# Supporting Information

# A sulfur rich electron acceptor and its $[Fe(Cp^*)_2]^+$ charge transfer salt with ferromagnetic interactions

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**General procedures :** NMR spectra were recorded on a Bruker AV300III spectrometer. Chemical shifts are reported in ppm referenced to TMS for $^1$H NMR and $^{13}$C NMR. Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. Mass spectra were recorded with Varian MAT 311 instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Column chromatography was performed using silica gel Merck 60 (70-260 mesh). The solvents were purified and dried by standard methods. The bis(cyanoethylthio)-1,3-thiazoline derivatives **3** was prepared according to literature procedures.[1] All other reagents were commercially available and used without further purification. Cyclic voltammetry were carried out on a $10^{-3}$ M solution of **1** in $CH_2Cl_2$, containing 0.1 M $nBu_4NPF_6$ as supporting electrolyte. Voltammograms were recorded at 0.1 $Vs^{-1}$ on a platinum disk electrode (A = 1mm$^2$). The potentials were measured *versus* Saturated Calomel Electrode.

**Synthesis of (*E*)-3,3'-diethyl-5,5'-bithiazolidinylidene-2,4,2',4'-tetrathione 1** To a dry two necked flask containing (biscyanoethylthio)-1,3-thiazoline-2-thione **3** (200 mg, 0.63 mmol) was added under nitrogen a solution of freshly prepared NaOMe (1.9 mmol) in dry methanol (from 44 mg of Na in 10 mL of dry MeOH). The solution was stirred for 1 hour. After the formation of the dithiolate, air was bubbled into the reaction mixture for 3 days at room temperature. The solvent was evaporated and $CH_2Cl_2$ (20mL) was added. The organic phase was washed with water, dried over $MgSO_4$ and purified on silica gel using $CH_2Cl_2$ as eluent to afford **1** in 50% yield. Crystals of sufficient quality for X-ray diffraction were obtained by slow evaporation of $CH_2Cl_2$. M.p 240-242°C; $^1$H NMR (300MHz, $CDCl_3$) δ 1.36 (t, 6H, $CH_3$, J = 7.2 Hz, 4.35 (q, 4H, $CH_2$, J = 7.2 Hz). $^{13}$C NMR (75MHz, $CDCl_3$) δ 11.4, 43.3, 133.6, 188.5, 201.0; UV-vis ($CH_2Cl_2$) λ (nm) (ε [$L.mol^{-1}cm^{-1}$]) 296 (19940), 456 (10319), 529 (15538), 570 (19920). ; Anal calcd for $C_{10}H_{10}N_2S_6.0.5CH_2Cl_2$ C, 33.11; H 2.78; N, 7.02. Found: C, 33.05; H 2.95; N, 7.09; HRMS (ESI) calcd for $C_{10}H_{11}N_2S_6$ $[M^+H]^+$: 350.92465. Found: 350.9244.

**Preparation of [Fe(Cp*)$_2$][1].** To a hot solution of **1** (20 mg, 0.057 mmol) in 15 mL of MeCN was added a hot solution of decamethylferrocene (21.4 mg, 0.0655 mmol) in 10 mL of MeCN. The reaction mixture was refluxed 15 mn and the solvent was slowly evaporated to afford purple dark crystals of sufficient quality for X-ray diffraction.

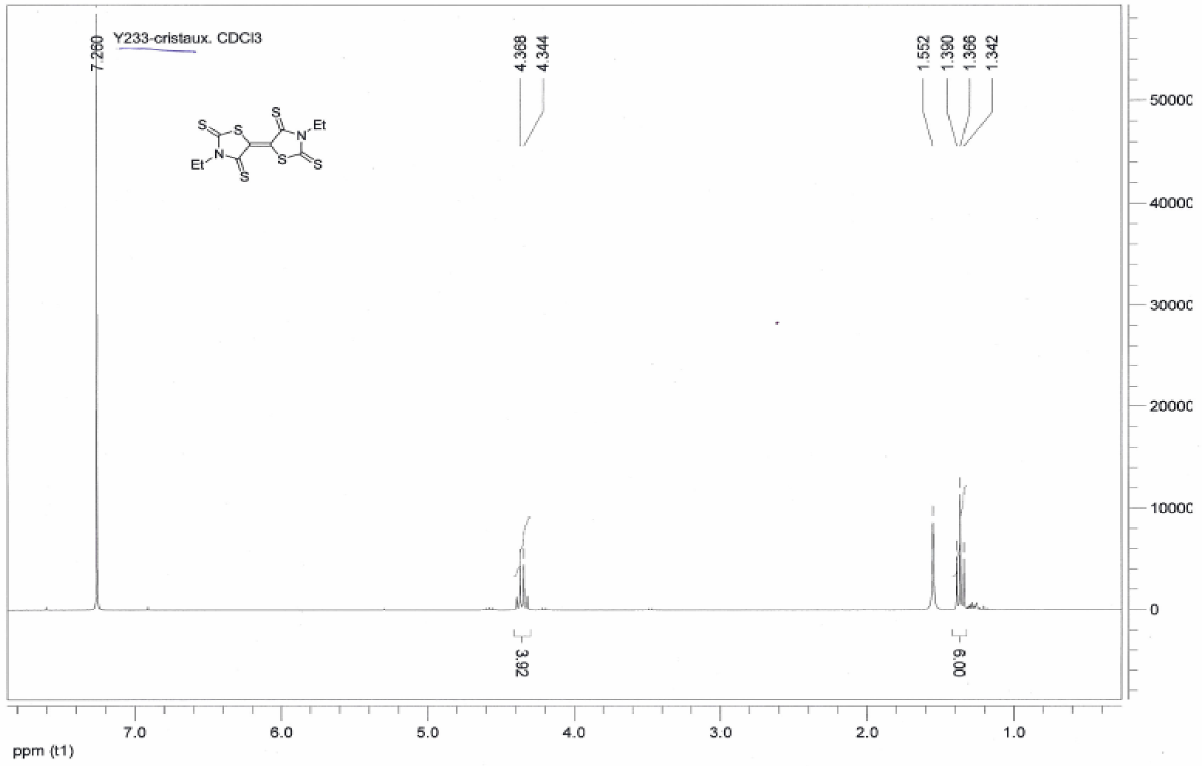

**Fig S2** $^1$H NMR spectrum of **1** in $CDCl_3$

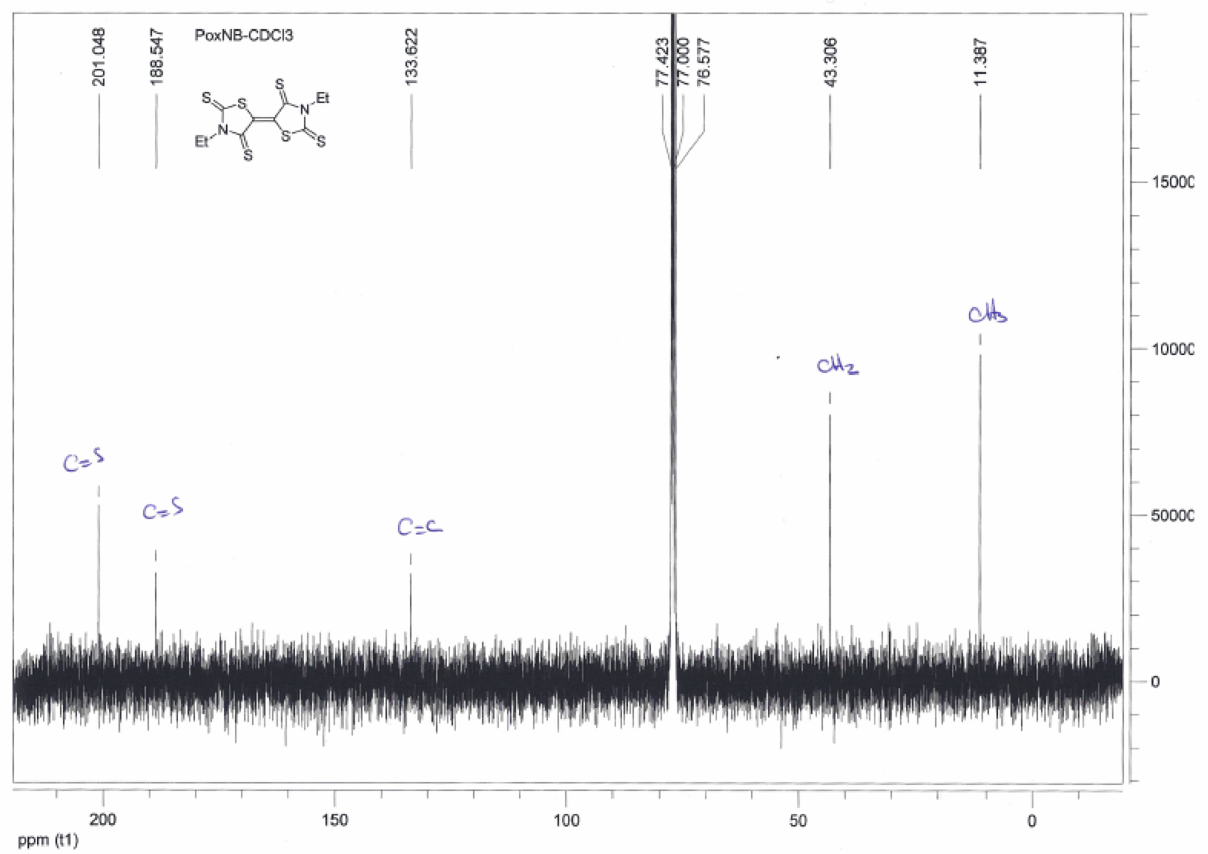

**Fig S2** $^{13}$C NMR spectrum of **1** in $CDCl_3$

***Crystallography***. Data were collected on an APEXII, Bruker-AXS diffractometer. The structure were solved by direct methods using the *SIR97* program,[2] and then refined with full-matrix least-square methods based on $F^2$ (*SHELXL-97*)[3] with the aid of the *WINGX*[4] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. Compound **1**( $2(C_{10}H_{10}N_2S_6)$); $M = 701.12$. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 150(2)$ K; triclinic $P$-1 (I.T.#2), a = 7.4387(5), b = 8.1655(7), c = 12.5242(9) Å, α = 108.826(4), β = 101.941(4), γ = 91.319(4) °, $V = 701.13(9)$ Å$^3$, $Z = 1$, $d = 1.661$ g.cm$^{-3}$, μ = 0.956 mm$^{-1}$. A final refinement on $F^2$ with 3185 unique intensities and 165 parameters converged at $\omega R(F^2) = 0.0716$ ($R(F) = 0.0332$) for 2678 observed reflections with $I > 2\sigma(I)$.

Complex **[Fe(Cp*)₂][1]** ($C_{20}$ $Fe_1$ $H_{30}$, $C_{10}$ $H_{10}$ $N_2$ $S_6$); $M = 676.84$. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 150(2)$ K; triclinic *P*-1 (I.T.#2), a = 9.3382(12), b = 9.6932(12), c = 10.4978(14) Å, α = 76.994(6), β = 64.923(6), γ = 70.853(6) °, $V = 808.93(18)$ Å$^3$, $Z = 1$, $d = 1.389$ g.cm$^{-3}$, $\mu = 0.877$ mm$^{-1}$. A final refinement on $F^2$ with 3662 unique intensities and 184 parameters converged at $\omega R(F^2) = 0.0911$ ($R(F) = 0.0396$) for 2971 observed reflections with $I > 2\sigma(I)$.

**Computational Details.**

Full geometry optimization of models of **1** and **1**$^{\cdot-}$ with Density Functional Theory (DFT)[5] calculations and Time-Dependant DFT calculations were performed with the hybrid Becke-3 parameter exchange functional (B3LYP)[6] and the Lee-Yang-Parr nonlocal correlation functional[7] implemented in the *Gaussian 03* (revision D.02) program suite.[8] The 6-311G** basis set[9] was used. The figures were generated with Molekel 4.3.[10]

### Cartesian coordinates for the optimized geometry of **1** and **1**$^{\cdot-}$

Cartesian Coordinates of **1**

Neutral species, singlet

| | | | |
|---|---|---|---|
| S | -1.45426 | 1.69175 | 0.04793 |
| S | -1.38866 | -2.56514 | -0.31271 |
| S | -4.42739 | 1.89168 | -0.15226 |
| C | -0.67939 | 0.10813 | -0.03656 |
| C | -1.69367 | -0.93766 | -0.19894 |
| N | -2.96840 | -0.39734 | -0.25009 |
| C | -3.06305 | 0.97021 | -0.13348 |
| C | -4.17544 | -1.23630 | -0.39899 |
| C | -4.72957 | -1.69992 | 0.94607 |
| S | 1.45415 | -1.69160 | -0.04836 |
| S | 1.38858 | 2.56532 | 0.31202 |
| S | 4.42716 | -1.89178 | 0.15306 |
| C | 0.67934 | -0.10795 | 0.03616 |
| C | 1.69365 | 0.93782 | 0.19852 |
| N | 2.96832 | 0.39743 | 0.25013 |

| | | | |
|---|---|---|---|
| C | 3.06292 | -0.97017 | 0.13353 |
| C | 4.17546 | 1.23621 | 0.39944 |
| C | 4.73046 | 1.69927 | -0.94546 |
| H | -3.89031 | -2.08399 | -1.02013 |
| H | -4.90465 | -0.62820 | -0.93180 |
| H | -4.00065 | -2.30648 | 1.48601 |
| H | -5.61981 | -2.31030 | 0.77607 |
| H | -5.01487 | -0.84780 | 1.56539 |
| H | 4.90419 | 0.62807 | 0.93281 |
| H | 3.89025 | 2.08418 | 1.02020 |
| H | 5.01594 | 0.84687 | -1.56431 |
| H | 5.62076 | 2.30951 | -0.77517 |
| H | 4.00203 | 2.30583 | -1.48605 |

Cartesian Coordinates of **1**$^{\cdot-}$

Radical anion, doublet

| | | | |
|---|---|---|---|
| S | 1.48901 | -1.67436 | 0.03896 |
| S | 1.39960 | 2.60388 | -0.32101 |
| S | 4.48223 | -1.87946 | -0.15664 |
| C | 0.69849 | -0.08334 | -0.04139 |
| C | 1.67484 | 0.93662 | -0.19714 |
| N | 2.97627 | 0.39641 | -0.24463 |
| C | 3.08106 | -0.95627 | -0.13510 |
| C | 4.16847 | 1.24242 | -0.39112 |
| C | 4.72790 | 1.69393 | 0.95709 |
| S | -1.48901 | 1.67435 | -0.03932 |
| S | -1.39955 | -2.60387 | 0.32096 |
| S | -4.48219 | 1.87949 | 0.15698 |
| C | -0.69848 | 0.08333 | 0.04102 |
| C | -1.67483 | -0.93663 | 0.19682 |
| N | -2.97624 | -0.39641 | 0.24455 |
| C | -3.08104 | 0.95627 | 0.13496 |
| C | -4.16842 | -1.24239 | 0.39140 |
| C | -4.72817 | -1.69400 | -0.95664 |
| H | 3.86991 | 2.10095 | -0.99117 |
| H | 4.90351 | 0.64763 | -0.93281 |
| H | 3.99006 | 2.28667 | 1.50074 |
| H | 5.61588 | 2.31321 | 0.79687 |
| H | 5.01556 | 0.83224 | 1.56259 |
| H | -4.90332 | -0.64756 | 0.93322 |
| H | -3.86972 | -2.10089 | 0.99145 |
| H | -5.01597 | -0.83235 | -1.56213 |
| H | -5.61612 | -2.31326 | -0.79615 |
| H | -3.99047 | -2.28680 | -1.50042 |

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