K mol^{-1}) are nearly identical to the numerical values of M_{sat} (in the unit of μ_B). Therefore, $\chi T \approx 1$ is found for **2**, after values of χT are corrected by spin concentration (M_{sat}). Although the χT vs. T plots are nearly flat (Fig. 4, inset plot), small errors in correction for diamagnetism may have significant impact on such plots, especially at higher temperatures. Thus, only a lower limit of more than 100–200 K (0.2–0.4 kcal mol^{-1}) for the singlet–triplet energy gap ($2J/k$) may be estimated. A more accurate value of $2J/k$ may be obtained from the χT vs. T plots in the solid state, using rigorous point-by-point correction for diamagnetism.

For solid diradical **2**, the χT vs. T plot shows a downward turn at lower temperatures from the value of $\chi T \approx 0.93$ emu K mol^{-1} at 290 K (Fig. 5). These data indicate that diradical **2** possesses a triplet ground state ($S = 1$) with the singlet–triplet energy gap, $2J/k$, that is comparable or greater than the thermal energy at room temperature ($2J/k \geq 300$ K), and the presence of the antiferromagnetic intermolecular interactions between the $S = 1$ diradical molecules.
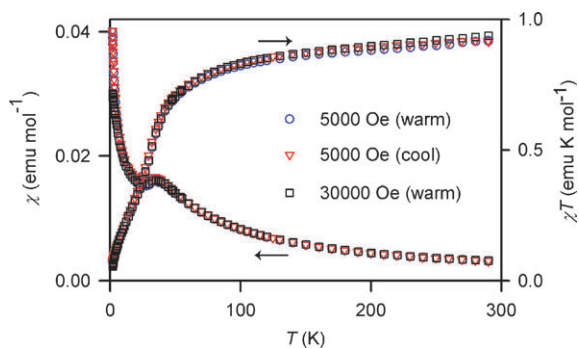

Fig. 5 SQUID magnetometry for solid diradical **2**.

In the χ vs. T plot, a broad maximum is observed at 37 K, indicating that these intermolecular antiferromagnetic interactions are stronger by about an order of magnitude compared to those in planar alkylarylnitroxide diradicals.[20] The broad maximum at 37 K is more pronounced in samples with lesser content of monoradical (Fig. S8, ESI†). Unlike for the planar alkylarylnitroxide diradicals,[20] neither the dimer model (Heisenberg pairs of $S = 1$ diradicals) or chain model (one-dimensional Heisenberg chains of $S = 1$ diradicals) provided good numerical fits, even if a monoradical was included in the fit. These relatively strong intermolecular antiferromagnetic interactions are expected to lower the value of χT, below 1.00 emu K mol^{-1} expected for an $S = 1$ state, even at room temperature.[24]

In summary, nitroxide diradical **2** is the first isolated diarylnitroxide diradical that is stable in the solid state at room temperature and it possesses the triplet ground state with strong ferromagnetic coupling.

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21 (a) F. A. Neugebauer and S. Bamberger, *Chem. Ber.*, 1974, **107**, 2362–2382; (b) For diradical **2** at 140 K, isotropic $g = (g_x + g_y + g_z)/3 = 2.0048$, Fig. S4 and Table S1, ESI†.
22 All simulated components of g-tensor, D-tensor, and ^{14}N-hyperfine tensor for **2** have slightly lower values compared to those for a planar alkylarylnitroxide diradical (ref. 20) (Table S1, ESI†). This is consistent with greater delocalization of spin density away from nitroxide into relatively extended π-system in diarylnitroxide diradical **2**.
23 EPR and ^{1}H NMR spectra for the identical sample of **2**, as well as EPR spectra for this SQUID sample, are shown in Fig. S6, S7 and S11 (ESI†).
24 The value of $\chi T \approx 0.93$ emu K mol^{-1} at 290 K may also be affected by the correction for diamagnetism, for which the accuracy may be decreased accuracy because of small weights of samples.