

CHEMISTRY A European Journal



Accepted Article

Title: Dithienopyrrole Derivatives with Nitronyl Nitroxide Radicals Offers Their Oxidation to Cationic High-Spin Molecules

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201905734

Link to VoR: http://dx.doi.org/10.1002/chem.201905734

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Dithienopyrrole Derivatives with Nitronyl Nitroxide Radicals Offers Their Oxidation to Cationic High-Spin Molecules

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Abstract: Three 1N-phenyl nitronyl nitroxide (NN) 4-substituted dithieno[3,2-*b*:2',3'-*d*]pyrrole (**DTP**) derivatives with $R^1 = 4$ -Phenyl-, 4H-, and 4-methylthiothiophenyl- (R^1_2 **DTP-Ph-NN**, $R^1 = H$, Ph and MeSTh) were designed, synthesized and characterized. The electrochemical properties were studied by cyclic voltammetry (CV). All the molecules exhibited two main oxidation peaks, first for radical cation and next for dication formation. The cation and dication formation were also confirmed by UV–vis absorption spectroscopy for **Ph**₂**DTP-Ph-NN** and **MeSTh**₂**DTP-Ph-NN** titrated with *tris*(4-bromophenyl)aminiumhexachloroantimonate (magic blue). In addition, the cation and dication formation were verified by EPR spectroscopy. Finally, the exchange interactions (*J*/*k*_B) of NN and radical cation were calculated by DFT studies.

Introduction

Organic high spin molecules are attractive due to their flexible and controllable electronic properties and those were obtained by different strategies.^[1] High spin molecules have been used for various applications such as spintronic device, and molecular magnets.^[1d, 2] The spin carrying units are very important in the high spin molecules, because of the kinetic stability issues of materials for further applications. To enhance the kinetic stability, nitronylnitroxide (NN) iminonitroxide (IN) were the most recognized spin units for the high spin organic molecules.^[3] Organic spin carrying unit linked with conjugated triarylaminium radical cations are also of interest.^[4] Their combination in mixed stable radical and one electron oxidized cation-diradical systems are more popular, because of their fair kinetic stability and synthetic accessibility. The parent triphenylaminium radical cation is not stable and quickly reacts via the para positions to form benzidines. Thus, introduction of an electron donating para substitutents eliminates this problem. Stable radical units linked with easily oxidizable aromatic amines are of particular interest for triplet ground state high spin molecules.[4a, 4b, 5] Thus, the mixed stable radical with radical-cation molecules were provided for high spin triplet ground state molecules.^[1d, 6] A series of nitronyl nitroxide (NN) substituted triarylamine (TAA-NN)[7], fused arylamine (FTAA-NN)^[8], pyrazine (NNDPP)^[9], thianthrene (TA-NN)^[10] phenothiazine (PTZ-NN)^[11] and pyrrole-based^[2b] molecules and their radical-cationic forms were reported (Figure S1), most of them afforded ground-state triplet diradicals upon

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one electron oxidation. Especially, 1-phenyl NN 4-substituted-2,5-di(thiophen-2-yl)-1H-pyrrole derivatives (TPT-Ph-NN),[12] NNsubstituted conjugated oligomers of dithienyl-N-methylpyrrole with methoxy substituents at the inner β -position of thiophene rings type of molecules (DTP-P-NN)^[13] were focused on the synthesis of cationic high-spin molecules. Since our interest is synthesis, stable-radical species substituted with π-conjugated electron donor systems and their radical cation formation for Dithieno[3,2-b:2,3-d]-pyrrole formation. (DTP) hiah spin derivatives are leading to better m-conjugation and lower ionization potential by electron-donating nature of the molecules. They also have two active positions at the thiophene, which serve to modify the energy levels to substitute different donor and or acceptor units which can assist to control the HOMO and LUMO energy level of the molecules. In our molecular design, two-phenyl (Ph) or -methylthiothiophene (MeSTh) groups were introduced to tune the electronic properties of the molecules in the DTP π -unit.^[14]

We report the design, synthesis, and structural characterization of three, NN substituted **DTP** molecules with R¹ = 4-Phenyl-, 4H-, and 4-di(methylthiothiophenyl dithieno[3,2-*b*:2',3'-*d*]pyrrole derivatives (R¹₂**DTP-Ph-NN** R¹ = H, Ph and MeSTh) together with the formation of their radical cationic (R¹₂**DTP-Ph-NN**)⁺ forms. Furthermore, intra-molecular exchange interactions were examined by DFT calculation.

Results and Discussion

Molecular design with DFT calculations

The computations were carried out to understand the electronic structure of the molecules. All the DFT calculations were performed using the Gaussian09 package.^[15] The full geometry optimizations were carried out by UB3LYP/6-31G(d) level for all the neutral radical molecules. The optimized structures and spin density distribution of the neutral radical molecules of **DTP-Ph-NN**, **Ph**₂**DTP-Ph-NN**, and **MeSTh**₂**DTP-Ph-NN** are shown in Figure 1.



Figure 1: Optimized structures (a), (b), and (c), spin density distributions (d), (e) and (f) for DTP-Ph-NN, Ph₂DTP-Ph-NN, and MeSTh₂DTP-Ph-NN), respectively, calculated by DFT using ub3lyp/6-31g(d) basis set.

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In order to get triplet ground state high spin molecules, one electron could be oxidized from HOMO of the neutral molecules. The proposed one electron oxidation mechanism is described in Figure S14 for spin polarized donor radicals. A similar mechanism was also reported using molecular orbital theory to analyses one electron oxidation of the amine-based spinpolarized donors radical and pyrrole derivatives molecules.[3b] Therefore, the energy level of the neutral molecules were analyzed using DFT calculations. The energy levels of the HOMO, LUMO and SOMO were summarized in the Figure 2 and table S1. The HOMO of the DTP-Ph-NN (-5.18 eV) is higher energy than HOMO (-5.19 eV) of the Ph2DTP-PhNN and MeSTh₂DTP-Ph-NN (-5.26 eV). The energy level of the SOMO for DTP-Ph-NN (-5.06 eV) is lower than for Ph2DTP-PhNN SOMO (-4.85 eV) and MeSTh2DTP-Ph-NN (-4.22 eV). The energy difference between HOMO and SOMO are gradually increased for DTP-Ph-NN, Ph2DTP-PhNN and MeSTh2DTP-Ph-NN, respectively. The results clearly indicate that the substitutions on their terminal sites in the core DTP π -unit with two-Ph or -MeSTh groups were changed the electronic properties of the molecules.



Figure 2: Relative energy levels of the HOMO green line, LUMO blue line and SOMO redline diagram of the DTP-Ph-NN, Ph₂DTP-Ph-NN, and MeSTh₂DTP-Ph-NN), respectively.

The bond distance between NN and Ph unit is 1.461 Å and Ph and DTP-backbone is 1.412, these values are same for all the derivatives. The torsion between NN and its attached phenyl is slightly varies for different derivatives such as 7.2°, 1.4°, and 1.7°, similarly between phenyl and DTP-backbone also varies as 39.9, 48.9 and 41.1 for **DTP-Ph-NN**, **Ph**₂**DTP-Ph-NN**, and **MeSTh**₂**DTP-Ph-NN**, respectively.

Synthesis

The syntheses of **R**₂**DTP-Ph-NNs** are demonstrated in scheme 1. Compound 1^[16] and 2^[17] were prepared by literature procedure and **3** obtained by modified procedure with improved yield.^[18] Ullman condensation of **3** with 2,3-bis(hydroxylamino)-2,3dimethylbutane (BHA) yielded **4**.^[19] Oxidation of **4** by NalO₄ offered **DTP-Ph-NN**. Then N–OH groups were protected for **4** with *tert*-butyldimethylsilyl (TBDMS) through *tert*butyldimethylsilyl chloride (*t*-BuMe₂SiCl) in the presence of imidazole in DMF as solvent to afford 5.^[20] Further compound **5** was reacted with *n*-butyllithium solution followed by trimethyltinchloride (Me₃SnCl) yielding **6**. Stille coupling was carried out between **6** and bromobenzene, or 2-bromo-5-(methylthio)thiophene^[21] yielding **7a** and **7b**, respectively. Further **7a** or **7b** were reacted with tetrabutylammoniumfluoride (TBAF) to yield **Ph₂DTP-Ph-NN** and **MeSTh₂DTP-Ph-NN**.^[20] All the diamagnetic precursors were characterized by NMR paramagnetic neutral radical molecules by Uv–vis EPR spectroscopy and HRMS mass spectrometry.





Reaction conditions: (a) Pd₂(dba)₃, *t*-Bu₃ONa, *t*-Bu₃P, toluene,125 °C, 46%, (b) BHA, DMF, 65 C, 52%, (c) NaIO₄, DCM, H₂O, 0 °C, 62%, (d) *t*-BuMe₂SiCl, imidazole, 55 °C, DMF, 83%, (e) *n*-BuLi, THF, -20 °C, Me₃SnCl, THF, 91%, (f) bromobenzene, Pd₂dba₃, P(o-tolyl)₃, toluene, 90 °C, (f) TBAF, THF.

X-ray crystallographic studies

The crystal structure analysis is important to understand magnetic interactions in the solid state. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of DCM solution for **MeSTh**₂**DTP-Ph-NN** and mixtures of DCM and PhCN solution for **Ph**₂**DTP-Ph-NN**.



Figure 3. X–ray crystal structure of (a) Ph₂DTP-Ph-NN, (b) molecular packing (c) and (d) MeSTh₂DTP-Ph-NN of the conformers, hydrogen atoms and PhCN for Ph₂DTP-Ph-NN are omitted for clarity.

The blue plate **Ph₂DTP-PhNN** was crystallized with PhCN solvent molecule in orthorhombic, Pbcn space group. The structure of the molecules is given in the Figure 3a. The torsions between the radical NN and phenyl are 14.0°. The torsions between the central phenyl and π -unit is 48.5°. Further, the molecular packing is displayed in Figure 3b, providing a short intermolecular distance (3.24 Å) between two oxygen atoms, in addition short π - π intermolecular distances are found as 3.45 Å for S11...C5 and 3.48 Å for S11...C4.

The green block MeSTh2DTP-Ph-NN was crystallized in dimeric triclinic form with P-1 space group (Figure S3a). The two structures of the unit cell are given in the Figures 3c and d. The two independent molecules differ mainly in the orientation of the thiophene unit and the torsion angles. In MeSTh₂DTP-PhNN-A, the sulfur atoms are arranged as S5 and S13 in syn-orientations, S8 and S20 in anti-orientations while in molecule MeSTh2DTP-Ph-NN-B, both S5 and S13, then S8 and S20 are arranged in anti-orientations. The torsions between the radical NN and Ph are also different in both molecules 34.0° and 15.1° for MeSTh₂DTP-Ph-NN-A, and MeSTh₂DTP-PhNN-B, respectively. Similarly slightly different torsion angles were found between the center Ph and DTP core as 30.2° and 27.6° for MeSTh2DTP-Ph-NN-A, and MeSTh₂DTP-Ph-NN-B, correspondingly. These variations are due to intermolecular interaction present between the molecules in the molecular packing.

Cyclic voltammetry studies

A prerequisite for generating a radical cationic molecule is that the arylamine of DPT moiety has a lower oxidation potential than those of the NN radical. Hence, the electrochemical properties of all the molecules were investigated by the cyclic voltammetry in acetonitrile for R_2DTP -Ph-NN, ($R^1 = H$, and Th), and benzonitrile for Ph₂DTP-PhNN at room temperature. The cyclic voltammograms are given in Figure 4 for Ph₂DTP-Ph-NN, and for R_2DTP -Ph-NN, ($R^1 = H$, and Th in Figure S4). The oxidative process with half-wave potentials are summarized versus ferrocene/ferrocenium (Fc/Fc⁺) in Table 1.



Figure 4. Cyclic voltammograms in PhCN solution of Ph₂DTP-Ph-NN at a 0.1 V/s scan rate, with 0.1M (n-C₄H₉)₄NBF₄ as supporting electrolyte, versus ferrocene/ferrocenium (Fc/Fc⁺).

The first oxidation wave occurs at +0.23, and +0.33, (\pm 0.02) V vs Fc/Fc⁺, for **Th**₂**DTP-Ph-NN** and **Ph**₂**DTP-Ph-NN** respectively. The first oxidation potentials were apparently lower than those of the NN unit,^[2b, 12] and similar compounds of **DTP-Ph**, **Ph**₂**DTP-Ph**, and **MeSTh**₂**DTP-Ph** reported in the literature.^[14d-f] All the

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Table 1. Oxidation potentials of half-wave potentials for R2DTP-Ph-NN			
	E _{1/2} ox1	E _{1/2} ^{ox2}	E _{1/2} ^{ox3}
DTP-Ph-NN	+0.38	+0.78	+1.14
Ph ₂ DTP-Ph-NN	+0.33	+0.48	+1.00
MeSTh2DTP-Ph-NN	+0.23	+0.41	+1.11

Oxidative process with half-wave potentials versus Fc/Fc^+ in V with (± 0.02 V).

molecules showed two reversible and one irreversible oxidation waves. The second and third oxidation waves probably correspond to the oxidation process of the NN groups and/or the oxidation process of the **DTP** core which allotted for the dication formation. The **DTP-Ph-NN** was polymerized and/or some other side reaction occurred at 0.8 V and 1.1 V (Figure S4b). The extension of the π -bridge is also benefits for better donor ability to the π -core. These two molecules exhibited both the first and second oxidation potentials lower than those of the NN radical. It means that first and second steps were radical cation and dication formations in the oligomer molecules (scheme 2).



Scheme 2. Oxidation and reduction of the R₂DTP-Ph-NN and oxidation of (R₂DTP-Ph-NN)* molecules.

UV-vis absorption studies

The optical properties were studied for $R^{1}_{2}DTP$ -Ph-NN ($R^{1} = H$, Ph and MeSTh) by UV–vis spectroscopy. The absorption spectra are displayed in Figure S5. Two main absorption bands appeared, one around 280–450 nm for π – π * transitions of the donor π -unit and another about 500-750 nm for n– π * transitions of NN radical units which is similar to typically reported nitronylnitroxide molecules.^[20]



The chemical oxidation reactions were conducted by *tris*(4-bromophenyl)aminiumhexachloroantimonate (magic blue, $(BrC_6H_4)_3N^{-+}SbCl_6^{--}$) as the oxidant at room temperature in air, and these reactions were monitored by UV-vis absorption

spectroscopy. During first oxidation two new peaks were formed at 521 and 805 nm for Ph₂DTP-Ph-NN (Figure 5) and at 539 and 945 nm for MeSTh₂DTP-Ph-NN (Figure S6) due to production of radical cation, at the mean time the absorption band at 380 for Ph₂DTP-Ph-NN and 425 for MeSTh₂DTP-Ph-NN for the neutral compounds were superseded. The absorption in the longer wavelength regions was assigned as the HOMO-SOMO and shorter for SOMO-LUMO transition, respectively. For second oxidation, another new peak appeared at 730 nm for Ph₂DTP-Ph-NN and 887 nm for MeSTh₂DTP-Ph-NN and former peaks decreased.

EPR studies

The EPR spectra of neutral radicals of DTP-Ph-NN, Ph2DTP-Ph-NN and MeSTh₂DTP-Ph-NN in toluene (~10⁻⁴ M) in argonsaturated solutions were measured at room temperature and in frozen solution at 130 K. The experiment spectra's with simulated are displayed in Figure S7a-c. All the molecules showed equally separated five lines at room temperature assigned to hyperfine coupling of two equivalent nitrogen nuclei of the NN unit. The g values ($g = 2.0070, \pm 0.02$) are nearly same for the all three neutral radicals. The variable temperature EPR spectra's of the Ph2DTP-Ph-NN and Th2DTP-Ph-NN are displayed in Figure S9. Moreover, frozen solution spectra's are asymmetric with an anisotropic component in the spectra, which gives the different number of the shoulders in both the side of the outermost region (Figure S7d-f). Initially, we tried to oxidize using magic blue as an oxidant in the oxidation process, but the reaction could not be monitored clearly by EPR spectroscopy. It might be the unreacted magic blue affected resolutions of the spectra. Further, the chemical oxidation reaction was carried out for all the neutral radicals by the silver hexafluoroantimonate (AgSbF₆) and the reaction was monitored with EPR spectroscopy. DTP-Ph-NN in DCM (blue solution) was titrated with AgSbF₆ as an oxidant and the spectra are given in Figure S8a. During addition of the oxidant, the blue solution of DTP-Ph-NN turned to green and the intensity of the five line spectra decreased. Finally, all the EPR lines disappeared, this is due to decomposition of the NN, and polymerisation of the molecules or some other side reaction occurred.



Figure 6. EPR spectra of the $(Ph_2DTP-Ph-NN)^{+}$ biradical cation monomer obtained by chemical oxidation titrated with AgSbF₆ as an oxidant in DCM at room temperature.

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The blue solution of Ph2DTP-Ph-NN in DCM become brown during addition of the AgSbF₆, in which the EPR spectra was recorded, there is a clear change in the spectrum where the center is shifted upfield and the total width narrowed as given in Figure S8b and Figure 4. After addition of one equivalent oxidant, 30 line EPR spectra were obtained (Figure 4), once the neutral precursor was consumed. The solution was cooled to 160 K to minimize decomposition of the biradical cations and (Figure S10b). The one very week signal was found at 160 K, this is due to dimerization occurred at lower temperature. Therefore, no zero field splitting could be observed. Then warmed and the variable temperature EPR spectra's of the oxidized specie of the (Ph2DTP-Ph-NN)'+ were measured (Figure S10b). While decreasing the temperature, the intensity of the EPR line also decreased until at 200 K, It is just above the melting point (176.5 K) of CH2Cl2. For MeSTh2DTP-Ph-NN in DCM the light blue/green solution became dark green during addition of the AgSbF₆, and formed dark green precipitate. The poor soluble materials might be dimerized radical cations. The new EPR line appeared during addition of AgSbF₆ along with MeSTh₂DTP-Ph-NN (5 line) but the spectra are not resolved as demonstrated in Figure S8d. The π-dimerization of dithienylpyrrole radical cation molecules is known from the literature.^[13, 22] Further addition of one more equivalent of the AgSbF₆, kept at -10 °C for 6 hours, five lines EPR spectra was retained for Ph2DTP-Ph-NN and MeSTh₂DTP-Ph-NN, the spectra are given the Figures S8e-f. These results indicate the dication formation on the DTP core without decomposition of the NN radical.

Magnetic interaction calculations using DFT calculations

The intra molecular interaction (J_{intra, calc}) of NN and radical-cation was calculated for (R12DTP-Ph-NN)'+ for all the molecules with density functional theory (DFT) and hybrid function BLYP, and basis set 6-31G(d) in the gas phase using Gaussian 09 package.^[15] The X-ray structure geometry of Ph2DTP-Ph-NN, MeSTh₂DTP-Ph-NN and optimized geometry for DTP-Ph-NN with positive charge were used for the calculationa. The $J_{intra,calc}$ values are -3580 K, +5000 K, +965 K for DTP-Ph-NN, Ph2DTP-Ph-NN MeSTh₂DTP-Ph-NN respectively. The interaction between NN and radical-cation is positive and ferromagneticinteraction with high-spin molecules for Ph2DTP-Ph-NN and MeSTh₂DTP-Ph-NN whereas for DTP-Ph-NN is negative indicating antiferromagnetic-interaction. The spin densities were also calculated for both the neutral R¹₂DTP-Ph-NN and charged (R2DTP-Ph-NN)'+ molecules. The spin density is mostly localized on Ph-NN for the neutral molecules while delocalized over the extended π-unit for charged molecules in Figure 5 for Ph2DTP-Ph-NN (Ph2DTP-Ph-NN)'+ and see in Figure S11-12 for R2DTP-PhNN, R¹₂DTP-Ph-NN and (R¹₂DTP-Ph-NN)⁺ (R = H, and Th). The Jintra, calc is nearly five time higher for (Ph2DTP-Ph-NN)'+ than for (MeSTh2DTP-Ph-NN)'+ because the positive charges are distributed equally over the entire molecule for (Ph2DTP-Ph-NN)'+ whereas in MeSTh2DTP-Ph-NN the positive charge and the spin are better delocalized over the extended π -unit and less spin is on the central phenyl.

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Figure 7. Spin density distributions of the (a) $Ph_2DTP-PhNN$ and (b) $(Ph_2DTP-PhNN)^{\star}\cdot$

The Jintra, calc is antiferromagnetic interaction for (DTP-PhNN)+ while ferromagnetic interaction for (Ph2DTP-PhNN)+ and (MeSTh₂DTP-PhNN)'+. To investigate this variation, vertical ionization potential ($IP_{ver} = E_{cation} - E_{neutral}$) calculation was used. These (IPver) calculations were performed by the DFT with BLYP, 6-31G(d) basis set in the gas phase using Gaussian 09 package (Figure S15-16). The NN was deleted from the X-ray structures for Ph2-DTP-Ph and MeSTh2-DTP-Ph whereas for DTP-Ph and Ph-NN optimised structure were used for calculation. The calculated IP_{ver} were 5.54 eV and 4.98 eV for Ph_2 -DTP and MeSTh₂-DTP-Ph respectively. These are much lower than 6.24 eV of NN-Ph (Figure S15). Therefore, neutral molecules of Ph2DTP-Ph-NN, MeSTh2DTP-Ph-NN are easily oxidized and form high spin ground state molecules. In case of DTP-Ph the vertical ionization potential is IPver = 6.37 eV which is higher than the IP_{ver} = 6.24 eV for phenyl nitronyl nitroxide radical (Ph-NN, Figure S13). Consequently, in DTP-Ph-NN'+ nitroxide is charged with a low spin ground state and the triplet is much higher in energy.

In another aspect from DFT, as we mention before to generate a radical cation is that the arylamine of DPT moiety has a lower oxidation potential than those of the NN radical. The important factor now is the energy difference between HOMO and SOMO must be high enough. In case of the DTP-Ph-NN, the energy level of the SOMO is -5.18 eV and HOMO is -5.06 eV. Then, the energy difference between HOMO and SOMO is only (0.12 eV) while the HOMO of the phenyl nitronyl nitroxide (Ph-NN) is -5.17 eV. It is very closer with the SOMO of the DTP-Ph-NN (-5.18 eV). Therefore, we cannot determine very clearly that the removal of the first electron is either from the SOMO or HOMO for DTP-Ph-NN during oxidation. In case of another two molecules the energy difference between HOMO and SOMO were -0.39 and -1.04 for Ph2DTP-PhNN and MeSTh2DTP-Ph-NN, respectively which are better enough to generate the cationic molecules.

Thus, three Ph-NN substituted donor π -core of (DTP) derivatives (**R**₂**DTP-Ph-NN**) molecules were prepared and characterized. The molecular structures and packing of **Ph**₂**DTP-Ph-NN** and **Th**₂**DTP-Ph-NN** were examined by single crystal x-ray structure analysis. The **Th**₂**DTP-Ph-NN** is crystalized in the dimeric form with shorter intermolecular distance of N-O...C-Ph (3.31 Å), while **Ph**₂**DTP-Ph-NN** crystalized in monomeric structure with smaller intermolecular distance found between two oxygen atoms for N-O...N-O (3.24 Å) in molecular packing. Upon one electron oxidation, the (R¹₂**DTP-Ph-NN**, R¹ = Ph and MeSTh)^{*+} offered triplet ground state radical-cationic high spin molecules. Although for (**DTP-Ph-NN**)^{*+} the calculated magnetic interaction is antiferromagnetic between the NN and radical-

cation. Further charged molecules will be isolated and analyzed for magnetic properties by magnetic susceptibility. Syntheses of similar radical cationic molecules are under way. The **Ph**₂**DTP-Ph-NN** and MeS**Th**₂**DTP-Ph-NN** type molecules are suitable for spintronic and molecular based magnetic materials application.

Experimental Section

The experimental details are given in the supporting information.

Acknowledgements

Dieter Schollmeyer for the X-ray structure analysis and we acknowledge the SFB-TR49 for financial support.

Keywords: • dithienopyrrole (DTP) • stable radical • nitronyl nitroxide • radical cation • high spin molecules.

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Dithienopyrrole Derivatives with phenyl and methylthiothiophenyl connected with phenylnitronylnitroxides were oxidized to their cations forming high spin S=1 molecules.