

## Supporting Information

### **Photo-recycling the Sacrificial Electron Donor: Towards Sustainable Hydrogen Evolution in a Biphasic System**

Peiyu Ge,<sup>[a]</sup> Mohamad Hojeij,<sup>[a]</sup> Micheál D. Scanlon,<sup>[b,c]\*</sup> and Hubert H. Girault<sup>[a]\*</sup>

[a] Dr. P. Ge, Dr. M. Hojeij, Prof. H.H. Girault

Laboratoire d'Électrochimie Physique et Analytique

École Polytechnique Fédérale de Lausanne, EPFL, Valais Wallis

Rue de l'industrie, 17, 1950 Sion (Switzerland)

E-mail: [hubert.girault@epfl.ch](mailto:hubert.girault@epfl.ch)

[b] Dr. M.D. Scanlon

The Bernal Institute and Department of Chemical Sciences

University of Limerick (UL)

Limerick V94 T9PX, Ireland

E-mail: [micheal.scanlon@ul.ie](mailto:micheal.scanlon@ul.ie)

[c] Dr. M.D. Scanlon

Marine and Renewable Energy Ireland (MaREI) centre

## Methods and Materials

### Chemicals

All chemicals were used as received without further purification. Decamethylferrocene (DcMFC, 99%) was obtained from ABCR and purified by vacuum sublimation at 140 °C. All aqueous solutions were prepared with ultra-pure water (18.2 MΩ·cm). Lithium tetrakis(pentafluorophenyl)borate diethyl etherate (LiTB) was provided by Boulder Scientific. Bis(triphenylphosphoranylidene)ammonium chloride (BACl, ≥ 98%) and 1,2-dichloroethane (DCE, ≥ 99.8%) were obtained from Fluka. Hydrochloric acid (HCl, 32%) was ordered from Merck. BATB was prepared by metathesis of 1:1 mixtures of BACl and LiTB in a methanol/water mixture (2/1, v/v), followed by recrystallization from acetone. TiO<sub>2</sub> nanoparticles (P25; Rutile:Anatase/85:15, 99.9 %, 20 nm) were purchased from Evonik Industries (Hanau, Germany). Nanocrystalline molybdenum(IV) sulphide (MoS<sub>2</sub>) with an average particle size of 6 μm (max. 40 μm) was purchased from Aldrich (catalogue number: 69860). XPS and TEM analysis of this material were reported by our group previously.<sup>[1]</sup> Citrate stabilised CdSe (Cd:Se molar ratio 4:1) and core-shell CdSe@CdS (Se:S molar ratio 10:1) nanoparticles were synthesised using the protocol described by Kotov and co-workers.<sup>[2]</sup> The obtained CdSe and CdSe@CdS nanoparticles had an average size around 2.5 to 3 nm as determined by transmission electron microscopy (TEM), reported by us previously.<sup>[3,4]</sup>

### Preparation of the decamethylferrocenium cation (DcMFC<sup>+</sup>)

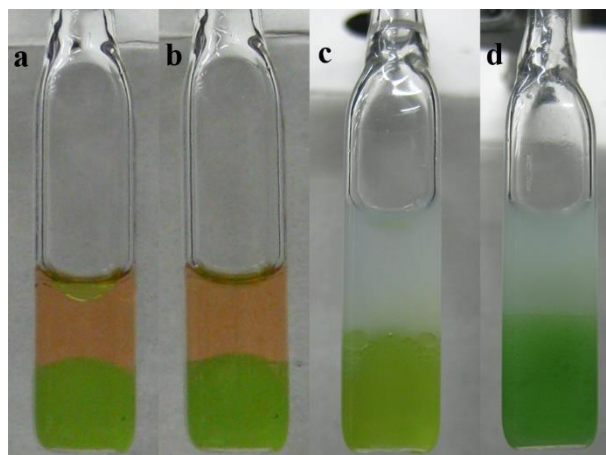
As reported by us previously,<sup>[5–7]</sup> DcMFC<sup>+</sup> was prepared by carrying out a biphasic reaction under anaerobic conditions in which the DCE organic phase containing 5 mM DcMFC (2 mL) was added first, followed by the aqueous phase containing 0.25 mM MoS<sub>2</sub> microparticles and 10 mM LiTB (2 mL, adjusted by HCl to pH 1) and vigorously stirred for 2.5 hours. The ITIES was polarised positively by the distribution of TB<sup>−</sup> between the phases, with protons pumped to the organic phase. The DCE phase turned green, indicating the oxidation of DcMFC to DcMFC<sup>+</sup> as confirmed by UV/vis spectroscopy using an Ocean Optics spectrometer (Ocean Optics Inc.). H<sub>2</sub> was evolved as confirmed by gas chromatography (GC) using a Perkin–Elmer GC (Clarus 400) equipped with packed 5 Å molecular sieves, 80/100 mesh, using a TCD detector and argon as the carrier gas.

### Biphasic photo-recycling of DcMFC<sup>+</sup>

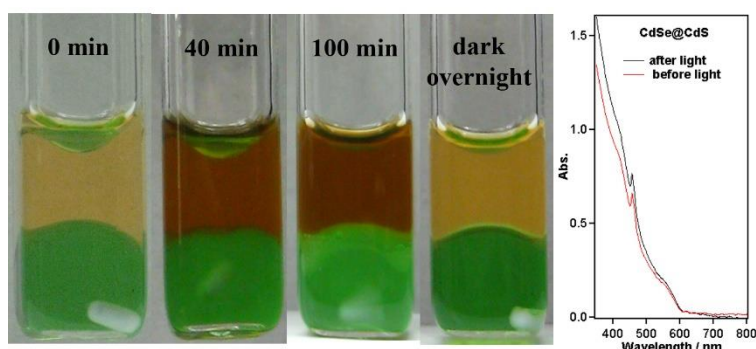
The photo-reaction was carried out in a quartz cell using a Xenon lamp (150 W) as a light source. The head space was analysed by GC and the oxidation state of DcMFC in both phases was monitored by UV/vis spectroscopy.

## Supplementary Figures

### Attempts to photo-recycle $\text{DcMfc}^+$ without polarising the ITIES



**Figure S1.** Experiments with (a, b) 50% (v/v) CdSe and (c, d) 50% (v/v)  $\text{TiO}_2$  (P25, 0.1 g/L) in the aqueous phase before and after photo-illumination. In each biphasic cell was 5 mM  $\text{DcMfc}^+$ , initially in the DCE phase. All experiments were performed under anaerobic conditions and each cell was photo-illuminated for 2.5 hours.



**Figure S2.** Experiments with 25% (v/v)  $\text{CdSe@CdS}$  in the aqueous phase before (0 min) and after (40 and 100 min) photo-illumination, plus one biphasic cell kept in the dark overnight. In each biphasic cell was 5 mM  $\text{DcMfc}^+$ , initially in the DCE phase. UV/vis spectra were taken by sampling the aqueous phase in the cell before photo-illumination (0 min, red line) and after being kept in the dark overnight (black line).

In Figures S1 and S2, it is clear that after photo-illumination at open circuit potential (OCP) conditions, the DCE phase remains green in colour indicating the presence of  $\text{DcMfc}^+$  and the absence of any photo-recycling. The colour change of the aqueous phase in Figure S2 after 40 and 100 mins. of photo-illumination may be attributed to photocorrosion of the CdS shell on the  $\text{CdSe@CdS}$  nanoparticles, as discussed in the main text. The  $\text{CdSe@CdS}$  are stable in the dark as shown by the identical UV/vis spectra in Figure S2 before and after being kept in the dark overnight.

### Supplementary References

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