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Supporting Information

Interrogating the Ultrafast Dynamics of an Efficient Dye for Sunlight Conversion

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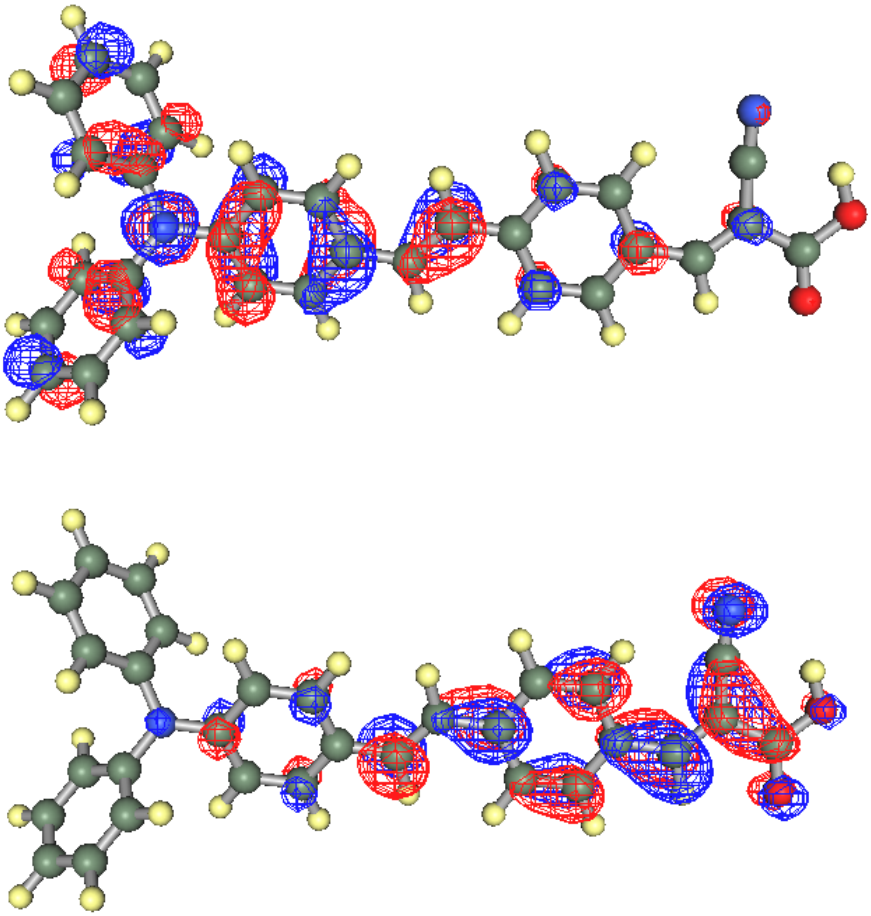
Scheme S1.

Frontier orbitals of the HOMO (upper) and LUMO (lower) calculated for TPC1 dye with DFT at B3LYP 6-31* level optimized in the ground state.



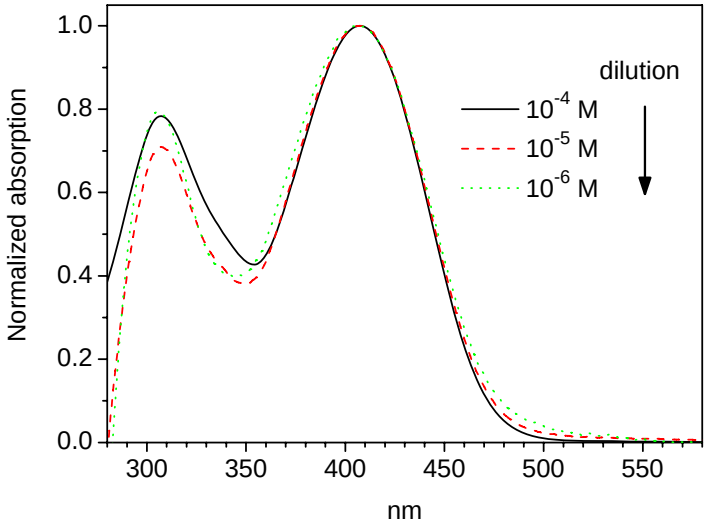


Figure S1.

Effect of changing the concentration of TPC1 in DCM containing 0.01 M of DBU on the normalized Uv-visible absorption spectrum.

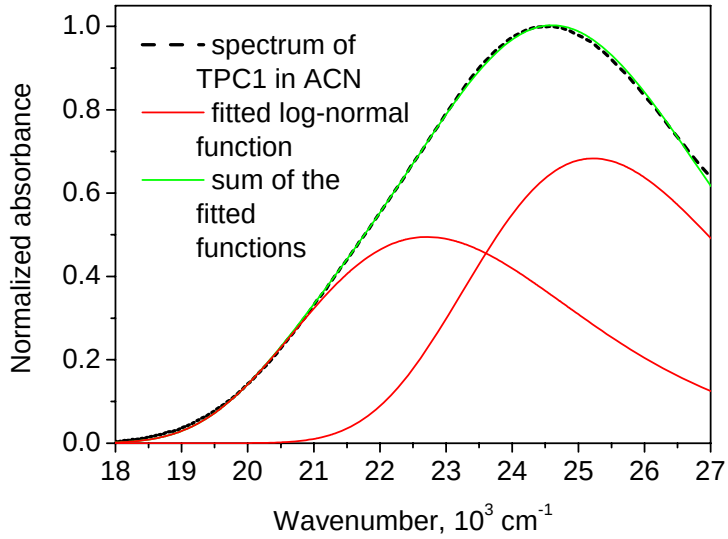


Fig. S2.

Example of the estimation of contribution of the normal form by fitting two log-normal functions to the stationary absorption spectrum of TPC1 in ACN (10^{-5} M). The formula of the used lognormal function is the following $y(\nu)=h\ \exp[-\ln(2)(\ln(1+2\gamma(\nu-\nu_p)/\Delta)/\ \gamma)^2]$, where h is the peak height, ν_p: the peak frequency, Δ: the width parameter, and γ: the asymmetry parameter. The fitted parameters are: h_1=0.68, γ_1=0.27, Δ_1=4.7, ν_{p1} = 25.22 cm^{-1}, h_2=0.49, γ_2=0.30, Δ_2=4.9 and ν_{p2} = 22.71 cm^{-1}.

Table S1.

Correlation of the solar cell efficiency for photovoltaic devices prepared under different bath (from H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt and L. Sun, *J. Phys. Chem. C*, 2008, **112**, 11023) with the contribution of normal form in th Uv-visible absorption spectrum of 10^{-5} M. A linear correlation between these values gives r^2=0.92. The estimation of normal form contribution was based on fitting two lognormal function to the stationary absorption spectrum of TPC1 in a given solvents for λ>370 nm (see an example in Fig. S2). The short wavelength band corresponds to that of the anion structure, and the long wavelength band – to the normal one. The width and asymmetry of the functions were taken from the fits of pure normal and anion form in DCM and DCM with DBU, respectively, while the amplitudes and maxima were left free in the fit. The calculation takes into account the ratio between the extinction coefficients (ε) of the normal and anion forms, which was found to be ε_{normal}=0.67 ε_{anion} in DCM.

Solvent	Contribution of normal form, %	Solar cell efficiency, %
DCM	100	5.33
ACN	52	4.59
EtOH	20	4.29
THF	9	3.61

Table S2.

Decay time constants (τ_i) and their fractional amplitudes (in %, normalized to 100%) at the indicated wavelengths of observation (λ_{em}) obtained from a global fit (χ^2<1.1) of the fluorescence decays of TPC1 in ACN for 10^{-5} M, and upon excitation at: (A) 433 nm and (B) 470 nm.

(A)

λ_{em} / nm	τ_1 = 83 ps	τ_2 = 2.65 ns
600	10	90
700	39	61
800	81	19

(B)

λ_{em} / nm	τ_1 = 69 ps	τ_2 = 2.61 ns
600	26	74
700	84	16
800	97	3

Table S3.

Decay time constants (τ_i) and their fractional amplitudes (in %, normalized to 100%) at the indicated wavelengths of observation (λ_{em}) obtained from a global fit (χ^2<1.1) of the fluorescence decays of TPC1 in DCM upon 433 nm excitation and for: (A) 10^{-4} M, (B) 10^{-5} M and (B) 10^{-6} M.

(A)

λ_{em} / nm	τ_1 = 40 ps	τ_2 = 770 ps	τ_3 = 2.54 ns
600	61	34	5
700	14	83	3
800	4	94	2

(B)

λ_{em} / nm	τ_1 = 40 ps	τ_2 = 780 ps	τ_3 = 2.53 ns
600	59	35	6
700	7	89	4
800	0	98	2

(C)

λ_{em} / nm	τ_1 = 40 ps	τ_2 = 780 ps	τ_3 = 2.77 ns
600	57	32	11
700	6	85	9
800	0	96	4

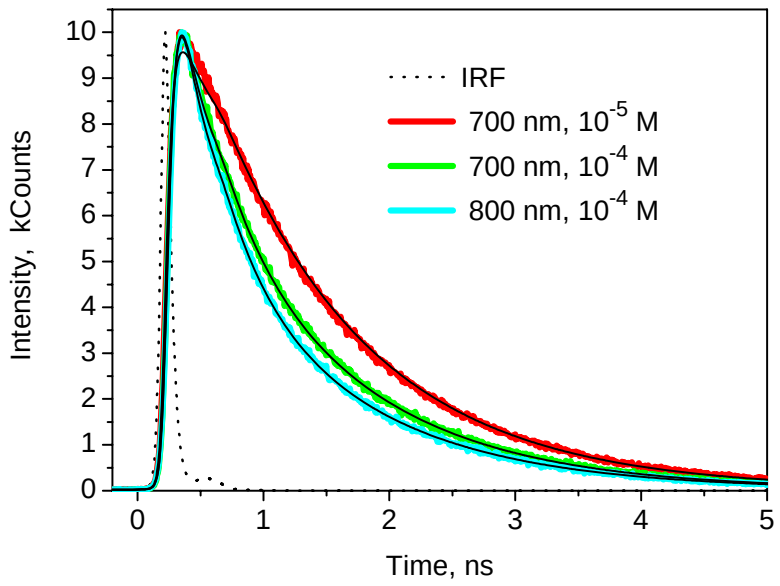


Figure S3.

The illustrative magic-angle fluorescence decays of TPC1 in EtOH under excitation at 433 nm and indicated observation wavelength and concentration of the dye. The solid line shows the multi-exponential function used to fit the experimental data (values in Table 2). The dotted black signal is of the instrument response function (IRF, FWHM=90 ps) measured at the excitation wavelength of a ludox suspension while the solid black lines are from the fit.

the illustrative original nanosecond emission transients

Table S4.

Time constants (τ_i) and their fractional amplitudes (A_i, normalized to 1, a negative value indicates a rise time) obtained from exponential functions fits to the fs-transients (convoluted with an IRF of 220 fs) at the indicated emission wavelengths (λ_{em}) of TPC1 in ACN (c=10^{-5} M). The excitation wavelength was 400 nm.

λ_{em} /nm	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3 / ps
500	0.60	0.05	0.36	0.51	0.04	2600
550	0.15	0.05	0.49	0.73	0.36	2600
600	0.10	0.05	0.21	1.5	0.69	2600
650	0.09	0.05	0.09	3.8	0.82	2600

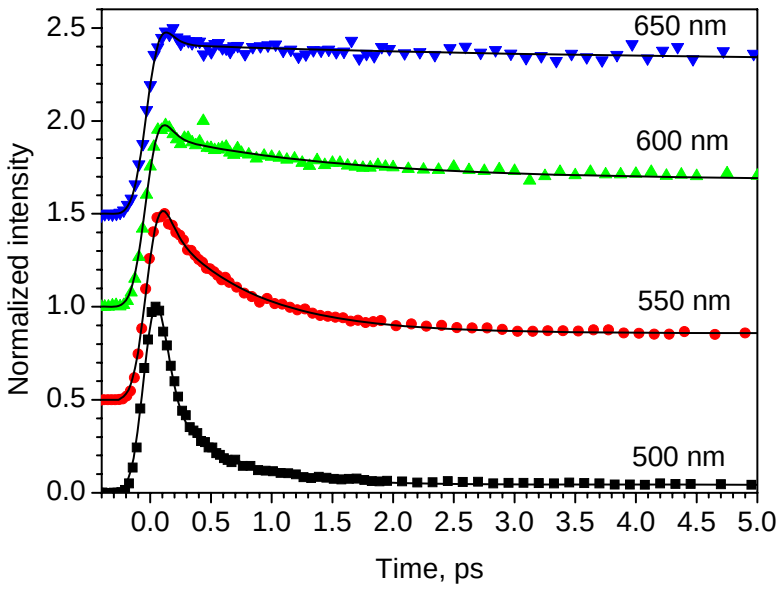


Figure S4.

Femtosecond (fs) emission transients of TPC1 in ACN (c=10^{-5} M) at the indicated wavelengths of observation, and upon excitation at 400 nm (a vertical offset is added for a better presentation). The solid lines are from the best fit (Table S4).

Table S5.

Time constants (τ_i) and their fractional amplitudes (A_i, normalized to 1, a negative value indicates a rise time) obtained from exponential functions fits to the fs-transients (convoluted with an IRF of 220 fs) at the indicated emission wavelengths (λ_{em}) of TPC1 in DCM (c=10^{-4} M) containing 0.01 M of DBU. The excitation wavelength was 400 nm.

λ_{em} /nm	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3 / ps
470	0.77	0.25	0.20	1.2	0.03	500
500	0.75	0.60	0.15	2.9	0.10	960
550	-0.16	0.18	0.45	2.1	0.55	1500
600	-0.43	0.51			1.00	2600
650	-0.44	0.67	-0.27	3.1	1.00	2600

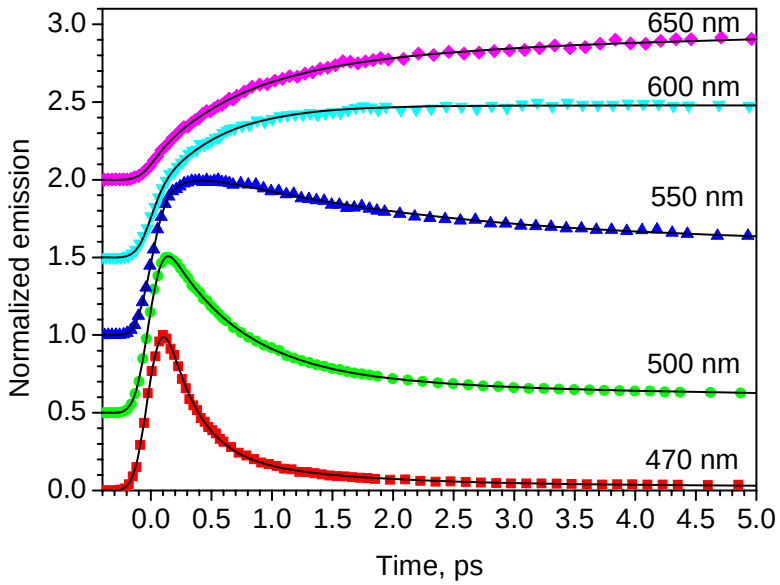


Figure S5.

Femtosecond (fs) emission transients of TPC1 in DCM (c=10^{-4} M) containing DBU at the indicated wavelengths of observation, and upon excitation at 400 nm (a vertical offset is added for a better presentation). The solid lines are from the best fit (Table S5).

Table S6.

Time constants (τ_i) and their fractional amplitudes (A_i, normalized to 1, a negative value indicates a rise time) obtained from exponential functions fits to the fs-transients at the indicated emission wavelengths (λ_{em}) of TPC1 in EtOH (c=10^{-4} M).

λ_{em} /nm	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3 / ps
475	0.50	0.18	0.38	1.52	0.12	10
500	0.35	0.23	0.44	2.31	0.21	16.3
525	0.39	0.98	0.50	9.6	0.11	83
550	0.28	2.22	0.57	16.6	0.15	217
575	0.45	11.3	0.39	49	0.16	1000
600	-0.19	0.63	0.59	23.8	0.41	444
625	-0.31	1.23	0.53	46	0.47	1000
650	-0.43	1.79	0.52	89	0.48	1000
675	-0.21	0.58	-0.40	4.0	1.00	320
700	-0.22	0.88	-0.50	7.5	1.00	340
725	-0.24	0.85	-0.70	15.4	1.00	295

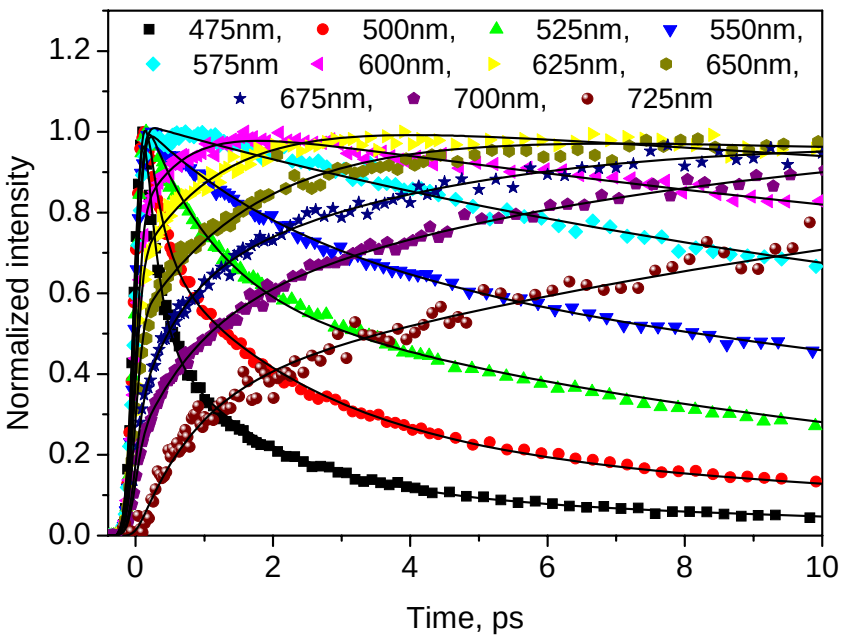


Figure S6.

Femtosecond (fs) emission transients of TPC1 in EtOH (c=10^{-4} M) at the indicated wavelengths of observation, and upon excitation at 400 nm. The solid lines are from the best fit (Table S6).

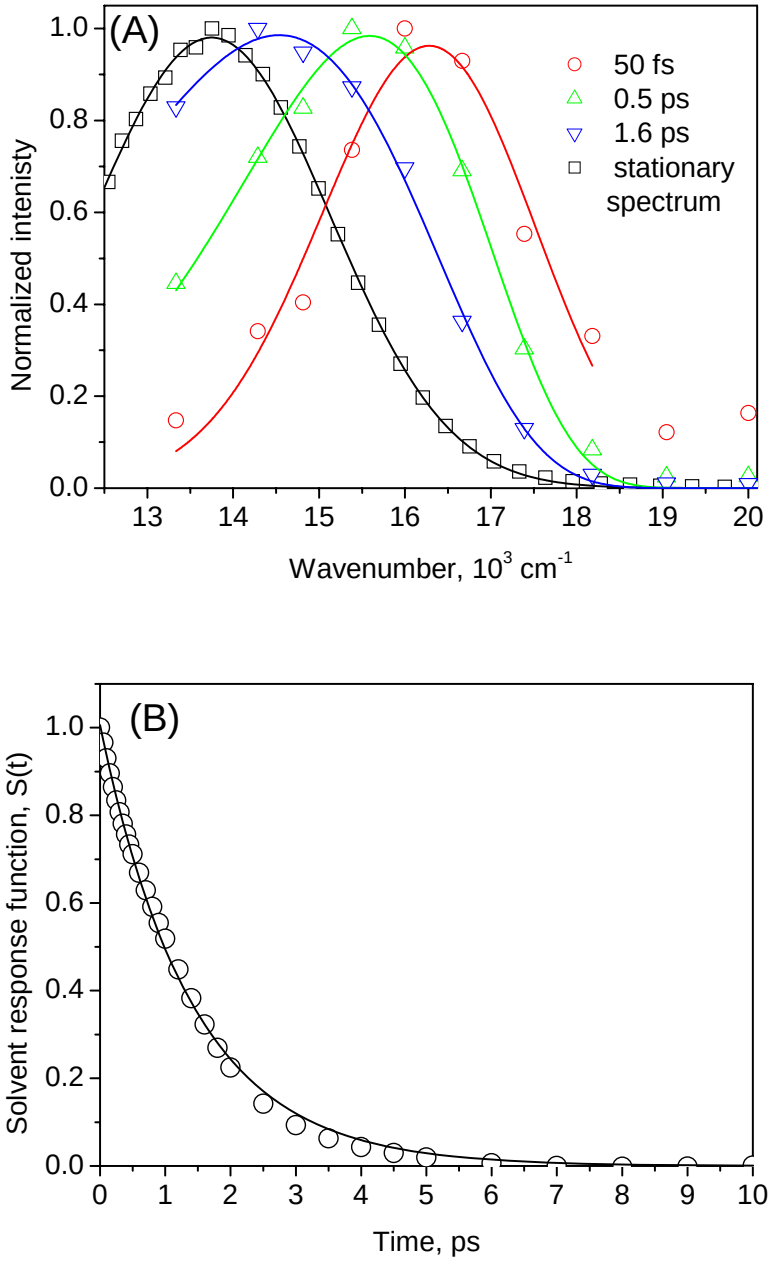


Figure S7.

(A) Normalized time-resolved emission spectra (TRES) of TPC1 in DCM (10^{-4} M) at the selected indicated time delays (points) with the fitted log-normal functions (lines). (B) Solvent response function S(t) measured from the shifts of the maximum of log-normal functions fitted to TRES of TPC1 in DCM (points) and one-exponential fits (lines) giving a solvent response time of 1.4 ps.