Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Assessment of permethylated transition-metal sandwich complexes as internal reference redox systems in ionic liquids

Angel A. J. Torriero, Jaka Sunarso, Maria Forsyth, Cristina Pozo-Gonzalo,*

Australian Research Council (ARC) Centre of Excellence for Electromaterials Science, Institute for Frontier Materials, Deakin University, Burwood, Victoria 3125, Australia. Fax: +61(3)92446868.

Phone: +61(3)92446897.

E-mail: angel.torriero@deakin.edu.au

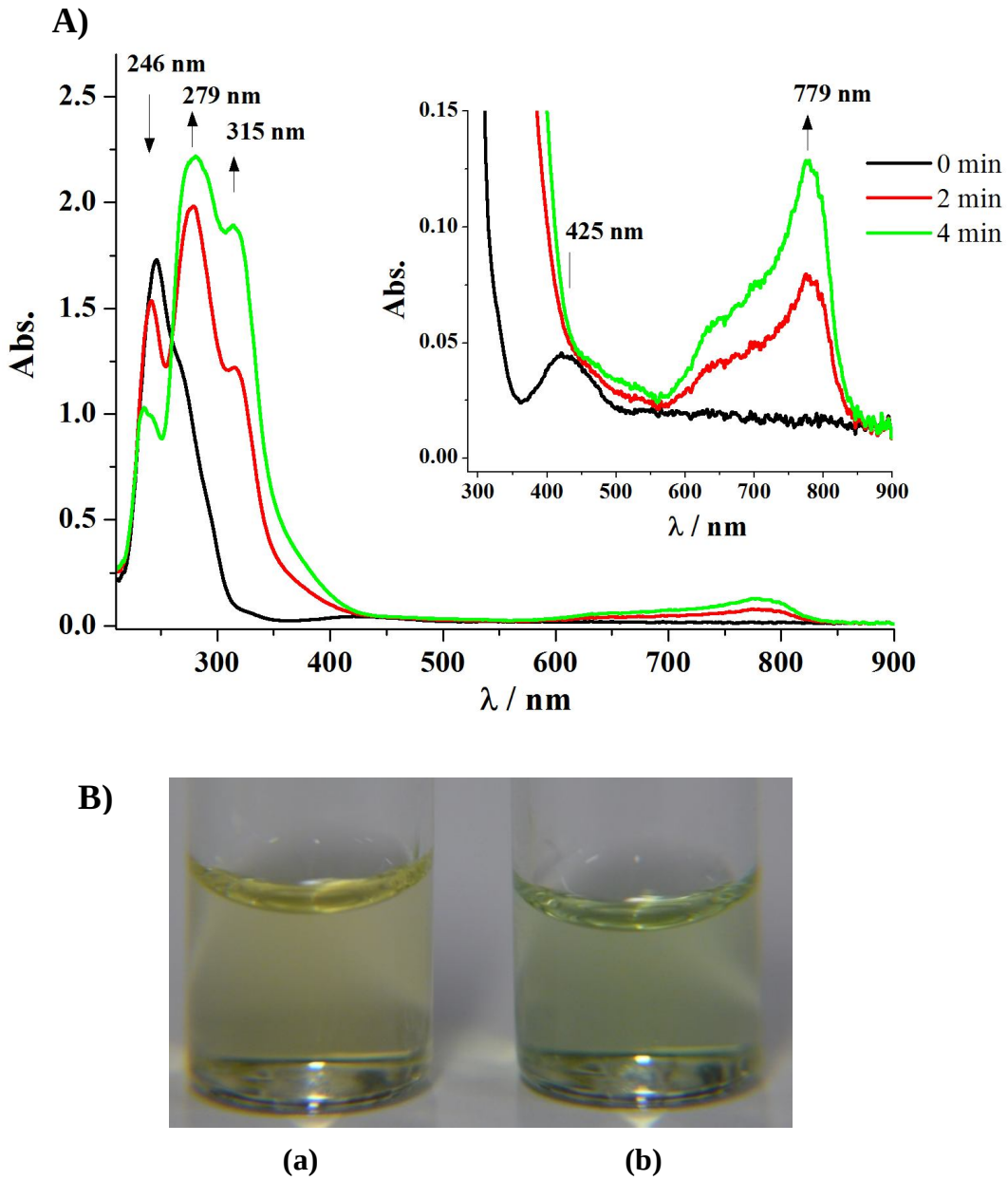

Figure S1. A) UV-visible spectra obtained from 1.15 mM DmFc solution in acetonitrile (0.1 M $[Bu_4N][PF_6]$) during the course of oxidative electrolysis at 0.2 V *vs.* $DmFc^{0/+}$. This experiment was performed with platinum gauze working electrode, a Pt wire auxiliary electrode separated from the Pt gauze by a fine porosity frit, and an Ag/Ag^+ (0.01 M $AgNO_3$, 0.1 M $[Bu_4N][PF_6]$) double junction reference electrode. A rectangular quartz cuvette (2.0 mm optical path length) was used as the electrochemical cell. Inset: amplification of A to show the DmFc spectra before bulk electrolysis. **B)** Comparison of a 1.15 mM DmFc solution in acetonitrile (0.1 M $[Bu_4N][PF_6]$) before (a) and after (b) oxidative electrolysis.

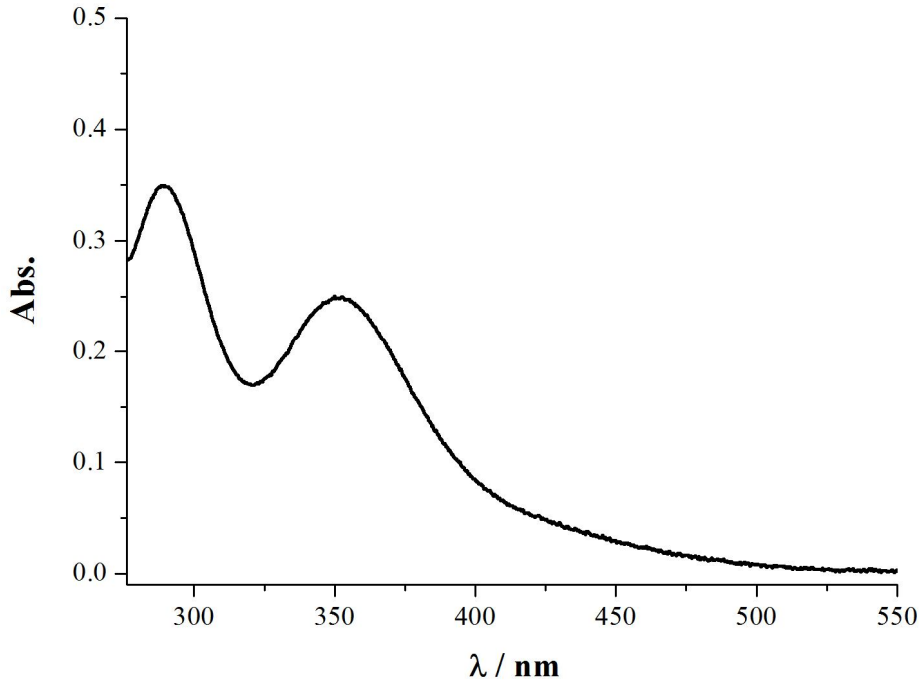

Figure S2. UV-visible spectra of triiodide formed in 2 mL of an aqueous phase after liquid-liquid extraction with 0.4 mL of $[C_4mim][NTf_2]$ and addition of 0.20 mmol potassium iodide. The IL phase, containing 2.27 mmol/Kg DmFc, was stirred in oxygen- and water-saturated atmosphere during two hours before contact with the aqueous phase. The spectrum was obtained with a 1 cm cuvette at 20 ± 1 °C.

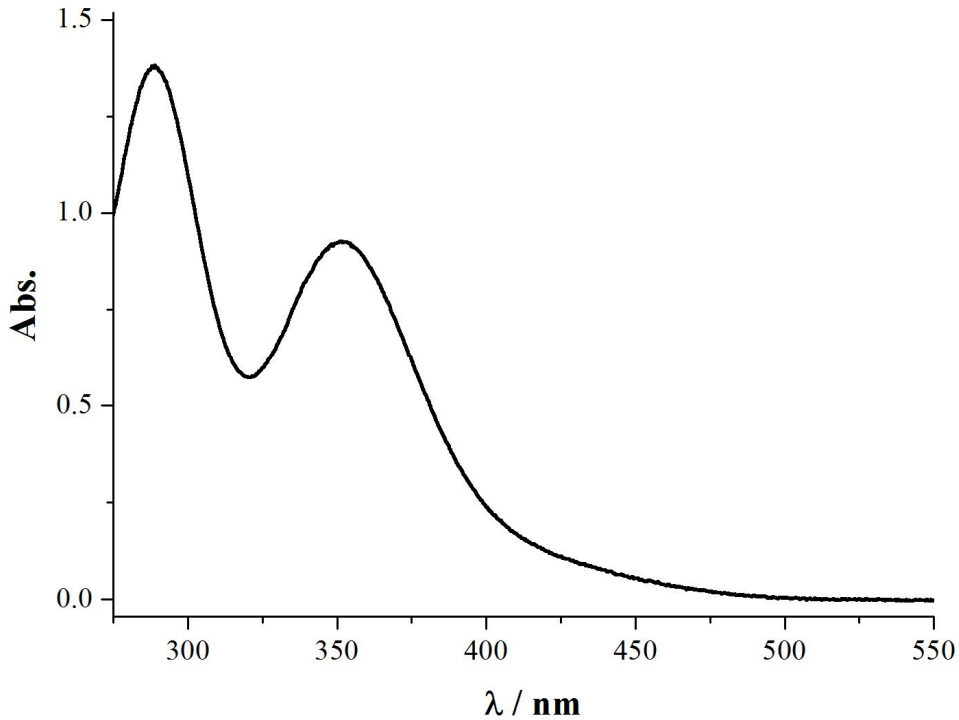

Figure S3. UV-visible spectra of triiodide formed in 2 mL of the aqueous phase after liquid-liquid extraction with 0.4 mL of $[C_4mpyr][NTf_2]$ and addition of 0.2 mmol potassium iodide. The IL phase, containing 2.19 mmol/Kg DmFc and 26.07 mmol $HNTf_2$, was stirred in oxygen- and water-saturated atmosphere during two hours before contact with the aqueous phase. The spectrum was obtained with a 1 cm cuvette at 20 ± 1 °C.