Electronic Supporting Information

Coupling of zinc porphyrin dyes and copper electrolytes: a springboard for novel sustainable dye-sensitized solar cells

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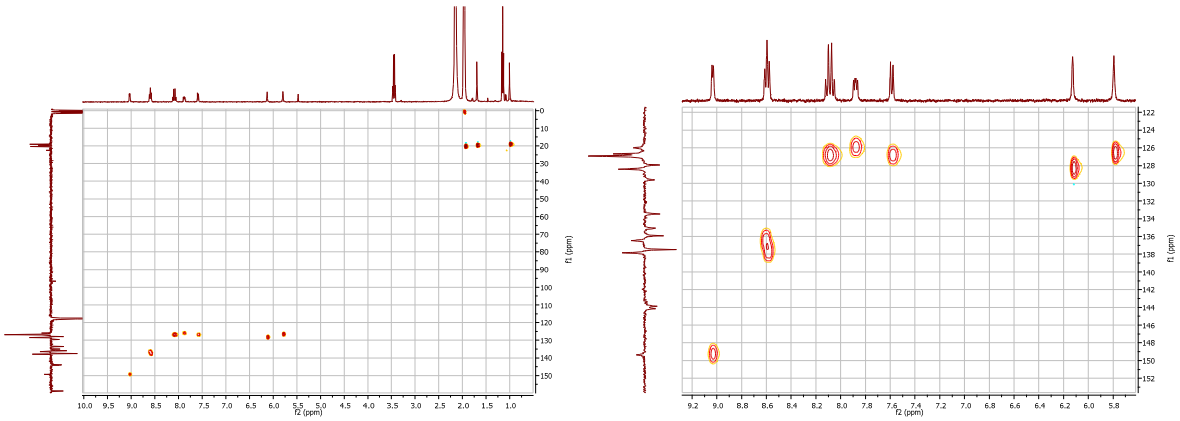


Figure S1 HSQC (^{1}H-^{13}C) spectrum of complex **1** in CD_3CN. Full window (left) and magnification of the aromatic region (right).

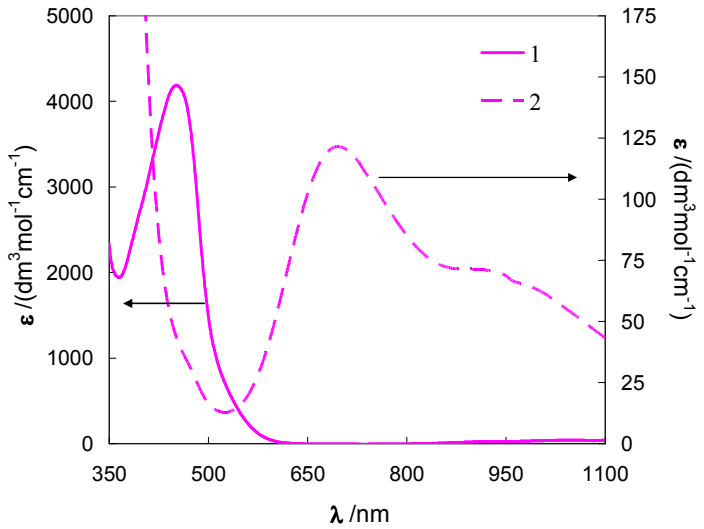


Figure S2 Absorption spectra of the new complexes **1** and **2** in acetonitrile.

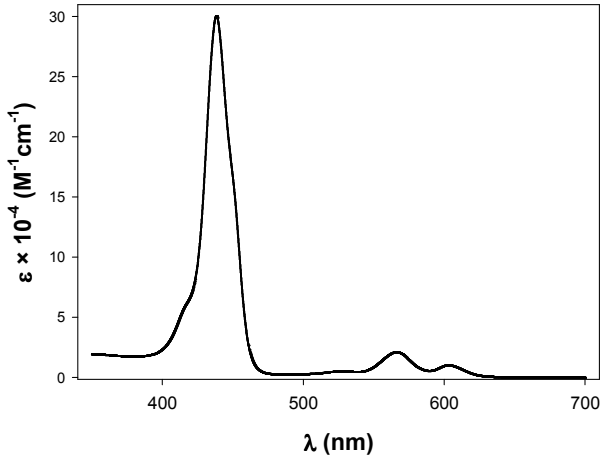


Figure S3 Absorption spectrum of Zn^{2+}-porphyrin **D2** in THF solution.

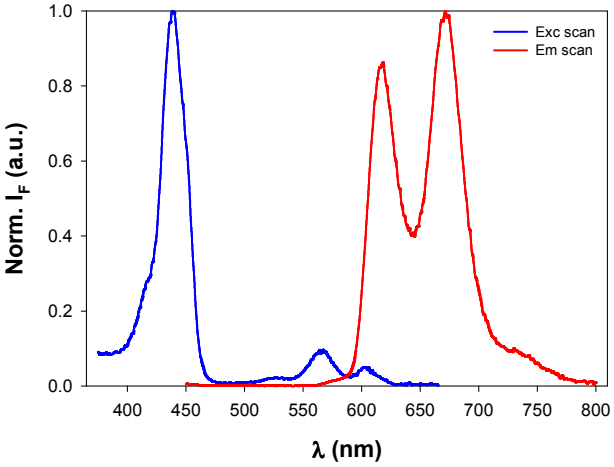


Figure S4 Excitation (λ_{em}: 672 nm) and emission (λ_{exc}: 438 nm) spectra of **D2** in THF solution.

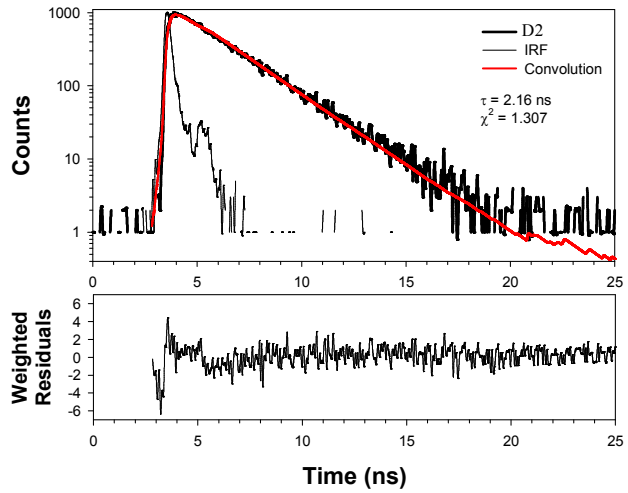


Figure S5. Fluorescence decay of **D2**, bold black line (λ_{exc} 445nm; λ_{em} 617 nm). Instrument response function (IRF) and convolution fit black line and red line respectively. Weighted residuals are shown under the decay curves.

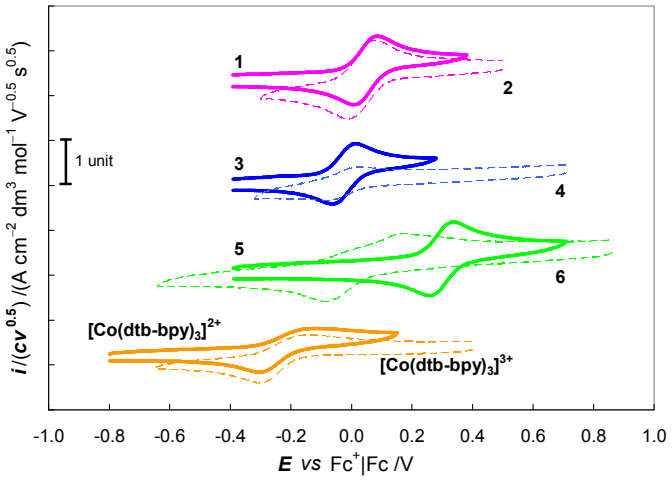


Figure S6 Cyclovoltammetric, CV, patterns of Cu-based redox mediators, **1-6**, in acetonitrile with 0.1 M $TBAPF_6$ on glassy carbon electrode at 0.2 Vs^{-1}. For sake of comparison the CVs of the cobalt tris-bipyridyl couple is also reported (bottom). CV of **2** was recorded in presence of a small excess of ascorbic acid.

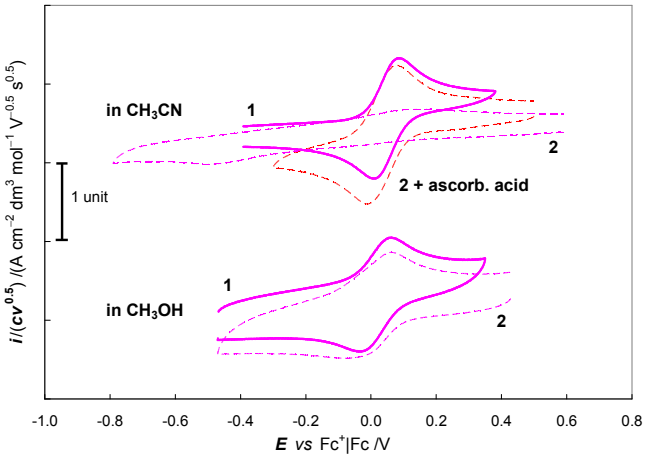


Figure S7 Cyclovoltammetric study to clarify the behaviour of Cu(II) complex **2** (thin dashed lines). Top: pristine complex **2** in acetonitrile (pink line) revealed an anomalous pattern respect to the Cu(I) analogue **1** (bold solid line), but after addition of ascorbic acid (red line) it perfectly resembled **1**. Bottom: pristine complex **2** in methanol showed the same pattern of the Cu(I) analogue **1** (bold solid lines). Supporting electrolyte: $TBAPF_6$ 0.1 M.

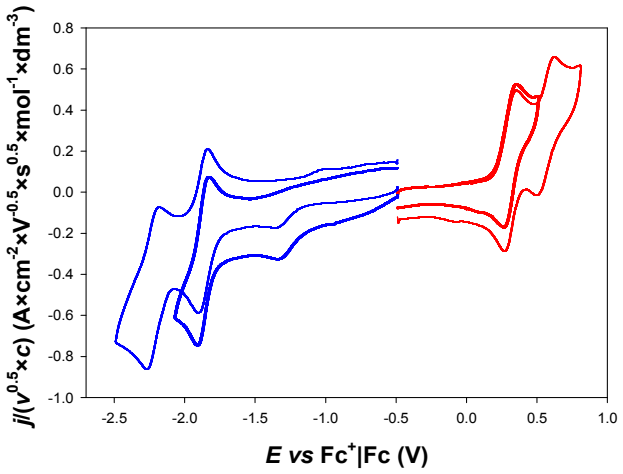
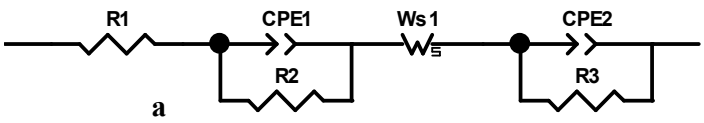
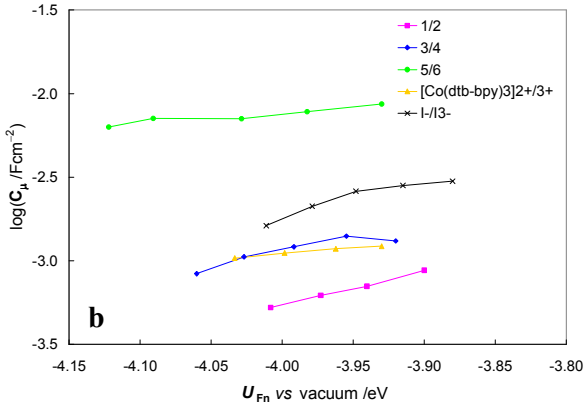
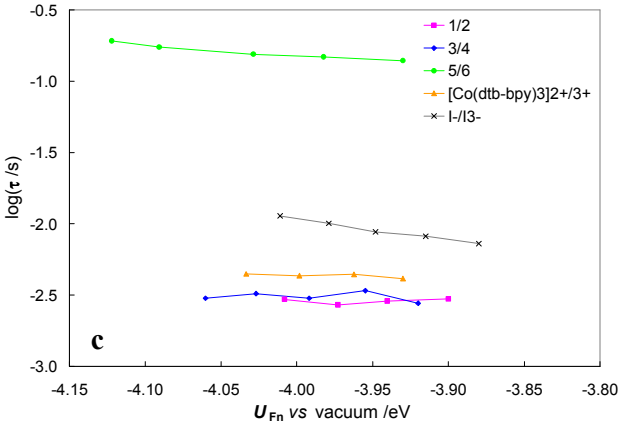


Figure S8 CV patterns of **D2** on glassy carbon electrode, in N,N'-dimethylformamide with 0.1 M TBAP, at 0.2 Vs^{-1}.







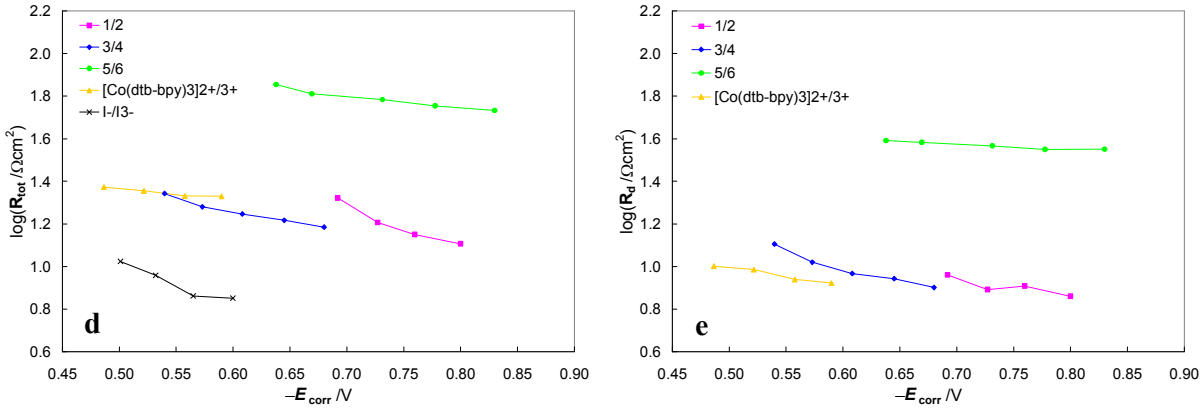


Figure S9 Equivalent circuit employed to fit EIS spectra of **D1**-sensitized DSSCs under 100 mW cm^{-2} irradiation (a): R1= serial ohmic resistance, R2= counter electrode charge transfer resistance, CPE1= counter electrode capacitance, R3= recombination resistance at TiO_2/electrolyte interface, CPE2= chemical capacitance of TiO_2, and Ws1= diffusional Warburg element; chemical capacitance C_μ (b) and electron lifetime $\tau = R_{rec}C_\mu$ (c) as a function of electron Fermi level in TiO_2, U_{Fn}; total resistance R_{tot} (d) and diffusional resistance R_d (e) as a function of corrected bias potential E_{corr}. Lines are added simply to guide the eyes.

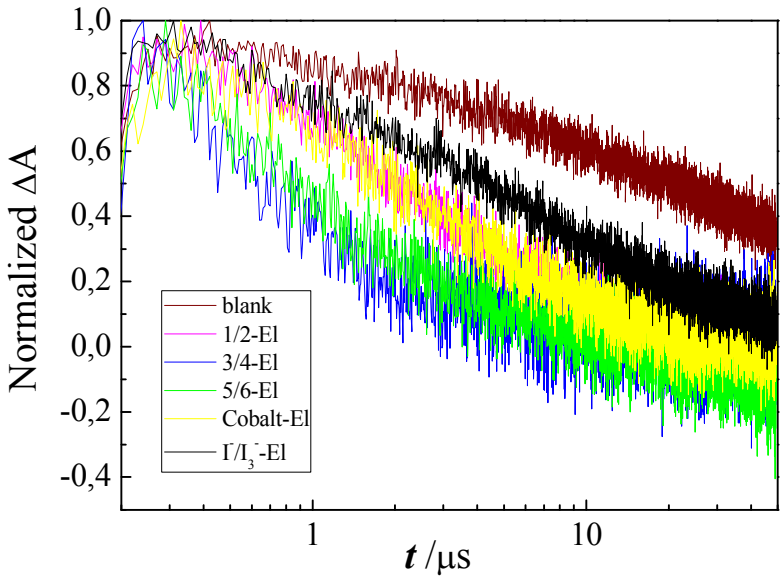


Figure S10: Dye recovery traces of transparent **D1**-sensitized TiO_2 anode by 0.17 M solution of electron donor **1**, **3**, **5**, $[Co(dtb\text{-}bpy)_3]^{2+}$, I^- and by a blank solution (*i.e.* dye-mediated electron recombination).

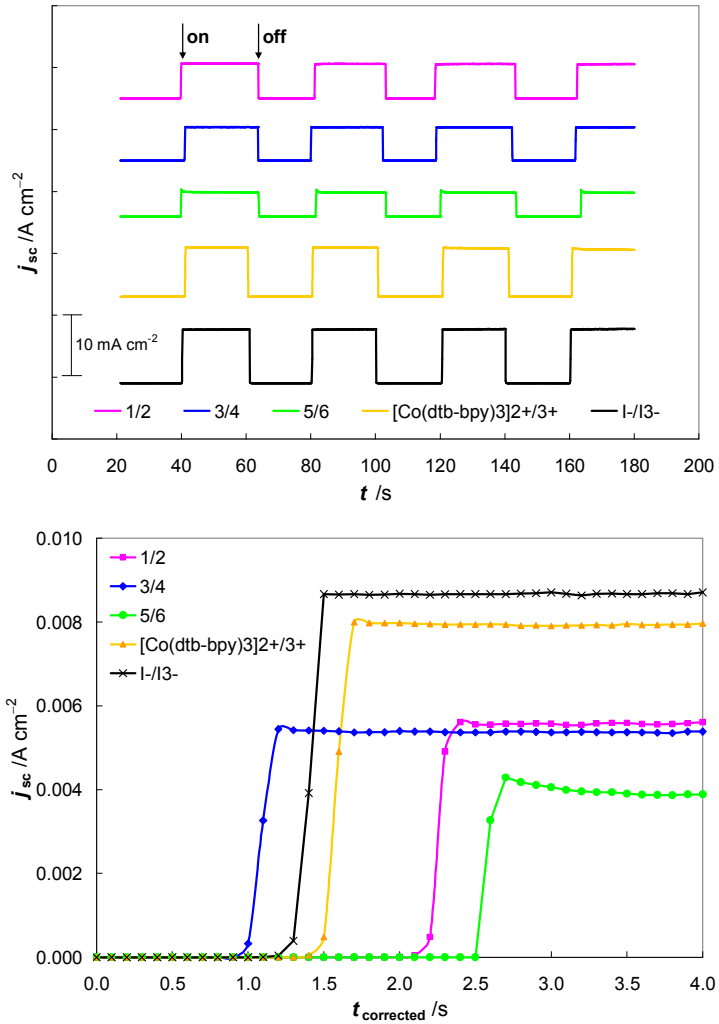


Figure S11 Top: chopped chronoamperometric traces at short circuit for **D1**-sensitized DSSCs. Bottom: magnification of the light-on edges to evidence possible diffusion limitations.

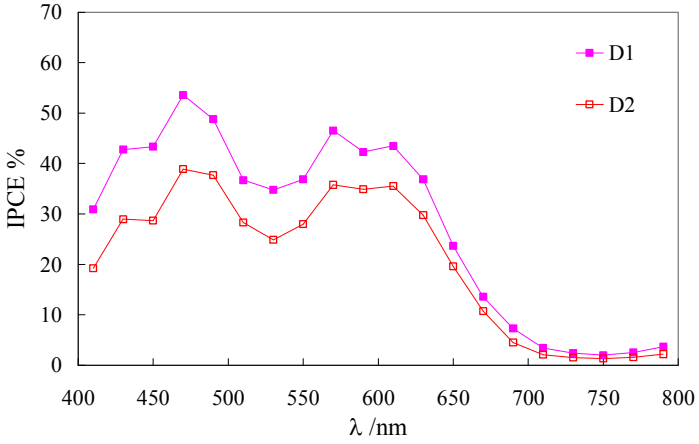


Figure S12. Under 100 mW cm^{-2} AM 1.5G illumination of **D1** or **D2**-sensitized DSSCs, filled with **1**/**2**-El. Photoaction spectra of the devices

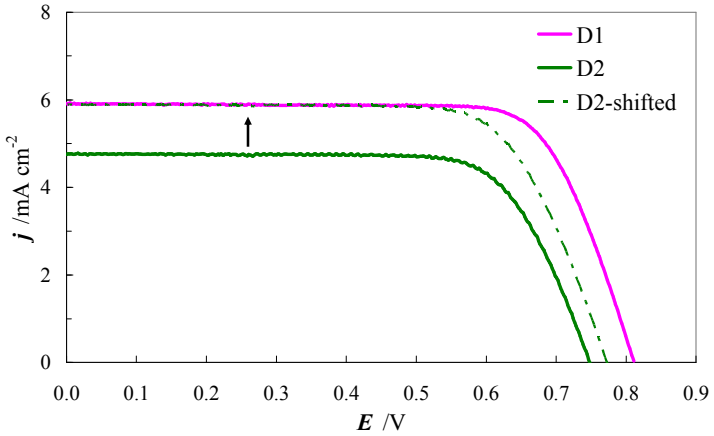


Figure S13 Comparison of **D1** versus **D2**-sensitized solar cells with **1**/**2**-El, after upshifting of **D2** trace until j_{sc} matches each others.

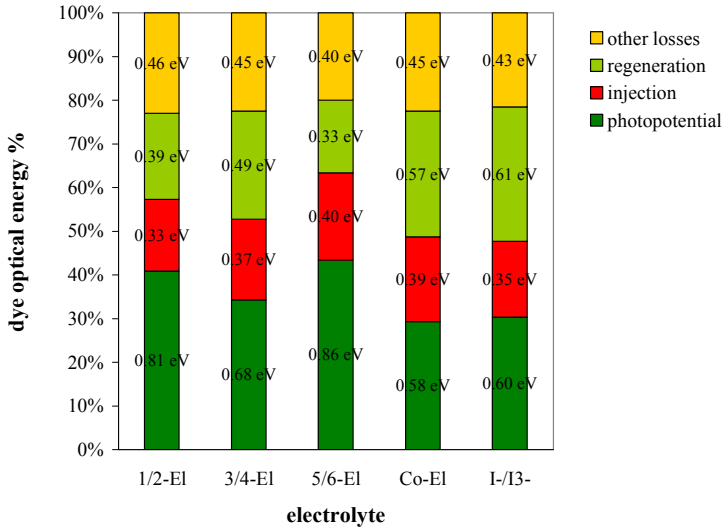


Figure S14 Profile of energy distribution for **D1-**sensitized DSSCs. Energy of the optical band gap 1.98 eV (from onset absorption) was taken as reference to evaluate percentage of each single process.

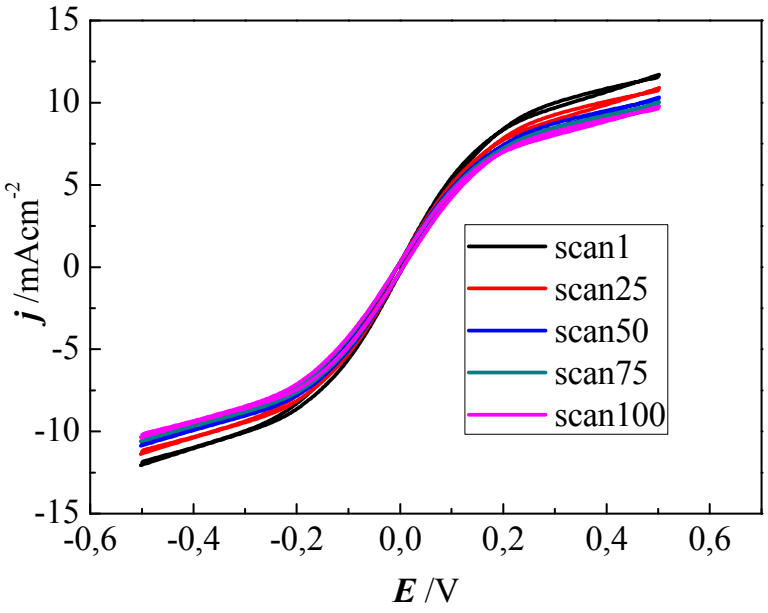


Figure S15: Stability test of **1/2**-El by scanning potential at 0.01 V s^{-1} scan rate up to 100-times in symmetrical PEDOT/FTO dummy cell.

Table S1 Half-wave potential, $E_{1/2}$, heterogeneous rate constant, k_{heter}, and apparent diffusion coefficient, D_{Rd}, of the reduced form of redox couples employed in the formulation of electrolytes for DSSCs. Data were obtained by *ca.* 0.001 M solution in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate on glassy carbon electrode (geometric area= 0.071 cm^2).

Complex	$E_{1/2}$ *vs* Fc^+|Fc /V [a]	k_{heter} (error) /cm s^{-1} [b]	D_{Rd} /cm^2 s^{-1} [c]
1	0.06	$9.1\cdot10^{-3}$ ($1\cdot10^{-4}$)	$8\cdot10^{-6}$ ($1\cdot10^{-6}$)
3	–0.02	$6.9\cdot10^{-3}$ ($1\cdot10^{-4}$)	$7\cdot10^{-6}$ ($1\cdot10^{-6}$)
5	0.30	$2.0\cdot10^{-2}$ ($2\cdot10^{-3}$)	$1.04\cdot10^{-5}$ ($8\cdot10^{-7}$)
$[Co(dtb\text{-}bpy)_3]^{2+}$	–0.21	$1.10\cdot10^{-3}$ ($2\cdot10^{-5}$)	$3.9\cdot10^{-6}$ [d] ($7\cdot10^{-7}$)

[a] From cyclic voltammograms.

[b] From averaged R_{ct} values from EIS fitting, defined as $k_{heter} = \frac{i_0}{FC_{Rd}} = \frac{RT}{F^2 R_{ct} C_{Rd}}$ where i_0 is the exchange current density, F the Faraday constant, C_{Rd} the concentration of the complex (in mol cm^{-3}), R is the gas constant, T the absolute temperature, and R_{ct} the charge transfer resistance evaluated by fitting EIS spectra with a Randles equivalent circuit.

[c] Obtained as an average between data resulted by $i_{p,a}$ *vs* $\nu^{0.5}$ plots (with ν the potential sweep) and by the analysis of the limiting currents, i_{lim}, of the stationary CV signals obtained from the corresponding non-stationary ones through the semi-integral algorithm [S1].

[d] Obtained by i_{lim} due to the poor correlation between $i_{p,a}$ *vs* $\nu^{0.5}$ attributable to the higher degree of quasi-reversibility of the electron transfer.

Table S2 Some electrochemical parameters of **D1** and **D2** sensitizers in solution.

Dye	$E_{1/2,I\ Ox}$ *vs* Fc^+|Fc /V [a]	$E_{1/2,I\ Rd}$ *vs* Fc^+|Fc /V [a]	$U_{0\text{-}0}$ /eV [b]	$E_{1/2}(D^*/D^+)$ *vs* Fc^+|Fc /V [c]
D1	0.29	–1.83	2.11	–1.82
D2	0.31	–1.87	2.12	–1.81

[a] From cyclic voltammetry, CV, in N,N'-dimethylformamide with tetrabutylammonium perchlorate 0.1M.

[b] 0-0 transition energy was estimated as $U_{0-0} = hc/\lambda_{cross}$ by the wavelength at the cross point, λ_{cross}, between normalized absorption and emission spectrum in THF solution [S2].

[c] Excited state half-wave potential was estimated as $E_{1/2}(D^*/D^+) = -\left(\frac{U_{0-0}}{e} - E_{1/2,IOx}\right)$, with e the unitary charge [S3]. The derived values are in very good agreement with the ground-state $E_{1/2,\ IRd}$ directly estimated by CV, considering the intrinsic uncertainty of 0.1 eV or more [S4].

Table S3 Parameter fitted by dye recovery traces for pseudo-first order regeneration kinetic constants, k'_{reg}, and for dye regeneration efficiency, η_{reg}, for **D1**-sensitized TiO_2 anodes. Apparent recombination constant, k'_{rec}, was estimated to be $2.9 \cdot 10^4$ s^{-1} from a blank solution (ACN + LiOTf 0.1M).

Electron donor	k_{reg} /s^{-1}	η_{reg} %
0.17 M **1**	$1.63 \cdot 10^5$	85
0.17 M **3**	$2.88 \cdot 10^5$	91
0.17 M **5**	$2.99 \cdot 10^5$	91
0.17 M $[Co(dtb\text{-}bpy)_3]^{2+}$	$1.71 \cdot 10^5$	85
0.17 M I^- (0.024 M LiI + 0.146 M PMIMI)	$7.25 \cdot 10^4$	71

References

S1 Bard, A. J.; Faulkner, L. R. *Electrochemical methods: Fundamental and Applications*, 2nd ed., Wiley, New York, 2001.

S2 William W. Parson, Modern Optical Spectroscopy. 2nd Edition, Springer, 2015

S3 Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord Chem Rev.* **1988**, *84*, 85.

S4 Jones W.E. Jr; Fox, M.A. *J. Phys. Chem*. **1994**, *98*, 5095.