

Supplementary Information

Enhanced Interfacial Electron Transfer Kinetics Between Co^{2+/3+} Complexes and Organic Dyes with Free Space Near Their Backbone

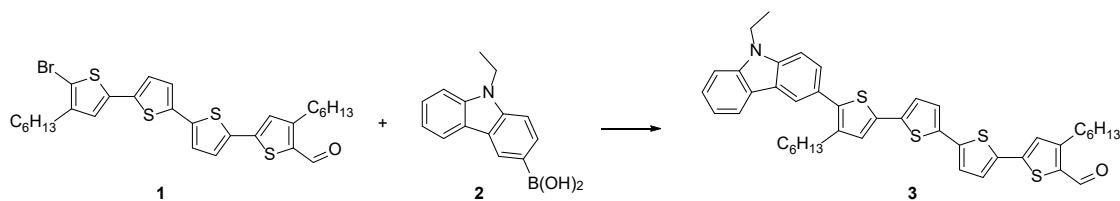
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Synthesis of PX47.

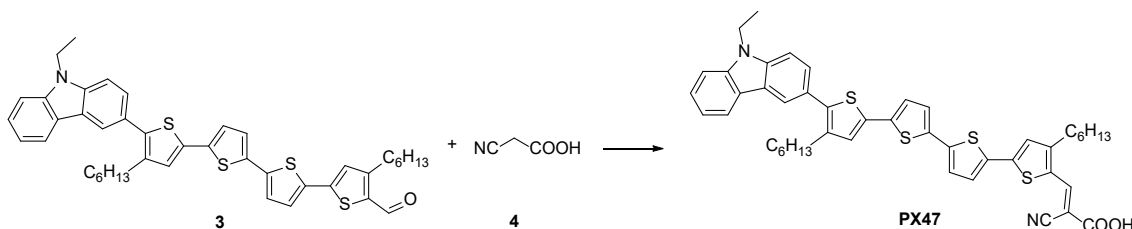
5'''-bromo-4,4'''-dihexyl-[2,2':5',2'':5'':2'''-quaterthiophene]-5-carbaldehyde **1** was synthesized according to previous report.¹ Other chemicals were obtained commercially and used as received.



5'''-(9-Ethylcarbazol-3-yl)-4,4'''-dihexyl-[2,2':5',2'':5'':2'''-quaterthiophene]-5-carbaldehyde **3**:

5'''-bromo-4,4'''-dihexyl-[2,2':5',2'':5'':2'''-quaterthiophene]-5-carbaldehyde **1** (125 mg, 2.1 μmol) and 9-ethylcarbazol-3-yl boronic acid **2** (3.2 μmol , 1.5 eq.) were dissolved in dimethoxyethane (15 mL), aqueous solution of potassium carbonate (1M, 5 mL) was added followed by $\text{Pd}(\text{PPh}_3)_4$ (10 mg, 0.1 μmol). The resulting mixture was stirred at 90°C for 16 h then cooled down. The mixture was extracted with dichloromethane. The organic layer was separated, dried over MgSO_4 and evaporated to dryness under vacuum. The remaining was purified on silica using hexane : dichloromethane (2:8) as an eluent.

Yield: 87%; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ_{H} : 9.99 (s, 1 H), 8.13 (dd, 1 H, $J = 0.9$ and 1.7 Hz), 8.11 (ddd, 1 H, $J = 0.9$, 1.7 and 7.7 Hz), 7.55 (dd, 1 H, $J = 1.7$ and 8.5 Hz), 7.50 (ddd, 1 H, $J = 0.9$, 1.7 and 8.0 Hz), 7.47 – 7.42 (m, 2 H), 7.28 – 7.23 (m, 2 H), 7.15 – 7.09 (m, 4 H), 7.06 (s, 1 H), 4.41 (q, 2 H, $J = 7.2$ Hz), 2.93 (t, 2 H, $J = 7.5$ Hz), 2.70 (t, 2 H, $J = 7.5$ Hz), 1.76 – 1.63 (m, 4 H), 1.48 (t, 3 H, $J = 7.2$ Hz), 1.43 – 1.22 (m, 12 H), 0.90 (t, 3 H, $J = 7.0$ Hz), 0.85 (t, 3 H, $J = 7.0$ Hz); HRMS: Found: $[\text{M}+\text{H}]^+$ 720.2469, molecular formula $\text{C}_{43}\text{H}_{46}\text{NOS}_4$ requires $[\text{M}+\text{H}]^+$ 720.2457.



2-Cyano-3-{5'''-(9-Ethylcarbazol-3-yl)-4,4'''-dihexyl-[2,2':5',2'':5'':2'''-quaterthiophen-5-yl]}acrylic acid **PX47**:

The aldehyde **3** (115 mg, 1.6 μmol) and cyanoacetic acid **4** (135 mg, 1.6 mmol) were dissolved in THF (3 mL), acetic acid (3 mL) was added followed by ammonium acetate (117 mg, 3 mmol). The resulting mixture was stirred at 70°C for 24 h. Afterwards, the mixture was cooled to r.t., water (50 mL) was added and the mixture was vigorously stirred for 15 min. The resulting dark powder was filtered off, washed several times with water then vacuum dried.

Yield: 99%; $^1\text{H NMR}$ (DMSO-d_6 , 400 MHz) δ_{H} : 8.22 (s, 1 H), 8.17 (d, 1 H, $J = 1.5$ Hz), 8.15 (d, 1 H, $J = 7.8$ Hz), 7.64 (d, 1 H, $J = 8.5$ Hz), 7.58 (d, 1 H, $J = 8.5$ Hz), 7.53 (d, 1 H, $J = 4.0$ Hz), 7.48 (s, 1 H), 7.47 (dd, 1 H, $J = 1.9$ and 8.5 Hz), 7.43 (dd, 1 H, $J = 1.2$ and 7.8 Hz), 7.37 (d, 1 H, $J = 3.8$ Hz), 7.35 (d, 1 H, $J = 3.8$ Hz), 7.28 (s, 1 H), 7.26 (d, 1 H, $J = 3.8$ Hz), 7.16 (dd, 1 H, $J = 7.8$ and 8.5 Hz), 4.42 (q, 2 H, $J = 7.2$ Hz), 2.73 (t, 2 H, $J = 7.6$ Hz), 2.62 (t, 2 H, $J = 7.6$ Hz), 1.62 – 1.49 (m, 4 H), 1.28 (t, 3 H, $J = 7.2$ Hz), 1.31 – 1.11 (m, 12 H), 0.80 (t, 3 H, $J = 6.9$ Hz), 0.71 (t, 3 H, $J = 6.9$ Hz); HRMS: Found: $[\text{M}+\text{H}]^+$ 787.2538, molecular formula $\text{C}_{46}\text{H}_{47}\text{N}_2\text{O}_2\text{S}_4$ requires $[\text{M}+\text{H}]^+$ 787.2515.

Surface adsorption density of the dyes (dye loading, mol cm⁻² μm⁻¹). Dye loading was determined using UV-vis spectroscopy (experimental details are described in Experimental section in the main manuscript). The number of dye molecules on the TiO₂ was obtained using pre-calculated molar extinction coefficient values. The number of dye molecules was divided by the area (0.64 cm²) and the thickness (μm) of the TiO₂ electrodes (see Table S1).

Arrangement of the dye molecules on the TiO₂ was estimated as follows;

Effective surface area (nm²) of TiO₂. Effective surface area of TiO₂ (A) for dye adsorption was calculated via eq S1,

$$A = s \times d \times \varphi \times V \quad \text{eq S1}$$

where *s* is the specific surface area of the TiO₂ nano particles (18NR-T) reported in the literature, 65 m² g⁻¹,² *d* is the density of the TiO₂, *φ* is the porosity of the TiO₂ (0.58 as per Safdari et al.²), *V* is the volume of the TiO₂ film (0.64 cm² × thickness determined by surface profilometer, Dektak 150). Calculated effective surface area values are shown in Table S1.

Calculating average distances between the dye molecules on the TiO₂. Average distances between the dye molecules were calculated using measured adsorption densities shown in Table S1 and estimated dimensions of MK2 and PX47 using Chem3D.

Table S1. Effective surface area, estimated in-plane backbone-to-backbone distance, estimated distance between dye planes, calculated number of dyes on the TiO₂ in full dye coverage based on calculated size and distance, measured adsorption density, measured number of dyes on TiO₂, and surface coverage compared to the calculated full adsorption density.

Dye	Effective surface area / nm ²	In-plane backbone - backbone distance / nm	Distance between planes / nm	Calculated number of dyes on TiO ₂ / mol	Measured adsorption density / mol cm ⁻² μm ⁻¹	Measured number of dyes on TiO ₂ / mol	Surface coverage / %
MK2	3.27 × 10 ¹⁶	1.75	0.55	3.65 × 10 ⁻⁸	1.81 × 10 ⁻⁸	3.55 × 10 ⁻⁸	97%
PX47	3.37 × 10 ¹⁶	1.75 × 0.65	0.55	5.81 × 10 ⁻⁸	2.69 × 10 ⁻⁸	5.68 × 10 ⁻⁸	98%
PX47 low	3.27 × 10 ¹⁶	-	-	7.73 × 10 ⁻⁹	4.03 × 10 ⁻⁹	-	15%

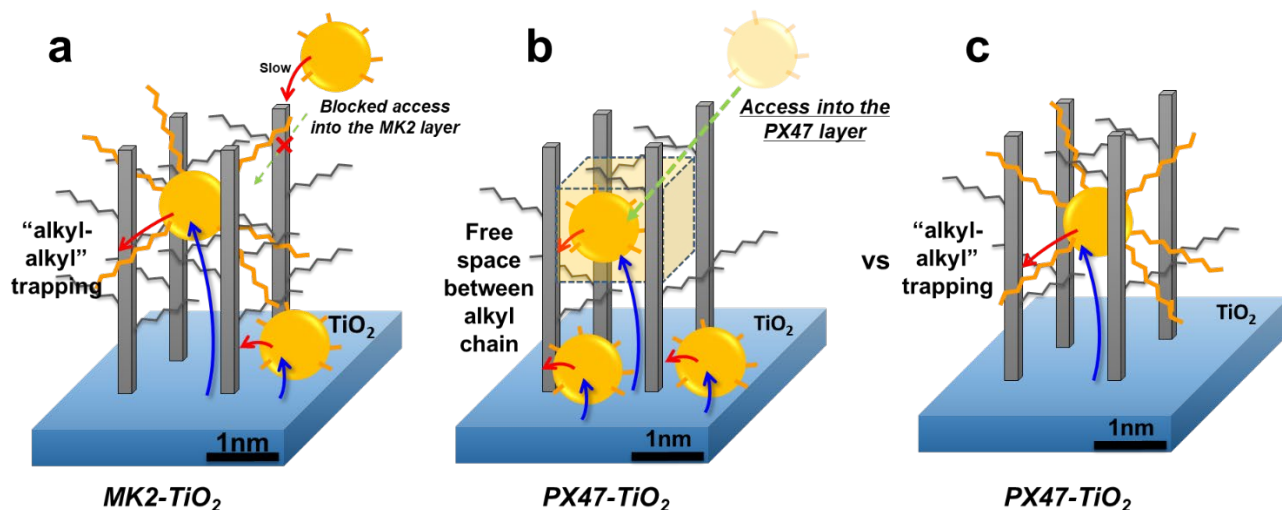


Figure S1. Proposed arrangement of Co(c1-bpy)₃ and Co(c9-bpy)₃ for regeneration and recombination reactions in combination with MK2 dye (a) adapted from ref 17. Proposed arrangement of Co(c1-bpy)₃ (b) and Co(c9-bpy)₃ (c) for regeneration and recombination reactions in combination with PX47 dye.

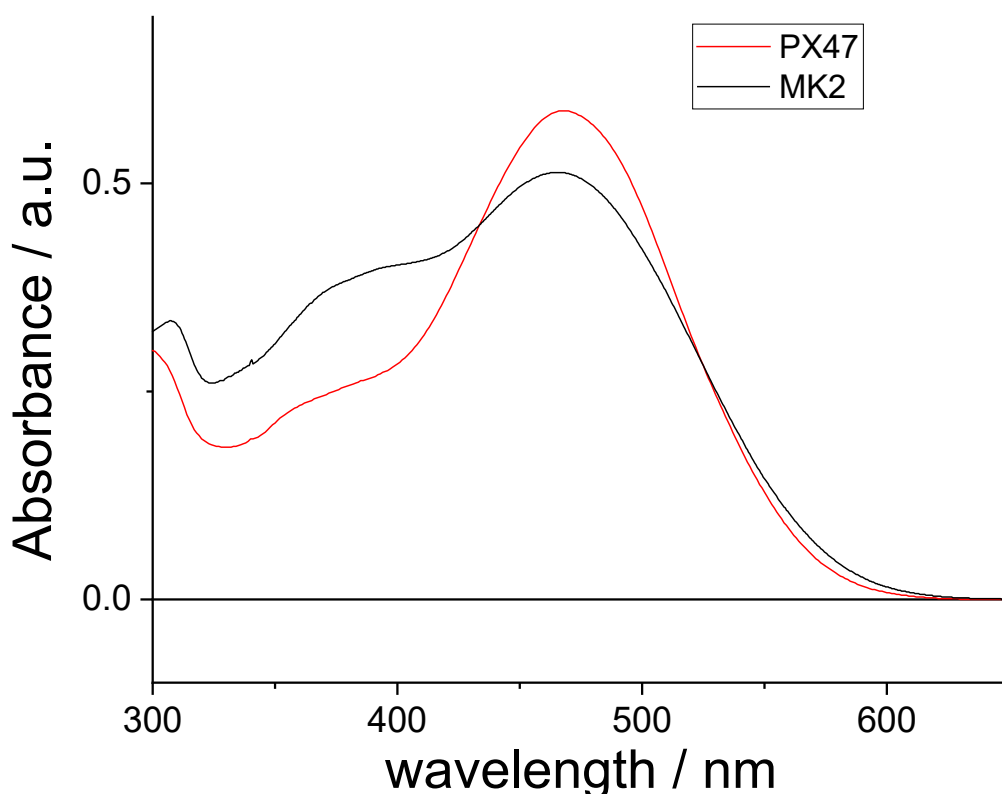


Figure S2. UV-vis absorption of MK2 and PX47 dissolved in acetonitrile : tert-butyl alcohol : toluene = 1:1:1 volume ratio, 0.015 mM dye concentration.

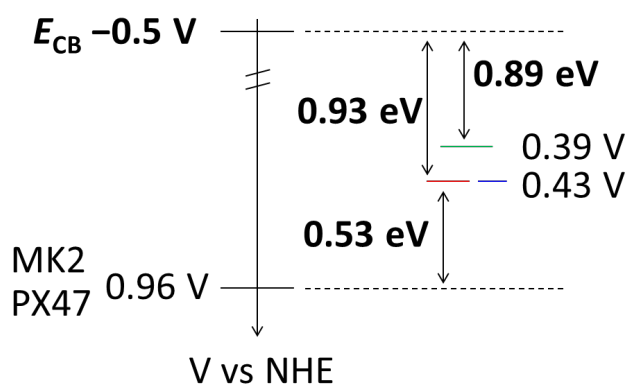


Figure S3. Energy diagram of the redox species employed in this work. $\text{Co}(\text{c1-bpy})_3$ (red), $\text{Co}(\text{dtb-bpy})_3$ (green), and $\text{Co}(\text{c9-bpy})_3$ (blue).

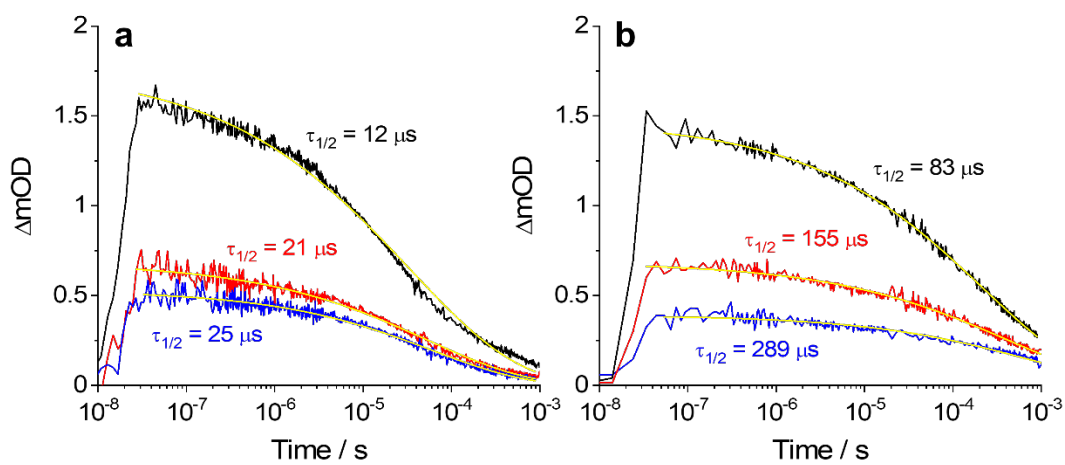


Figure S4. Transient absorption (TA) decays of (a) PX47 adsorbed TiO_2 (PX47- TiO_2) and (b) MK2 adsorbed TiO_2 (MK2- TiO_2) immersed in acetonitrile containing 0.2 M LiClO_4 at three pump (532 nm) intensities of 10 , 5 , 3 $\mu\text{J cm}^{-2}$.

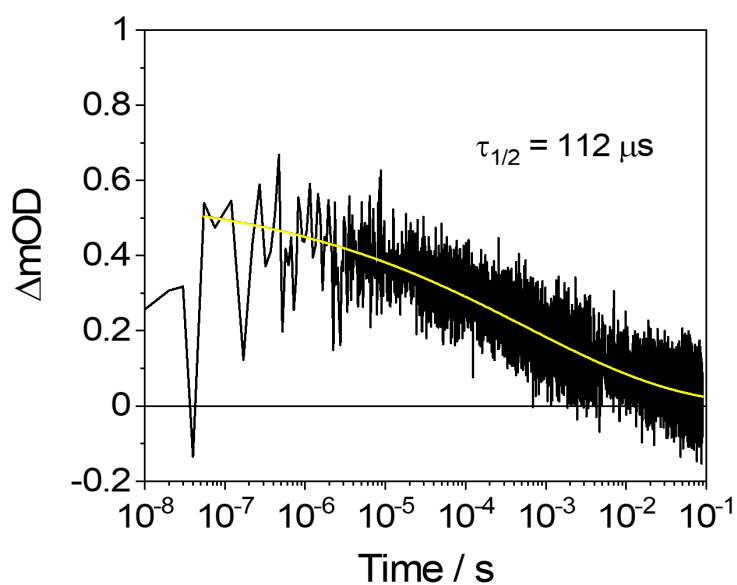


Figure S5. TA decay of PX47-TiO₂ immersed in acetonitrile containing 0.2 M LiClO₄. The PX47 was attached to the TiO₂ in the diluted PX47 solution (0.03 mM in toluene/acetonitrile/tert-butanol=1/1/1 vol.) for 1 h.

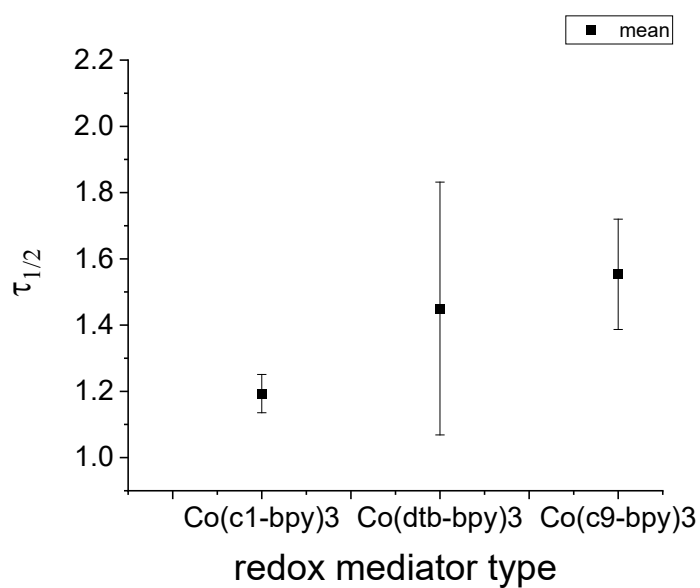


Figure S6. Mean and standard deviation of $\tau_{1/2}$ of TA decay for PX47-TiO₂ immersed in acetonitrile containing 0.2 M LiClO₄ and 0.2 M / 0.02 M of Co(c1-bpy)₃, Co(dtb-bpy)₃, and Co(c9-bpy)₃. The PX47 was attached to the TiO₂ in the diluted PX47 solution (0.03 mM in toluene/acetonitrile/tert-butanol=1/1/1 vol.) for 1 h.

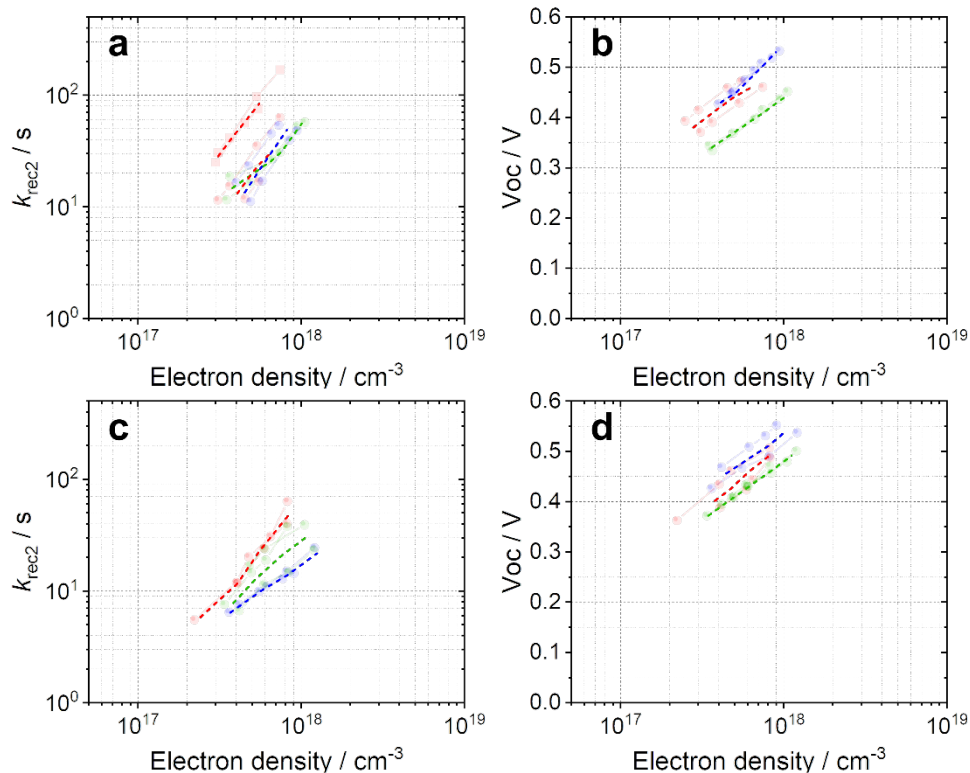


Figure S7. Trend lines among identically prepared samples (determined by eyes) in Figure 7. (a) $k_{\text{rec}2}$ and (b) V_{oc} versus electron density for PX47-TiO₂ samples and (c) $k_{\text{rec}2}$ and (d) V_{oc} versus electron density for MK2-TiO₂ samples. The samples were containing 0.2 M LiClO₄ in AN as electrolytes in the presence of 0.2 M/0.02 M [Co(c1-bpy)₃]^{2+/3+} (red), [Co(dtb-bpy)₃]^{2+/3+} (green), and [Co(c9-bpy)₃]^{2+/3+} (blue).

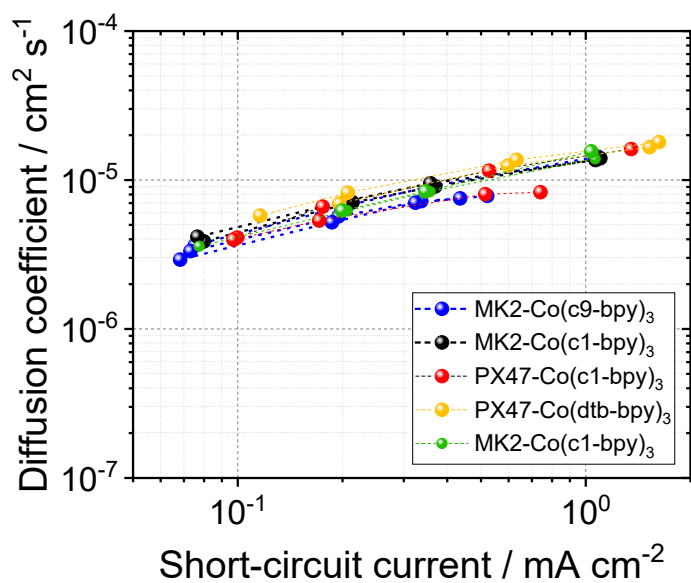


Figure S8. Diffusion coefficient of injected electrons in MK2-TiO₂ and PX47-TiO₂ immersed in acetonitrile (AN) containing 0.2 M/0.02 M Co^{2+/3+} complexes and 0.2 M LiClO₄.

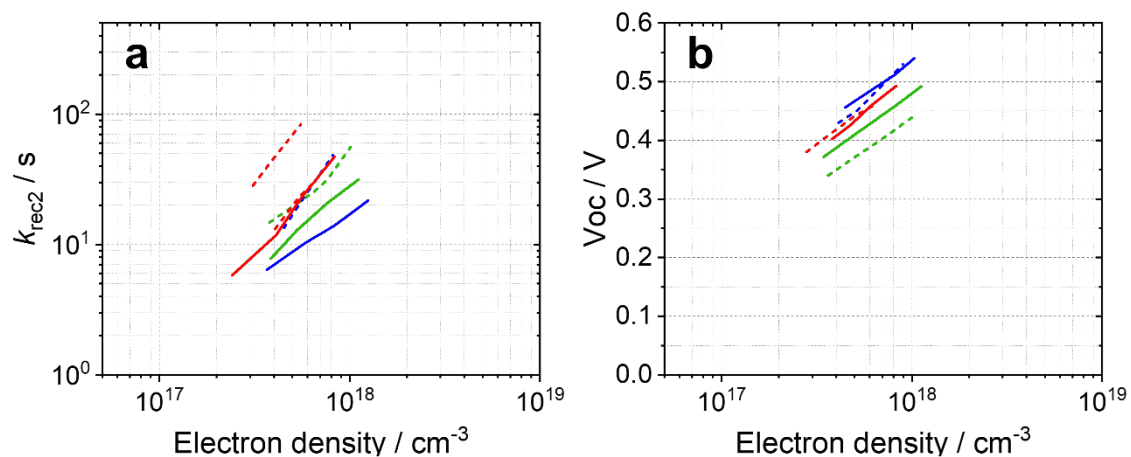


Figure S9. The trend lines in Figure S7 were merged into the same plot. (a) $k_{\text{rec}2}$ and (b) V_{oc} versus electron density for PX47-TiO₂ samples (dashed lines) and MK2 (solid lines) The samples were containing 0.2 M LiClO₄ in AN as electrolytes in the presence of 0.2 M/0.02 M [Co(c1-bpy)₃]^{2+/3+} (red), [Co(dtb-bpy)₃]^{2+/3+} (green), and [Co(c9-bpy)₃]^{2+/3+} (blue).

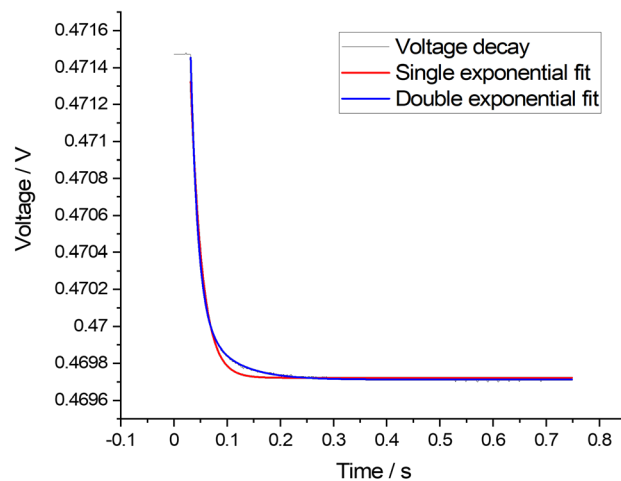


Figure S10. Photo-voltage versus time of PX47-TiO₂ immersed in AN containing 0.2 M LiClO₄ in the presence of 0.2 M/0.02 M [Co(c1-bpy)₃]^{2+/3+}.

Stretched-exponential fitting to obtain $\tau_{1/2}$ of the TA decays. TA decays presented in the manuscript was fitted using a stretched-exponential decay function.

$$\Delta OD(t) = \Delta OD_{(t=0)} e^{-\left(\frac{t}{\tau_{ww}}\right)^\beta} \quad (\text{eq. S1})$$

where, $\Delta OD_{(t=0)}$ is the initial signal magnitude, τ_{ww} is the stretched-exponential lifetime, and β is the stretch parameter. Some decays showed biphasic-decay was fitted using a double stretched-exponential function (Eq S2).

$$\Delta OD(t) = \Delta OD_{(t=0)} e^{-\left(\frac{t}{\tau_{ww}}\right)^\beta} + \Delta OD_{S(t=0)} e^{-\left(\frac{t}{\tau_{ww}^s}\right)^{\beta_s}} \quad (\text{eq. S2})$$

where, $\Delta OD_{S(t=0)}$ is the initial signal magnitude, τ_{ww}^s is the stretched-exponential lifetime, and β_s is the stretch parameter of the second phase. $\tau_{1/2}$ values of the decays then were calculated using eq. S3 which is a solution of eq.1 when $\Delta OD(t) = 0.5\Delta OD_{(t=0)}$. In the case of the bi-phasic decay, parameters of the first stretched-exponential component which is assigned to the regeneration reaction was used. k_{reg} was calculated using eq. S4, where $\tau_{1/2,inert}$ is the half-decay time in the absence of Co complexes in the electrolyte.

$$\tau_{1/2} = \tau_{ww} (\ln 2)^{\frac{1}{\beta}} \quad (\text{eq. S3})$$

$$k_{reg} = 1/\tau_{1/2} - 1/\tau_{1/2,inert} \quad (\text{eq. S4})$$

References

1. I. Cho, P. Wagner, P. C. Innis and A. J. Mozer, *Physical Chemistry Chemical Physics*, 2021., 23, 13001-13010.
2. M. Safdari, P. W. Lohse, L. Häggman, S. Frykstrand, D. Högberg, M. Rutland, R. A. Asencio, J. Gardner, L. Kloo and A. Hagfeldt, *RSC advances*, 2016, 6, 56580-56588.