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Rigid nitronyl-nitroxide-labelled anchoring molecules: syntheses, structural and magnetic investigations

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Abstract—The syntheses of two rigid organic molecular rods bearing a nitronyl-nitroxide radical and a terminal nitrogen-based functionality like a pyridine or a cyano group are reported. Both new paramagnetic molecules are fully characterized, including crystal structure analysis. Furthermore their magnetic behaviours in the crystalline state are investigated and their spin concentration corroborate their excellent purity. While the pyridine functionalized rod is synthesized by converting the corresponding benzaldehyde to the phenyl-nitronyl-nitroxide radical, the synthesis of the cyano functionalized rod demonstrates the accessibility of highly sophisticated spin-labelled molecules via cross-coupling reaction with a *meta*-iodo-phenyl-nitronyl-nitroxide moiety.

The presence of unpaired electrons in organic molecules is of great interest as the promising combination of the virtually unlimited structural diversity of organic chemistry and the amazing physics of paramagnetic scaffolds. Stable organic radicals have been used as spin-labels for biological and medical applications.[1] Paramagnetic molecules have also been used in the field of molecular magnetism to investigate the interaction either between their unpaired electrons[2] or with other unpaired electrons of the neighbouring radicals[3] or paramagnetic metals.[4] More recently, several groups focussed on the interaction between an unpaired electron of a stable organic radical and excited electrons. The combination of various chromophores with radicals has been achieved for that purpose.[5]

In the course for the investigation of the behaviour of unpaired electrons in different environments, a challenging goal is the design of paramagnetic molecular rods for the functionalization of surfaces. Together with the observation of organic radicals on surfaces, the investigation of their properties in two dimensions is fascinating. However, even if several conjugated systems bearing radicals have been published,[6] spin-labelled conjugated organic anchoring molecules are not frequently described in literature and their use for surface or nanoparticle coating are rare.[7]

Moreover, the interaction between an unpaired electron of an organic radical and an electron flow is unprecedented to our knowledge. In fact, only few studies with paramagnetic metal-containing molecules have been reported like a paramagnetic metal complex connected between two gold electrodes, showing a particular behaviour due to the presence of an unpaired electron spin.[8]

The synthesis of more and more sophisticated molecules with specific properties or shapes will therefore be of valuable interest to increase the knowledge about their behaviours on different types of surfaces and the new properties they could induce.

In this communication, we present the syntheses of the two rigid rod π-conjugated paramagnetic molecules combining a nitronyl-nitroxide moiety and a terminal nitrogen donor atom as anchoring functionality. To the best of our knowledge, elongated conjugated molecules bearing a nitronyl-nitroxide spin-containing unit together with an anchor group have not been reported.

The X-ray crystal structures and magnetic measurements are shown for both compounds, pointing at the efficiency of the applied reaction strategies. In particular, the efficient integration of an iodo-phenyl-nitronyl-nitroxide as modular building block of a functionalized

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Keywords: Stable radical; Rigid rod; Molecular magnet; Sonogashira coupling reaction.

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molecular structure is here demonstrated for the first time by a cross-coupling reaction.

The different terminal anchor groups of **1** and **2** required two synthetic strategies.

(a) The synthetic strategy for radical **1** follows the classical Ullman synthesis. First the backbone of the rigid rod structure is assembled. Containing an aldehyde function as placeholder, this intermediate is subsequently transformed in two steps to the nitronyl-nitroxide radical as displayed in Scheme 1.[9] In more details, the aldehyde **3** has been obtained by a Sonogashira-type coupling reaction with the commercially available hydrochloride salt of the bromo-pyridine and the 3-ethynyl-benzaldehyde[10] in a THF/*i*-Pr_2NH mixture at rt in 47–52% yield. A multiple condensation with the *N*,*N′*-dihydroxy-2,3-diamino-2,3-dimethyl-butane **4**[11] in MeOH gave the bis-*N*-hydroxyl amine **5** in 62% yield.[12] This intermediate product was oxidized by $NaIO_4$ in a CH_2Cl_2/H_2O biphasic mixture to give the desired blue nitronyl-nitroxide **1** in 84% yield.[13]

(b) An unlike synthetic strategy has been developed for radical **2**. The backbone of the rigid rod is assembled in the final step by a Sonogashira–Hagihara type cross-coupling reaction of molecular units, one of them bearing already the nitronyl-nitroxide radical (Scheme 2). To the best of our knowledge, this is the first synthesis with a *meta*-iodo-phenyl-nitronyl-nitroxide showing the excellent spin concentration of the product. Such a reaction step has been documented for the synthesis of substituted pyridine derivatives or phenyl analogues without additional substituents.[14] Using the similar NEt_3/pyridine solvent mixture reported for couplings with aryl-nitronyl-nitroxides at rt,[15] the blue target radical was obtained with 59% yield and with excellent spin concentration (vide infra).[16]

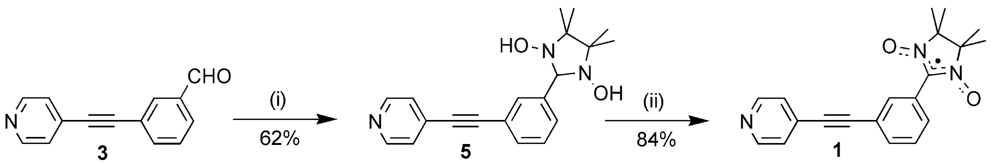
These two desired radicals are stable violet solids as shown by the relatively high melting points. The products were characterized by MALDI-TOF, UV–vis, IR spectroscopy, elemental analysis and single crystal X-ray structure analysis. The MALDI-TOF spectra of both radicals show the molecular peak and fragmentations corresponding to the loss of both oxygen atoms of the nitronyl-nitroxides. The characteristic ν_{NO} vibration band can be seen on the IR spectra ($1364\,cm^{-1}$ for **1** and **2**). As expected, the $\nu_{C\equiv C}$ or $\nu_{C\equiv N}$ vibration bands are also observed (**1**: $2210\,cm^{-1}$, **2**: $2226\,cm^{-1}$). On the UV–vis spectra, the absorption band corresponding to the characteristic $n\rightarrow\pi^*$ of aryl-nitronyl-nitroxide (586nm for **1** and for **2**) corroborates also the characterization of the two coloured molecules.

X-ray crystal structures of both compounds were determined on single crystals obtained by slow evaporation of a CH_2Cl_2–hexane mixture.[17] Both compounds crystallize monoclinic in the space group $P2_1/c$. The ORTEP views of both molecules are shown in Figures 1a and 2a, respectively.

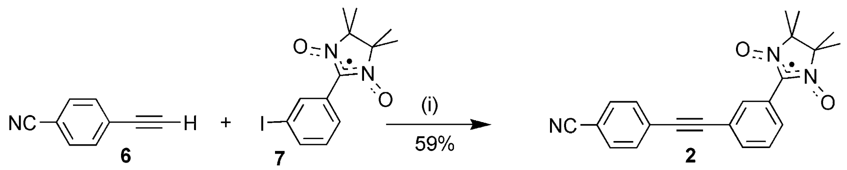
The nitronyl-nitroxides have characteristic bond lengths of such radicals having an unpaired electron equally shared between two equivalent NO groups ($d_{NO} = 1.27$–1.28 Å). The dihedral angle between the mean planes of the radical and the adjacent phenyl ring is also typical of such molecules (28.8° for **1**, 29.9° for **2**). Interestingly, the π system of the anchoring fragment formed by the two aromatic rings and the triple bond is highly conjugated as shown by the low dihedral angle between the rings (13.6° for **1** and 2.3° for **2**).

In both crystal structures, the packing shows π-stacking between the terminal aromatic ring with the anchor group and the benzene ring bearing the radical. The distances between the atoms of these aromatic systems are in the range of 3.3–3.5Å. Finally, two radicals are disposed in a head-to-tail manner with a relatively large intermolecular distance between the O atom of one radical and the central C atom of the neighbouring radical (4.30Å for **1** and 4.21Å for **2**).

Magnetic measurements were done with a SQUID susceptometer for both radicals on poly-crystalline samples from 2 to 300K. The corresponding magnetic behaviours versus temperature are reported, respectively, in Figures 1b and 2b.



Scheme 1. Reagents and conditions: (i) **4**, MeOH, 7d, rt; (ii) $NaIO_4$, CH_2Cl_2, H_2O, 1h, rt.



Scheme 2. Reagents and conditions: (i) $PdCl_2\,(PPh_3)_2$ 10mol%, CuI 5mol%, NEt_3/Py 1/4, 1.5h, rt.

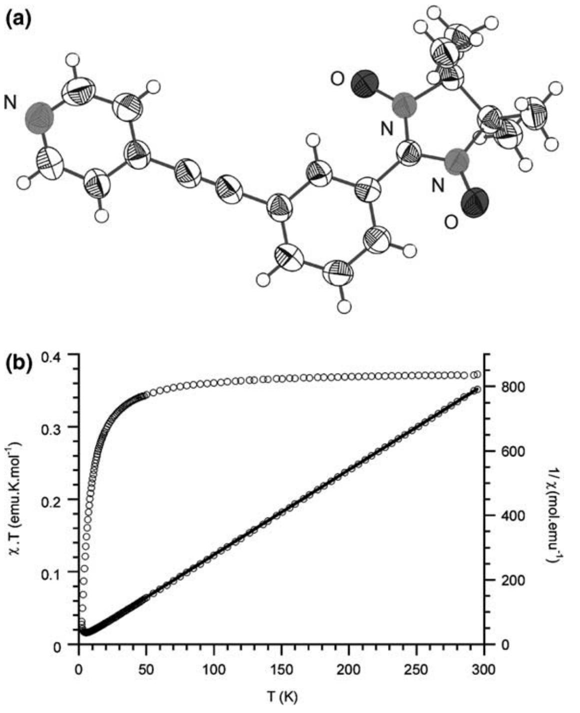


Figure 1. (a) ORTEP view of the molecular structure of **1**. (b) Magnetic behaviour of compound **1** versus temperature.

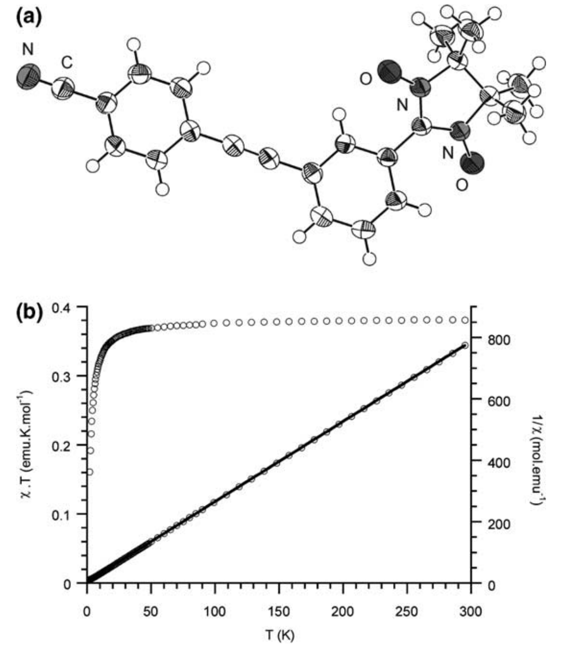


Figure 2. (a) ORTEP view of the molecular structure of **2**. (b) Magnetic behaviour of compound **2** versus temperature.

At high temperature, the $\chi \cdot T$ versus T curve for compound **1** is horizontal and located near the expected value for one isolated $S = 1/2$ spin ($\chi \cdot T = 0.371\,\mathrm{emu\,K\,mol^{-1}}$ at 300 K). This value is consistent with an excellent spin concentration and high purity of the sample. The curve remains horizontal down to ca. 100 K. By lowering further the temperature, a decrease of the curvature is observed, revealing the presence of an antiferromagnetic behaviour. A mean-field correction θ parameter of -5.4 K is obtained by fitting the $1/\chi = f(T)$ curve with a Curie–Weiss law above 10 K.

A similar shape is observed for compound **2**. At high temperature, the $\chi \cdot T$ product is near the expected value for one isolated $S = 1/2$ spin ($\chi \cdot T = 0.381\,\mathrm{emu\,K\,mol^{-1}}$) and the curve is horizontal down to ca. 50 K. This confirms again the high spin concentration and the purity of the sample prepared by the cross-coupling reaction in the presence of a radical. Here again, the curve decreases by lowering further the temperature due to intermolecular antiferromagnetic interactions. The best fit with a Curie–Weiss law gave a θ parameter of -1.9 K.

In summary, two different synthetic strategies allowed the preparation of rigid and conjugated paramagnetic anchor molecules with different end groups. While the frequently used and well-known Ullman synthesis of nitronyl-nitroxide radicals is well suited for the introduction of various functional groups in good yields, the modular nature of the Sonogashira–Hagihara cross-coupling reaction is very promising for the assembly of more complex nitronyl-nitroxide radicals bearing molecular structures. Seeing that, the enlargement of the tool kit of acetylene scaffolding with iodo-phenyl-nitronyl-nitroxide derivatives will further be promoted. Furthermore, the interactions between radical-bearing subunits on surfaces, their coupling with the surface and structure–property correlations of the rigid rod structure are currently in the focus of our investigations.

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13. R_f (SiO$_2$, CH$_2$Cl$_2$/MeCN 4/6): 0.45. MALDI-TOF (1,8,9-anthracenetriol): 335.9 (65) [M+H]$^+$, 319.9 (100) [M−O+H]$^+$, 303.9 (30) [M−2O+H]$^+$. IR (KBr pellets): 3449, 3040, 3023, 2975, 2210 ($\nu_{\mathrm{C\equiv C}}$), 1590, 1449, 1416, 1403, 1393, 1364 (ν_{NO}), 1217, 1166, 1138, 1123, 990, 899, 863, 824, 802, 683, 541, 455. UV–vis (CH$_2$Cl$_2$) λ nm (ε, M^{-1}cm^{-1}): 225 (20490), 282 (36390), 300 (25270), 353 (sh, 7560), 368 (10800), 586 (430), 621 (sh, 415), 682 (sh, 180). Mp: 122–128 °C. Anal. Calcd for $C_{20}H_{20}N_3O_2$ ($M_r = 334.39$): C, 71.84; H, 6.03; N, 12.57. Found: C, 72.02; H, 6.07; N, 12.65.
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16. R_f (SiO$_2$, CH$_2$Cl$_2$/MeCN 97/3): 0.18. MALDI-TOF (1,8,9-anthracenetriol): 359.9 (42) [M+H]$^+$, 343.9 (100) [M−O+H]$^+$, 327.9 (30) [M−2O+H]$^+$. IR (KBr pellets): 3436, 2977, 2226 ($\nu_{\mathrm{C\equiv N}}$), 1604, 1502, 1451, 1414, 1392, 1364 (ν_{NO}), 1311, 1274, 1220, 1164, 1139, 842, 797, 681, 554, 541, 455. UV–vis (CH$_2$Cl$_2$) λ nm (ε, M^{-1}cm^{-1}): 226 (23480), 285 (34920), 298 (38210), 316 (33830), 586 (465). Mp: 183–185 °C. Anal. Calcd for $C_{22}H_{20}N_3O_2$ ($M_r = 358.41$): C, 73.72; H, 5.62; N, 11.72. Found: C, 73.69; H, 5.53; N, 11.33.
17. Crystal data and structure refinement for **1** and **2**: Data were collected at 200 K on a STOE diffractometer with graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) using θ–2θ scans. The structures were solved by direct methods and refined by full-matrix least-squares analysis. **1**, $M = 334.39$, monoclinic, space group $P2_1/c$, with $a = 14.289(3)$, $b = 12.149(2)$, $c = 11.164(2)$ Å, $\beta = 111.44(3)°$, $V = 1804.1(6)$ Å^3, $Z = 4$, D$_c = 1.231$ Mg/m^3, $\mu = 0.081$ mm^{-1}. Parameters (226) were refined using 2302 unique observed reflections [$I > 1\sigma(I)$] to give $R1 = 0.0745$ and $wR2 = 0.1349$ (all data). Compound **2**, $M = 358.41$, monoclinic, space group P_1/c, with $a = 13.647(3)$, $b = 12.340(3)$, $c = 11.547(2)$ Å, $\beta = 100.98(3)°$, $V = 1909.1(7)$ Å^3, $Z = 4$, $D_c = 1.247$ Mg/m^3, $\mu = 0.082$ mm^{-1}. Parameters (244) were refined using 2760 unique observed reflections [$I > 1\sigma(I)$] to give $R1 = 0.0589$ and $wR2 = 0.1081$ (all data). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 249046 for **1** and CCDC 249047 for **2**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.