

Supplementary Information

The impact of insufficient time resolution on dye regeneration lifetime determined using transient absorption spectroscopy

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Synthesis of the compounds.

Sodium 4-hexyl-2-thienylboronate 1,¹ Co(bpy)₃^{2+/3+},² and GD1³ were synthesized according to previously reported procedures. The other reagents were obtained commercially and were used without further purification.

[Co(terpy)₂]²⁺ Cobalt chloride hexahydrate (0.88 g, 3.7 mmol) was dissolved in hot methanol (10 mL) then 2,2':6',2''-terpyridine was added (1.91 g, 8.2 mmol). The resulting mixture was refluxed for 2 h. LiTFSI (7.76 g, 22.0 mmol) was added to the hot solution and allowed to cool down to r. t. over 1 h. The bright red solid was filtered off, washed with methanol then vacuum dried at 60°C overnight.

Yield: 95 %; Elemental Analysis: found: C 38.01 %, H 2.15 %, N 9.96; requires for C₃₄H₂₂N₈CoF₁₂O₈S₄: C 37.61 %, H 2.04 %, N 10.32 %.

[Co(terpy)₂]³⁺ Cobalt complex (0.76 g, 7 × 10⁻⁴ mol) was dissolved in dry acetonitrile (10 mL) then NOBF₄ (0.11 g, 9 × 10⁻⁴ mol) was added. The resulting mixture was stirred at room temperature for 1 h. Afterwards LiTFSI was added (1.22 g, 4.2 mmol) and the stirring continued for another 30 min. The solvent was removed under reduced pressure at 50°C and the resulting viscous oil was treated with water (50 mL). The solid was filtered off, washed with water then vacuum dried at 60°C overnight.

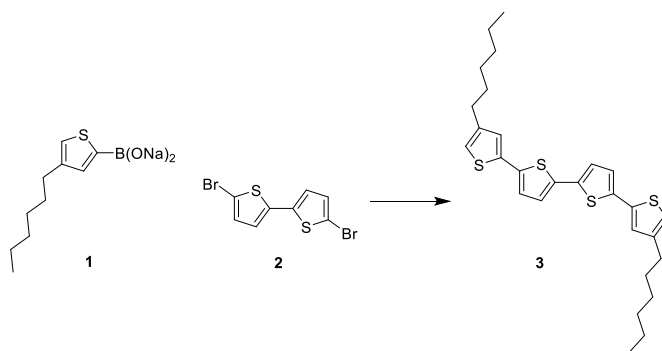
Yield: 97 %; Elemental Analysis: found: C 31.84 %, H 1.42 %, N 9.05; requires for C₃₆H₂₂N₉CoF₁₈O₁₂S₆: C 31.66 %, H 1.62 %, N 9.23 %.

[Co(bpy-dmetho)₃]²⁺ Cobalt chloride hexahydrate (1.74 g, 7.3 mmol) was dissolved in hot methanol (100 mL) then 4,4'-dimethoxy-2,2'-bipyridine was added (5.00 g, 23.1 mmol). The resulting mixture was refluxed for 2 h. LiTFSI (15.75 g, 55.1 mmol) was added to the hot solution and allowed to cool down to 0°C over 1 h. The resulting yellow-orange solid was filtered off, washed with methanol then vacuum dried at 60°C overnight.

Yield: 98 %; Elemental Analysis: found: C 37.44 %, H 3.00 %, N 8.72; requires for C₄₀H₃₆N₈CoF₁₂O₁₄S₄: C 37.89 %, H 2.86 %, N 8.84 %.

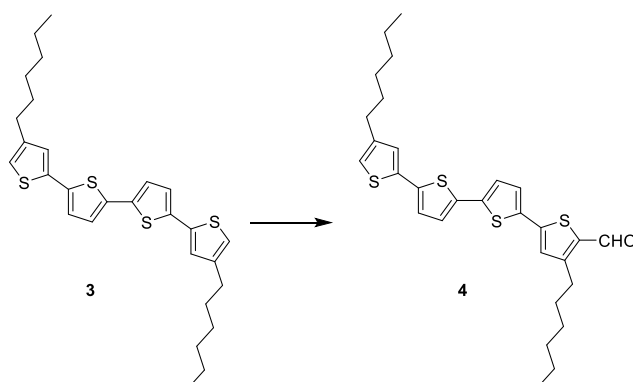
[Co(bpy-dmetho)₃]³⁺ Cobalt complex (1.1 g, 7 × 10 mmol) was dissolved in dry acetonitrile (20 mL) then NOBF₄ (0.20 g, 1.3 mmol) was added. The resulting mixture was stirred at room temperature for 1 h. Afterwards LiTFSI was added (1.82 g, 6.2 mmol) and the stirring continued for another 30 min. The solvent was removed under reduced pressure at 50°C and the resulting viscous oil was treated with water (50 mL). The yellow solid was filtered off, washed with water then vacuum dried at 60°C overnight.

Yield: 95 %; Elemental Analysis: found: C 32.87 %, H 2.41 %, N 8.05; requires for C₄₂H₃₆N₉CoF₁₈O₁₈S₆: C 32.59 %, H 2.32 %, N 8.14 %.



4,4''-Dihexyl-2,2':5',2'':5'':2'''-quaterthiophene 3: Sodium boronate 1 (4.84 g, 19.5 mmol) and 4,4'-dibromo-2,2'-bithiophene 2 were dissolved in dimethoxyethane (60 mL) and brought to reflux. Saturated aqueous sodium bicarbonate solution (30 mL) was added followed by Pd(PPh₃)₄ (0.55 g, 0.5 mmol). The resulting mixture was refluxed overnight under argon. After cooling, the yellow solid was filtered off and washed with water then methanol. The solid was dissolved in dichloromethane and filtered through pad of silica. The solvent was removed under reduced pressure at 50°C. The yellow solid was redissolved in minimal amount of dichloromethane and precipitated by methanol.

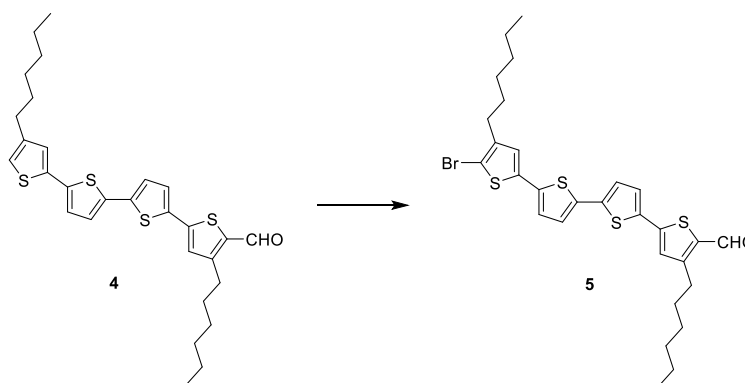
Yield: 73%; ¹H NMR (CDCl₃, 400 MHz) δ_H: 7.05 (d, 2H, J = 3.9 Hz), 7.04 (d, 2H, J = 3.9 Hz), 7.01 (d, 2H, J = 1.3 Hz), 6.81 (d, 2H, J = 1.3 Hz), 2.58 (t, 4H, J = 7.7 Hz), 1.68 – 1.58 (m, 4H), 1.41 – 1.28 (m, 12H), 0.90 (t, 6H, J = 6.7 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ_C: 144.2, 136.7, 136.6, 135.7, 125.1, 124.1, 124.0, 119.2, 31.7, 30.5, 30.4, 29.0, 22.6, 14.1; HRMS: Found: [M+H]⁺ 499.1634, molecular formula C₂₈H₃₅S₄ requires [M+H]⁺ 499.1616.



4,4''-Dihexyl-[2,2':5',2'':5'':2'''-quaterthiophene]-5-carbaldehyde 4: To DMF (0.97 g, 6.3 mmol) cooled to 0°C, POCl₃ (0.56 g, 7.6 mmol) was added dropwise. The mixture was stirred at 0°C for 15 min then solution of 3 (1.21 g, 2.4 mmol) in chloroform (25 mL) was added and the mixture was refluxed for 30 min. After that time,

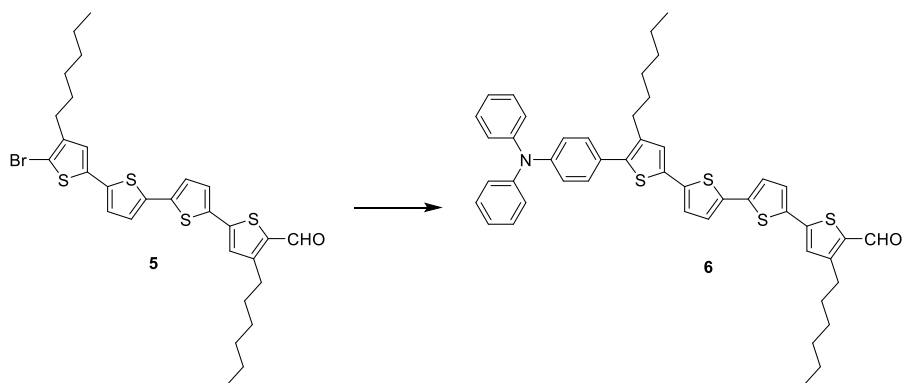
another batch of the Vilsmeier reagent (prepared from the same amount of reagents as the first one) was added and the resulting mixture was refluxed for additional 15 min. The reaction mixture was poured into cold water (200 mL) and diluted with chloroform (100 mL). The organic layer was washed twice with water then saturated water solution of sodium bicarbonate. The organic layer was separated, triethylamine (3 mL) was added and the mixture was dried over magnesium sulfate then evaporated to dryness under reduced pressure at 50°C. The remaining solid was purified on silica using dichloromethane as an eluent.

Yield: 64%; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ_{H} : 9.99 (s, 1H), 7.24 (d, 1H, $J = 3.9$ Hz), 7.11 (d, 1H, 3.8 Hz), 7.07 (d, 1H, $J = 3.8$ Hz), 7.06 (d, 1H, $J = 4.0$ Hz), 7.05 (s, 1H), 7.03 (d, 1H, $J = 1.3$ Hz), 6.83 (d, 1H, $J = 1.3$ Hz), 2.93 (t, 2H, $J = 7.8$ Hz), 2.59 (t, 2H, $J = 7.8$ Hz), 1.72 – 1.58 (m, 12H), 0.92 – 0.88 (m, 6H); HRMS: Found: $[\text{M}+\text{H}]^+$ 527.1579, molecular formula $\text{C}_{29}\text{H}_{35}\text{OS}_4$ requires $[\text{M}+\text{H}]^+$ 527.1565.



5''-Bromo-4,4''-dihexyl-[2,2':5',2'':5'':2''']-quaterthiophene-5-carbaldehyde 5: Aldehyde 4 (0.73 g, 1.4 mmol) was dissolved in dichloromethane (25 mL) then NBS (0.27 g, 1.5 mmol) was added in one portion. The resulting mixture was stirred at r. t. overnight then precipitated by methanol (50 mL) to give 5 as orange powder.

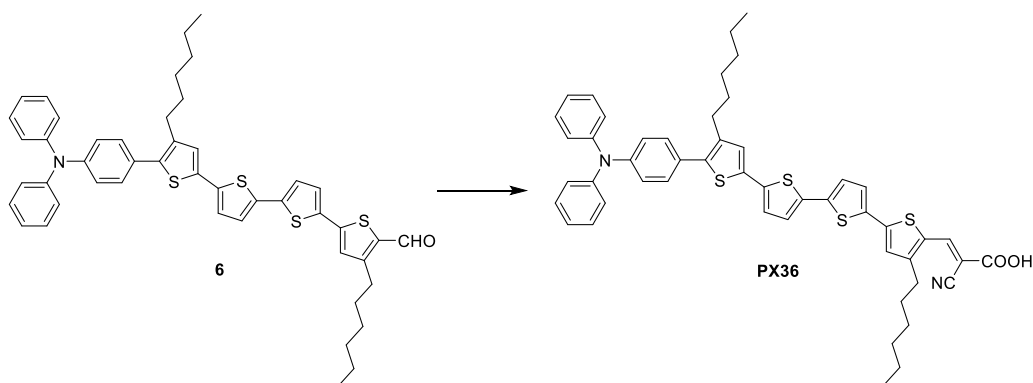
Yield: 92%; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ_{H} : 9.99 (s, 1H), 7.25 (d, 1H, $J = 3.9$ Hz), 7.11 (d, 1H, $J = 3.7$ Hz), 7.10 (d, 1H, $J = 3.7$ Hz), 7.05 (s, 1H), 7.01 (d, 1H, $J = 3.9$ Hz), 6.88 (s, 1H), 2.92 (t, 2H, $J = 7.5$ Hz), 2.55 (t, 2H, $J = 7.5$ Hz), 1.75 – 1.66 (m, 2H), 1.65 – 1.56 (m, 2H), 1.45 – 1.28 (m, 12H), 0.90 (t, 3H, 6.5 Hz), 0.89 (t, 3H, 6.5 Hz); HRMS: Found: $[\text{M}+\text{H}]^+$ 605.0658, molecular formula $\text{C}_{29}\text{H}_{34}\text{BrOS}_4$ requires $[\text{M}+\text{H}]^+$ 605.0670.



5'''-[4-(diphenylamino)phenyl]-4,4'''-dihexyl-[2,2':5',2'':5'':2'''-quaterthiophene]-5-carbaldehyde 6: Aldehyde

5 (0.16 g, 3×10^{-4} mol) and 4-(diphenylamino)phenylboronic acid (0.12 g, 4.5×10^{-4} mol) were dissolved in dimethoxyethane (15 mL) and brought to reflux. The aqueous solution of potassium carbonate (1M, 5 mL) was added followed by $\text{Pd}(\text{PPh}_3)_4$ (13 mg, 1.2×10^{-5} mol). The resulting mixture was stirred at 90°C overnight. After cooling, the mixture was diluted with chloroform; the organic layer was separated, dried over magnesium sulfate and evaporated to dryness under reduced pressure at 50°C . The resulting red viscous oil was purified on short silica column using dichloromethane as an eluent.

Yield: 57%; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ_{H} : 9.99 (s, 1H), 7.32 – 7.24 (m, 6H), 7.18 – 7.01 (m, 14H), 2.93 (t, 2H, $J = 7.1$ Hz), 2.65 (t, 2H, $J = 7.1$ Hz), 1.76 – 1.67 (m, 2H), 1.66 – 1.59 (m, 2H), 1.44 – 1.27 (m, 12H), 0.90 (t, 3H, $J = 6.9$ Hz), 0.88 (t, 3H, $J = 6.9$ Hz); HRMS: Found: $[\text{M}+\text{H}]^+$ 770.2627, molecular formula $\text{C}_{47}\text{H}_{48}\text{NOS}_4$ requires $[\text{M}+\text{H}]^+$ 770.2613.



2-cyano-3-{5'''-[4-(diphenylamino)phenyl]-4,4'''-dihexyl-[2,2':5',2'':5'':2'''-quaterthiophen-5-yl]} acrylic acid

PX36: Aldehyde 6 (132 mg, 1.6×10^{-4} mol) and cyanoacetic acid (135 mg, 1.6 mmol) were dissolved in THF : acetic acid mixture (1 : 1, 6 mL), ammonium acetate (117 mg, 1.6 mmol) was added and the resulting mixture was stirred at 70°C for 24 h. Afterwards, water (50 mL) was added and the mixture was stirred vigorously for 15

min. The resulting red powder was filtered off, washed several times with water then vacuum dried at 60°C overnight.

Yield: 99%; $^1\text{H NMR}$ (DMS- d_6 , 400 MHz) δ_{H} : 8.30 (s, 1H), 7.61 (d, 1H, $J = 3.7$ Hz), 7.55 (s, 1H), 7.43 (d, 1H, $J = 3.9$ Hz), 7.42 (d, 1H, $J = 3.9$ Hz), 7.39 – 7.30 (m, 8H), 7.13 – 7.09 (m, 6H), 7.04 – 7.01 (m, 2H), 2.81 (t, 2H, $J = 7.5$ Hz), 2.64 (t, 2H, $J = 7.5$ Hz), 1.67 – 1.56 (m, 4H), 1.36 – 1.27 (m, 12H), 0.88 (t, 3H, $J = 6.9$ Hz), 0.85 (t, 3H, $J = 6.9$ Hz); HRMS: Found: $[\text{M-H}]^-$ 835.2517, molecular formula $\text{C}_{50}\text{H}_{47}\text{NO}_2\text{S}_4$ requires $[\text{M-H}]^-$ 835.2526.

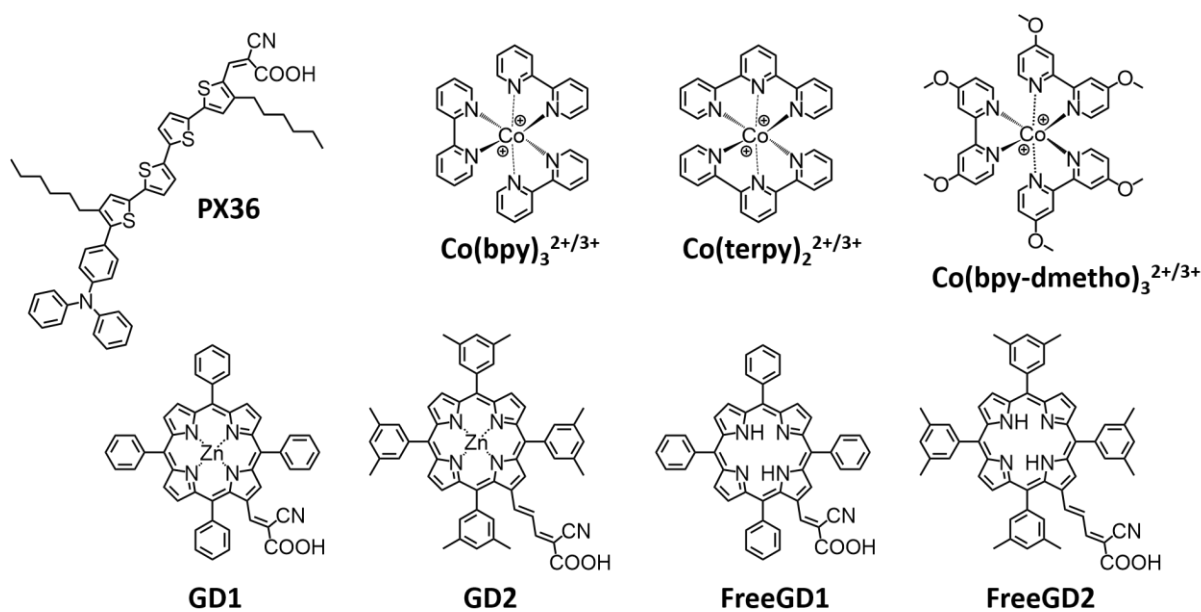


Fig. S1. Chemical structures of the dyes and the redox mediators employed in this work.

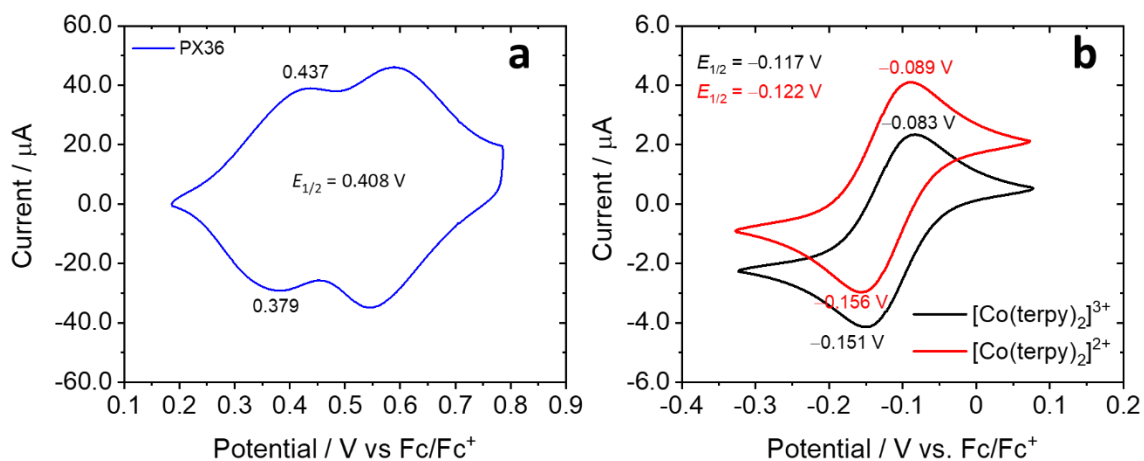


Fig. S2. Current versus potential curves and the half-wave potentials ($E_{1/2}$) of PX36-sensitised TiO₂ (a) and 1 mM [Co(terpy)₂]^{2+/3+} (b) in AN containing 0.1 M tetrabutylammonium perchlorate (TBAP).

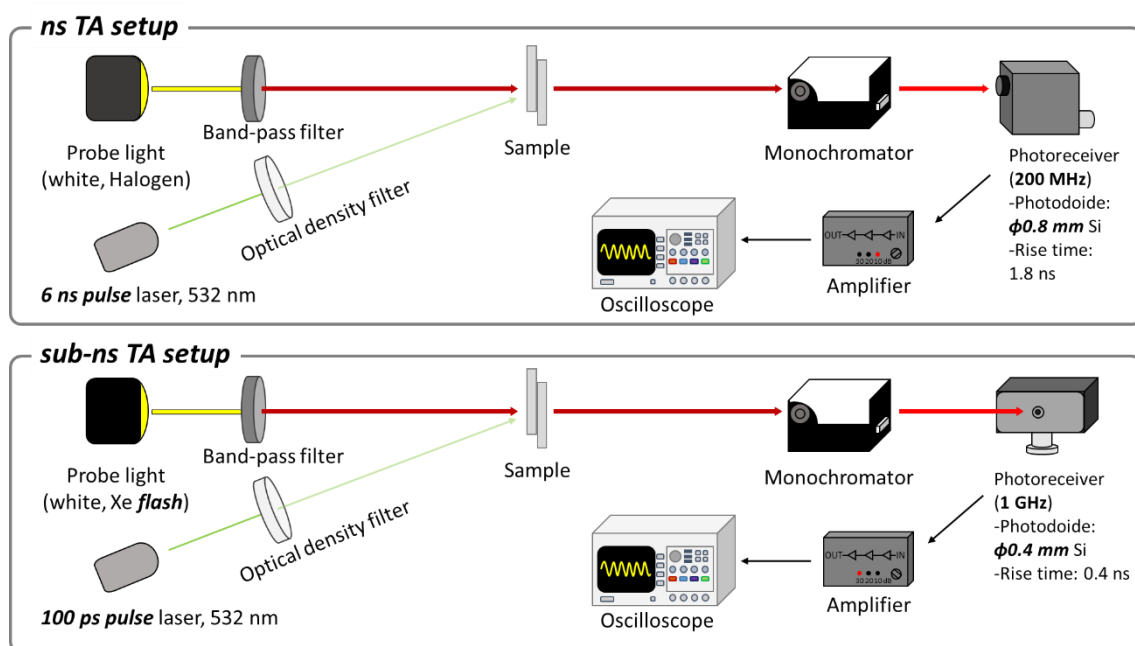


Fig. S3. Schematic illustration of two transient absorption (TA) setups employed in this work.

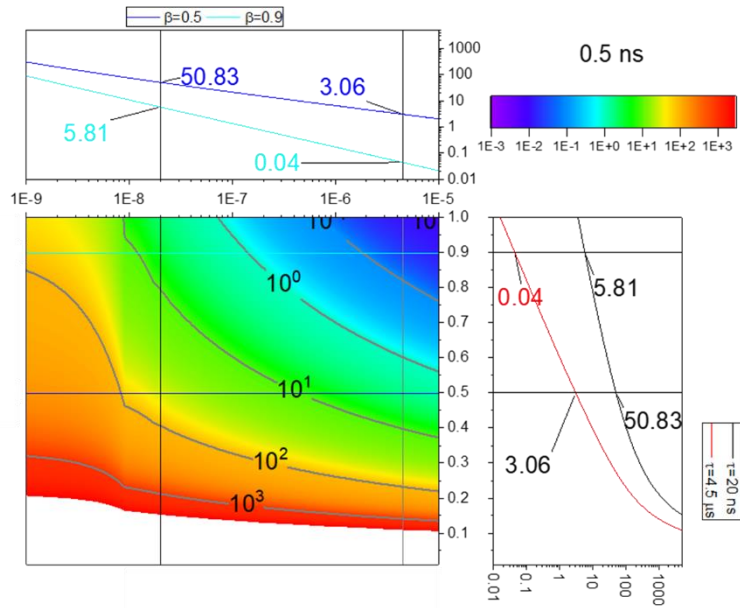


Fig. S4. Contour plot of calculated error as a function of τ_{wv} (x-axis) and β (y-axis) at 0.5 ns time resolution.

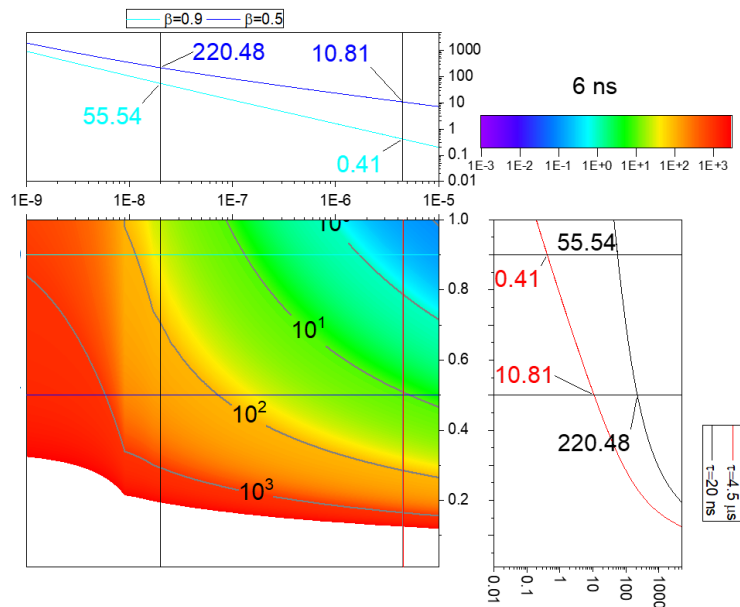


Fig. S5. Contour plot of calculated error as a function of τ_{wv} (x-axis) and β (y-axis) at 6 ns time resolution.

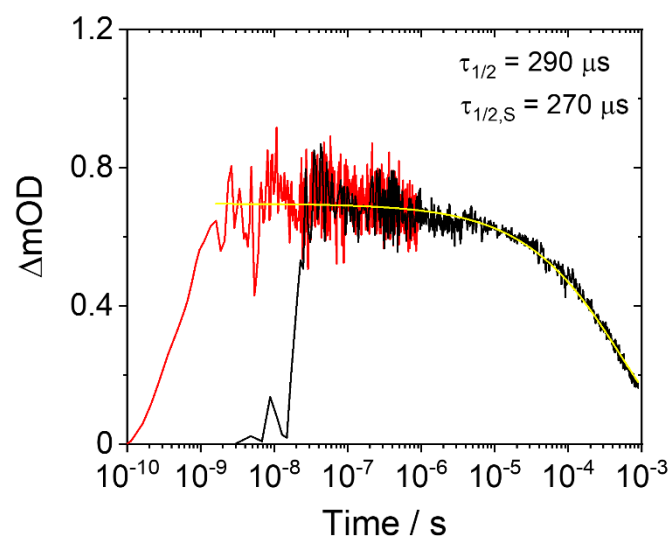


Fig. S6. TA signals of PX36-sensitised TiO₂ in the inert AN containing 0.2 M LiClO₄. Red and black curves were recorded using sub-ns and ns TA setups, respectively, and the yellow line is stretched-exponential fit on the merged curve.

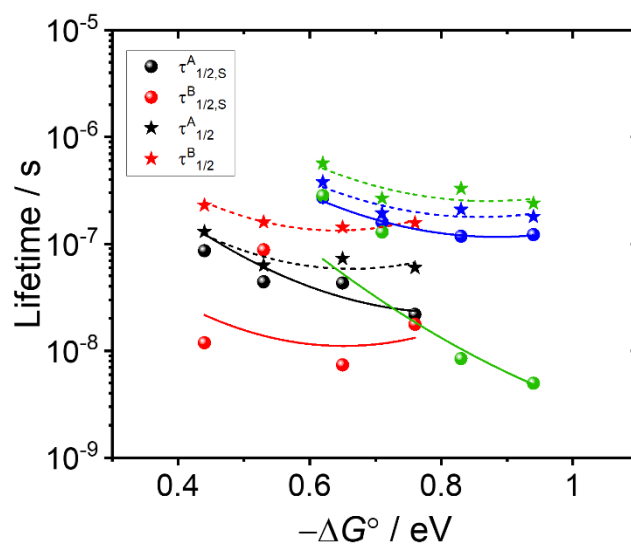


Fig. S7. Unrestricted Marcus fits to the regeneration lifetime using Co(bpy)₃ (red and black) and Co(bpy-dmetho)₃ (blue and green) paired with a series of porphyrin-based dyes as a function of $-\Delta G^\circ$.

Table S1 Electronic coupling (H_{DA}) and reorganisation energy (λ) of the unrestricted Marcus fits shown in Fig. S7.

Regeneration lifetime	λ / eV		H_{DA} / 10^{-5} eV	
	Co(bpy) ₃	Co(bpy-dmetho) ₃	Co(bpy) ₃	Co(bpy-dmetho) ₃
$\tau^A_{1/2,s}$	0.82	0.88	4.88	2.19
$\tau^B_{1/2,s}$	0.59	1.38	5.96	23.66
$\tau^A_{1/2}$	0.66	0.86	2.88	1.76
$\tau^B_{1/2}$	0.64	0.87	1.89	1.49

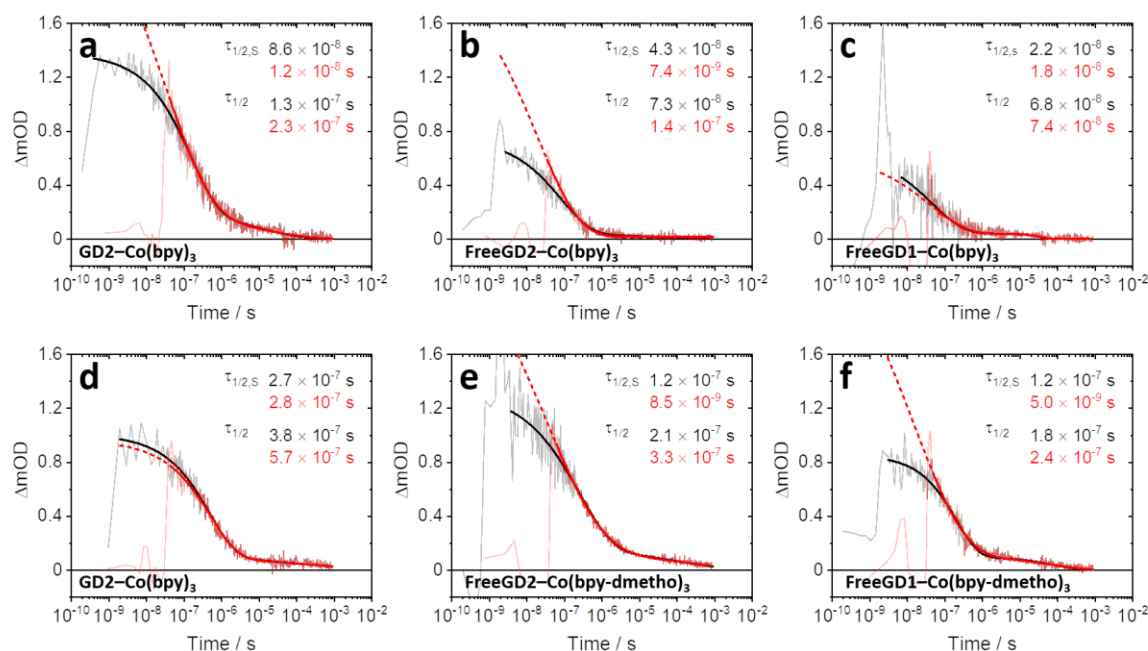


Fig. S8. TA signals measured by sub-ns TA setup (black) and by ns TA setup (red) and stretched-exponential fits to the measured curves.

Discussion of the significantly different fits between TA curves by sub-ns and ns setups, shown in Figs S8a, S8b, S8e, S8f. Photoluminescence signal was subtracted from the ns TA measurement by measuring ΔOD decays with and without probe on ($\Delta OD_{\text{pump+probe}} - OD_{\text{pump}}$). However, the presence of strong photoluminescence signal saturating the detector results in the reduction of the effective bandwidth of the photoreceiver, leading to the exponential-like RC decay of the positive ΔOD signal shown in **Fig. S8**. Stretched-exponential fitting on this erroneous detector signal results in overestimation of the initial signal magnitude and a much shorter apparent dye regeneration lifetime. The sub-ns setup is equipped by a spectrometer with a narrower bandwidth, therefore the photoluminescence signal is filtered out to a level not saturating the detector. Therefore, this artefact is eliminated. This benefit is unique to our setups therefore not included in the discussion in Fig. 4.

Stretched-exponential fitting. Since the decays presented in the manuscript showed biphasic-decay behaviour, therefore two stretched-exponential functions (Eq S1) were used to fit the curves.

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

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. As explained in Experimental section in the main manuscript, fitting parameters of the first phase were used to calculate $\tau_{1/2,S}$.

References

1. J. Pei, J. Ni, X.-H. Zhou, X.-Y. Cao and Y.-H. Lai, *The Journal of organic chemistry*, 2002, **67**, 4924-4936.
2. I. Cho, M. Koshika, P. Wagner, N. Koumura, P. C. Innis, S. Mori and A. J. Mozer, *Journal of the American Chemical Society*, 2018, **140**, 13935-13944.
3. Q. Wang, W. M. Campbell, E. E. Bonfantani, K. W. Jolley, D. L. Officer, P. J. Walsh, K. Gordon, R. Humphry-Baker, M. K. Nazeeruddin and M. Grätzel, *The Journal of Physical Chemistry B*, 2005, **109**, 15397-15409.