

# Hexathiophenalenylium Cations: Syntheses, Structures, and Redox Chemistry

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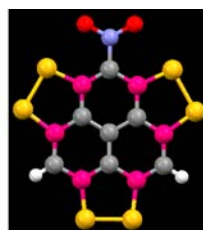
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## ABSTRACT



HTPLY



Nitro-HTPLY

Preparations of two hexathiophenalenylium compounds as stable salts from the reaction of 3,4,6,7-tetrathio-9-hydroxyphenalenone with Lawesson's reagent have been reported. The presence of three disulfide linkages on the periphery of the core phenalenyl unit is confirmed by X-ray crystallographic characterizations. Electrochemical cell potentials are lower than those of related dithio- and tetrathio-bridged phenalenyl radicals, and the hexathiophenalenyl radical shows a strong electron paramagnetic resonance (EPR) signal in the solid state.

The past few decades have witnessed the continuing interest in organic conductors based on charge transfer salts.<sup>1–4</sup> There are a number of alternative approaches,<sup>5</sup> one of which makes use of neutral radicals possessing an unpaired electron that could function as organic conductors in analogy with the classical monatomic metals and superconductors.<sup>6–8</sup> There are, however, several difficulties in pursuing the neutral radical conductor model: (1) dimerization of the radical molecules either by  $\sigma$ - or by  $\pi$ -association can compete with the metallic ground state; (2) the half filled band, coupled with a low value of the ratio of the bandwidth ( $W$ ) to the Coulomb repulsion energy ( $U$ ), can lead to Mott insulators. Thus, the design of materials with a higher ratio of  $W/U$  is crucial to improve the conductivities.

Considerable progress has been made in this field by using heterocyclic and phenalenyl (PLY) based radicals.<sup>9–40</sup>

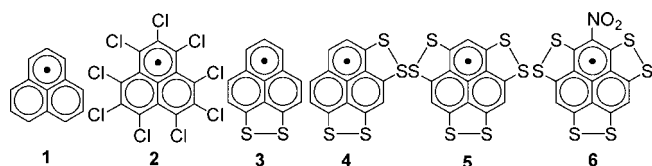
The phenalenyl radical<sup>41,42</sup> and related alkyl derivatives undergo facile dimerization either by  $\pi$ - or  $\sigma$ -association,<sup>43–46</sup> but recent progress in phenalenyl

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chemistry<sup>19,20,22,25,27–29,47,48</sup> has led to the isolation of the radical in the crystalline state through the introduction of bulky substituents.<sup>22,25,26,29</sup> To obtain stable neutral radicals with less steric hindrance and further delocalization of an unpaired electron, we have designed and pursued both chalcogen and halogen substitution at the periphery of the PLY unit (Figure 1).<sup>22–24,49,50</sup> Chalcogens have been



**Figure 1.** Mono-PLY radicals.

popular atoms for incorporation into the periphery of the molecular building blocks for organic conductors because these atoms do not require additional functionality to

terminate their valences and they are often associated with strong intermolecular interactions.<sup>51,52</sup> Furthermore, they seem to be able to stabilize multiple oxidation states and to effectively delocalize spin density.<sup>49</sup>

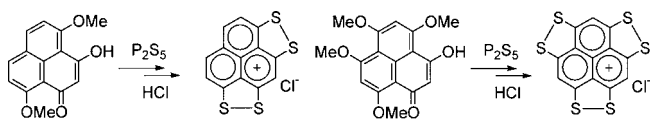
In principle three dithio-bridged derivatives of PLY are possible; dithiophenalenyl (DTPLY, **3**),<sup>23,49</sup> tetra-thiophenalenyl (TTPLY, **4**),<sup>24</sup> and hexathiophenalenyl (HTPLY, **5**). DTPLY was prepared in 1978, and solution EPR and electrochemical measurements were reported.<sup>49</sup> Subsequent studies led to the crystallization of the 1,9-dithiophenalenyl radical (**3**) which gave rise to a  $\pi$ -dimer, and this was the first example of a radical based on a single phenalenyl unit that has been stabilized against  $\sigma$ -dimerization in the solid state by electronic effects rather than by the presence of sterically bulky substituents.<sup>23,49</sup> Recently, we made use of the cationic species  $4^+ \text{SbF}_6^-$  to prepare and characterize the tetrathiophenalenyl radical (**4**).<sup>24</sup> The synthesis of the TTPLY framework is a further development of the chemistry used to produce DTPLY.<sup>49</sup> The crystals of TTPLY are diamagnetic in the solid state and the X-ray structure confirmed the sulfur bridged dimer structure, although dissolution of the crystals in toluene affords a well resolved EPR spectrum corresponding to the TTPLY radical. In principle, HTPLY, which has yet to be prepared, should have a threefold symmetrical molecular skeleton although a sulfur bridged dimeric structure may prevail.<sup>24</sup>

The presence of two disulfide groups in the TTPLY radical (**4**) leads to the lowest disproportionation potential observed for a monofunctional phenalenyl derivative. In this respect sulfur substitution is much more successful than the introduction of other heteroatoms in reducing the value of  $\Delta E_{2-1}$ ,<sup>34</sup> and thus we pursued the synthesis of HTPLY in order to further reduce the disproportionation potentials. Herein, we report the preparation and X-ray crystal structures of the cationic salt of HTPLY ( $5^+ \text{TFAB}^-$ ,  $\text{TFAB}^-$  = tetrakis(pentafluorophenyl)borate) and its nitro derivative ( $6^+ \text{BPh}_4^-$ ,  $\text{BPh}_4^-$  = tetraphenylborate). The salts were synthesized by following a modification of our previous route for introduction of the disulfide unit,<sup>23,49</sup> in which 3,4,6,7-tetrathio-9-hydroxyphenalenone serves as the starting material. The HTPLY radical (**5**) was characterized by solid state EPR and electrochemical studies.

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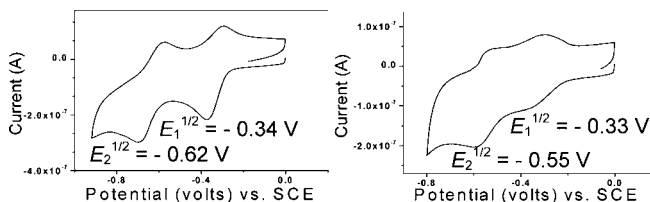
### Scheme 1. Synthesis of TTPLY Salt



The synthesis of the TTPLY (**4**) framework is related to that developed for DTPLY (**3**); reaction of 4,9-dimethoxy-3-hydroxyphenalenone with  $P_2S_5$ , followed by treatment with HCl, affords [TTPLY] $^+Cl^-$  (Scheme 1), but this oxidative strategy is not useful in the present connection. The replacement of the alkoxy groups of 3-hydroxy-4,6,7,9-tetramethoxyphenalenone (**II**) by sulfur substitution proved to be difficult (Scheme 1). Hence we turned our attention to a route involving the stepwise introduction of the disulfide linkages, and thus we focused on the tetrathio derivative of 9-hydroxyphenalenone as our initial goal. Recently, we developed a versatile synthetic approach for the introduction of chalcogenide substituents into the phenalenyl ring system which involved the introduction of better leaving groups at the active positions of 9-hydroxyphenalenone in order to facilitate their replacement by nucleophiles.<sup>34</sup> The synthesis of the precursor salts to radicals **5** and **6** began with the addition of the ethyl malonyl group to 1,3,6,8-tetramethoxynaphthalene (Scheme 2).<sup>26</sup> The product of this reaction was cyclized with concentrated hydrochloric acid and then demethylated using pyridine-hydrochloride.<sup>34</sup> We introduced the mesyl groups ( $-OMs$ ) into the active positions of the 9-hydroxyphenalenone unit, and this increased the reactivity of these positions toward nucleophilic substitution by potassium thioacetate. By carrying out the reaction in the atmosphere, 3,4,6,7-tetramesyate-9-hydroxyphenalenone reacts smoothly with potassium thioacetate to produce the corresponding disulfide bridged 3,4,6,7-tetrathio-9-hydroxyphenalenone as the only isolable product (Scheme 2). Reaction of 3,4,6,7-tetrathio-9-hydroxyphenalenone with Lawesson's reagent, followed by

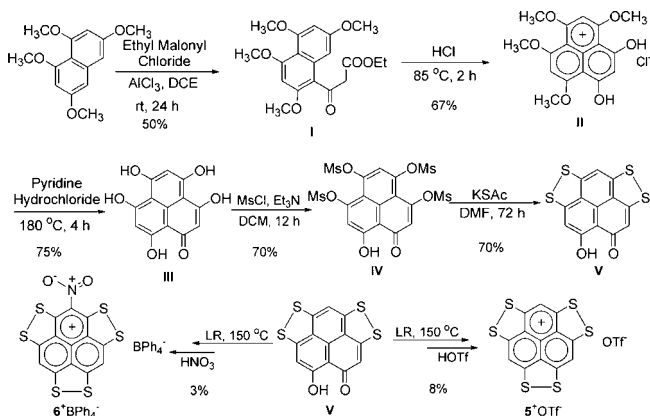
treatment with triflic acid (HOTf), affords [HTPLY] $^+OTf^-$  in pure form; metathesis with  $K^+TFAB^-$  and recrystallization from dichloromethane/hexane yield [HTPLY] $^+TFAB^-$  as black crystals. The tetraphenylboron salt of nitro-HTPLY (**6** $^+BPh_4^-$ ) was obtained by the use of nitric acid instead of triflic acid, followed by a metathesis reaction using sodium tetraphenylborate. The yields of the reactions for the oxidative introduction of the third disulfide bridge into the tetrathiophenalenone moiety were quite low (3–10%).

The cyclic voltammograms for the salts (**5** $^+OTf^-$  and **6** $^+BPh_4^-$ ) in 1,2-dichlorobenzene showed two reversible waves (Figure 2) corresponding to the expected triad of oxidation states: a reversible (0/+1) wave and a reversible (–1/0) wave. The reduction potentials and disproportionation potentials ( $\Delta E_{2-1}$ ) are given in Table 1. Additionally, we carried out cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments for **5** using DMF as solvent (Figure S1, Supporting Information), and the reduction potentials are tabulated in Table 1. The estimated cell potentials are substantially smaller than those found for other reported mono-PLY systems (**1–4**), a conclusion that argues for a low onsite Coulomb potential in solids based on these radicals. Preliminary results indicate that the cationic salt [**5** $^+TFAB^-$ ] can be reduced to the radical, as evidenced by the strong solid state EPR observed for the HTPY (**5**) radical with  $g = 2.0055$  (Figure S4, Supporting Information).



**Figure 2.** Cyclic voltammograms in 1,2-dichlorobenzene for **5** $^+OTf^-$  (left) and **6** $^+BPh_4^-$  (right), with half wave  $E_{1/2}$  potentials. The internal reference  $Fc/Fc^+$  (0.56 V) is not shown.

### Scheme 2. Syntheses of Hexathiophenalenyliums

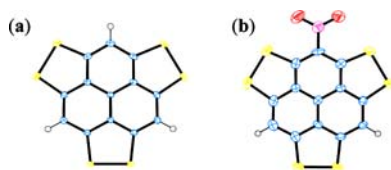


**Table 1.** Half-Wave Potentials and Disproportionation Potentials (volts vs SCE) of Monophenalenyl Salts

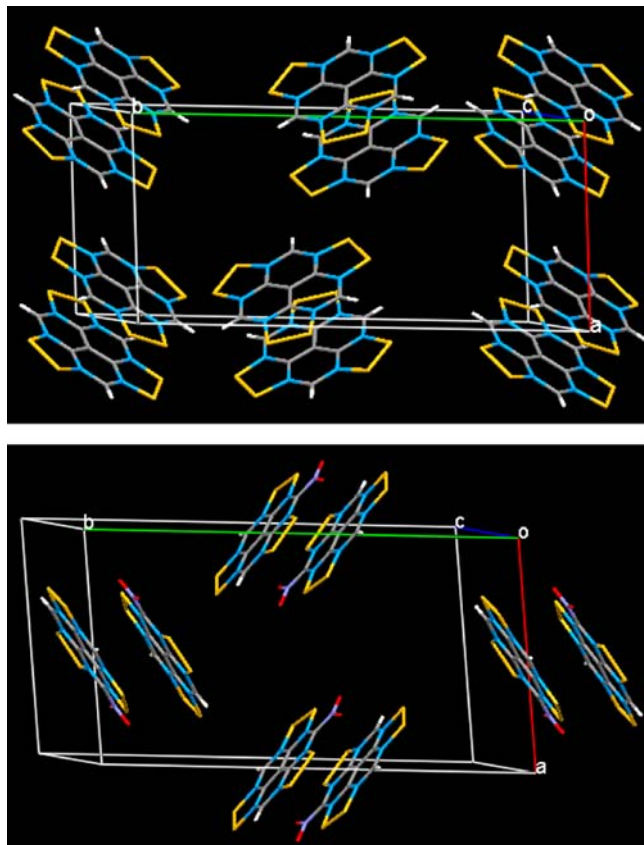
compd	$E_{1/2}$ (V)	$E_{2/2}$ (V)	$\Delta E_{2-1} = E_{2/2} - E_{1/2}$ (V)
PLY ( <b>1</b> $^+BF_4^-$ ) <sup>a</sup>	0.7	–0.9	–1.6
PCPLY ( <b>2</b> $^+GaCl_4^-$ ) <sup>b</sup>	1.14	–0.08	–1.22
DTPLY ( <b>3</b> $^+OTf^-$ ) <sup>a</sup>	–0.23	–0.80	–0.57
TTPLY ( <b>4</b> $^+SbF_6^-$ ) <sup>b</sup>	–0.34	–0.71	–0.33
HTPLY ( <b>5</b> $^+OTf^-$ ) <sup>c</sup>	–0.42	–0.60	–0.18
HTPLY ( <b>5</b> $^+OTf^-$ ) <sup>d</sup>	–0.34	–0.62	–0.28
Nitro-HTPLY ( <b>6</b> $^+BPh_4^-$ ) <sup>d</sup>	–0.33	–0.55	–0.22

<sup>a</sup> Acetonitrile. <sup>b</sup> 1,2-Dichloroethane. <sup>c</sup> *N,N*-Dimethylformamide. <sup>d</sup> 1,2-Dichlorobenzene.



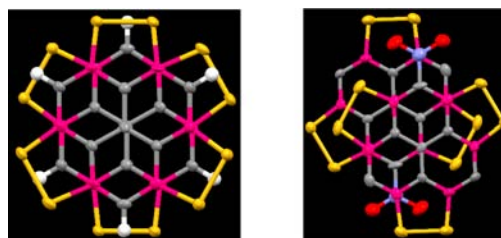


**Figure 3.** X-ray crystal structures of the salts,  $5^+\text{TFAB}^-$  and  $6^+\text{BPh}_4^-$ . The asymmetric units contain a single (a) hexathiophenalenyl cation unit and a (b) nitro-hexathiophenalenyl cation unit.



**Figure 4.** Packing of the cationic molecules of  $5^+\text{TFAB}^-$  (top) and  $6^+\text{BPh}_4^-$  (bottom) (anions and solvent molecules are omitted for clarity).

Syntheses and characterizations of the radicals (**5** and **6**) in the solid state are underway. However, we were able to establish the crystal structures of the two hexathiophenalenyl salts (Figure 3). These determinations confirmed the presence of the three dithio-bridged functional groups in both compounds and also established unequivocally the



**Figure 5.** Dimeric pairs of cations for  $5^+\text{TFAB}^-$  and  $6^+\text{BPh}_4^-$ .

position of nitration on the phenalenyl ring in the nitro-hexathiophenalenyl framework. X-ray crystal structures were obtained for  $5^+\text{TFAB}^-$  and  $6^+\text{BPh}_4^-$ , and the crystal data are provided in Table S1 (Supporting Information).

The asymmetric unit of  $5^+\text{TFAB}^-$  is composed of a single cation/anion pair within the monoclinic,  $P2(1)/c$  space group, whereas, for  $6^+\text{BPh}_4^-$ , there are two dichloromethane molecules as solvent of crystallization in addition to a single cation/anion pair within the monoclinic  $P2(1)/n$  space group. Packing diagrams of the cations ( $5^+$  and  $6^+$ ) are given in Figure 4; the HTPLY $^+$  units for both compounds occur as dimers in the lattice which are oriented along the  $b$  axis and the molecules in the dimer of  $6^+\text{BPh}_4^-$  are rotated with respect to each other. Perpendicular views of the dimer pairs are given in Figure 5. The interplanar separation between the two PLY rings within each dimer is 3.42 Å for compound  $5^+\text{TFAB}^-$  and 3.39 Å for compound  $6^+\text{BPh}_4^-$ .

In summary, we have developed a synthetic strategy which allows the isolation and characterization of the precursor salts for hexathiophenalenyl radicals, and preliminary studies suggest the formation of the HTPLY radical by chemical reductions. Finally, the enhancement in spin delocalization of phenalenyl radicals, occasioned by the attachment of successive disulfide substituents and the concomitant improvement in their electrochemical cell potentials, suggests that these materials may be important for exploration of new organic materials having interesting electrical and magnetic properties.

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**Supporting Information Available.** Experimental procedures, CV and DPVs,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, an EPR spectrum of **5**, crystal information, and CIF files for compounds  $5^+\text{TFAB}^-$  and  $6^+\text{BPh}_4^-$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.