Isolable Polyradical Cations of Polyphenylenediamines with Populated High-Spin States

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The chemical approach to preparation of organic magnetic materials requires molecular and intermolecular dissection and control of electron spin interactions.[1] An important component of the molecule-based magnet strategy is the design and synthesis of new stable, high-spin organic polyradical building blocks. We have been designing new organic spin units that are spin tunable. Our approach is to use redox-active groups covalently linked to favor their intramolecular ferromagnetic interaction. In such systems, the neutral molecule serves as a recyclable precursor to sequentially more highly charged molecular states whose multiplicities are, by design, a function of the redox level of the unit and are, therefore, electrochemically (or chemically) switchable.

Previous work on tris(arylamino)benzene radical cations has demonstrated the viability of multistage redox-activation of high-spin organic substrates.[2] However, the polycations in that series were disappointingly short-lived,[3] having lifetimes much shorter than those of the corresponding constituent monomeric radical ions.[4] It is therefore apparent that monomeric radical ion stability is not always a sufficient indicator of the corresponding polyradical cation lifetime. Here, we report the preparation and properties of two new polyradical ion spin systems based on the phenylenediamine redox function—1,3,5-tris[*N*-[4-(diphenylamino)phenyl]phenyl-amino]benzene (**1**) and 1,3,5-tris[*N*-[4-(di-4-anisylamino)phenyl]-4-anisylamino]benzene (**2**). We find that polyradical ion stability is enhanced in this series, which yields isolably stable **2**$^+$, **2**$^{2+}$, and **2**$^{3+}$ salts, with **2**$^{3+}$ (PF$_6^-$)$_3$ being the first example of an isolable organic quartet triradical cation of which we are aware.[5]

Substrate **1**[6] is prepared in 21% overall yield by an iodine-catalyzed 3× condensation[7] between phloroglucinol dihydrate and *N*-phenyl-*p*-phenylenediamine, followed by treatment of the resulting tris(*N*-arylphenylene-diamino)benzene with copper and *p*-iodobenzene to effect a 6× Ullmann reaction. Substrate **2** is prepared analogously in overall 22% yield.

The cyclic voltammogram of **1**, overlaid by that of monomeric tetraphenyl-*p*-phenylenediamine (TPPD), is
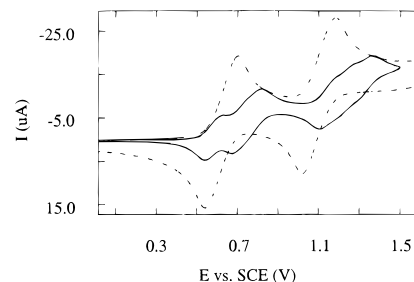

Figure 1. Cyclic voltammogram of **1** (solid line) and TPPD (dashed line) in CH$_2$Cl$_2$ (0.1 M *n*-Bu$_4$NBF$_4$) at 298 K and 50 mV/s scan rate.

shown in Figure 1. The associated formal oxidation potentials are difficult to determine precisely because of wave overlap but are approximately (n,+) 0.59, (+,2+) 0.72, (2+,3+) 0.79, (3+,4+) 1.15, (4+,5+) 1.24, (5+,6+) 1.33 V vs SCE for **1**. A similar CV response is observed for **2** oxidation and yields the following approximate $E°'$ values: (n,+) 0.41, (+,2+) 0.54, (2+,3+) 0.61, (3+,4+) 0.97, (4+,5+) 1.01, (5+,6+) 1.08 V vs SCE. These data show that oxidation states +1 through +6 of both **1** and **2** have solution lifetimes ≥ a few seconds at 298 K.

R	
H	**1**$^{3+}$
MeO	**2**$^{3+}$
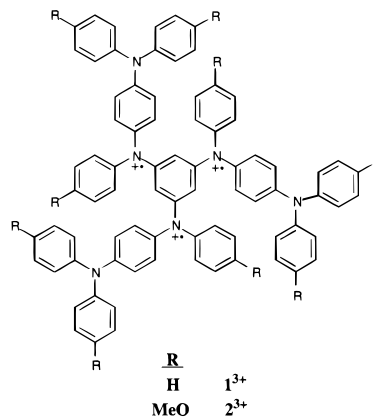
Chemical oxidation of **1** (1 mM) by 1 molar equiv of thianthrenium perchlorate[8] (TH$^+$ClO$_4^-$) in CH$_2$Cl$_2$ at ambient temperature yields a green solution that shows a single broad-line ESR spectrum with a spectral width of ~35 G. We assign this signal to **1**$^+$. No hyperfine coupling is observed, presumably because numerous small, unresolved splittings effectively line broaden the signal. The radical cation **2**$^+$, prepared similarly, also displays a single broad-line ESR signal under these conditions and shows a strong UV−vis transition with λ_m 1028 nm (ϵ 2.8 × 10^4 L mol^{-1} cm^{-1}) in CH$_2$Cl$_2$.

Treatment of either **1** or **2** in butyronitrile[9] with 2 molar equiv of TH$^+$ClO$_4^-$ yields the corresponding in-

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(1) For some reviews of organic molecule-based magnets see: (a) Iwamura, H. *Adv. Phys. Org. Chem.* **1990,** *26,* 179−253. (b) Dougherty, D. A. *Acc. Chem. Res.* **1991,** *24,* 88. (c) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 385. (d) Rajca, A. *Chem. Rev.* **1994,** *94,* 871.

(2) Stickley, K. R.; Blackstock, S. C. *J. Am. Chem. Soc.* **1994,** *116,* 11576.

(3) Trication triradical lifetimes are milliseconds to minutes at 195 K. See: (a) Stickley, K. R.; Blackstock, S. C. *Tetrahedron Lett.* **1995,** *36,* 1585. (b) Stickley, K. R.; Blackstock, S. C. *Mol. Cryst. Liq. Cryst.* **1995,** *272,* 81.

(4) For triarylamine radical cation properties see (a) Hagopian, L.; Günter, K.; Walter, R. I. *J. Phys. Chem.* **1967,** *71,* 2290. (b) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966,** *88,* 3498.

(5) For a description of some isolable neutral quartet organic molecules see: (a) Veciana, J.; Rovira, C.; Ventosa, N.; Crespo, M. I.; Palacio, F. *J. Am. Chem. Soc.* **1993,** *115,* 57. (b) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Phys. Chem.* **1993,** *97,* 13267. (c) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993,** *115,* 2396. (d) Weissman, S. I.; Kothe, G. *J. Am. Chem. Soc.* **1975,** *97,* 2537.

(6) For a previous preparation see: Ishikawa, W.; Noguchi, K.; Kuwabara ,Y.; Shirota, Y. *Adv. Mater.* **1993,** *5,* 559.

(7) Buu-Hoï, N. P. *J. Chem. Soc.* **1952,** 4346.

(8) Caution! Thianthrenium perchlorate (TH$^+$ClO$_4^-$) is a shock-sensitive explosive solid and should be handled with due care. For preparation and properties see: Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969,** *34,* 3368.

(9) Generally, 5% trifluoroacetic acid and 5% trifluoroacetic anhydride is added to the solvent to quench trace nucleophiles such as water, which tend to decompose the electrophilic polyradical cations.
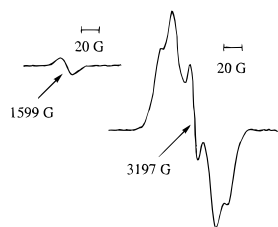
Figure 2. ESR spectrum of 0.25 mM $\mathbf{1}^{2+}(ClO_4^-)_2$ in butyronitrile at 93 K.
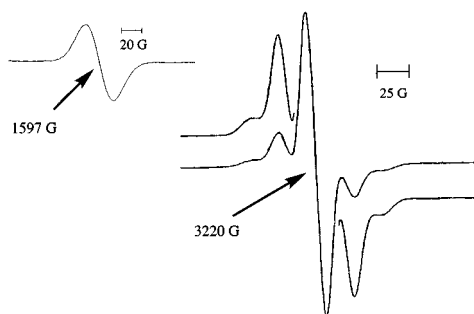

Figure 3. ESR spectrum of 10 mM $\mathbf{1}^{3+}$ $(ClO_4^-)_3$ in butyronitrile at 93 K.

tensely green dications. For $\mathbf{1}^{2+}$, the fluid solution gives a broad singlet ESR spectrum, but when frozen at 93 K, a four-line pattern characteristic of a triplet species with $E \approx 0$ is observed (Figure 2). In addition, a $\Delta m_s = 2$ transition at ~1599 G is detected. From these data, we find a $|D|/hc$ value of 0.0035 cm^{-1} for triplet $\mathbf{1}^{2+}$. This value is smaller than that of Schlenk's hydrocarbon (0.0064 cm^{-1})[10] or hexaanisyl-substituted 1,3,5-triaminobenzene dication (HATAB^{2+}) (0.0065 cm^{-1})[2] as expected for the more highly delocalized π system of $\mathbf{1}^{2+}$ in which the average odd-electron separation is expected to be greater. A similar ESR triplet signal is observed for $\mathbf{2}^{2+}$ (UV−vis λ_m 1050 nm, ϵ 4.2 × 10^4 L mol^{-1} cm^{-1} in CH$_2$Cl$_2$), which yields a $|D|/hc$ value of 0.0026 cm^{-1}.

Oxidation of **1** with 3 molar equiv of TH$^+$ClO$_4^-$ yields a green sample whose matrix ESR spectrum at 93 K shows a five-line signal with a line separation of ~28 G (Figure 3). This spectrum is that expected for an axially symmetric quartet state, and we assign it to $\mathbf{1}^{3+}$. A $\Delta m_s = 2$ transition for $\mathbf{1}^{3+}$ is observed at ~1597 G, but no $\Delta m_s = 3$ transition for this species has yet been detected.[11] The $|D|/hc$ value is 0.0026 cm^{-1}, slightly less than that reported for the hexa-*p*-biphenyl-substituted 1,3,5-trimethylenebenzene triradical (0.0037 cm^{-1}),[12] a similarly highly delocalized, axially symmetric π-triradical. Similarly prepared $\mathbf{2}^{3+}$ (λ_m 1090, ϵ 6.6 × 10^4 L mol^{-1} cm^{-1} in CH$_2$Cl$_2$) gives a quartet ESR signal in butyronitrile at 98 K with $|D|/hc$ of 0.0018 cm^{-1}.

For $\mathbf{1}^{3+}$ and $\mathbf{2}^{3+}$, Curie−Weiss plots of the ESR signal intensity over a limited temperature range of 90−120 K are linear ($r^2 \geq 0.99$), consistent with high-spin ground states or nearly degenerate high- and low-spin states for these species. Susceptibility measurements in CDCl$_3$

solution at 298.5 K by the Evans ^{1}H NMR shift method[13] yield the following effective magnetic moment (μ_{eff}) values: $\mathbf{1}^+$ (1.77), $\mathbf{1}^{2+}$ (2.61), $\mathbf{1}^{3+}$ (3.05), $\mathbf{2}^+$ (1.76), $\mathbf{2}^{2+}$ (2.79), and $\mathbf{2}^{3+}$ (3.04). Theoretical μ_{eff} values for singlet, triplet, and quartet species are 1.73, 2.83, and 3.87, respectively. The monocation moments are very close to those expected for pure doublet species as required.[14] Treatment of the dication μ_{eff} values as resulting from mixed singlet/triplet populations according to $(\mu_{eff})^2 = (\mu_L)^2 X_L + (\mu_H)^2(1 - X_L)$ suggests that $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ are 85% and 97% triplet populated in solution and thus possess triplet ground states.[15] Similar analysis of the $\mathbf{1}^{3+}$ and $\mathbf{2}^{3+}$ NMR shift data gives quartet populations of 53% and 52%, respectively and suggests a slight preference for low spin (doublet) ground states in these triradical cations.[16,17] More extensive investigation of the low-temperature magnetic properties of the above polycations is in progress.

Both trications $\mathbf{1}^{3+}$ and $\mathbf{2}^{3+}$ are solution stable at room temperature for hours to days. Moreover, $\mathbf{2}^{3+}$ is unreactive toward oxygen as indicated by no loss of ESR signal intensity upon purging its solutions with O$_2$. The methoxy-substituted cations $\mathbf{2}^+$, $\mathbf{2}^{2+}$, and $\mathbf{2}^{3+}$ all survive isolation and have been prepared as PF$_6^-$ salts by NOPF$_6$ oxidation of **2**. Redissolved $\mathbf{2}^{3+}(PF_6^-)_3$ yields, quantitatively, the characteristic quartet ESR spectrum and ^{1}H NMR paramagnetic shifts observed from in situ-generated samples of $\mathbf{2}^{3+}$.[18]

Lastly, we point out that the p-phenylenediamine redox group is not only a low $E°'$, kinetically stable radical-cation spin carrier, but it also affords considerable synthetic potential for construction of larger spin ensembles. For example, extending the redox array via N,N′-bridging of a phenylenediamine gives a precursor to a potential sextet pentacation. Further work along these lines is in progress.

Supporting Information Available: Synthesis of **1** and **2**, ESR sample preparations, ESR spectra of $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{2}^{2+}$, and $\mathbf{2}^{3+}$, Curie−Weiss plots for $\mathbf{1}^{3+}$ and $\mathbf{2}^{3+}$, and NMR susceptibility data (11 pages).

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(11) This transition is expected to be quite weak and difficult to observe. Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi, J.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 5994.

(12) Kothe, G.; Ohmes, E.; Brickmann, J.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 938.

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(14) The μ_{eff} values of two other standard samples of known multiplity [(1,1,3,3-tetramethylisoindolin-2-yl)oxyl μ_{eff} 1.71 (1.73 theoretical) and Cr(III)(acac)$_3$ μ_{eff} 3.92 (3.87 theoretical)] were also determined to demonstrate the viability of the NMR shift method under our conditions.

(15) μ_L is the low-spin μ value, μ_H is the high-spin μ value, and X$_L$ is the mole fraction of the low spin-state population in the sample.

(16) It should be noted that the triplet state is statistically favored over the singlet state by a factor of 3 and that the quartet state is similarly favored over the doublet state by a factor of 2.

(17) The doublet trications are probably best viewed as triradicals rather than as trications containing a phenylenediamine dication (singlet) and a single phenylenediamine radical cation (doublet) in the same molecule. The latter state is related to the triradical trication by internal disproportionation of two phenylenediamine radical cations, the energetic cost of which is given by $E'_2 - E°'_1$ of a single phenylenediamine unit or ~11.5 kcal/mol according to Figure 1. This energetic requirement would appear to rule out the latter electronic configuration as a major contributor to the doublet trication structures.

(18) The elemental purity of solid $23^+(PF_6^-)_3$ has been established by C, H, N combusion analysis.