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PAPER

Sulfur and selenium substituted spiro-biphenalenvl-boron neutral radicals[†]

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We report a synthetic scheme for the preparation of alkylthio, dithio-bridged and diseleno-bridged 9hydroxyphenalenones and associated spiro-biphenalenyl boron neutral radicals. We show that the strategy of sulfur substitution at the active positions of the phenalenyl units reduces the electrochemical disproportionation potential ($\Delta E_{2-1} = E_2^{\vee_2} - E_1^{\vee_2}$, where $E_1^{\vee_2}$ and $E_2^{\vee_2}$ are the first and second reduction potentials of corresponding cations) of the alkylthio-radicals [3,7-SR-PLY(O,O)]₂B, (R = Me, 9), (R = Et, 10) and (R = Pr, 11), but brings about a significant reduction of the ΔE_{2-1} value in the case of disulfide and diselenide substitution, [3,4-S,S-PLY(O,O)]₂B (12) and [3,4-Se,Se-PLY(O,O)]₂B (13). The crystal structures of 10 and 11 show that the radicals exist as one dimensional (1-D) π -chains of superimposed phenalenyl units, and the molecular units pack more efficiently than the oxygensubstituted analog [3,7-OMe-PLY(O,O)]₂B (8). Magnetic susceptibility measurements indicate that in the solid state the radicals remain paramagnetic while there is spin-spin interaction between the molecules along the π -chains. Band structure calculations are in accordance with the magnetic measurement data and indicate the presence of interactions between the molecules. The room temperature electrical conductivities of both compounds are found to be $\sigma_{RT} = 1.5 \times 10^{-2} \text{ S cm}^{-1}$.

Introduction

Neutral organic radicals contain an unpaired electron just as in classical (mono) atomic metals such as sodium, and they are promising units for the construction of intrinsic molecular metals and superconductors.¹ Molecular conductors have been widely explored in the areas of optoelectronics, magnetooptics and spintronics,²⁻⁶ and phenalenyl radicals have been the subject of a number of recent reviews.⁷⁻⁹ Recently phenalenyl radicals have been shown to display phase transitions that include reversible thermochromism that affect the conductivity, transparency and magnetism.10,11

In organic molecular conductors, improved conductivities usually result from the design of materials with a higher ratio of W/U, that is, by increasing the bandwidth $(W)^{12-14}$ or by reducing

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the on-site Coulomb repulsion (U) which is primarily a molecular property and measures the energy change for an ionic fluctuation and clearly relates to the ease with which a conduction electron can migrate through the lattice.^{15–18} In the pursuit of phenalenyl (PLY)-based neutral radical molecular conductors,1 several mono-, 19-27 bis-, 28-39 and tris-40,41 phenalenyl-based radicals have been synthesized and crystallized (Scheme 1).7-9 Progress in the single phenalenyl based molecular conductors led to the isolation of the radical in the crystalline state by the introduction of bulky or delocalizing substituents which prevent intermolecular σ - or π -association.^{19-27,42} Recently we have introduced substituents into the bis- and tris-phenalenyl compounds with the goal of lowering the value of U in order to improve the conductivity.^{39,41} The substituents have been selected in a way which would not seriously perturb the desirable electronic properties of the PLY

nucleus or inhibit intermolecular interactions in the solid state. The introduction of sulfur and selenium into organic molecular conductors is well known to enhance the intermolecular interactions and electronic stabilization of various oxidation states which results in improved solid state properties.43-51

We have recently succeeded in crystallizing and characterizing the dithiophenalenyl (DTPLY) radical 1 in the solid state (Scheme 1);²⁴ the isolation of 1 as its π -dimer shows that sulfur substitution electronically stabilizes the radical. The electrochemistry of 1 and 2 reveals that sulfur substitution significantly reduces the solution based disproportionation potential $(\Delta E_{2-1} = E_2^{\frac{1}{2}} - E_1^{\frac{1}{2}}$, where $E_1^{\frac{1}{2}}$ and $E_2^{\frac{1}{2}}$ are the first and second reduction potentials of corresponding cations) which is closely related to the on-site Coulomb repulsion (U).

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[†] Electronic supplementary information (ESI) available: Cyclic voltammetry of 9⁺ TFPB⁻, 10⁺ TFPB⁻ and 11⁺ TFPB⁻ in acetonitrile and 12⁺ TFAB⁻ in 1,2-dichlorobenzene reversed after 1st and 2nd reduction and at scan rates of 5 and 10 mV S⁻¹; differential pulse voltammogram of 9+ TFPB- in acetonitrile and 12+ TFAB-, 13 TFPB- in 1,2-dichlorobenzene; details of crystallographic data collection and refinement of 100 K and 293 K structures of 10 and 11 and 100 K structure of 9⁺ TFPB⁻ including crystallographic CIF files. CCDC reference numbers 867315-867319. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm16001c



Scheme 1

An important advantage of the spiro biphenalenyl boron radicals is the quarter-filled band which reduces the onsite coulomb potential in comparison to that which is characteristic of the half-filled band which results for radicals containing a single phenalenyl unit.²² Our most recent results show that alkoxy-substitution in the spiro-biphenalenyl boron compounds can lower the ΔE_{2-1} value, as observed in the biphenalenyl radical (8).³⁹

In the present manuscript we extend this approach by exploring the further introduction of sulfur and selenium substituents into the phenalenyl nucleus by modifying the 9hydroxyphenalenone building block, which allows the synthesis of the sulfur and selenium substituted spirobiphenalenyl boron compounds 9-13 as an alternative strategy to produce radicals with low values of the disproportionation potential. Electrochemistry of the cationic species reveals that sulfur and selenium substitution is effective in lowering the disproportionation potentials; radicals 10 and 11 have been crystallized and shown to have the lowest disproportionation potential among the radicals characterized in the solid state whereas compounds 12 and 13 have the lowest ΔE_{2-1} value so far reported for any organic radical. Radicals 10 and 11 show better overlap in the solid state than the oxygen substituted analogue (8), and the physical properties are improved.

Results and discussion

Synthesis of phenalenyl precursors and spiro-biphenalenyl salts

Our main goal was the synthesis of the disulfide and diselenide bridged and dithioalkyl substituted phenalenyls, while maintaining the 9-hydroxyphenalenone functionality; the disulfidebridged phenalenyls 1 and 2 have been already synthesized according to Scheme 2a,^{25,42} but this oxidative strategy is not useful in the present connection. The nucleophilic replacement of the alkoxy group with thiols is successful in 9-alkoxy-1-phenalenone (Scheme 2b),⁵² but replacement of the methoxy groups of



3,4-dimethoxy-9-hydroxy phenalenone by sulfur substitution proved to be difficult (Scheme 2c). Thus we focused on the introduction of a better leaving group in these positions in order to facilitate the replacement by nucleophiles derived from thiols and hydrogen sulfide [-SR (R = alkyl or H)], and we targeted the *p*-toluenesulfonate derivatives. By reacting *p*-toluenesulfonyl chloride with the previously reported 3,7,9-trihydroxy phenalenone (23) and the newly synthesized 3,4,9-trihydroxy phenalenone (28, Scheme 3) we were able to produce the 3,7- and 3,4-ditosylate derivatives (24 and 29). Compound 24 reacted smoothly with methanethiol, ethanethiol and 1-propanethiol in the presence of potassium carbonate to produce ligands $L^{1}-L^{3}$, whereas reaction of compound 29 with hydrogen sulfide gave the disulfide bridged ligand L⁴ directly, after spontaneous aerial oxidation of the initial reaction product; ligand L⁵ was obtained in a similar manner but using potassium selenoacetate to introduce the desired functionality. This synthetic protocol provides a route to the full range of chalcogenide derivatives of the 9-hydroxyphenalenone nucleus and the corresponding spirobiphenalenvl radicals.

The syntheses of radicals **9–13** followed the same basic procedure that has been used to prepare radicals **3–8**; we first prepared the chloride salts (9^+ Cl⁻ to 13^+ Cl⁻) and finally employed the TFPB⁻ or TFAB⁻ anions to obtain the required solubility properties of the salts (Scheme 4). The salts 9^+ TFPB⁻, 10^+ TFPB⁻, 11^+ TFPB⁻, 12^+ TFAB⁻, and 13^+ TFPB⁻ were purified as air-stable red crystals by recrystallization from dichloromethane and hexane.

Preparation and electrochemistry of 9-13

The cyclic voltammetry (CV) of 9^+-13^+ , X^- showed two reversible waves corresponding to the expected triad of oxidation states (Fig. 1): reversible waves for (0/+1) and (-1/0) couples, together with additional reductions in the case of 12 and 13;^{25,42} the reduction potentials and the disproportionation potentials are given in Table 1. Fig. 1 shows the CV of 9–13 recorded in 1,2dichlorobenzene (the CVs of compounds 9–11 recorded in acetonitrile are shown in the ESI†). The cyclic voltammetry of 12 and 13 in acetonitrile was not reversible; the strong cathodic wave suggests electroreduction of the material coating the electrode.²⁵





The first two reductions for 12 and 13 are very close (Fig. 1c and d) and are nearly merged in the CV experiments, so differential pulse voltammograms (DPVs) were recorded (ESI[†]) to confirm the presence of the two reduction processes. Thus we concluded based on the CV and DPV data (ESI[†]) that compounds 12⁺ and 13⁺ each gave rise to three reductions with potentials of -0.51 V, -0.64 V, and -0.93 V (12⁺), and -0.47 V, -0.55 V, and -0.63 V (13⁺) in acetonitrile, although it may be seen that the second reduction process of 12⁺ (Fig. 1c) is not well behaved.

The reductions of the new compounds 9^+-13^+ occur at less negative potentials than other spirobiphenalenyl boron compounds with the exception of 6^+ and 7^+ . However, the disproportionation potentials (ΔE_{2-1}) of 9-11 are lower than those of the previously reported compounds (1-8) (Table 1 and Fig. 2a; nomenclature based on a previous publication);⁴¹ whereas compounds **12** and **13** show an extremely low value of $\Delta E_{2-1} < -0.1$ V (lowering of ΔE_{2-1} of **12** and **13** with respect to the oxygen substituted compound has also been verified by recording the CVs of **6**, **8**, **9** and **10** in 1,2-dichlorobenzene; Table 1 and Fig. 2b).

We crystallized radicals 10 and 11 by using a chemical reductant (Scheme 4) in an H-cell and obtained a good yield of high quality, long red needles of radical crystals; radicals 9, 12 and 13 have not yet been crystallized due to their very low solubility in common organic solvents. Tetrakis-(dimethylamino)ethylene (TDAE) was used as a reductant as its oxidation potential ($E^{1/2} = -0.7$ V) falls slightly below the first reduction potentials of 9⁺-13⁺. To ensure high crystal quality for radicals 10 and 11 the H-cell was loaded in a dry box and the solvent (acetonitrile) was degassed three times on a vacuum line before mixing the reductant and salt. Crystal growth started on the glass frit after 6 hours standing, and the crystals reached their optimum size and quality in about 24 hours. The crystals are sufficiently stable to allow ambient chemical analyses, X-ray crystallography and solid-state measurements.

X-Ray crystal structures of 10 and 11

The structures of 10 and 11 were determined at two different temperatures (100 K and room temperature (RT) for 10 and 200 K and RT for 11); the room temperature structures did not show any significant change in structural parameters from the low temperature structures ruling out the occurrence of phase transition in this temperature range. Table 2 provides crystal data, and Fig. 3 shows ORTEP drawings of both the radicals. The most important point is the absence of simple σ - or π -dimerization of these radicals in the solid state. There are four molecules of 10 and 11 in the unit cell; the asymmetric units of both of the radicals are composed of half of the molecule, indicating symmetric solid-state packing. The main differences between the molecular structures

Table 1	The half-wave potentials and	disproportionation potent	als (volts vs. SCE) of	f phenalenyl-based	boron and silicon salts
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Salt	Structure	$E_1^{\frac{1}{2}}$	$E_2^{\frac{1}{2}}$	$\Delta E_{2-1}{}^b$	Solvent ^a
1+ OTf-	DTPLY	-0.23	-0.80	-0.57	CH ₃ CN
2^+ BPh ₄ ⁻	TTPLY	-0.33	-0.65	-0.32	$C_2H_4Cl_2$
3^+ BPh ₄ ⁻	$[PLY(O, N R)]_2B; R = Bu$	-0.73	-1.09	-0.36	CH ₃ CN
4^+ BPh ₄ ⁻	[PLY(O,N Et)] ₃ Si	-0.89	-1.24	-0.35	CH ₃ CN
5^+ BPh ₄ ⁻	$[PLY(N Me, N R_1)]_2B; R_1 = Me$	-1.02	-1.37	-0.35	CH ₃ CN
6^+ BPh ₄ ⁻	$[PLY(O,O)]_2B$	-0.36	-0.65	-0.29	CH ₃ CN
6 ⁺ TFAB ⁻	$[PLY(O,O)]_2B$	-0.30	-0.69	-0.39	$C_6H_4Cl_2$
7 ⁺ TFPB ⁻	$[5 \text{ Me-PLY}(O,O)]_2B$	-0.36	-0.64	-0.28	CH ₃ CN
8+ TFPB-	$[3,7-OMe-PLY(O,O)]_2B$	-0.78	-0.99	-0.21	CH ₃ CN
8+ TFPB-	$[3,7-OMe-PLY(O,O)]_2B$	-0.74	-1.04	-0.30	$C_6H_4Cl_2$
9+ TFPB-	[3,7-SMe-PLY(O,O)] ₂ B	-0.55	-0.75	-0.20	CH ₃ CN
9+ TFPB-	$[3,7-SMe-PLY(O,O)]_2B$	-0.40	-0.68	-0.28	$C_6H_4Cl_2$
10 ⁺ TFPB ⁻	[3,7-SEt-PLY(O,O)] ₂ B	-0.60	-0.80	-0.20	CH ₃ CN
10 ⁺ TFPB ⁻	[3,7-SEt-PLY(O,O)] ₂ B	-0.45	-0.74	-0.29	$C_6H_4Cl_2$
11 ⁺ TFPB ⁻	[3,7-SPr-PLY(O,O)] ₂ B	-0.61	-0.82	-0.21	CH ₃ CN
12+ TFAB-	[3,4-S,S-PLY(O,O)] ₂ B	-0.49	-0.56	-0.07^{b}	$C_6H_4Cl_2$
13 ⁺ TFPB ⁻	[3,4-Se,Se-PLY(O,O)] ₂ B	-0.47	-0.55	-0.08^{b}	C ₆ H ₄ Cl ₂

^{*a*} CH₃CN = acetonitrile; $C_2H_4Cl_2 = 1,2$ -dichloroethane; $C_6H_4Cl_2 = 1,2$ -dichlorobenzene. ^{*b*} ΔE_{2-1} evaluated from differential pulse voltammetry experiments (ESI[†]).

of **10** and **11** are (i) 23.5° bending of the PLY plane at the oxygen atoms in **11** and (ii) disorder of one of the alkyl carbons in **11** (Fig. 3 and Table 2). However, these differences in molecular geometry do not influence the packing and solid state properties of these radicals (see later sections).

The sulfur atoms and the carbon atoms connected to sulfur are almost coplanar with the PLY rings and thus we conclude that the sulfur atoms are sp²-hybridized and remain in conjugation with the phenalenyl units in these radicals (Fig. 3). The spiroconjugated phenalenyl rings in these molecules deviate from the usual perpendicular orientation (dihedral angles of 79° and 81° for 10 and 11, respectively). The solid state structures of 10 and 11 reveal that the radicals pack in a continuous array of π -stacked neighboring phenalenyl units with parallel orientation and very short intermolecular carbon-carbon contacts so as to form a polymeric network of neutral radicals (Fig. 4 and 5). It has been previously established that the orientation of the radical molecules in the well-spaced, narrow bandwidth lattices plays the determining role in influencing the conductivity properties.³⁰ In the present case, it is clear that the carbon atoms with short intermolecular contacts possess π -orbitals which are oriented for efficient overlap in radicals 10 and 11. The previously reported analogous oxygen substituted compound 8 is structurally different from 10 and 11. Radical 8 did not show a continuous chain structure at room temperature and carbon-carbon contacts as well as interplanar separations are higher in the case of radical 8 (ref. 39) than those in radicals 10 and 11. Examination of the packing of molecules reveals that phenalenyl units of nearest neighbor molecules are parallel to each other and are involved in a superimposed π -overlap by selective registry between all six pairs of spin-bearing carbon atoms. Thus there is an almost complete superposition of all six active carbon atoms of the phenalenyl nucleus with all intermolecular distances between the spin-bearing carbon centers well below the sum of the van der Waals atomic separations for carbon (Fig. 4), with the closest C-C distance of 3.20 Å at low temperature for both radicals and mean plane separations of 3.23 Å for 10 and 3.26 Å

for 11. This configuration minimizes the steric interference and maximizes the overlap between the singly occupied molecular orbitals (SOMOs) of the adjacent phenalenyl units. By repeating this superimposed π -overlap, both molecules 10 and 11 form a highly symmetrical π -chain structure along the z axis and diagonal to the xz plane.

An important aspect in the packing of radical 10 is the presence of intermolecular S–S interactions (Fig. 4); the sulfur atoms of the superimposed phenalenyls are at a distance of 3.54 Å which is shorter than the sum of the van der Waals atomic separations for sulfur (3.6 Å). Thus in the crystal lattices of 10 and 11, the molecules form a quasi one-dimensional structure which is dominated by 1-D π -chains with very short intermolecular contacts, providing an obvious pathway for conduction.

Magnetic susceptibility of 10 and 11

The temperature dependence of the magnetic susceptibility (χ) of 10 and 11 was measured over the range of 8–330 K and is shown in Fig. 6a as the paramagnetic susceptibility χ_p (after correction for the sample diamagnetism). In both the radicals, χ_p increases with decreasing temperature below 330 K and reaches a broad maximum at $T_{\text{max}} = 81$ K (10) and 57 K (11). We used the analytical form of the Bonner-Fisher model for the S = 1/2antiferromagnetic Heisenberg chain of isotropically interacting spins, ^{53,54} to fit $\chi(T)$ in the temperature range 40–330 K[†], and we obtained an intrachain exchange constant, J = -47 cm⁻¹ for 10 and J = -40 cm⁻¹ for 11, corresponding to antiferromagnetic interactions which dominate the magnetic susceptibilities at low temperature. The uniform Heisenberg model^{53,54} is appropriate because of the regular chain structures of 10, in which the radical spins couple through a single type of interaction (fully superimposed π -overlap, Fig. 4).

Electrical resistivity of 10 and 11

The single crystal conductivities of radicals **10** and **11** were measured using a four probe configuration, and the temperature



Fig. 1 Cyclic voltammetry of (a) 9^+ TFPB⁻, (b) 10^+ TFPB⁻, (c) 12^+ TFAB⁻ and (d) 13^+ TFPB⁻ in 1,2-dichlorobenzene ($E^{1/2}$ are taken from differential pulse voltammetry in the ESI⁺); referenced to SCE *via* internal ferrocene (not shown).



Fig. 2 (a) Comparison of $E_1^{\nu_{\beta}}$, $E_2^{\nu_{\alpha}}$ and ΔE_{2-1} for a variety of phenalenyl radicals in acetonitrile; (b) comparison of $E_1^{\nu_{\beta}}$, $E_2^{\nu_{\alpha}}$ and ΔE_{2-1} for a variety of spiro-biphenalenyl-boron radicals in 1,2-dichlorobenzene.

 Table 2
 Crystal data for radicals 10 and 11

Compound	10	11
Formula	$C_{34}H_{30}BO_4S_4$	C38H38BO4S4
Fw	641.63	697.73
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Ż	4	4
Temp./K	100(2)	200(2)
a/Å	19.019(4)	9.2187(3)
b/Å	8.549(2)	21.9894(7)
c/Å	18.248(3)	16.5888(6)
α/deg	90	90
β/deg	106.965(4)	92.6085(6)
γ/deg	90	90
θ range/deg	2.24-32.22	2.22-29.36
Cell volume/Å ³	2838.1(9)	3359.3(2)
Measured reflections used	5192	6243
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0345	R1 = 0.0411
	wR2 = 0.0865	wR2 = 0.1006
R indices (all data)	R1 = 0.0468	R1 = 0.0546
	wR2 = 0.0933	wR2 = 0.1089
Mean plane separation	3.23	3.26
between phenalenyls/Å		
Dihedral angles between phenalenyls/°	79.0	81.0
Bending at oxygen atoms/°	0	23.5



Fig. 3 ORTEP diagrams of radicals (a) 10 and (b) 11.



Fig. 4 Superimposed π -overlap in 10 and 11, showing the six pairs of spin bearing carbon atoms of the adjacent phenalenyl units which interact with each other with a closest C–C distance of 3.20 Å. The interactions between the sulfur atoms in radical 10 (3.54 Å) are also within van der Waals separation (alkyl groups are omitted for clarity, intermolecular distances of 11 are shown within the brackets).





Fig. 5 Extended representation of solid-state packing of (a) 10 and (b) 11, showing that a single type of repeating superimposed π -overlap leads to an infinite spiro-conjugated chain in the crystal lattice along the *z* axis for 10 and along the diagonal of *xz* plane for 11 (alkyl groups are omitted for clarity).

dependence of the conductivity is shown in Fig. 6c. The conductivity shows a semiconducting temperature dependence with activation energy $\Delta = 0.28$ eV and 0.25 eV for radicals **10** and **11** respectively. The room temperature conductivity



Fig. 6 Solid-state properties of crystalline 10 (blue) and 11 (red), showing the strong similarities in the solid state properties of the radicals: (a) paramagnetic susceptibility as a function of temperature, where the solid line represents the fit of the magnetic susceptibility data of 10 to the Bonner– Fisher model for the S = 1/2 antiferromagnetic Heisenberg chain of isotropically interacting spins, with J = -47 cm⁻¹; (b) fraction of Curie spins and χ_p^*T product (right axis) as a function of temperature; (c) single-crystal conductivity as a function of temperature; (d) single-crystal infrared transmission spectra. (b) Shows the effective fraction of Curie spins per molecule ($8\chi_pT/3$) as a function of temperature; at high temperatures, these values approach the Curie free-spin value of one unpaired electron per molecule, a signature of the neutral radicals we have reported previously.^{28,29,33-35}

 $(\sigma_{\rm RT} = 1.5 \times 10^{-2} \text{ S cm}^{-1})$ of radicals **10** and **11** compares favourably to the other neutral radicals in the same class (1–7). The higher value of the room temperature conductivity in **10** and **11** in comparison with their oxygen substituted analogue **8** $(\sigma_{\rm RT} = 3 \times 10^{-3} \text{ S cm}^{-1})$ may result from the packing and lower value of ΔE_{2-1} in **10**.

Optical measurement of 10 and 11

To obtain further information on the electronic structure, we measured the transmission spectra of single crystals of radicals **10** and **11** (Fig. 6d). The most important feature in the transmission spectra is a strong decrease of absorption between 0.37 eV (E_g) and 0.25 eV (E_g') in correlation with the activation energy of the electrical conductivity ($\Delta = 0.28$ eV, Fig. 6c).

Band electronic structures of 10 and 11

We carried out extended Hückel theory (EHT) band structure calculations,⁵⁵ on the crystal structures of radicals **10** and **11**. Such calculations have been very useful in understanding the electronic structure of organic molecular superconductors,^{56,57} and thin-film field effect transistors,⁵⁸ but cannot be expected to provide a complete picture of the electronic structure in situations where the tight-binding approximation is not applicable. Fig. 7 shows the results obtained for band structure calculations carried out on the lattices found in the X-ray crystal structures. The eight bands shown in Fig. 7a and b are derived from the two

LUMOs of 10^+ and 11^+ respectively, for each of the four molecules of radicals 10 and 11 in the unit cell; basically these consist of the symmetric and antisymmetric combinations of the 1,3,7,9tetrasubstituted phenalenyl LUMO.^{28,59} Alternatively they can be viewed as arising from the nonbonding molecular orbitals of each of the eight phenalenyl units in the unit cell.^{1,60} In this picture these eight orbitals now accommodate a total of four electrons, leading to a quarter-filled band complex with two filled and six vacant bands.

The maximum band dispersions in **10** are 0.04 eV (along a^*), 0.12 eV (b^*), 0.05 eV (c^*) and 0.14 eV, 0.06 eV, 0.16 eV and 0.17 eV along the diagonal directions (Fig. 7a), whereas the maximum band dispersions in **11** are 0.19 eV (along a^*), 0.02 eV (b^*), 0.04 eV (c^*) and 0.18 eV, 0.21 eV, 0.05 eV and 0.19 eV along the diagonal directions (Fig. 7b).

It may be seen that the band dispersions found for 10 and 11 are higher than those for some of the previously reported phenalenyl based radicals such as 1^{24} 3 (R = propyl, pentyl, hexyl, octyl),^{28,30,32,34} 4,⁴⁰ 5,³⁵ and their oxygen substituted analogue 8.³⁹

Radical 10 is the first of the spirobiphenalenyl-based neutral radical conductors to possess a 1-D electronic structure with intermolecular S–S interactions. The band dispersion is reflected in the electronic spectrum (Fig. 6d), where the width of the band-like absorptions is greater than those of a number of other members of this series such as 3 ($\mathbf{R} = \text{ethyl}$, propyl, butyl, pentyl, hexyl, octyl), 4, 5 and 8.^{28–30,32,34,35,39,40}

The presence of a half molecule in the asymmetric unit of the solid-state structure at all temperatures confirms the high



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molecular symmetry and the delocalized nature of the 1-D electronic structure; thus the new radicals may possess the resonating valence bond (RVB) ground state which is characteristic of selected members of the spiro-biphenalenyl radical conductors that were previously reported [3 (R = benzyl, cyclohexyl), 6, and 7].^{33,36,37,61,62}

Conclusion

-7.2

-7.4

-7.6

-7.8

-8.0

-8.2

-8.4

-8.6

-8.8

-7.4

-7.6

-7.8

-8.0

-8.2

-8.4

-8.6

-8.8

D

-7.4

-7.6

-7.8

-8.0

-8.2

-8.4

-8.6

-8.8

-7.4

-7.6

-78

-8.0

-8.2

-8.4

-8.6

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7

Υ

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A convenient and broadly applicable route for the synthesis of thioalkyl as well as dithio-bridged substituted-phenalenyl derivatives and their corresponding spiro-biphenalenyl boron compounds is reported. The first two members (10 and 11) of a new family of spiro-bis(3,7-dithioalkyl 1,9-di-oxophenalenyl) boron neutral radical conductors have been synthesized and characterized in the solid-state. The strategy of thioalkyl as well as dithio- and diseleno-bridge substitution at the active positions of the PLY system is shown to be successful in lowering the electrochemical disproportionation energy ($\Delta E_{2-1} = E_2^{\frac{1}{2}} - E_1^{\frac{1}{2}}$) of radicals 9-13. In the solid state, radicals 10 and 11 pack in a continuous array of π -stacked phenalenyl units; sulfur substitution at the 3, 7 positions not only lowers the ΔE_{2-1} value but also leads to a reduced interplanar separation between π stacked phenalenyls and intermolecular C-C contacts in comparison with their oxygen analogue 8. The solid state properties are dictated by the π -chain structure and the sulfur substitution at the 3, 7 positions. Magnetic susceptibility measurements support the idea that the radicals do not exist as isolated free radicals in the crystalline state, and there are spin-spin interactions between the molecules in the solid state. Band-structure calculations support the magnetic measurement data and indicate the presence of significant interactions between the spin bearing carbons. The low value of ΔE_{2-1} (-0.20 V) and the more efficient solid-state packing in 10 and 11 may be responsible for the order of magnitude increase in the conductivity in comparison to the oxygen analogue 8. The results indicate that appropriate functionalization of the phenalenyl ring system can increase the conductivities in this class of compounds.

Experimental section

Materials

Boron trichloride (Aldrich), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) (Boulder Scientific Company), potassium tetrakis(pentafluorophenyl)borate (KTFAB) (Boulder Scientific Company), sodium tetrakis[3,5bis(trifluoromethyl)phenyl]borate (NaTFPB) (Boulder Scientetrakis(dimethylamino)ethylene (TDAE) (Aldrich), tific). *p*-toluenesulfonyl chloride (Aldrich), ethanethiol (Aldrich), methanethiol (Aldrich), 1-propane thiol (Aldrich) and acetonitrile (dry solvent) (Aldrich) were all commercial products and were used as received. 3,7,9-Trihydroxyphenalenone (23) and 3hydroxy-4,9-dimethoxy phenalenone (27) were prepared according to literature procedures.39,63 Potassium selenoacetate was prepared according to literature procedures.^{64,65} 1,2-Dichloroethane was distilled from CaH₂ just prior to use. The NMR spectra were recorded on a Bruker 300 spectrometer. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer at 2 cm^{-1} resolution. Mass spectra (MALDI) were

-8.8

run on a Voyager-DE STR BioSpectrometry Workstation mass spectrometer. Elemental analyses were performed by the Microanalysis Laboratory, University of Illinois, Urbana, IL.

Preparation of 24

3,7,9-Trihydroxy phenalenone (23) (1.4 g, 6.1 mmol) was dissolved in acetone (200 mL) and anhydrous potassium carbonate (2 g, 12.8 mmol) was added. The mixture was stirred for 2 h, *p*-toluenesulfonylchloride (2.55 g, 12.8 mmol) was added and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by thin layer chromatography [$R_f = 0.6$, dichloromethane]. After 2 h the solution was filtered and the solvent was removed from the filtrate using a rotary evaporator. The compound was purified by column chromatography (SiO₂; dichloromethane). Evaporation of the solvent yielded 1.6 g (49%) of a yellow solid. Mp 195 °C. MS (ESI), m/z = 537.07 (MH⁺). ¹H NMR (CDCl₃): δ 16.70 (s, 1H), 8.24 (d, 2H), 7.88 (d, 4H), 7.56 (t, 1H), 7.37 (d, 4H), 6.89 (s, 2H), 2.46 (s, 6H). Anal. calcd (found) for C₂₇H₂₀O₈S₂: C, 60.44 (60.29); H, 3.76 (3.60)%.

Preparation of 28

A mixture of 3-hydroxy-4,9-dimethoxy phenalenone (**27**) (1.0 g, 0.004 mol) and pyridine hydrochloride (3.0 g, 0.026 mol) was heated to 225 °C in an argon atmosphere for 15 min. The reaction mixture was allowed to cool to room temperature and then dissolved in 200 mL 2(N) sodium hydroxide solution. Hydrochloric acid, 3(N), was added slowly to adjust the pH of the solution to 7 at which point the desired compound precipitated. The brown solid was isolated by filtration, washed several times with water and dried (0.8 g, 90% yield). Mp > 300 °C. MS (ESI), $m/z = 229.05 \text{ (MH}^+$). ¹H NMR (CD₃OD): δ 8.84 (d, 2H), 6.82 (d, 2H), 5.97 (s, 1H). Anal. calcd (found) for C₁₃H₈O₄: C, 68.42 (68.65); H, 3.53 (3.57)%.

Preparation of 29

3,4,9-Trihydroxy phenalenone (**28**) (1.4 g, 6.1 mmol) was dissolved in acetone (200 mL) and anhydrous potassium carbonate (2.0 g, 12.8 mmol) was added. The mixture was stirred for 2 h, *p*-toluenesulfonylchloride (2.55 g, 12.8 mmol) was added and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by thin layer chromatography [$R_f = 0.6$, dichloromethane]. After 1 h the solution was filtered and the solvent was removed from the filtrate using a rotary evaporator. The compound was purified by column chromatography (SiO₂; dichloromethane). Evaporation of the solvent yielded 1.2 g (36%) of a yellow solid. Mp 180 °C. MS (ESI), *m*/*z* = 537.07 (MH⁺). ¹H NMR (CDCl₃): δ 16.29 (s, 1H), 8.04 (d, 1H), 7.97 (d, 1H), 7.79 (d, 2H), 7.67 (d, 2H), 7.42 (d, 1H), 7.30 (d, 2H), 7.25 (d, 2H), 7.18 (d, 1H), 6.86 (s, 1H), 2.42 (br-s, 6H). Anal. calcd (found) for C₂₇H₂₀O₈S₂: C, 60.44 (60.12); H, 3.76 (3.68)%.

Preparation of L¹

Compound **24** (0.4 g, 0.7 mmol) was dissolved in acetone (50 mL) and anhydrous potassium carbonate (0.5 g, 3.6 mmol) was added. A slow stream of methanethiol (gas) was bubbled for 2 h at 0 $^{\circ}$ C and the progress of the reaction was monitored by thin

layer chromatography [$R_f = 0.5$, dichloromethane]. After 24 h the solvent was evaporated and the residue was washed with water and then with hexane to yield 0.15 g (70%) of a yellow solid. Mp 180 °C. MS (ESI), m/z = 289.04 (MH⁺). ¹H NMR (CDCl₃): δ 16.49 (s, 1H), 8.40 (d, 2H), 7.55 (t, 1H), 6.85 (s, 2H), 2.65 (s, 6H). Anal. calcd (found) for C₁₅H₁₂O₂S₂: C, 62.47 (62.85); H, 4.19 (4.26)%.

Preparation of L²

Compound **24** (0.4 g, 0.7 mmol) was dissolved in acetone (50 mL) and anhydrous potassium carbonate (0.5 g, 3.6 mmol) was added. A large excess of ethanethiol (1.0 mL) was added to the mixture and the reaction mixture was stirred for 24 h; the progress of the reaction was monitored by thin layer chromatography [$R_f = 0.5$, dichloromethane]. After 24 h the solvent was evaporated and the residue was washed with water and then with hexane to yield 0.16 g (68%) of a yellow solid. Mp 175 °C. MS (ESI), m/z = 317.07 (MH⁺). ¹H NMR (CDCl₃): δ 16.49 (s, 1H), 8.42 (d, 2H), 7.54 (t, 1H), 6.90 (s, 2H), 3.16 (q, 4H), 1.51 (t, 6H). Anal. calcd (found) for C₁₇H₁₆O₂S₂: C, 64.52 (64.10); H, 5.10 (4.96)%.

Preparation of L³

Compound **24** (0.4 g, 0.7 mmol) was dissolved in acetone (50 mL) and anhydrous potassium carbonate (0.5 g, 3.6 mmol) was added. Excess of 1-propanethiol (0.5 mL) was added to the mixture and the reaction mixture was stirred for 24 h; the progress of the reaction was monitored by thin layer chromatography [$R_f = 0.6$, dichloromethane]. After 24 h the solvent was evaporated and the residue was washed with water and then with hexane to yield 0.17 g (66%) of a yellow solid. Mp 165 °C. MS (ESI), m/z = 345.1 (MH⁺). ¹H NMR (CDCl₃): δ 16.50 (s, 1H), 8.44 (d, 2H), 7.54 (t, 1H), 6.90 (s, 2H), 3.11 (t, 4H), 1.88 (m, 4H), 1.51 (t, 6H). Anal. calcd (found) for C₁₉H₂₀O₂S₂: C, 66.24 (66.87); H, 5.85 (5.96)%.

Preparation of L⁴

Compound **29** (0.4 g, 0.7 mmol) was dissolved in acetone (50 mL) and anhydrous potassium carbonate (0.5 g, 3.6 mmol) was added. A slow stream of hydrogen sulfide was bubbled for 3 h and the progress of the reaction was monitored by thin layer chromatography [$R_f = 0.3$, dichloromethane]. After 24 h the solvent was evaporated and the residue was washed with water and then with hexane to yield 0.10 g (52%) of a brown solid. Mp 170 °C (dec.). MS (ESI), m/z = 258.99 (MH⁺). ¹H NMR (CDCl₃): δ 16.05 (s, 1H), 8.18 (d, 1H), 8.11 (d, 1H), 7.62 (d, 1H), 7.37 (d, 1H), 7.08 (s, 1H). Anal. calcd (found) for C₁₃H₆O₂S₂: C, 60.44 (61.37); H, 2.34 (2.56)%.

Preparation of L⁵

Compound **29** (1.3 g, 2.6 mmol) was dissolved in acetone (60 mL). Potassium selenoacetate, KSeAc (1.7 g, 10.4 mmol), was added slowly to the reaction mixture. The reaction mixture was stirred overnight (8 h) at room temperature. Acetone was evaporated completely using a rotary evaporator and the solid residue was washed with water and diethylether to yield 0.55 g

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(60%) of a brown solid. Mp 105 °C (dec.). MS (ESI), $m/z = 353.86 \text{ (MH}^+$). ¹H NMR (CDCl₃): δ 16.31 (s, 1H), 8.18 (d, 1H), 8.02 (d, 1H), 7.69 (d, 1H), 7.35 (d, 1H), 7.32 (s, 1H). Anal. calcd (found) for C₁₃H₆O₂Se₂: C, 44.34 (43.89); H, 1.72 (2.11)%.

Preparation of 9⁺ Cl⁻

0.15 g (0.53 mmol) of L¹ in 1,2-dichloroethane (10 mL) was treated with boron trichloride (0.26 mL of 1 M solution in dichloromethane, 0.26 mmol) under argon and the mixture was stirred for 24 h. Hexanes were added to the reaction mixture to give a yellow precipitate. The compound was isolated as a red solid (0.110 g) by filtration and used for the next step without further purification. MS (MALDI), m/z = 585 (cation, M⁺).

Chloride salts 10^+ Cl⁻ and 11^+ Cl⁻ were synthesized by a procedure similar to that used for the preparation of 9^+ Cl⁻.

Preparation of 10⁺ Cl⁻

Starting materials. L² (0.15 g, 0.47 mmol); boron trichloride (0.24 mL of 1 M solution in dichloromethane, 0.24 mmol). The compound was isolated as a red solid (0.12 g). MS (MALDI), m/z = 641 (cation, M⁺).

Preparation of 11⁺ Cl⁻

Starting materials. L³ (0.15 g, 0.44 mmol); boron trichloride (0.22 mL of 1 M solution in dichloromethane, 0.22 mmol). The compound was isolated as a red solid (0.12 g). MS (MALDI), m/z = 698 (cation, M⁺).

Preparation of 12⁺ Cl⁻

Starting materials. L⁴ (0.15 g, 0.58 mmol); boron trichloride (0.29 mL of 1 M solution in dichloromethane, 0.29 mmol). The compound was isolated as a dark red solid (0.1 g). MS (MALDI), m/z = 525 (cation, M⁺).

Preparation of 13⁺ Cl⁻

Starting material L⁵ (0.1 g, 0.28 mmol) was dissolved in 25 mL of toluene by heating at 70 °C, 0.14 mL (0.14 mmol) of boron trichloride (1 M solution in dichloromethane) was added and the reaction mixture was stirred at 70 °C for 6 h. The compound was isolated as a dark brown solid (0.080 g, 76%). MS (MALDI), m/z = 713 (cation, M⁺).

Preparation of 9⁺ TFPB⁻

Solid NaTFPB (0.176 g, 0.19 mmol) was added to the dichloromethane solution of 9^+ Cl⁻ (0.12 g, 0.19 mmol) and stirred for 3 h to give a red solution which was filtered and the solvent was evaporated under vacuum to give a red solid. The crude product was purified by recrystallization from dichloromethane/hexane to give red crystals of the desired compound (0.180 g, 64%). Mp 210 °C. MS (MALDI), m/z = 585 (cation, M⁺). ¹H NMR (CDCl₃): δ 8.75 (d, 4H), 7.83 (t, 2H), 7.70 (br s, 8H), 7.50 (s, 4H), 6.99 (s, 4H), 2.69 (s, 12H). Anal. calcd (found) for C₆₂H₃₄B₂F₂₄O₄S₄: C, 51.4 (51.25); H, 2.37 (2.26)%.

Compounds 10^+ TFPB⁻ and 11^+ TFAB⁻ were synthesized by a procedure similar to that used for the preparation of 9^+ TFPB⁻.

Preparation of 10⁺ TFPB⁻

Starting materials. NaTFPB (0.176 g, 0.19 mmol); 10^+ Cl⁻ (0.13 g, 0.19 mmol). The crude product was purified by recrystallization from dichloromethane/hexane to give red crystals of the desired compound (0.19 g, 66%). Mp 190 °C. MS (MALDI), m/z = 641 (cation, M⁺). ¹H NMR (CDCl₃): δ 8.75 (d, 4H), 7.81 (t, 2H), 7.68 (br s, 8H), 7.49 (s, 4H), 7.02 (s, 4H), 3.19 (q, 8H), 1.51 (t, 12H). Anal. calcd (found) for C₆₆H₄₂B₂F₂₄O₄S₄: C, 52.68 (52.80); H, 2.81 (2.51)%.

Preparation of 11⁺ TFPB⁻

Starting materials. NaTFPB (0.176 g, 0.19 mmol); **11**⁺ Cl⁻ (0.14 g, 0.19 mmol). The crude product was purified by recrystallization from dichloromethane/hexane to give red crystals of the desired compound (0.19 g, 66%). Mp 180 °C. MS (MALDI), m/z = 698 (cation, M⁺). ¹H NMR (CDCl₃): δ 8.77 (d, 4H), 7.81 (t, 2H), 7.69 (br s, 8H), 7.50 (s, 4H), 7.02 (s, 4H), 3.15 (t, 8H), 1.89 (m, 8H), 1.12 (t, 12H). Anal. calcd (found) for C₇₀H₅₀B₂F₂₄O₄S₄: C, 53.86 (53.60); H, 3.23 (3.11)%.

Preparation of 12⁺ TFAB⁻

Starting materials. KTFAB (0.136 g, 0.19 mmol); 12⁺ Cl⁻ (0.11 g, 0.19 mmol). The crude product was purified by recrystallization from dichloromethane/hexane to give red crystals of the desired compound (0.19 g, 80%). The material was further purified by dissolution in dichloromethane and re-precipitated by addition of hexane. Mp 160 °C. MS (MALDI), m/z = 525 (cation, M⁺). ¹H NMR (CDCl₃): δ 8.68 (d, 2H), 8.61 (d, 2H), 8.14 (d, 2H), 7.67 (d, 2H), 7.56 (s, 2H). Anal. calcd (found) for C₅₀H₁₀B₂F₂₀O₄S₄: C, 49.86 (49.66); H, 0.84 (0.97)%.

Preparation of 13⁺ TFPB⁻

0.25 g (0.28 mmol) of NaTFPB was treated with 0.21 g (0.28 mmol) of 13^+ Cl⁻ in 25 mL of dichloromethane for $\frac{1}{2}$ h. The reaction mixture was filtered and the filtrate was evaporated to give a dark red solid (0.20 g, 45%). Mp 125 °C, MS (MALDI), m/z = 713 (cation, M⁺). ¹H NMR (CDCl₃): δ 8.63 (d, 2H), 8.43 (d, 2H), 8.09 (d, 2H), 7.72 (s, 8H), 7.58 (d, 2H), 7.49 (s, 4H), 7.27 (s, 2H). Anal. calcd (found) for C₅₈H₂₂B₂O₄F₂₄Se₄: C, 44.20 (44.21), H, 1.41 (1.57)%.

Crystallization of 10

An invertible H-cell with a glass D frit was loaded in a dry box. A solution of 80 mg of 10^+ TFPB⁻ (0.05 mmol) in 10 mL of dry acetonitrile was placed in one container, and 30 mg of TDAE (0.15 mmol) dissolved in 13 mL of dry acetonitrile in the other container. The H-cell was removed from the dry box and attached to the vacuum line, and the containers were taken through three cycles of freeze, pump and thaw to degas the solutions. The H-cell was inverted slowly and the solutions were allowed to diffuse through the glass frit. After sitting in the dark for 48 h, the cell yielded 10 mg (30%) of dark red shining needle shaped crystals. Anal. calcd (found) for C₃₄H₃₀BO₄S₄: C, 63.64 (62.46); H, 4.71 (4.45)%.

Crystallization of 11

An invertible H-cell with a glass D frit was loaded in a dry box. A solution of 90 mg of 11^+ TFPB⁻ (0.05 mmol) in 10 mL of dry acetonitrile was placed in one container, and 30 mg of TDAE (0.15 mmol) dissolved in 13 mL of dry acetonitrile in the other container. The H-cell was removed from the dry box and attached to the vacuum line, and the containers were taken through three cycles of freeze, pump and thaw to degas the solutions. The H-cell was inverted slowly and the solutions were allowed to diffuse through the glass frit. After sitting in the dark for 48 h, the cell yielded 11 mg (28%) of dark red shining needle shaped crystals. Anal. calcd (found) for C₃₈H₃₈BO₄S₄: C, 65.41 (66.67); H, 5.49 (5.76)%.

X-Ray crystallography

X-Ray intensity data were collected at 100 K and 293 K on a Bruker APEX2 (version 2.0-22) platform-CCD X-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å, 50 kV/40 mA power). The crystallographic parameters and the unit cell dimensions for 100 K data are summarized in Table 2. Full details of data collections are given in the ESI[†].

Cyclic voltammetry

Cyclic voltammetric measurement was performed using a CH Instruments Electrochemical Analyzer, with scan rates of 100 mV s^{-1} on solutions (< 10^{-3} M) of **9**⁺ TFPB⁻, **10**⁺ TFPB⁻, **11**⁺ TFPB⁻, **12**⁺ TFAB⁻ and **13**⁺ TFPB⁻ in oxygen-free acetonitrile (distilled from CaH₂) or 1,2-dichlorobenzene containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Potentials were scanned with respect to the saturated calomel reference electrode in a single-compartment cell fitted with Pt electrodes and reference to the Fc/Fc⁺ couple of ferrocene at 0.38 V *vs.* SCE for acetonitrile and -0.56 V *vs.* SCE for 1,2-dichlorobenzene.

Single-crystal near- and mid-infrared transmission spectroscopy

The infrared transmission measurements were carried out in a FTIR Nicolet Nexus 670 ESP spectrometer integrated with a Continuum Thermo-Nicolet FTIR microscope.

Magnetic susceptibility measurements

The magnetic susceptibilities were measured with a George Associates Faraday balance operating at 0.5 T. The calculated diamagnetic susceptibilities were $\chi_0 = -377.1$ and -424.3 emu mol⁻¹ for **10** and **11** respectively.

Electrical conductivity measurements

The single-crystal conductivities (σ) of **10** and **11** were measured in a four-probe configuration using in-line contacts which were attached with silver paint. The needle-like crystals were freely positioned on a sapphire substrate, and the electrical connections between the silver paint contacts on the crystal and the indium pads on the substrate were made by thin, flexible 25 µm diameter silver wires to relieve mechanical stress during thermal cycling of the crystal. The temperature dependence of the conductivity was measured using a custom made helium variable temperature

Band-structure calculations

The band-structure calculations made use of a modified version of the extended Hückel theory (EHT) bandstructure program supplied by M.-H. Whangbo. The parameter set is chosen to provide a reasonably consistent picture of bonding in heterocyclic organic compounds.^{58,66}

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