

# Supporting information

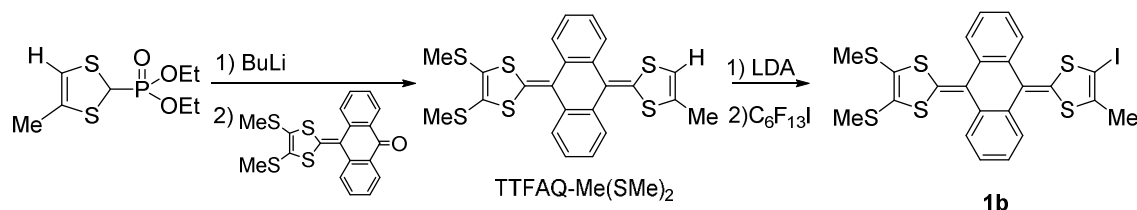
## How the anchoring site on two extended tetrathiafulvalenes impacts the electronic communication through a bis(acetylide)ruthenium linker

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### Synthesis of TTFAQ 1b



**TTFAQ-Me(SMe)<sub>2</sub>.** To a solution of the dithiole phosphonate (3.15 g, 12.4 mmol) in dry THF (320 mL), at -78°C and under argon, *n*BuLi was added (9 mL, 14.4 mmol). After 1h stirring at -78°C, the anthraquinone derivative<sup>1</sup> (1.38 g, 3.57 mmol) was added to the medium and the reaction mixture was allowed to warm to room temperature and stirred for 15h. The solvent was evaporated under reduced pressure and the residue was solubilized with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was washed with water (2x100 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent evaporated to obtain a yellowish powder that was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether (1:2) to afford TTFAQ-Me(SMe)<sub>2</sub> as a yellow powder in 95% yield. mp >220°C; <sup>1</sup>HNMR: δ 7.69 (m, 2H), 7.53 (m, 2H), 7.29 (m, 4H), 5.87 (q, 1H, *J*=1.5 Hz), 2.38 (s, 6H; 2(SMe)), 2.06 (s, 3H, *J*=1.5 Hz; Me); HMRS calcd for C<sub>23</sub>H<sub>18</sub>S<sub>6</sub>: 485.97273. Found : 485.9728.

**TTFAQ 1b.** To a solution of TTFAQ-Me(SMe)<sub>2</sub> (1.5 g, 3 mmol) in dry THF (300 mL), under argon and at -78°C, LDA (6.4 mmol) was slowly added. After 1h stirring at -78°C, perfluoro-

<sup>1</sup> Batsanov, A. S.; Bryce, M. R.; Coffin, M. A.; Green, A.; Hester, R. E.; Howard, J. A. K.; Lednev, I. K.; Martin, N.; Moore, A. J.; Moore, J. N.; Orti, E.Sánchez, L.; Savirón, M. Viruela, P.M.; Viruela, R.; Ye, T. Q. *Chem. Eur. J.* **1998**, *4*, 2580-2592.

1-iodohexane (1.3 mL, 6 mmol) was slowly added to the medium and the reaction mixture was allowed to warm to room temperature and stirred for 15h. The solvent was evaporated under reduced pressure and the residue was solubilized with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was washed with water (2x100 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent evaporated to obtain a powder that was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether as eluent (1:2) to afford TTFAQ **1b** as a dark red powder in quantitative yield. mp >220°C; <sup>1</sup>HNMR: δ 7.56 (m, 4H); 7.31 (m, 4H); 2.39 (s, 6H; 2(SMe)); 2.06 (s, 3H; Me); <sup>13</sup>CNMR: δ (ppm) 134.5, 126.3, 126.1, 125.4, 125.1, 122.7, 19.1, 18.8, 1.01; HMRS calcd for C<sub>23</sub>H<sub>17</sub>S<sub>6</sub>I:611.86938. Found: 611.8696 (0 ppm)

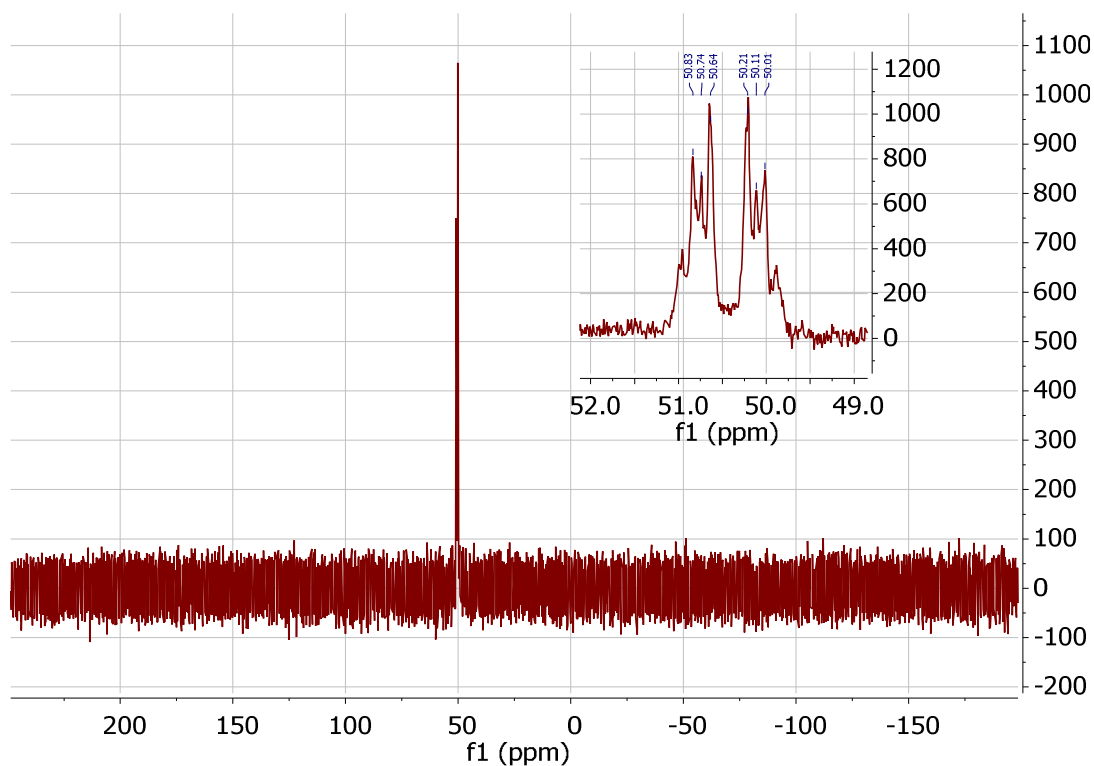
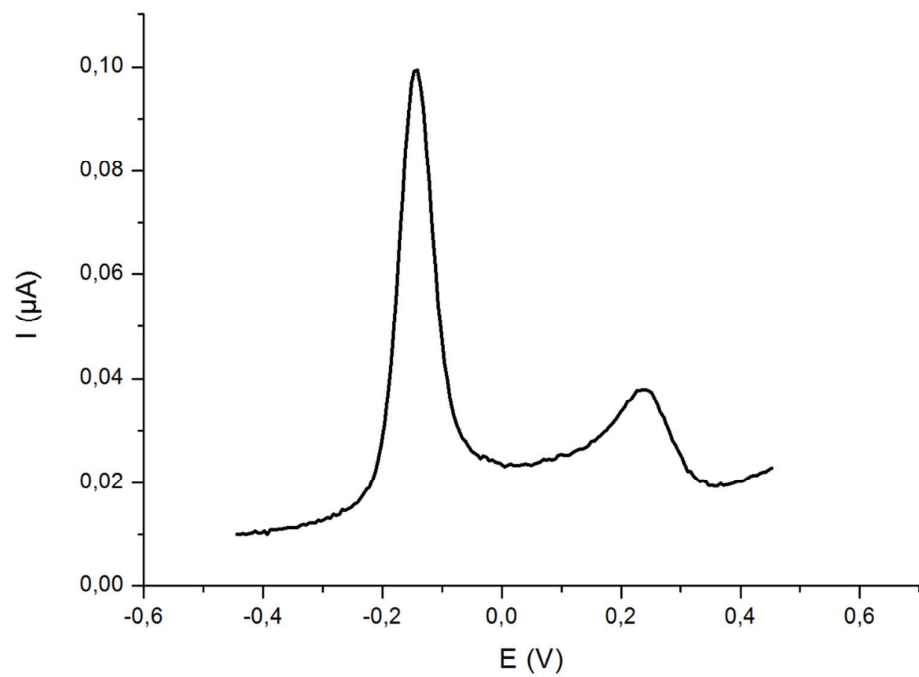
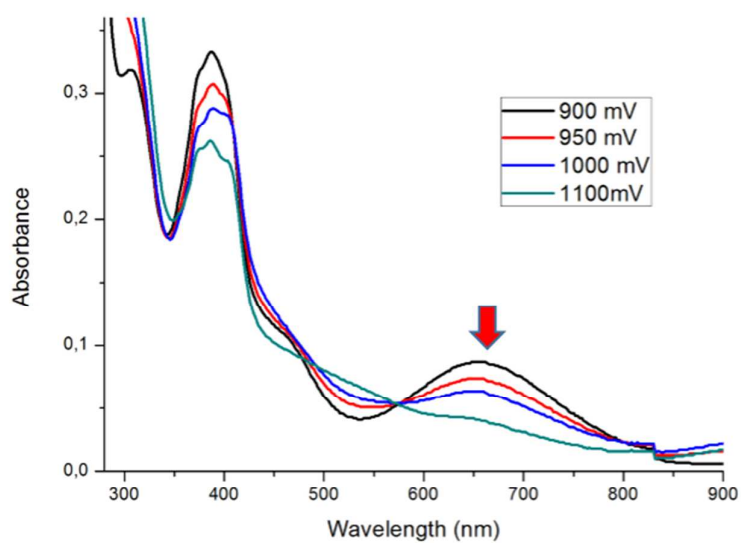


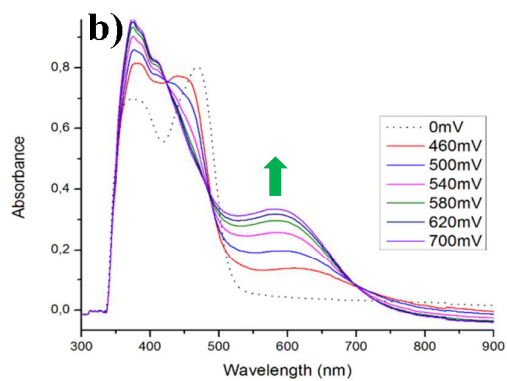
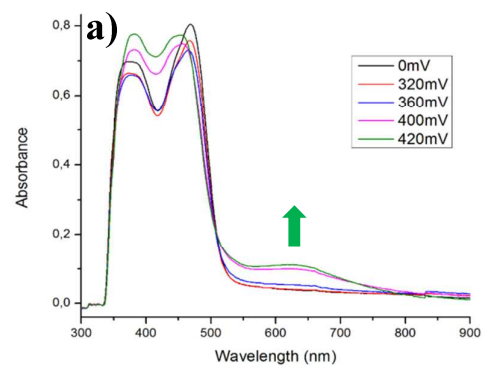
Figure S1. <sup>31</sup>P NMR of complex 5a



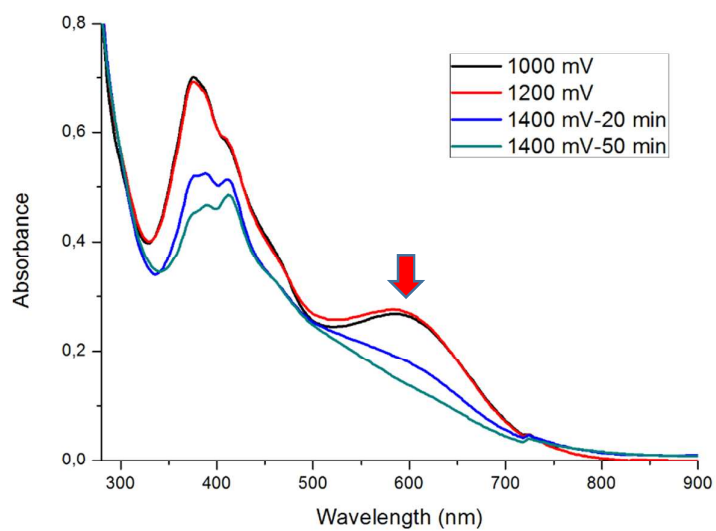
**Figure S2.** DPV of complex **8**. E in V vs Fc



**Figure S3.** UV-vis-NIR monitoring of the electrochemical oxidation of D-Ru **5a** in  $\text{CH}_2\text{Cl}_2$  containing 0.2 M  $\text{Bu}_4\text{NPF}_6$  to the full oxidation state.



**Figure S4** UV-vis-NIR monitoring of the electrochemical oxidation of **6b** in  $\text{CH}_2\text{Cl}_2$  containing  $0.2 \text{ M Bu}_4\text{NPF}_6$ , potentials are quoted vs SCE. a) gradual oxidation to the dication  $\mathbf{6b}^{2+}$  b) to the tetracation  $\mathbf{6b}^{4+}$ .



**Figure S5.** UV-vis-NIR monitoring of the electrochemical oxidation of D-Ru-D **6b** in  $\text{CH}_2\text{Cl}_2$  containing 0.2 M  $\text{Bu}_4\text{NPF}_6$  to the full oxidation state.