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Tetrathiophenalenyl Radical and its Disulfide-Bridged Dimer

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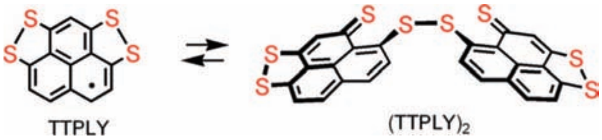
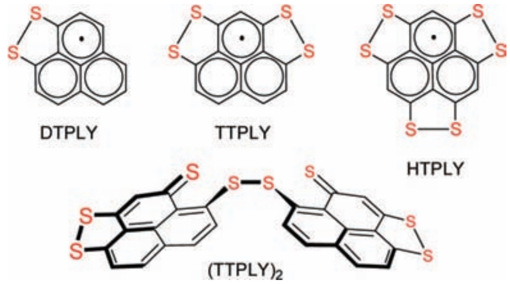
ABSTRACT



The presence of two disulfide groups in the tetrathiophenalenyl radical TTPLY leads to a highly delocalized spin distribution and the lowest cell potential ever observed for a monofunctional phenalenyl derivative. While the heteroatom substituents successfully block C−C bond formation, TTPLY nonetheless associates in the solid state to afford the hypervalent S−S-bonded dimer (TTPLY)$_2$.

The highly delocalized spin distribution in the phenalenyl (PLY) radical and its accessible triad of stable oxidation states make it an attractive candidate for the design of neutral radical conductors.[1] While PLY dimerizes through a C−C interaction in the solid state, the use of sterically bulky substituents has proven effective in preventing this mode of dimerization,[2,3] albeit at the expense of electronic communication between the radical molecules. As a result, the large onsite Coulomb repulsion energy U and small bandwidth W for these materials make it impossible to approach the necessary condition that $W > U$ for a metallic conductor. An alternative way to suppress C−C bond formation, while at the same time encouraging low U and high W values, is to use disulfide substituents.[4] Recently, we reported the preparation of the dithiophenalenyl radical DTPLY (Scheme 1) and demonstrated that the enhanced delocalization provided by the peripheral heteroatoms was indeed sufficient to suppress localized C−C σ-dimerization, although the radicals crystallized as π-dimers.[5]

Scheme 1. Disulfide-Substituted PLY Radicals



This finding encouraged further investigation into the effect of substitution of the phenalenyl core by multiple disulfide units. Herein, we report the preparation and spectral (EPR),

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[1] (a) Haddon, R. C. *Aust. J. Chem.* **1975**, *28*, 2343–2351. (b) Haddon, R. C. *Nature* **1975**, *256*, 394–396.

[2] Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomi, D.; Takui, T.; Kubota, M.; Kobayashi, T.; Yakusi, K.; Ouyang, J. *J. Am. Chem. Soc.* **1999**, *121*, 1619–1620.

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[5] Beer, L.; Mandal, S. K.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Donnadieu, B.; Haddon, R. C. *Crys. Growth Des.* **2007**, *7*, 802–809.

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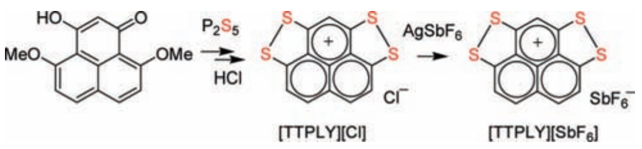
electrochemical, and solid-state characterization of tetrathiophenalenyl TTPLY. While this radical displays a highly delocalized spin distribution and excellent electrochemical characteristics, it undergoes cleavage of one of the dithiole rings to afford the S−S σ-bonded dimer $(TTPLY)_2$. Synthesis of the TTPLY framework (Scheme 2) builds off that developed for DTPLY. Reaction of 4,9-dimethoxy-3-hydroxyphenalenone[6] with P_2S_5, followed by treatment with HCl, affords [TTPLY][Cl] in crude form. Metathesis with $AgSbF_6$ and recrystallization from MeCN/PhCl yields [TTPLY][SbF_6] as deep red needles.

Scheme 2. Synthesis of TTPLY



The electrochemical behavior of TTPLY is more complex than that of DTPLY[5] and raises the possibility of radical association. Cyclic voltammetry (Figure 1) on solutions of [TTPLY][SbF_6] in MeCN (Pt electrodes, 0.1 M n-Bu_4NPF_6 supporting electrolyte) reveals a reversible +1/+2 wave at 1.60 V (vs SCE) and two irreversible waves corresponding to the 0/+1 and −1/0 couples with E_{pc} values of −0.41 and −0.76 V, the strong cathodic wave of the latter suggesting electroreduction of material coating the electrode.

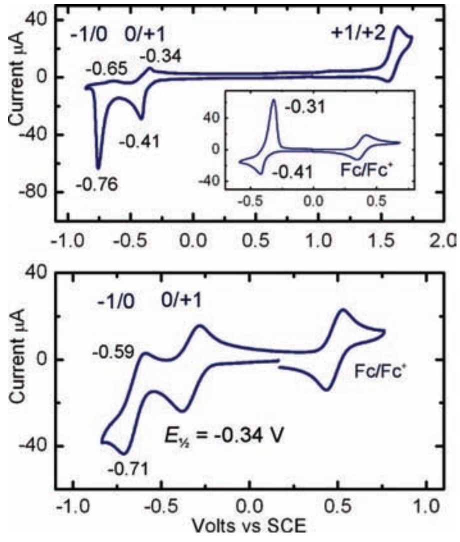


Figure 1. Cyclic voltammograms of [TTPLY][SbF_6] in MeCN (top) and $C_2H_4Cl_2$ (bottom), with half-wave $E_{1/2}$ and cathodic/anodic peak potentials E_{pc}/E_{pa}. The internal reference Fc/Fc^+ couple is also shown.

By contrast, when $C_2H_4Cl_2$ is used as solvent, a reversible 0/+1 wave with $E_{1/2} = -0.34$ V is observed, along with a quasi-reversible −1/0 process with $E_{pc} = -0.71$ V. Based on the separation of the two E_{pc} values (−1/0 and 0/+1), we estimate a cell potential ΔE of −0.33 V, a value substantially smaller than that found for DTPLY (−0.57 V),[5] a conclusion that augurs well for a low onsite Coulomb potential U.

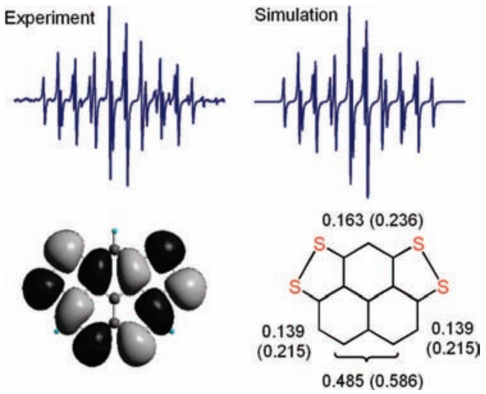


Figure 2. X-band EPR spectrum ($g = 2.0067$) of TTPLY in toluene, with derived a_H values (in mT). The B3LYP/6-31G(d,p) singly occupied molecular orbital and calculated a_H values (in parentheses) are also shown.

Chemical reduction of [TTPLY][SbF_6] in MeCN by slow codiffusion with a solution of tetrakisdimethylaminoethylene in MeCN affords small black needles. The crystals are diamagnetic (by EPR) in the solid state, but upon dissolution in toluene a weak but well-resolved EPR spectrum (Figure 2) corresponding to the TTPLY radical is obtained. The three hyperfine coupling constants a_H for the radical, as derived by spectral simulation, have been assigned by comparison with values predicted by B3LYP/6-31G(d,p) calculations. While the TTPLY radical can be generated in solution at room temperature and is stable indefinitely in the absence of oxygen, the absence of an EPR signal in the solid state suggests that the radical is associated. X-ray crystallographic analysis[7] of the black needles confirmed this inference. Figure 3A shows the molecular structure of the $[TTPLY]^+$ cation, as found in the salt [TTPLY][SbF_6]; the C−C and S−S bond lengths are similar to those seen in the $[DTPLY]^+$ cation.[5] By contrast, the structure of the reduced material reveals the rupture of one of the dithiole rings and the formation of the bis(phenalenethione)disulfide $[TTPLY]_2$.

As shown in Figure 3B,C the hypervalent disulfide linkage, which straddles a crystallographic 2-fold axis, consists of a long disulfide unit clamped between two thione-to-sulfide

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[6] Haddon, R. C.; Hirani, A. M.; Kroloff, N. J.; Marshall, J. H. *J. Org. Chem.* **1983**, *48*, 2115–2117.

[7] Crystal data for [TTPLY][SbF_6] at 173(2) K: $C_{13}H_5F_6S_4Sb$, M = 525.16, orthorhombic, space group *Pnma*, with $a = 10.4642(16)$ Å, $b = 16.0532(2)$ Å, $c = 21.759(3)$ Å, $V = 1534.0(4)$ Å^3, $Z = 4$, $D_{calcd} = 2.435$ g cm^{-3}, $\mu = 2.401$ mm^{-1}; 166 parameters were refined using 2524 unique reflections to give $R = 0.0399$ and $R_w = 0.1033$. Crystal data for $[TTPLY]_2$ at 173(2) K: $C_{26}H_{10}S_8$, $M = 578.82$, orthorhombic, space group *Pbcn*, with $a = 18.403(6)$ Å, $b = 8.002(3)$ Å, $c = 21.759(3)$ Å, $V = 2123.0(12)$ Å^3, $Z = 4$, $D_{calcd} = 1.811$ g cm^{-3}, $\mu = 0.859$ mm^{-1}; 154 parameters were refined using 2171 unique reflections to give $R = 0.0609$ and $R_w = 0.1028$.

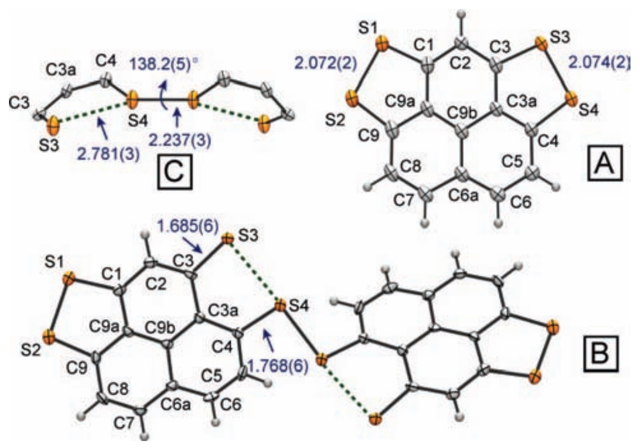
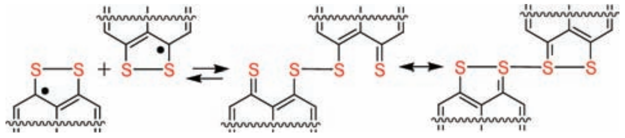


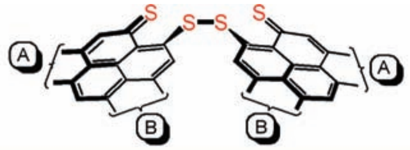
Figure 3. ORTEP drawings (50% probability ellipsoids), with selected distances (Å) and torsion angles (deg), in the $TTPLY^+$ cation in $[TTPLY][SbF_6]$ (A), the dimer $[TTPLY]_2$ (B), and the disulfide unit in $[TTPLY]_2$ (C).

S3−S4 bridges (Scheme 3). While stabilization of disulfides by lone-pair donation from a saturated sulfur center is well-known,[8] the use of an unsaturated thione sulfur in such a bonding arrangement, to produce a formally hypervalent disulfide, is not common.[9] Indeed, simple aromatic thiones (unless complexed to a metal) are themselves rare,[10] but the C3−S3 distance in $[TTPLY]_2$ indicates that these bonds are comparable to those found in thioureas.[11] The torsion angle C4−S4−S4′−C4′ is much larger than the 90° twist (gauche conformation) that typifies a standard RSSR disulfide,[12] but not as large (180°) as in thiazyl radical dimers bridged by hypervalent disulfide linkages.[9]

Scheme 3. Dimerization of TTPLY to $[TTPLY]_2$



The formation of a lateral S−S σ-bonded dimer for TTPLY is in marked contrast to the structure of DTPLY, in which the single dithiole ring remains intact in the solid state. It is apparent that the increased electron richness provided by the second dithiole ring leads to a destabilization of the π-electron framework and a greater propensity for rupture of the disulfide bonds. The observation of the TTPLY radical in solution by EPR nonetheless attests to the relative ease of dissociation of the dimer. This qualitative conclusion is supported by the calculated bond dissociation enthalpies (BE) of the various S−S-bonded dimers possible for DTPLY, TTPLY, and HTPLY. As shown in Figure 4, $[DTPLY]_2$ is calculated to be only slightly more stable than its radical, while the two possible modifications[13] of $[TTPLY]_2$ are both substantially favored relative to the radical TTPLY. The putative and, to date, elusive HTPLY radical appears destined to exist as a dimer.



	DTPLY	TTPLY		HTPLY
A	H,H	H,H	S,S	S,S
B	H,H	S,S	H,H	S,S
BE (kcal mol^{-1})	5.7	11.9	12.9	19.9

Figure 4. B3LYP/6-31G(d,p) bond enthalpies (BE) for disulfide-substituted phenalenyls.

In summary, 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 should be highly effective building blocks for neutral radical conductors. However, increasing the number of disulfide units also leads to a greater tendency for ring opening and spin quenching dimerization via hypervalent S−S linkages.

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Supporting Information Available: Details of experimental procedures and crystallographic data (CIF) for $[TTPLY][SbF_6]$ and $(TTPLY)_2$. Full numerical details of theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Association of TTPLY through a hypervalent disulfide bond can give rise to two possible isomers, with unruptured dithiole located at the **A** or **B** positions (Figure 4). The experimentally observed structure has the dithiole ring in the **A** position.