



Organic radicals based on phenalenyl and verdazyl units

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ABSTRACT

Stable phenalenyl (PLY) radicals without sterically bulky substituents need to be synthesized for application as neutral organic molecular conductors. Verdazyl radicals, which have high stability even without sterically bulky substituents, were combined with PLY radicals to produce two novel radicals. The stability of the dimethylthiourea substituted PLY radical is supported by the experimental results and quantum chemical calculations.

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Neutral organic radicals are generally known for their reactive and transient nature. Despite this, research has focused on stabilization and isolation of new neutral organic radicals because of their potential as molecule-based magnetic materials and single component organic conductors.^{1–4} Neutral phenalenyl (PLY) radical, which has a highly spin-delocalized planar π -structure, was suggested as a potential neutral organic molecular conductor many years ago.^{5,6} However, this hydrocarbon radical easily undergoes σ -dimerization through a C–C interaction.^{7,8} Although the σ -dimerization could be suppressed by introducing sterically bulky substituents on the periphery of PLY molecule,^{9–12} the bulky substituents also simultaneously prevent the π -electron orbital overlap between the adjacent PLY molecules, and accordingly lead to a Mott insulating state.⁷ Haddon and co-workers later reported that introduction of disulfide substituents on the PLY skeleton could stabilize the radical by electronic effects.^{8,13} This opened the door to design new stable PLY radicals with non-bulky substituents.

Nitroxide, nitronyl nitroxide, and verdazyl radicals are also known for their exceptional stability, which makes them attractive for possible application as molecular magnets.^{14–18} Especially, the stability of verdazyl radicals does not require addition of sterically bulky substituents.^{19,20} However, none of them show electrical

conductivity. If the verdazyl structure could be introduced into the PLY skeleton (Fig. 1), the unpaired electron would have highly delocalized spin distribution, and the obtained novel PLY radical should become more stable. More importantly, the radicals may show good electrical conductivity. Herein, we report the synthesis and characterization of two novel PLY radicals, **1** and **2**, based on both PLY and verdazyl units.

Consulting the synthesis of phenalene-phosphazene complexes reported by Haddon et al.,²¹ we selected the synthetic routes for

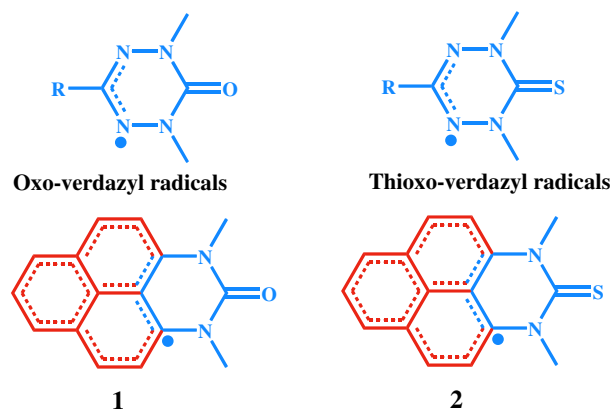


Figure 1. Structures of oxo-verdazyl and thioxo-verdazyl radicals and PLY radicals **1** and **2**.

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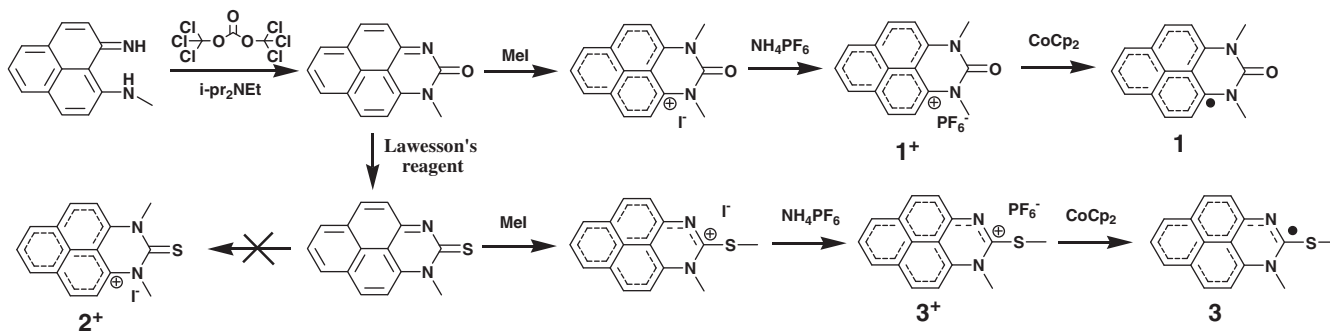
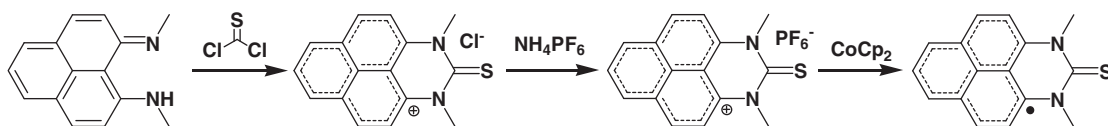
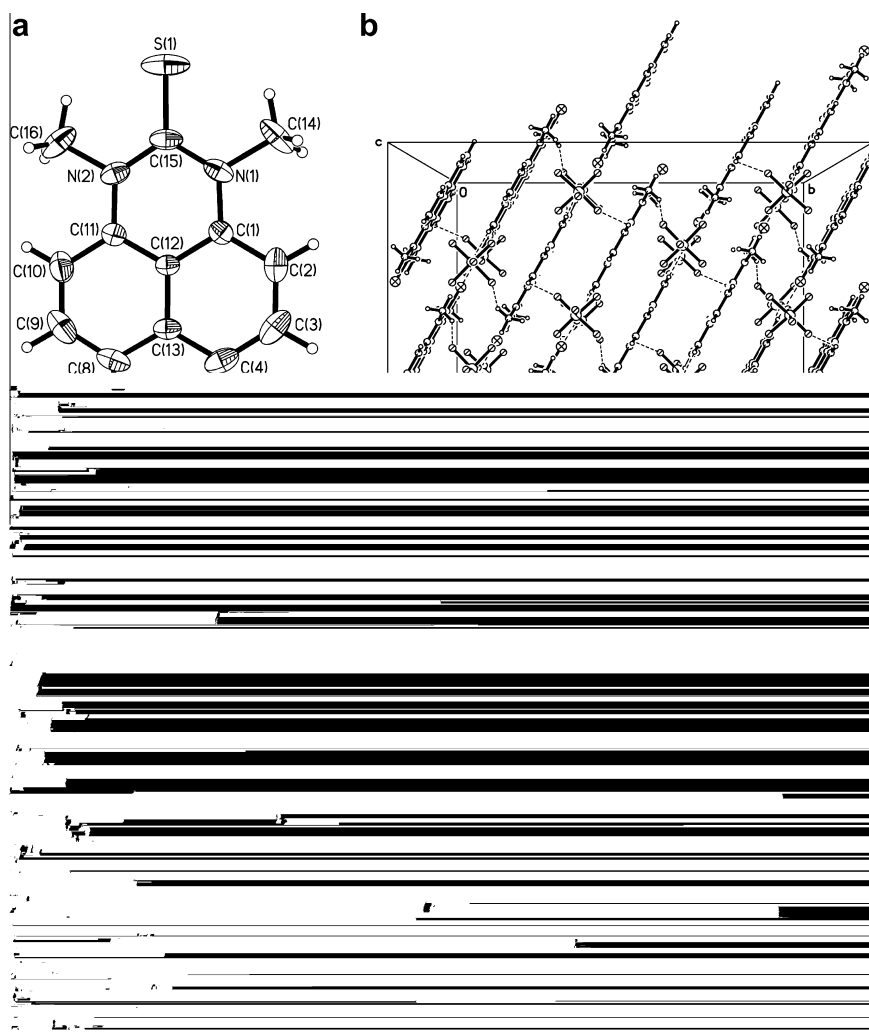
Scheme 1. Synthetic routes of the PLY salts 1^+PF_6^- and 3^+PF_6^- .Scheme 2. Synthetic route of the PLY salt 2^+PF_6^- .

Figure 2. (a) Molecular structure of PLY cation 2^+ ; (b) packing structure of PLY salts 2^+PF_6^- in the single crystal; (c) one row of 2^+ in the single crystal. Thermal ellipsoids have been drawn at the 30% probability level.

the PLY radical precursors 1^+PF_6^- and 2^+PF_6^- (Scheme 1). The PLY salt 1^+PF_6^- was easily obtained as a golden platelike crystal. Lawesson's reagent could convert the carbonyl into thiocarbonyl.

However, when we prepared the salt 2^+PF_6^- using the same method, unexpectedly the only product was PLY salt 3^+PF_6^- . For the nucleophilic addition reaction, S shows higher reactivity than N.

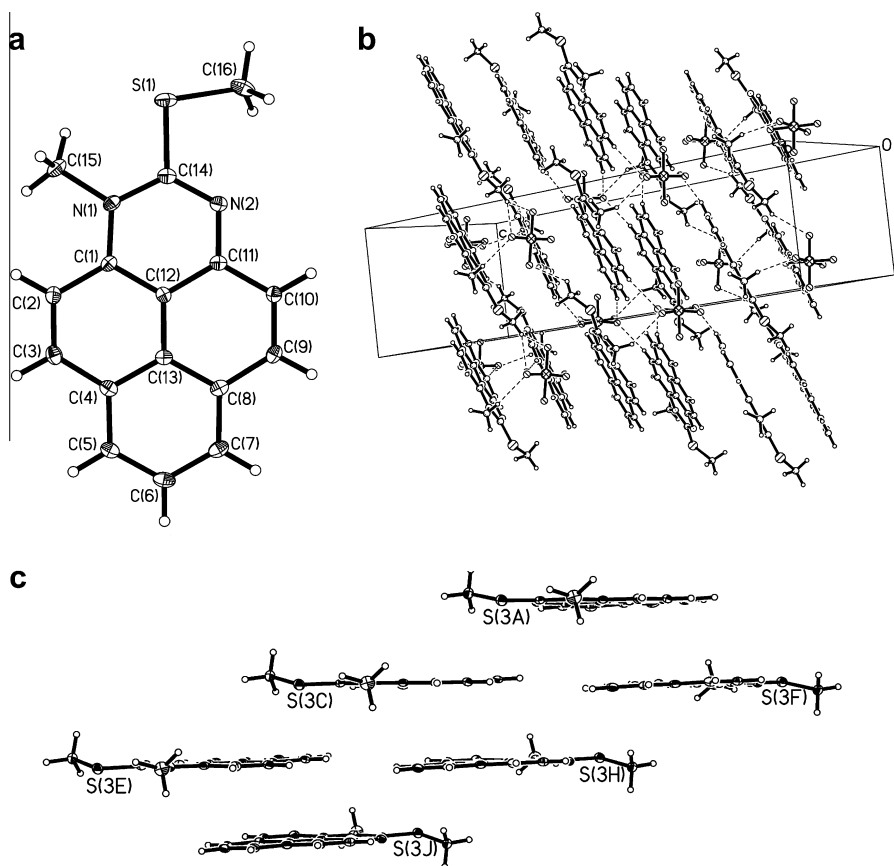


Figure 3. (a) Molecular structure of 3^+ ; (b) packing structure of PLY salts $3^+PF_6^-$ in the single crystal; (c) two adjacent parallel rows of 3^+ in the single crystal. Thermal ellipsoids have been drawn at the 30% probability level.

The PLY salt $2^+PF_6^-$ was fortunately obtained as the red solid when thiophosgene was used to react with 9-*N*-methylamino-1-*N'*-methylimino-phenalene, followed by metathesis with NH_4PF_6 (Scheme 2).

Single crystals of PLY salts $2^+PF_6^-$ and $3^+PF_6^-$ were obtained by recrystallization from CH_3CN /ether at room temperature.²² They were fully characterized by X-ray crystallographic, and their crystal structures are depicted in Figure 2 ($2^+PF_6^-$) and Figure 3 ($3^+PF_6^-$). Clearly, the PLY cation 2^+ is planar. Moreover, the two methyl substituents are also in the plane of the skeleton of PLY cation. The salt $2^+PF_6^-$ forms a layered structure, wherein the PLY cations are stacked in a head-to-tail fashion. The separation between two adjacent parallel cations is 3.43 Å. The PLY cation 3^+ is also planar, but with a different stacking mode to cation 2^+ . The PLY cations assembled into slipped arrays, and could still form head-to-tail π - π overlap with those in the adjacent array, which were separated by a distance of 3.45 Å.

We conducted cyclic voltammetry (CV) of the PLY salts $1^+PF_6^-$, $2^+PF_6^-$ and $3^+PF_6^-$ to investigate the redox abilities of their corresponding radicals **1**, **2** and **3** (Fig. 4). All of the salts showed two well-behaved reversible redox curves. Each of the redox couples corresponds to a one-electron reduction process, which indicates the successive generation of radical and anion. For the three PLY salts, the disproportionation potentials ΔE ($\Delta E = E_2^{1/2} - E_1^{1/2}$) are about 1 V, which corresponds to the energy gap between the singly occupied molecular orbitals (SOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the corresponding neutral radicals.²³

According to the redox potentials of the PLY salts $1^+PF_6^-$, $2^+PF_6^-$ and $3^+PF_6^-$, cobaltocene was chosen as the reductant because its oxidation potential ($E^{1/2} = -1.33$ V vs Fc/Fc^+)²⁴ falls between $E_1^{1/2}$

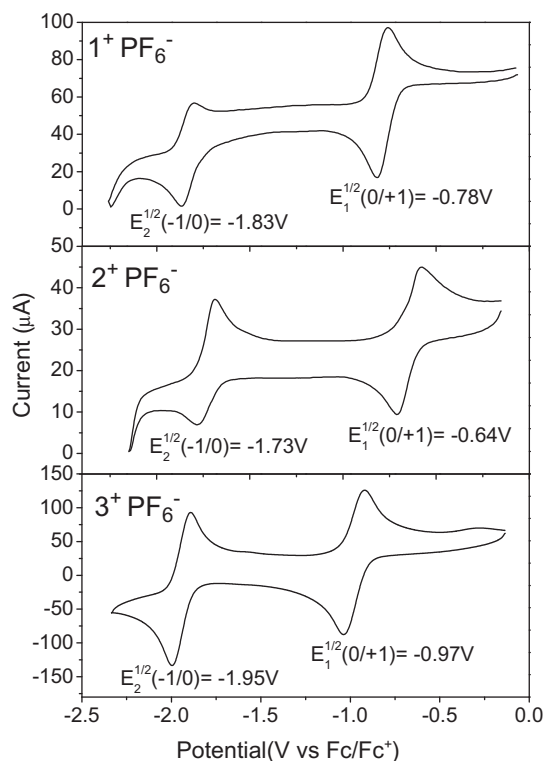


Figure 4. Cyclic voltammograms of the PLY salts $1^+PF_6^-$, $2^+PF_6^-$ and $3^+PF_6^-$ in MeCN, $n - Bu_4N^+PF_6^-$ supporting electrolyte.

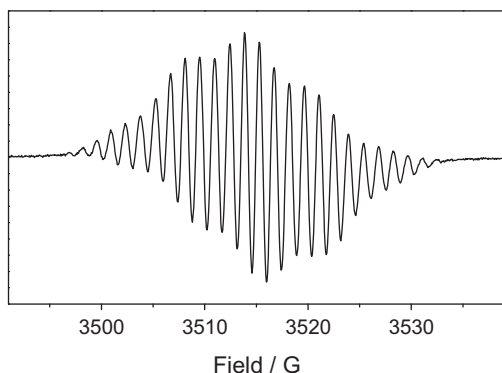


Figure 5. The EPR spectrum for radical **2**, which was recorded in degassed CH_2Cl_2 at 293 K.

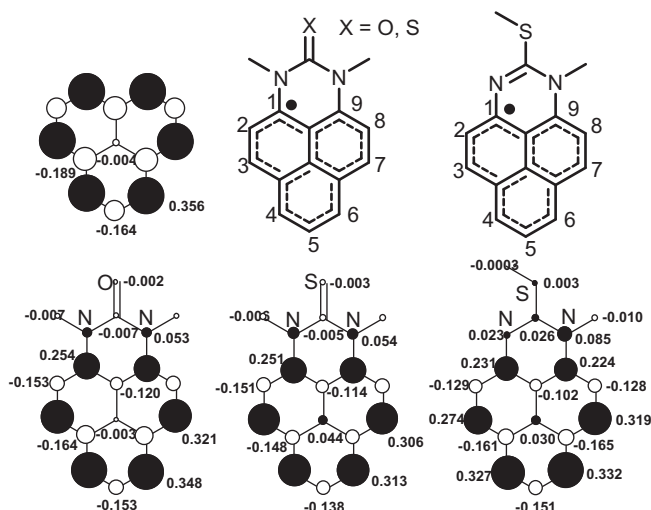


Figure 6. The π -spin density distributions of the radicals **1**, **2**, **3** and the unsubstituted PLY radical. Vacant and filled circles denote negative and positive π -spin density, respectively.

and $E_2^{1/2}$ of the three salts. All of the PLY salts could rapidly react with cobaltocene in acetonitrile to afford black solids. However, only an EPR spectrum with well-resolved hyperfine coupling pattern was observed for the degassed CH_2Cl_2 solution of the product from $\mathbf{2}^+\text{PF}_6^-$ (Fig. 5). The g -factor was 2.0022, which shows that the EPR signal comes from radical **2**. The signal could be observed even after the solution was left at room temperature for two days. For the radical solid placed in a sealed glass tube, the EPR signal could be observed for two weeks, indicating that radical **2** is stable.

To investigate why an EPR spectrum was only observed for radical **2**, the π -spin density distributions of the radicals **1**, **2**, **3** and the unsubstituted PLY radical were calculated by the DFT method using their optimized structures (Fig. 6). Obviously, for the radicals **1**, **2**, **3**, most of the spin densities are populated on the PLY nucleus, and only a very small amount of the spin densities are distributed on the N atoms (approximately 6%). The spin distributions on C_3 , C_4 , C_6 , C_7 are more than those on C_1 , C_9 . For all this, the spin densities on C_3 , C_4 , C_6 , C_7 of radical **2** were much lower than those of the unsubstituted PLY radical. However, for radical **1**, the spin densities on C_4 and C_6 were very close to those on the unsubstituted PLY radical. Because there are no sterically bulky substituents on C_3 , C_4 , C_6 , C_7 , radical **1** may follow the σ -dimerization reactions on C_4 or C_6 as the unsubstituted PLY radical.⁶ For radical **3**, there

also exists a greater spin density on C_6 , where the σ -dimerization reaction may occur for the same reason.

In summary, three novel PLY radical precursors were prepared and showed highly amphoteric redox properties. Among them, the dimethylthiourea substituted PLY salt $\mathbf{2}^+\text{PF}_6^-$ could be reduced and offer the corresponding stable PLY radical. Even without the protection of sterically bulk substituents, its stability is supported by the experimental results and quantum chemical calculations. These encourage full investigation of its solid-state properties, such as crystal packing, magnetism and conductivity, and this work is underway.

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Supplementary data

Supplementary data (the synthetic details and crystallographic data for PLY salts $\mathbf{2}^+\text{PF}_6^-$ and $\mathbf{3}^+\text{PF}_6^-$) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.05.031.

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