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# Synthesis and Characterization of Some Novel Homo- and Hetero-Diradicals of Hydrazyl and Nitroxide Type

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Starting from the well known stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH; **2a**) and its congener 2,2-diphenyl-1-(4-cyano-2,6-dinitrophenyl)hydrazyl **2b**, or from their reduced hydrazine counterparts **1a,b**, it was possible to obtain the *p*-quinonoid compounds **4a,b** by oxidation with ceric (Ce<sup>4+</sup>) sulfate, which by reduction gave the corresponding hydroxyl derivatives 2-phenyl-2-(4-hydroxyphenyl)-1-picrylhydrazine **5a** or 2-phenyl-2-(4-hydroxyphenyl)-1-(4-cyano-2,6-dinitrophenyl)hydrazine **5b**. These hydroxyl derivatives (**5a,b**) react with 4-carboxy-TEMPO or 2,2-diphenyl-1-(4-carboxy-2,6-dinitrophenyl)hydrazine to form the corresponding esters **6a,b** or **8a,b**. These esters (**6a,b** and **8a,b**) lead to the hybrid hetero diradicals (nitroxide–hydrazyl type) **7a,b** or homo biradicals (hydrazyl–hydrazyl type) **9a,b** by oxidation with lead dioxide or potassium permanganate. The new compounds were characterized by UV-vis, NMR, EPR, and MS analysis, and their magnetic behaviour was investigated.

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## Introduction

The chemistry of stable hydrazyl radicals is nowadays well understood,<sup>[1–4]</sup> finding their roots in 1922 with the pioneering work of Goldschmidt and Renn,<sup>[5]</sup> at a time when electron paramagnetic resonance (EPR or ESR) spectroscopy was not yet discovered and the study of stable free radicals was conducted only by chemical means. Since then, the strange and marvellous chemical behaviour of stable free radicals has attracted many chemists.<sup>[6–10]</sup> Nowadays, stable free radicals are usually classified into general types of oxygen-, carbon-, or nitrogen-centred free radicals, or subdivided into hydrazyl, verdazyl, nitroxide (TEMPO, PROXYL, DOXYL), and galvinoxyl congeners.<sup>[1]</sup>

Hydrazyl radicals are most suitable as multifunctional compounds, because of the possibility of their involvement in different chemical processes such as reduction–oxidation (redox) or acid–base reactions.<sup>[4,11,12]</sup> It is worth remembering that both these processes are accompanied by dramatic changes in structure and properties: for example, the 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical is perfectly stable for years as a purple compound, which can be reduced to the corresponding yellow hydrazine DPPH-H in a reversible redox process. This DPPH• radical can also be involved in a reversible acid– base reaction, which leads to the corresponding diamagnetic red anion DPPH<sup>-</sup>. All these processes may be observed with the naked eye by the colour change.<sup>[4,11,13]</sup> It is also known that hydrazyl radicals can be used not only as redox or acid–base sensors, but also as nitrogen dioxide sensors.<sup>[4,13,14]</sup>

Some crystals constructed from high-spin organic molecules act as molecular magnets.<sup>[15]</sup> In 1989 the first nitroxide-based

ferrimagnets (as a complex with transition metals) were reported, although in earlier decades many molecular magnets had been discovered.<sup>[16,17]</sup> Diradicals of the hydrazyl type have been known since 1964,<sup>[18]</sup> but the compound synthesized by Weil was extremely unstable (see structure A in Fig. 1), probably because of the corresponding zwitterion structure, while more stable DPPH-based diradicals were reported later (structure B, Fig. 1).<sup>[19–21]</sup>

Our previous papers have shown that the DPPH<sup>•</sup> radical and its congeners reacted with *N*-alkoxypicramides, which leads to the formation of diazenium betaine compounds.<sup>[22]</sup> These compounds were obtained by a *radical* + *radical* coupling reaction, from a stable hydrazyl radical and a picryl-*N*-alkoxy short-lived



Fig. 1. Dihydrazyl radicals from the literature.



Scheme 1. Formation of the deeply coloured diazenium betaine.



Scheme 2. Proposed mechanism of formation for compounds 3 and 4 ( $\mathbf{a}, R = NO_2$ ;  $\mathbf{b}, R = CN$ ).

radical, generated in situ by the hydrazyl radical (by hydrogen abstraction) (Scheme 1).

The present paper deals with the synthesis of the title compounds and their physico-chemical properties.

#### **Results and Discussion**

## Formation of Quinonoid Compounds 4a,b

Ceric sulfate is a very strong oxidant ( $E^0$  1.44 V) and reacts with compounds **1a**,**b** in the first step to give the corresponding well known stable hydrazyl radicals 2a,b, identified by TLC ( $R_F$ value), and EPR and UV-vis spectroscopy.<sup>[1]</sup> It is well established that the preferred position for a radical + radical coupling reaction in the case of DPPH<sup>•</sup> is the *para*-position on a phenyl ring.<sup>[14,22,23]</sup> We believe that the next step in the mechanism is a one-electron abstraction, which leads to the formation of a carbocation, which in the presence of water and excess oxidant finally forms the quinonoid compounds 4a,b (Scheme 2). As supplementary arguments to our proposed mechanism, we mention that when starting from the corresponding *p*-nitro derivative of 1a,b, no quinonoid compounds are formed. The presence of the sulfate anion also seems to be necessary, because on replacing the sulfate anion with acetate (ceric acetate), no quinonoid compound is formed.

#### Physico-Chemical Properties of Compounds 4a,b

Compounds **4a**,**b** have an extremely intense pink-red colour (Fig. 2 and Table 1), and can be easily reduced to the corresponding phenol derivatives **5a**,**b**, in a two-step redox process, the reduction also being accompanied by a dramatic colour change to yellow. The process is totally reversible: upon oxidation the regeneration of the parent compounds is achieved



Fig. 2. UV-Vis spectrum of 4a (in DCM).

(Scheme 3). The intermediate radical compounds 3a,b were detected by means of EPR spectroscopy (Fig. 3); the hyperfine coupling constants  $a_N$  correspond to the common values of hydrazyl radicals (Table 1).

The NH hydrogen is acidic, owing to the strong electronwithdrawing effect of the picryl group, and can be removed by bases, such as ammonia. This acid–base process yields anions  $5a^{-}$  and  $5b^{-}$  and is also accompanied by a colour change (well known in the literature),<sup>[11,23]</sup> see Table 1.

#### Synthesis of Diradicals

Starting from compounds **5a,b** stable hybrid diradicals of hydrazyl or nitroxide type are obtained.<sup>[13,23]</sup> Thus, from reaction of phenolic compounds **5a,b** with 4-carboxy-TEMPO (Scheme 4) or 2,2-diphenyl-1-(2,6-dinitrobenzoic acid)hydrazine (Scheme 5), followed by oxidation, stable diradicals **7a,b** (Scheme 4) and **9a,b** (Scheme 5) are prepared.

Compound	$R_{\rm F}{}^{\rm A}$	$\lambda_{max} \ [nm]^{B}$	$a_{\rm N}  [{\rm G}]^{\rm C}$	$G^{\mathrm{D}}$
3b			7.72	2.0039
			7.62	(2.0039)
4a	0.190	537		—
4b	0.119	526		_
5a	0.131	327		_
5a-	_	412		_
5b	0.083	380		_
5b <sup>-</sup>	_	413		_
6a	0.155	312	15.39	2.0057
6b	0.107	365	15.37	2.0057
6a-		428		_
6b-	_	375		_
7a	0.190	530	15.42	2.0057
			12.29	2.0039
			4.07	(2.0039)
7b	0.107	635	15.38	2.0057
			12.15	2.0039
			3.97	(2.0039)
8a	0.592	392		—
8a-		410		_
8b	0.529	392		_
8b <sup>-</sup>	_	409		_
9a	0.543	528	4.30	2.0039
			4.30	(2.0039)
			4.30	2.0039
			4.30	(2.0039)
9b	0.488	628	4.35	2.0039
			4.35	(2.0039)
			4.35	2.0039
			4.35	(2.0039)
				```

Table	1.	Physico-chemical	properties	of	the	compounds
		described	l in this stud	v		

<sup>A</sup>Silica gel/CH<sub>2</sub>Cl<sub>2</sub>. <sup>B</sup>In CH<sub>2</sub>Cl<sub>2</sub> (for anions, in CH<sub>2</sub>Cl<sub>2</sub> with 5% NH<sub>3</sub> in methanol). <sup>C</sup>In deoxygenated toluene at 290 K. <sup>D</sup>g values measured against solid DPPH standard (g 2.0037).



Scheme 3. Two-step redox process.

## EPR Spectra (Simulation in Red)

The values of the hyperfine coupling constants in the EPR spectra, recorded for the newly synthesized compounds, are compiled in Table 1. Fig. 4 shows the recorded EPR spectra of the free-radical compounds (in black), together with the



Fig. 3. EPR spectra of 3b (simulation in red).



Scheme 4. Synthesis of the hybrid diradicals **7a**,**b** of nitroxyl–hydrazyl type.

simulated spectra (in red). These spectra can be divided into three types: monoradical spectra of nitroxide type (**6a**,**b**), hybrid hetero-diradical spectra of nitroxide–hydrazyl type (**7a**,**b**), and homo-biradical spectra of hydrazyl–hydrazyl type (**9a**,**b**).

The EPR spectra of nitroxide radicals present three lines with equal intensity (1:1:1), while for hydrazyl radicals they usually present five lines with 1:2:3:2:1 intensities (as a result of the presence of two almost equivalent nitrogen atoms: if they are non-equivalent, a maximum number of nine lines can appear).

The spectra of **6a,b** are indeed the expected triplet; in the case of hybrid biradicals **7a,b**, their EPR spectra can be regarded as two superimposed spectra: one arising from the nitroxide (the sharp triplet) and one from the hydrazyl radical (the broad lines). Simulation of the recorded diradicals EPR spectra for **7a,b** as an equal mixture of two species (nitroxide + hydrazyl) give a good fit (Fig. 4).

A more interesting case is noticed for the hydrazyl-hydrazyl biradical spectra (**9a,b**), which cannot be simulated as a simple mixture of two hydrazyl radicals because of the spin-spin coupling (or spin-exchange). However, simulation as a biradical with  $J \gg a_N$  does give a good fit (*J* is the exchange interaction).<sup>[23]</sup>

An easy method to see (and sometimes to evaluate or measure) the spin–spin interaction is to record the EPR spectra at low temperature. Fig. 5 shows the EPR spectrum of compounds 6 and 9 at 100 K. In the case of monoradicals 6, the well known rigid limit EPR spectrum of a nitroxide is seen, while in the case of biradicals 9 the broadening of the spectra is very noticeable.



Scheme 5. Synthesis of the hybrid biradicals **9a**,**b** of hydrazyl–hydrazyl type.



Fig. 4. EPR spectra of compounds 6, 7, and 9 (top: 6a,b; middle: 7a,b; bottom: 9a,b; a left; b right; simulation in red).



Fig. 5. EPR spectra of the radicals 6 and 9 in a solid state (frozen toluene).



**Fig. 6.**  $\chi_M T$  versus *T* plot for compound **7a**. The red solid line represents the fit of experimental data to Eqn (2), see text.

## The Magnetism of the Diradicals 7a and 9a

There is current interest in the study of diradical magnetism.<sup>[24–31]</sup> The magnetic properties of compounds 7a and 9a have been investigated in the temperature range of 2–300 K, under an applied magnetic field of 5 kG. The  $\chi_{M}T$  versus T plots  $(\chi_{\rm M}$ : molar magnetic susceptibility), and the corresponding fits of the experimental data to the modified Bleaney-Bowers equation (Eqn 1), which describes the magnetic behaviour of a radical dimer that interacts weakly with their neighbours, are depicted in Figs 6 and 7. The room-temperature values of  $\chi_{M}T$  of 0.73 and  $0.71 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for **7a** and **9a**, respectively, are slightly lower than the expected value of  $0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for two S = 1/2uncorrelated spins.  $\chi_{M}T$  is practically constant down to approx. 100 K, below which it continuously decreases to reach values of 0.42 (for 7a) and 0.23 (for 9a)  $cm^3 mol^{-1} K$  at 2 K. This behaviour suggests dominant antiferromagnetic interactions in both compounds.

$$\chi_{\rm dimer} = \frac{2Ng^2\beta^2}{k_{\rm B}T} \frac{1}{3 + \exp(-2J_1/k_{\rm B}T)}$$
(1)

$$\chi T = \frac{\alpha \chi_{\text{dimer}} T}{1 - \frac{2zJ_2}{N\sigma^2 \beta^2} \cdot \chi_{\text{dimer}}}$$
(2)

The experimental magnetic data were fitted to the Bleaney– Bowers equation,<sup>[32]</sup> modified to take into account weak intermolecular interactions in the molecular field, and approximation by Eqn (2),<sup>[33]</sup> where  $\chi_{\rm M}$  is the experimental molar paramagnetic susceptibility expected for a magnetically isolated dimer (*T* is the temperature,  $k_{\rm B}$  the Boltzmann constant, *z* the number of neighbouring dimers that interact magnetically with each dimer, and  $\alpha$  denotes the purity).

The g-factor was fixed as g = 2.0048 for **7a** and 2.0039 for **9a**, as derived from EPR spectroscopy. The least-squares fitting



**Fig. 7.**  $\chi_M T$  versus *T* plot for compound **9a**. The red solid line represents the fit of experimental data to Eqn (2), see text.

leads to  $J_1 = -0.001 \text{ cm}^{-1}$ ,  $zJ_2 = -2.8 \text{ cm}^{-1}$ , and  $\alpha = 0.98$  $[R(\chi_{\rm M}T) = 1.5 \times 10^{-4}]$  for 7a, and  $J_1 = -0.002 \,{\rm cm}^{-1}$ ,  $zJ_2 =$  $-8.0 \text{ cm}^{-1}$ , and  $\alpha = 0.97 [R(\chi_{\text{M}}T) = 7.0 \times 10^{-5}]$  for **9a**. It is worth noting that the quality of the fit does not change substantially by fixing  $J_1$  at a value lying between -1 and  $+3 \text{ cm}^{-1}$ , so that this exchange parameter cannot be accurately determined from this fitting. However, its value has to be small. We further fitted the magnetic susceptibility data using the Curie-Weiss law  $[\chi_M = C/(T - \theta)]$ , with  $C = 0.73 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and  $\theta = -1.96$  K for 7a, and C = 0.73 cm<sup>3</sup> mol<sup>-1</sup> K and  $\theta = -5.56$  K for 9a]. The Curie constant (C) is in agreement with the expected value for organic biradicals with a g factor close to 2. The results show that the intra-dimer exchange-coupling is negligible in both compounds, and that the overall antiferromagnetic behaviour observed is a result of some inter-dimer interactions, which are stronger in the case of compound 9a (dipole-dipole interactions).

### Conclusions

It has been shown that oxidation of some hydrazine derivatives with ceric sulfate followed by reduction with sodium ascorbate leads to their hydroxylation in very high yields. By classical coupling reactions between these hydroxyl derivatives and other stable free radicals (or precursors) which contain a carboxylic group it was possible to synthesise novel homo- and heterodiradicals of hydrazyl and nitroxide type. Their characterization by UV-vis spectroscopy, MS, EPR spectroscopy, and magnetic behaviour is described. These compounds can be involved in acid—base or redox processes that are easily monitored by visible or EPR spectra.

#### Experimental

All solvents used were purchased from Aldrich or Lancaster and used without further purification. Ceric sulfate, compounds **1a**,

2a, and other common reagents were from Aldrich. Compound 1b was prepared as described previously.[11] NMR spectra were recorded on a Jeol EX270 instrument, EPR spectra on Jeol RE1X or Bruker ESP300 spectrometers, UV-vis spectra on a Hitachi U-3000 spectrometer, and MS spectra on a VG Autospec spectrometer. Simulations of the EPR spectra were performed using the WinSim free software. Typical settings used for the EPR measurements follows: concentration of the sample  $10^{-4}$  M, number of scans 1, centre field 3360 G, sweep field 100 G, frequency 9.42 GHz, power 1 mW, sweep time 60 s, time constant 0.1 s, modulation frequency 100 kHz, gain 100, and modulation width 1 G. Variable-temperature (2-300 K) magnetic susceptibility measurements were carried out on polycrystalline samples, using a Quantum Design MPMS-XL SQUID magnetometer operated at a 5 kG magnetic field. Diamagnetic corrections for the compounds were estimated from Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder. All J values quoted in this paper are based on the 2J formalism  $(H = -2J\Sigma S_i S_i)$ , with a positive J implying a ferromagnetic interaction. Where necessary, values from the literature have been converted into third formalism for consistency.

#### General Procedure for Obtaining Compounds 4

Compound **1a** or **2a** (1 mmol) dissolved in dichloromethane (40 mL) was stirred overnight with a slurry formed from ceric sulfate (20 g) and water (10 mL). The organic phase was then separated, dried over anhydrous sodium sulfate, and the solvent was removed under vacuum. The residue was dissolved in dichloromethane and chromatographed on a silica column (or on preparative TLC plates), using 9:1 dichloromethane/ether as eluent, to yield the pure compound **4a** as a dark solid (after removal of the solvent). Starting from **1b** (or **2b**), the **4b** derivative was obtained. The final yield was around 90%.

Compound 4a.  $R_{\rm F}$  (silica/dichloromethane) 0.190. m/z 409 (C<sub>18</sub>H<sub>11</sub>N<sub>5</sub>O<sub>7</sub>, *M* 409).  $\delta_{\rm H}$  (CD<sub>2</sub>Cl<sub>2</sub>) 8.62 (s, 2H, picryl CH), 8.03 (dd, 1H, *J* 13.1, 6.0, quinone CH), 7.55–7.37 (m, 5H, phenyl), 6.93 (dd, 1H, *J* 12.2, 4.0, quinone CH), 6.67 (dd, 1H, *J* 13.1, 6.0, quinone CH), 6.36 (dd, 1H, *J* 12.2, 4.0, quinone CH).  $\delta_{\rm C}$  (CD<sub>2</sub>Cl<sub>2</sub>) 144.01, 139.54, 133.15, 132.29, 130.67, 129.95, 129.60, 129.13, 127.25, 124.66.  $\lambda_{\rm max}/{\rm nm}$  537.

Compound 4b.  $R_F$  (silica/dichloromethane) 0.119. *m/z* 389 (C<sub>19</sub>H<sub>11</sub>N<sub>5</sub>O<sub>5</sub>, *M* 389).  $\delta_H$  (CD<sub>2</sub>Cl<sub>2</sub>) 8.00 (dd, 1H, *J* 12.1, 2.4, quinone CH), 7.55–7.35 (m, 5H, phenyl), 6.90 (dd, 1H, *J* 12.1, 2.4, quinone CH), 6.64 (d, 1H, *J* 10.0, quinone CH), 6.33 (d, 1H, *J* 10.0, quinone CH).  $\delta_C$  (CD<sub>2</sub>Cl<sub>2</sub>) 143.09, 132.02, 131.89, 130.56, 129.81, 129.58, 128.58, 128.54, 127.13, 115.44.  $\lambda_{max}/mm$  526.

#### General Procedure for Obtaining Compounds 5

Compound **4a** or **4b** (100 mg) dissolved in dichloromethane (50 mL) was stirred with a 5% aqueous solution of sodium ascorbate (50 mL) till the colour changed from red to yellow (depending on the stirring rate, this took from minutes to hours). The organic phase was then separated, dried over anhydrous sodium sulfate, and the solvent was removed under vacuum to yield **5a** (or **5b**) as a yellow solid. The yield was almost quantitative and the purity of the compounds was adequate for further reactions. Analytically pure samples were obtained by column chromatography (or preparative TLC) on silica.

Compound 5a.  $R_{\rm F}$  (silica/dichloromethane) 0.131. m/z 410 (C<sub>18</sub>H<sub>13</sub>N<sub>5</sub>O<sub>7</sub>, M411).  $\delta_{\rm H}$  (CD<sub>2</sub>Cl<sub>2</sub>) 9.98 (s, 2H, NH, OH), 9.17

(s, 1H, picryl CH), 8.51 (s, 1H, picryl CH), 7.31–6.77 (m, 9H, phenyl).  $\delta_{\rm C}$  (CD<sub>2</sub>Cl<sub>2</sub>) 154.84, 146.77, 142.21, 139.56, 129.19, 124.94, 124.33, 117.98, 116.48.  $\lambda_{\rm max}$ /nm 327. In a basic medium (dichloromethane and ammonia in methanol) the corresponding anion **5a**<sup>-</sup> was obtained, with  $\lambda_{\rm max}$ /nm 412.

Compound **5b**.  $R_{\rm F}$  (silica/dichloromethane) 0.083. m/z 390 (C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>O<sub>5</sub>, *M* 391).  $\delta_{\rm H}$  (CD<sub>2</sub>Cl<sub>2</sub>) 9.86 (s, 2H, NH, OH), 8.58 (s, 1H, CH–NO<sub>2</sub>), 7.87 (s, 1H, CH–NO<sub>2</sub>), 7.29–6.75 (m, 9H, phenyl).  $\delta_{\rm C}$  (CD<sub>2</sub>Cl<sub>2</sub>) 155.02, 146.84, 141.03, 139.30, 128.97, 124.97, 123.99, 117.68, 116.37, 116.56, 100.60.  $\lambda_{\rm max}/{\rm nm}$  380. In a basic medium (dichloromethane and ammonia in methanol) the corresponding anion **5b**<sup>-</sup> was obtained, with  $\lambda_{\rm max}/{\rm nm}$  413.

#### General Procedure for Obtaining Compounds 6

A mixture of **5a** or **5b** (0.2 mmol) and 4-carboxy-TEMPO (0.22 mmol) dissolved in dichloromethane (50 mL) was treated with DCC (0.25 mmol) and DMAP (20 mg), and the mixture was left overnight. The dichloromethane solution was washed sequentially with 0.1 N aqueous hydrochloric acid, aqueous sodium hydrogen carbonate, and water, and then the organic layer was dried over anhydrous sodium sulfate. Removal of dichloromethane afforded the crude compounds **6**, which were purified by chromatography on silica. The overall yield was  $\sim$ 70%.

Compound 6a.  $R_{\rm F}$  (silica/dichloromethane) 0.155. m/z 592 (C<sub>28</sub>H<sub>29</sub>N<sub>6</sub>O<sub>9</sub>, *M* 593).  $\lambda_{\rm max}/\rm{nm}$  312. In a basic medium (dichloromethane and ammonia in methanol) the corresponding anion 6a<sup>-</sup> was obtained, with  $\lambda_{\rm max}/\rm{nm}$  428. EPR (toluene):  $a_{\rm N}$  15.39 G, g 2.0057.

Compound **6b**.  $R_{\rm F}$  (silica/dichloromethane) 0.107. m/z 572 (C<sub>29</sub>H<sub>29</sub>N<sub>6</sub>O<sub>7</sub>, *M* 573).  $\lambda_{\rm max}/{\rm nm}$  365. In a basic medium (dichloromethane and ammonia in methanol) the corresponding anion **6b**<sup>-</sup> was obtained, with  $\lambda_{\rm max}/{\rm nm}$  375. EPR (toluene):  $a_{\rm N}$  15.37 G, g 2.0057.

#### General Procedure for Obtaining Compounds 7

Compound **6a** or **6b** (20 mg) dissolved in dichloromethane (20 mL) was stirred with 2.0 g of lead dioxide or potassium permanganate for 2 h. The solution was then filtered, and the solvent removed under vacuum. The yield was almost quantitative, and an analytical sample was obtained by preparative TLC on silica.

Compound 7a.  $R_{\rm F}$  (silica/dichloromethane) 0.190. m/z 592 (C<sub>28</sub>H<sub>28</sub>N<sub>6</sub>O<sub>9</sub>, *M* 592).  $\lambda_{\rm max}$ /nm 530. EPR (toluene):  $a_{\rm N}$  15.42/ 12.29/4.07 G, g 2.0039/2.0057.

Compound 7b.  $R_{\rm F}$  (silica/dichloromethane) 0.107. m/z 572 (C<sub>29</sub>H<sub>28</sub>N<sub>6</sub>O<sub>7</sub>, *M* 572).  $\lambda_{\rm max}$ /nm 635. EPR (toluene):  $a_{\rm N}$  15.38/ 12.15/3.97 G, g 2.0039/2.0057.

#### General Procedure for Obtaining Compounds 8

Compounds **8a,b** were obtained in the same manner as **6a,b**, using 2,2-diphenyl-1-(2,6-dinitro-4-benzoic acid)hydrazine instead of 4-carboxy-TEMPO.

Compound 8a.  $R_{\rm F}$  (silica/dichloromethane) 0.592. *m/z* 786 (C<sub>37</sub>H<sub>25</sub>N<sub>9</sub>O<sub>12</sub>, *M* 787).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 10.17 (s, 1H, NH), 9.40 (s, 1H, NH), 9.07 (s, 1H, CH–NO<sub>2</sub>), 8.97 (s, 1H, CH–NO<sub>2</sub>), 8.49 (s, 1H, CH–NO<sub>2</sub>), 8.37 (s, 1H, CH–NO<sub>2</sub>), 7.38–7.11 (m, 19H, phenyl).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 161.47, 147.36, 146.09, 145.51, 144.23, 143.99, 141.77, 141.37, 136.46, 129.71, 129.36, 128.80, 126.34, 125.42, 122.25, 121.03, 120.92, 120.34, 118.35.  $\lambda_{\rm max}/{\rm nm}$  392. In a basic medium (dichloromethane and ammonia in methanol) the corresponding anion **8a**<sup>-</sup> was obtained, with  $\lambda_{\rm max}/{\rm nm}$  410.

Compound **8b**.  $R_{\rm F}$  (silica/dichloromethane) 0.529. m/z 766 (C<sub>38</sub>H<sub>25</sub>N<sub>9</sub>O<sub>10</sub>, *M* 767).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 9.96 (s, 1H, NH), 8.99 (s, 1H, CH–NO<sub>2</sub>), 8.66 (s, 1H, NH), 8.54 (s, 1H, CH–NO<sub>2</sub>), 8.33 (s, 1H, CH–NO<sub>2</sub>), 7.81 (s, 1H, CH–NO<sub>2</sub>), 7.29–7.05 (m, 19H, phenyl).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 161.69, 147.52, 146.28, 145.86, 144.24, 141.45, 140.71, 136.98, 129.65, 129.37, 126.09, 125.39, 122.32, 121.06, 120.98, 120.42, 118.69, 115.43, 101.23.  $\lambda_{\rm max}/{\rm nm}$  392. In a basic medium (dichloromethane and ammonia in methanol) the corresponding anion **8b**<sup>-</sup> was obtained, with  $\lambda_{\rm max}/{\rm nm}$  409.

## General Procedure for Obtaining Compounds 9

Compounds **9a**,**b** were obtained in the same manner as **7a**,**b**.

Compound **9a**.  $R_{\rm F}$  (silica/dichloromethane) 0.543. m/z 785 (C<sub>37</sub>H<sub>23</sub>N<sub>9</sub>O<sub>12</sub>, *M* 785).  $\lambda_{\rm max}$ /nm 528. EPR (toluene):  $a_{\rm N}$  4.30/4.30/4.30/4.30 G, g 2.0039/2.0039.

Compound **9b**.  $R_{\rm F}$  (silica/dichloromethane) 0.488. m/z 765 (C<sub>38</sub>H<sub>23</sub>N<sub>9</sub>O<sub>10</sub>, *M* 765).  $\lambda_{\rm max}$ /nm 628. EPR (toluene):  $a_{\rm N}$  4.35/4.35/4.35/4.35/6, g 2.0039/2.0039.

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