Stable triplet-state di(cation radical)s of a *N*-phenylaniline oligomer

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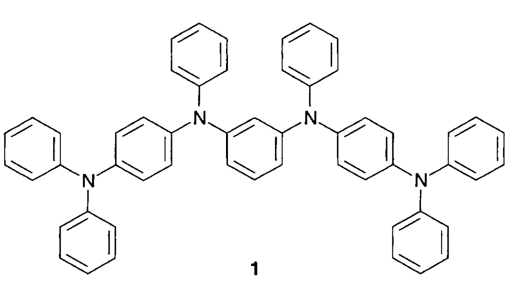
Two-electron oxidation of *N,N'*-bis[4-(diphenylamino)-phenyl]-*N,N'*-diphenyl-1,3-diaminobenzene produces a room temperature stable di(cation radical) with a triplet ground state as evidenced from EPR spectroscopy.

A promising strategy towards high-spin organic oligomers and polymers is the concept of a polaronic ferromagnetic chain, based on an alternating sequence of dopable π-conjugated segments and ferromagnetic spin coupling units.[1] Oxidative or reductive doping of such a polymer may result in polaronic (radical ion) segments that are ferromagnetically coupled to yield a high-spin polyradical, possibly leading to an organic magnetic material. The process of redox doping bears a strong resemblance to the well-established doping of fully π-conjugated polymers to conducting materials. Recently, there is a renewed theoretical[2] and experimental[3] interest in polaronic ferromagnets. Dougherty *et al.*[3] have examined a number of possible polaronic ferromagnets based on dopable building blocks consisting of 2,5-thiophene, 1,2-vinylene and 2,7-indoloindole, linked *via m*-phenylene coupling units. It was shown that in several instances ferromagnetic coupling of polarons occurs along the chain after oxidative doping.

It is well known that at high doping levels, most conducting polymers bear no resulting spin, due to the conversion of polarons to spinless bipolarons[4] and/or interchain π-dimers.[5] One noticeable exception to the absence of resulting electron spin in conducting polymers is the emeraldine salt of polyaniline in which bipolarons are unstable with respect to the formation of two polarons through an internal redox reaction.[6] In addition, it has been recently shown that the *m*-phenylene unit can give rise to ferromagnetic coupling of nitrogen cation radicals.[7] With this knowledge in mind we have designed the *N*-phenylaniline oligomer **1** that comprises alternating *para* and *meta* substituted phenylene rings to give the desired chemical stability from the *p*-diaminobenzene unit and ferromagnetic coupling from the *m*-diaminobenzene unit after two-electron oxidation.

N,N'-bis[4-(diphenylamino)phenyl)]-*N,N'*-diphenyl-1,3-diaminobenzene **1** was synthesised from 4-iodo-*N,N*-diphenylaminobenzene and *N,N'*-diphenyl-1,3-diaminobenzene in diphenyl ether at 200 °C, using butyllithium and copper(I) iodide as a catalyst.[8] The product was isolated by column chromatography (SiO_2; chloroform–hexane, 2:1) in 61% yield. Analytical data confirm the proposed structure.†

Cyclic voltammetry on **1** revealed four chemically reversible one-electron transfers with a peak separation between anodic and cathodic peak potentials of 62–65 mV, independent of the scan rate between 50 and 200 mV s^{-1} (Fig. 1). One-electron transfers occur at potentials of $E_1^0 = 0.54$, $E_2^0 = 0.68$, $E_3^0 = 1.13$ and $E_4^0 = 1.22$ V *vs.* SCE. Comparison with oxidation potentials for the corresponding all-*para*-substituted analogue of **1** (0.42, 0.68, 1.15 and 1.31 V),‡,[8] reveals that E_2^0 and E_3^0 are identical, whereas the E_1^0 and E_4^0 are higher and lower for **1**, respectively. The decreased separation between E_1^0 and E_2^0 as well as between E_3^0 and E_4^0 for **1**, is consistent with the non-resonant *meta* substitution on the central phenylene ring.



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Oxidation of **1** with less than one equivalent of thianthrenium perchlorate[7] in dichloromethane solution produces the monocation radical $\mathbf{1}^{+\bullet}$. The EPR spectrum of $\mathbf{1}^{+\bullet}$ at room temperature exhibits a 1:2:3:2:1 five-line pattern resulting from two equivalent ^{14}N nuclei with $A_{iso}(N) = 16$ MHz, identical to the hyperfine coupling constant reported for the cation radical of *N,N,N',N'*-tetraphenyl-1,4-diaminobenzene (TPDB).[9] The interaction with two ^{14}N nuclei demonstrates that the unpaired electron is localised on only one of the two *p*-diaminobenzene units. The anisotropic EPR spectrum of $\mathbf{1}^{+\bullet}$ recorded at 100 K [Fig. 2(*a*)] can be successfully simulated using anisotropic hyperfine coupling parameters $A_{\parallel}(N) = 37$ and $A_{\perp}(N) = 5$ MHz.

Further oxidation of $\mathbf{1}^{+\bullet}$ using thianthrenium perchlorate in the presence of TFA results in the formation of the di(cation radical) $\mathbf{1}^{2+2\bullet}$.§ The EPR spectrum of $\mathbf{1}^{2+2\bullet}$ at 4 K [Fig. 2(*b*)] reveals the characteristic zero-field spitting associated with a high-spin molecule. Direct spectral evidence for the triplet-state of $\mathbf{1}^{2+2\bullet}$ is obtained from the $\Delta M_s = \pm 2$ transition at half field [inset of Fig. (2*b*)]. The triplet-state di(cation radical) $\mathbf{1}^{2+2\bullet}$ can be kept in solution at room temperature for several weeks without appreciable decay of EPR signal intensity.

The zero-field splitting parameters have been determined from the $\Delta M_s = \pm 1$ transitions to be $D = 110$ MHz and $E \approx 0$ MHz using spectral simulation. Assuming a point dipole approximation for the zero-field splitting, the D parameter can be used to estimate the average distance d(Å) between the two interacting electrons *via* the relation $D = 7.8 \times 10^4 \, d^{-3}$. From $D = 110$ MHz, we find $d = 8.9$ Å, consistent with the separation of 9.8 Å between the centres of the two *p*-diaminobenzene units as estimated from standard bond lengths,

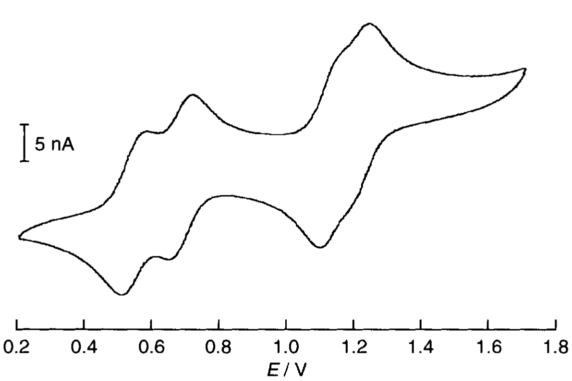

Fig. 1 Cyclic voltammogram of **1** in $CH_2Cl_2/Bu_4{}^+NPF_6{}^-$ (0.1 mol dm^{-3}) at 295 K, scan rate 50 mV s^{-1}, potential *vs.* SCE calibrated using Fc/Fc$^+$ (0.470 V)

assuming a coplanar geometry. The temperature dependence of the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ transitions follows Curie behaviour ($I = C/T$) in the range from 4 to 100 K, indicating a triplet ground state for $\mathbf{1}^{2+2\bullet}$ or possibly a degeneracy of singlet and triplet states.

In conclusion we have demonstrated the feasibility of alternating *meta* and *para* oligo(*N*-phenylaniline) as a stable building block for future polaronic ferromagnetic polymer chains. Further studies will be directed towards investigating the oxidation behaviour in more detail and exploring the concept of high-spin *m*-*p*-oligoanilines in larger systems.

We wish to thank Professor E. W. Meijer and Dr E. E. Havinga for stimulating discussions and valuable comments.

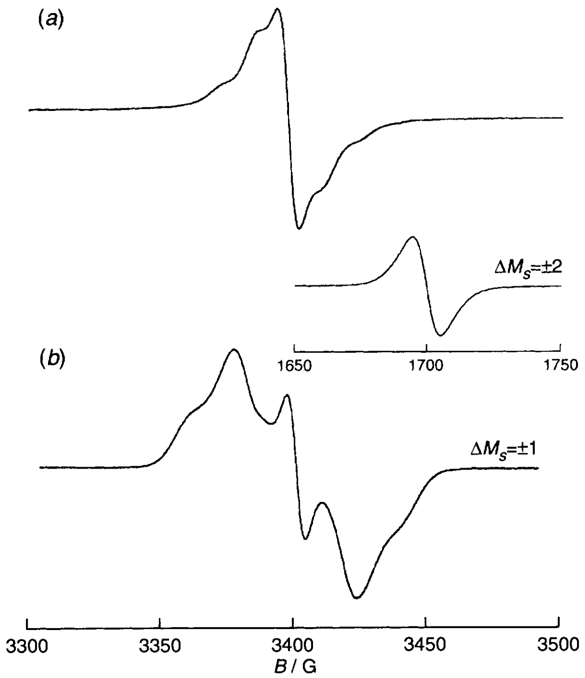

Fig. 2 EPR spectra (*a*) of $\mathbf{1}^{+\bullet}$ in CH_2Cl_2 recorded at 100 K using microwave power of 2 mW, and (*b*) of $\mathbf{1}^{2+2\bullet}$ in CH_2Cl_2–TFA recorded at 4 K using microwave power of 200 nW for $\Delta M_s = \pm 1$ and 1.2 mW for $\Delta M_s = \pm 2$. The central line in the $\Delta M_s = \pm 1$ spectrum is due to a remainder of $\mathbf{1}^{+\bullet}$.

Footnotes

† *Selected data* for **1**: mp 216–218 °C; ^{1}H NMR ($CDCl_3$) δ 6.68 (2 H, dd, *J* 8.0, 2.0 Hz, *m*-PhH-4), 6.86 (1 H, t, *J* 2.0 Hz, *m*-PhH-2), 6.94–7.01 (14 H, m, *p*-PhH-2, *p*-PhH-3, *di*-PhH-4, PhH-4), 7.06–7.12 (13 H, m, *m*-PhH-5, *di*-PhH-2, PhH-2), 7.19–7.25 (12 H, m, *di*-PhH-3, PhH-3); ^{13}C NMR ($CDCl_3$) δ 117.4, 118.6, 122.4, 123.4, 123.7, 123.8, 125.3, 125.6, 128.9, 129.1, 129.2, 129.7 (CH), 142.6, 143.0, 147.6, 147.9, 148.6 (*ipso*-C).

‡ The values reported in ref. 8 have been scaled by +0.12 V to correct for the difference in E_0 of the Fc/Fc$^+$ couple, resulting from different experimental conditions [E_0 = 0.35 V (ref. 8) *vs* E_0 = 0.47 V in present study].

§ While it has been reported that strongly acidic conditions do not influence the oxidation of TPDB (G. Durand, G. Morin and B. Trémillon, *Nouv. J. Chem.*, 1979, **7**, 463), we found that for **1** the presence of a strong acid (TFA, sulfonic acids) is required to observe the EPR spectrum of the triplet state di(cation radical) in combination with most oxidising agents (*e.g.* thianthrenium perchlorate, ferric chloride, tetrabutylammonium periodate), the only exception being nitrosonium tetrafluoroborate so far. Further studies are in progress to assess the role of acidity for **1** in more detail.

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