Supporting Information

Sulfur and Selenium Substituted Spiro-Biphenalenyl-Boron Neutral Radicals

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Details of X-ray Structure Determination for Radical 10 at 100K

A black prism fragment (0.14 x 0.08 x 0.06 mm^3) was used for the single crystal x-ray diffraction study of $C_{34}H_{30}BO_4S_4$ (sample rh173_0m). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2[1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 4.8550 cm from the crystal.

A total of 2400 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω, starting ω and 2θ angles at $–31^o$, and ϕ angles of 0^o, 90^o, 180^o, and 270^o for every 600 frames, 60 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package,[2] and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 22496 reflections at a maximum 2θ angle of 61.00^o (0.70 Å resolution), of which 4325 were independent reflections (R_{int} = 0.0447, R_{sig} = 0.0336, redundancy = 5.2, completeness = 99.9%) and 3506 (81.1%) reflections were greater than $2\sigma(I)$. The unit cell parameters were, **a** = 19.0190(35) Å, **b** = 8.5496(16) Å, **c** = 18.2482(33) Å, β = $106.9653(37)^o$**,** V = 2838.1(9) $Å^3$, Z = 4, calculated density D_c = 1.502 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.377 mm^{-1}; max/min transmission = 0.9785/0.9474) to the raw intensity data using the SADABS program.[3]

The Bruker SHELXTL software package[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.982) and systematic absent reflections indicated two possible space groups, C2/c and Cc. The space group C2/c (#15) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was half a molecule of $C_{34}H_{30}BO_4S_4$ present in the asymmetry unit of the unit cell. The molecule was located on a 2-fold rotation axis parallel to the **b**-axis.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0345, wR2 = 0.0865, with intensity $I>2\sigma$ (I). The largest peak/hole in the final difference map was 0.554/-0.254 e/$Å^3$.

Detail of X-ray Str. Determination for Radical 10 at 296K

A black prism fragment (0.14 x 0.08 x 0.06 mm^3) was used for the single crystal x-ray diffraction study of $C_{34}H_{30}BO_4S_4$ (sample rh173_296K_0m). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 296(2) K on a Bruker APEX2 [1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 4.8550 cm from the crystal.

A total of 2400 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω, starting ω and 2θ angles at –30^o, and ϕ angles of 0^o, 90^o, 180^o, and 270^o for every 600 frames, 60 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package[2] and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 16785 reflections at a maximum 2θ angle of 60.04^o (0.71 Å resolution), of which 4247 were independent reflections (R_{int} = 0.0459, R_{sig} = 0.0434, redundancy = 4.0, completeness = 99.9%) and 2944 (69.3%) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 19.1710(33) Å, **b** = 8.6743(15) Å, **c** = 18.2733(33) Å, β = 106.8288(30)^o**,** V = 2908.6(9) Å^3, Z = 4, calculated density D_c = 1.465 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.368 mm^{-1}; max/min transmission = 0.9790/0.9486) to the raw intensity data using the SADABS program.[3]

The Bruker SHELXTL software package[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.988) and systematic absent reflections indicated two possible space groups, C2/c and Cc. The space group C2/c (#15) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified.

There was half a molecule of $C_{34}H_{30}BO_4S_4$ present in the asymmetry unit of the unit cell. The molecule was located on a 2-fold rotation axis parallel to the **b**-axis.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0434, wR2 = 0.1034, with intensity $I>2\sigma$ (I). The largest peak/hole in the final difference map was 0.400/-0.218 e/Å^3.

Detail of X-ray Str. Determination for 9^+TFPB at 100K

A red fragment of a prism (0.51 x 0.15 x 0.11 mm^3) was used for the single crystal x-ray diffraction study of $[C_{30}H_{22}BO_4S_4]^+[C_{32}H_{12}BF_{24}]^-$ (sample rh171_0m). The crystal was coated with perfluoropolyethers (PFPE) oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2[1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 4.8650 cm from the crystal.

A total of 3600 frames were collected for a sphere of reflections (with scan width of 0.3^o in ω, starting ω and 2θ angles of –30^o, and ϕ angles of 0^o, 90^o, 120^o, 180^o, 240^o, and 270^o for every 600 frames, 60 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package[2] and using a narrow-frame integration algorithm. Based on a triclinic crystal system, the integrated frames yielded a total of 128000 reflections at a maximum 2θ angle of 53.46° (0.79 Å resolution), of which 28725 were independent reflections (R_{int} = 0.0551, R_{sig} = 0.0470, redundancy = 4.5, completeness = 99.9%) and 19089 (66.5%) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 17.2914(14) Å, **b** = 21.5371(18) Å, **c** = 21.8259(18) Å, α = 112.1825(15)°**,** β = 98.9048(15)°**,** γ = 108.7214(15)°**,** V = 6766.1(10) $Å^3$, Z = 4, calculated density D_c = 1.514 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.257 mm^{-1}; max/min transmission = 0.9733/0.8809) to the raw intensity data using the SADABS program.[3]

The Bruker SHELXTL software package[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.968) and no systematic absent reflections indicated two possible space groups, P-1 and P1. The space group P-1 (#2) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There were two cations of $[C_{30}H_{22}BO_4S_4]^+$, two disordered anions of $[C_{32}H_{12}BF_{24}]^-$ (four CF_3-disordered site occupancy factor ratios were 62%/38%, 60%/40%, 43%/27%/30%, 48%/16%/36%, 58%/29%/13%) and three partially occupied solvent molecules of $C_4H_{10}O$ (site occupancy factors 84.6%, 84.7%, 83.5%) present in the asymmetry unit of the unit cell. The SADI, SUMP, DFIX, SIMU and DELU restraints were used to stabilize the final refinement of the disordered anions and partially occupied solvents.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0485, wR2 = 0.1226, with intensity, $I>2\sigma(I)$. The largest peak/hole in the final difference map was 0.684/-0.600 e/Å^3.

Details of X-ray Structure Determination for Radical 11 at 200K

A black needle fragment (0.52 x 0.19 x 0.11 mm^3) was used for the single crystal x-ray diffraction study of $C_{38}H_{38}BO_4S_4$ (sample rh174r_200K_0m). The crystal was mounted on to a glass fiber with epoxy resin. X-ray intensity data were collected at 200(2) K on a Bruker APEX2[1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 4.8550 cm from the crystal.

A total of 2400 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω, starting ω and 2θ angles at –30^o, and ϕ angles of 0^o, 90^o, 180^o, and 270^o for every 600 frames, 10 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package[2] and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 24807 reflections at a maximum 2θ angle of 58.26^o (0.73 Å resolution), of which 4529 were independent reflections (R_{int} = 0.0295, R_{sig} = 0.0206, redundancy = 5.5, completeness = 99.9%) and 3564 (78.7%) reflections were greater than $2\sigma(I)$. The unit cell parameters were, **a** = 9.2187(3) Å, **b** = 21.9894(7) Å, **c** = 16.5888(6) Å, β = 92.6085(6)^o**,** V = 3359.3(2) Å^3, Z = 4, calculated density D_c = 1.380 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.325 mm^{-1}; max/min transmission = 0.9652/0.8499) to the raw intensity data using the SADABS program.[3]

The Bruker SHELXTL software package[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.985) and systematic absent reflections indicated two possible space groups, C2/c and Cc. The space group C2/c (#15) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was half a molecule of $C_{38}H_{38}BO_4S_4$ present in the asymmetry unit of the unit cell. The molecule was located at the 2-fold rotation axis parallel to the **b**-axis. Note that the CHECKCIF report of Alert level B indicating a short intermolecular H..H contact between the H5A and H15D (of the disordered propyl-group) is probably due to the H-atoms of the CH_3-group are not at optimal calculated positions [similarly for the short intra-molecular H…H contact between H8A and H13D (of the disordered propyl-group) that generates an Alert level C].

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0411, wR2 = 0.1006, with intensity $I > 2\sigma$ (I). The largest peak/hole in the final difference map was 0.384/-0.701 e/Å^3.

Details of X-ray Structure Determination for Radical 11 at 296K

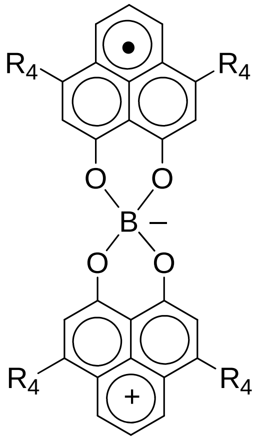
A black prism fragment (0.39 x 0.33 x 0.23 mm^3) was used for the single crystal x-ray diffraction study of $C_{38}H_{38}BO_4S_4$ (sample rh174_296K_0m). The crystal was mounted on to a glass fiber with epoxy resin. X-ray intensity data were collected at 296(2) K on a Bruker APEX2[1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 4.8550 cm from the crystal.

A total of 2400 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω, starting ω and 2θ angles at –30^o, and ϕ angles of 0^o, 90^o, 180^o, and 270^o for every 600 frames, 20 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package[2] and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 26790 reflections at a maximum 2θ angle of 60.06^o (0.71 Å resolution), of which 5005 were independent reflections (R_{int} = 0.0199, R_{sig} = 0.0139, redundancy = 5.4, completeness = 99.8%) and 3924 (78.4%) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 9.3401(2) Å, **b** = 22.0917(6) Å, **c** = 16.6081(4) Å, β = 92.7623(4)^{o}**,** V = 3422.91(14) Å^{3}, Z = 4, calculated density D_c = 1.354 g/cm^{3}. Absorption corrections were applied (absorption coefficient μ = 0.318 mm^{-1}; max/min transmission = 0.9309/0.8856) to the raw intensity data using the SADABS program.[3]

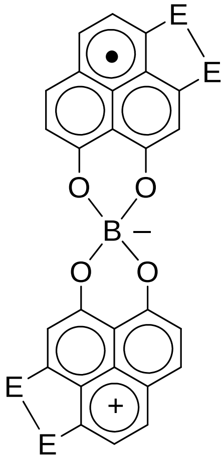
The Bruker SHELXTL software package[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.985) and systematic absent reflections indicated two possible space groups, C2/c and Cc. The space group C2/c (#15) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was half a molecule of $C_{38}H_{38}BO_4S_4$ present in the asymmetry unit of the unit cell. The molecule was located at the 2-fold rotation axis parallel to the **b**-axis.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0400, wR2 = 0.1097, with intensity I>2σ (I). The largest peak/hole in the final difference map was 0.341/-0.290 e/Å^{3}.

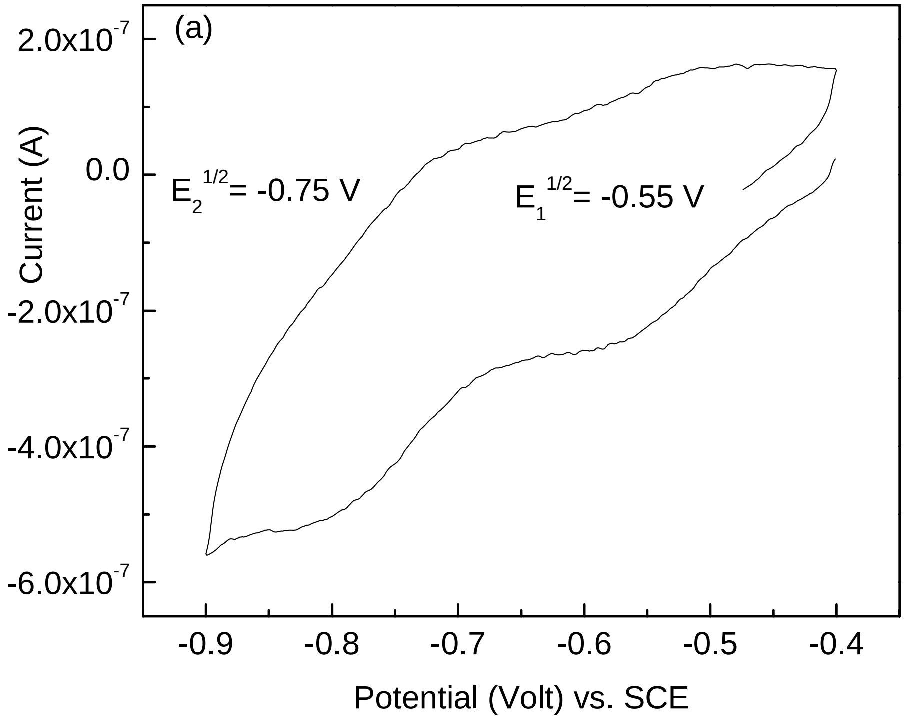
Electrochemistry of $9^+ – 13^+$, X^-

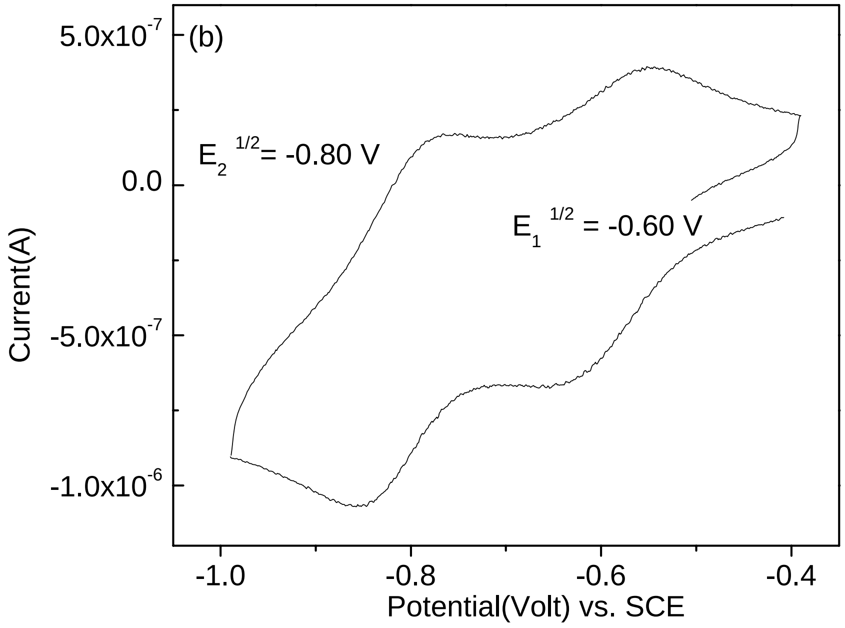


9; $[3,7\text{-}R_4\text{-PLY(O,O)}]_2B$; R_4 = SMe
10; $[3,7\text{-}R_4\text{-PLY(O,O)}]_2B$; R_4 = SEt
11; $[3,7\text{-}R_4\text{-PLY(O,O)}]_2B$; R_4 = SPr



E = S (**12**)
E = Se (**13**)


(a)
$E_2^{1/2}$= -0.75 V
$E_1^{1/2}$= -0.55 V
Current (A)
2.0x10^{-7}
0.0
-2.0x10^{-7}
-4.0x10^{-7}
-6.0x10^{-7}
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
Potential (Volt) vs. SCE


(b)
$E_2^{1/2}$= -0.80 V
$E_1^{1/2}$ = -0.60 V
Current(A)
5.0x10^{-7}
0.0
-5.0x10^{-7}
-1.0x10^{-6}
-1.0
-0.8
-0.6
-0.4
Potential(Volt) vs. SCE

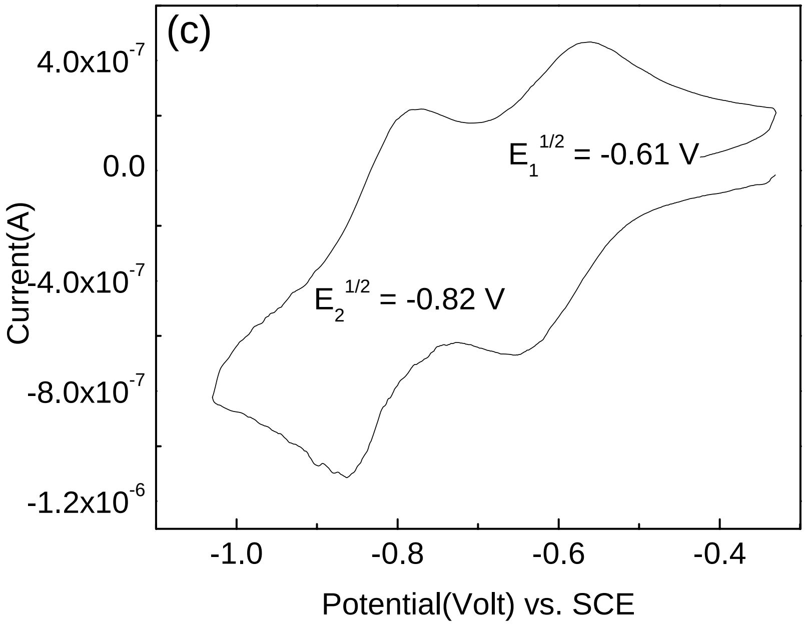


Figure S-1 Cyclic voltammetry of (a) **9**$^{+}$TFPB^{-} (b) **10**$^{+}$TFPB^{-} (c) **11**$^{+}$TFPB^{-} in acetonitrile; referenced to SCE via internal ferrocene (not shown).

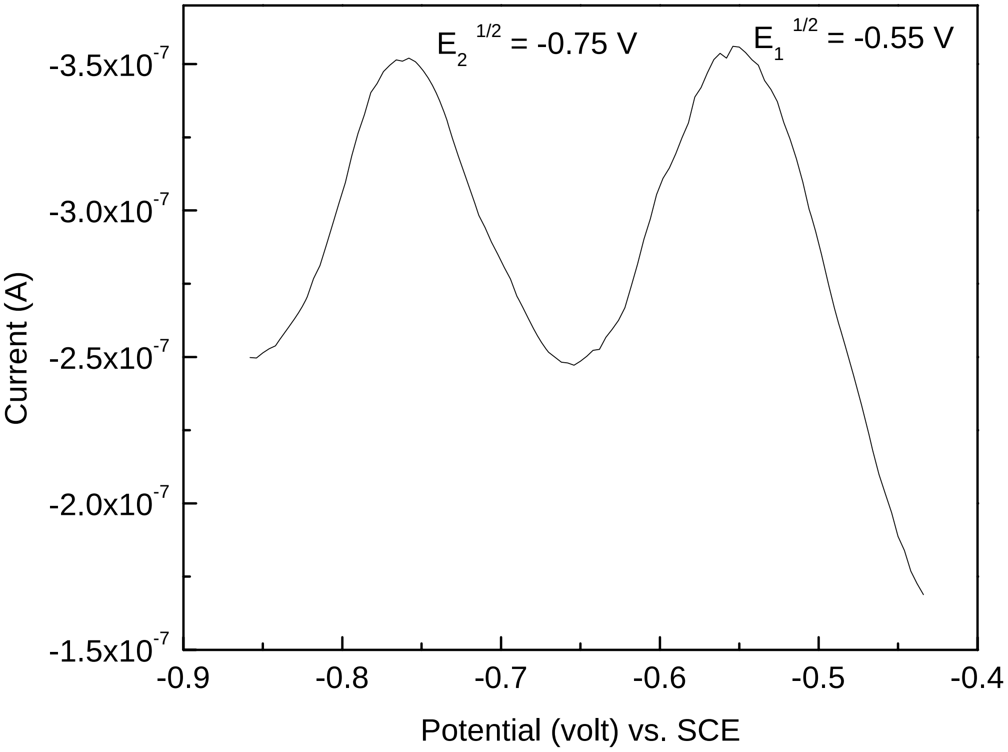


Figure S-2 Differential pulse voltammetry (DPV) of **9**$^+$TFPB$^-$ in acetonitrile; referenced to SCE via internal ferrocene (not shown).

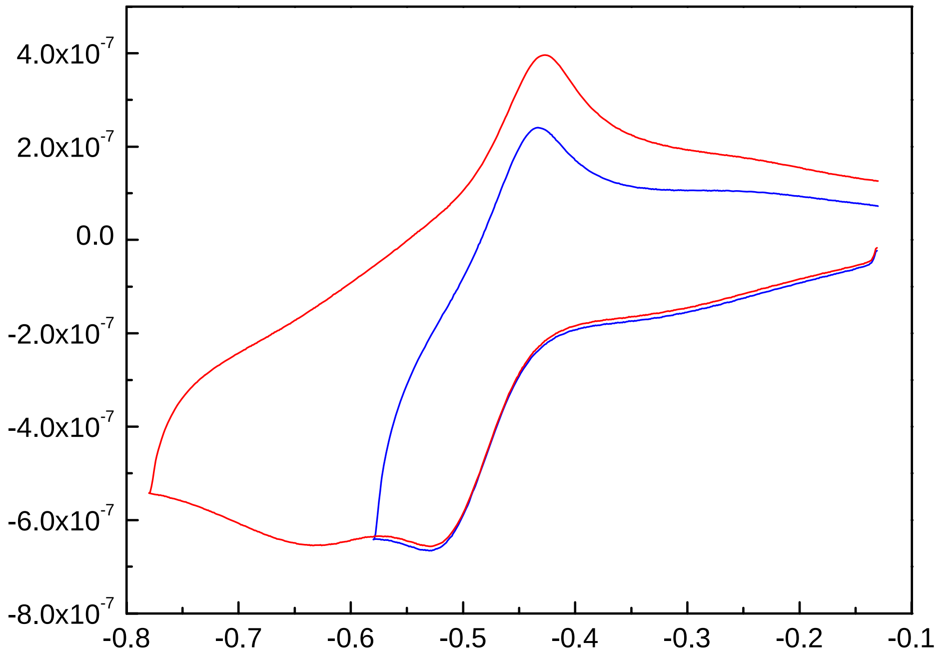


Figure S-3 Cyclic voltammetry of **12**$^+$TFAB in 1, 2-dichlorobenzene, reference to SCE (scan rate 100 mV/s); the sweep was reversed after the first (blue) and second reductions.

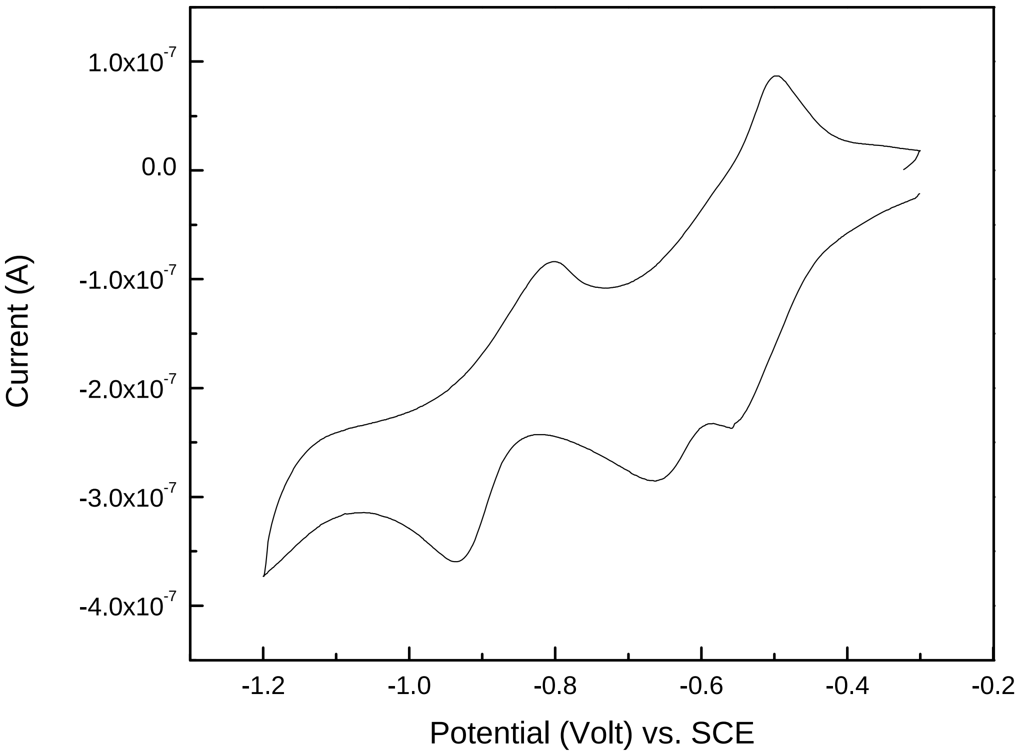


Figure S-4 Cyclic voltammetry of **12**$^+$TFAB in 1, 2-dichlorobenzene, reference to SCE (scan rate 10 mV/S). showing the broadening of the cyclic voltammogram

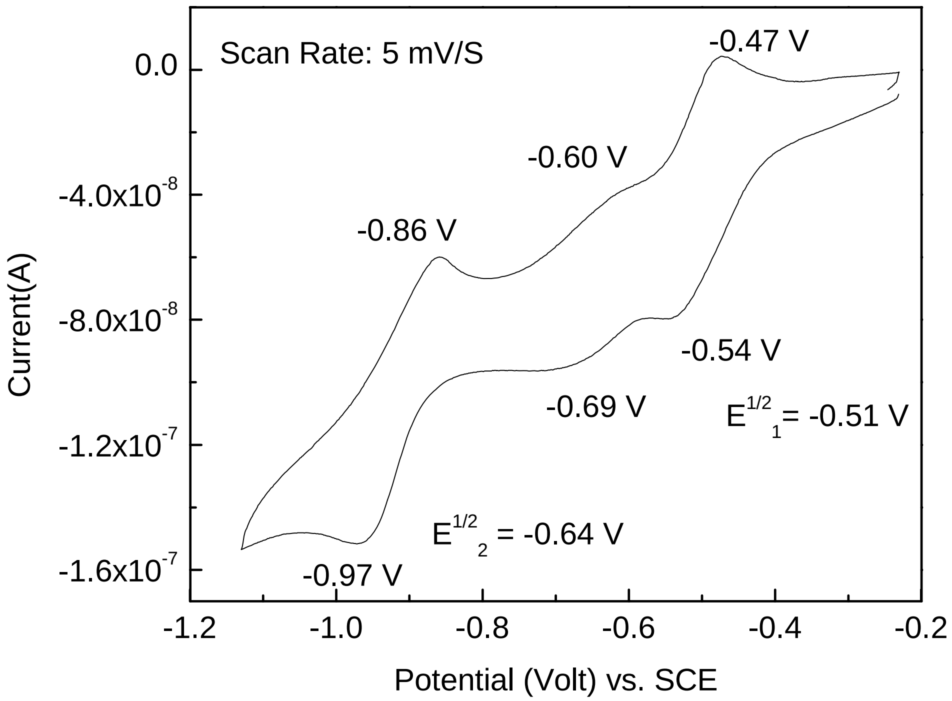


Figure S-5 Cyclic voltammetry of **12**$^+$TFAB in 1, 2-dichlorobenzene, reference to SCE (scan rate 5 mV/s).

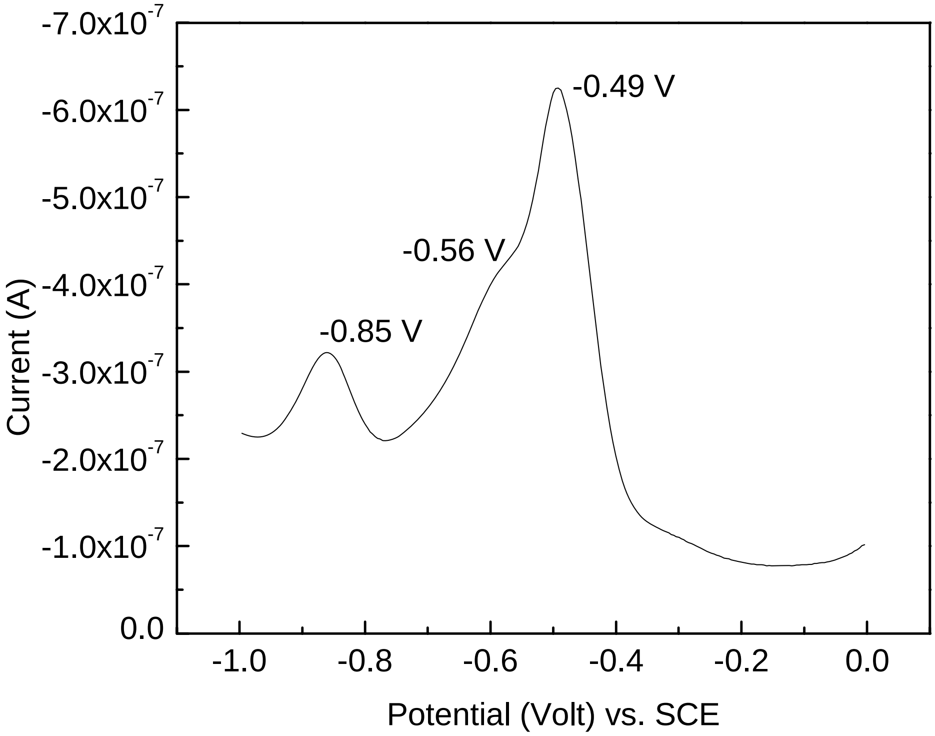


Figure S-6 Differential pulse voltammetry (DPV) of **12**$^{+}$TFAB^{-} in 1, 2-dichlorobenzene referenced to SCE via internal reference ferrocene (not shown).

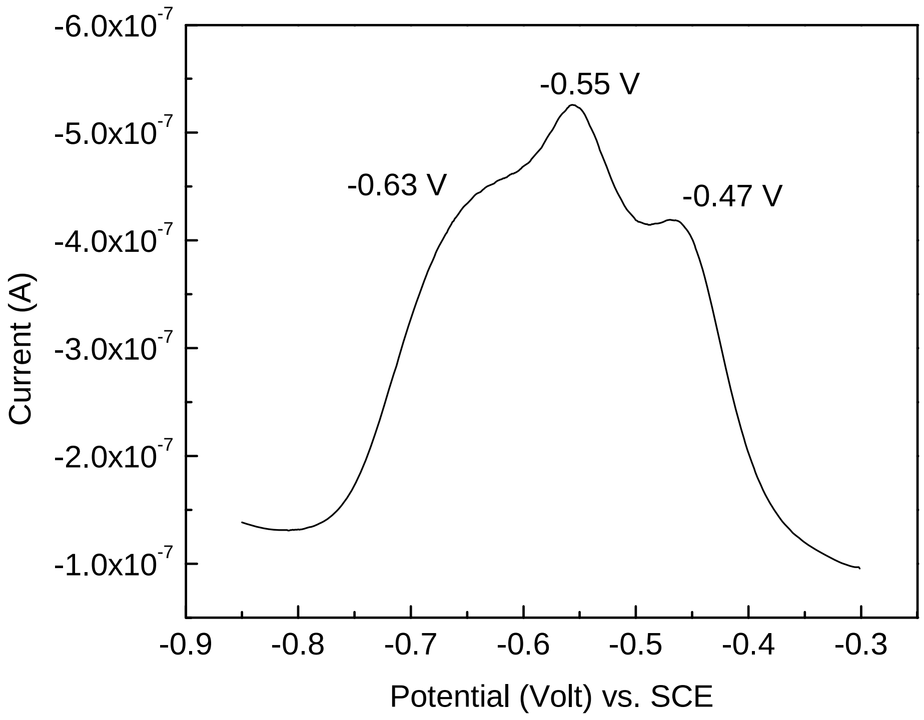


Figure S-7 Differential pulse voltammetry (DPV) of **13**$^{+}$TFPB^{-} in 1, 2-dichlorobenzene; referenced to SCE via internal reference ferrocene (not shown).

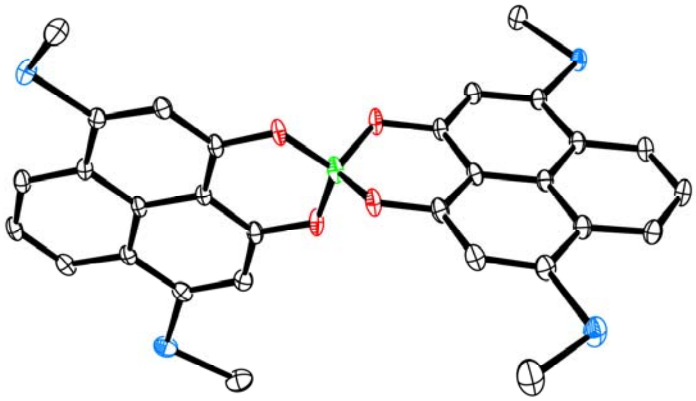


Figure S-8 Molecular structure of **9**$^{+}$TFPB^{-} (counter ion TFPB^{-} is not shown for clarity).

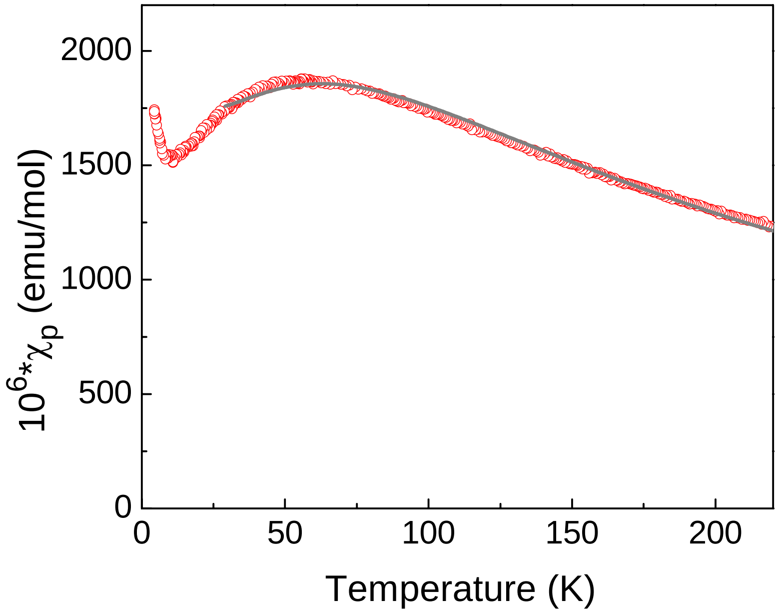


Figure S-9 Paramagnetic susceptibility of **11** as a function of temperature with the red curve showing the fit to the Bonner-Fisher model for the S = 1/2 antiferromagnetic Heisenberg chain of isotropically interacting spins with J=-40 cm^{-1}.

References

(1) *APEX 2,* version 2010.3-0, Bruker (2010), Bruker AXS Inc., Madison, Wisconsin, USA.

(2) *SAINT,* version V7.60A, Bruker (2009), Bruker AXS Inc., Madison, Wisconsin, USA.

(3) *SADABS,* version 2008/1, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.

(4) *SHELXTL,* version 2008/4, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.