SUPPORTING INFORMATION

Photo-induced electron transfer study of an organic dye anchored on the surfaces of TiO_2 nanotubes and nanoparticles

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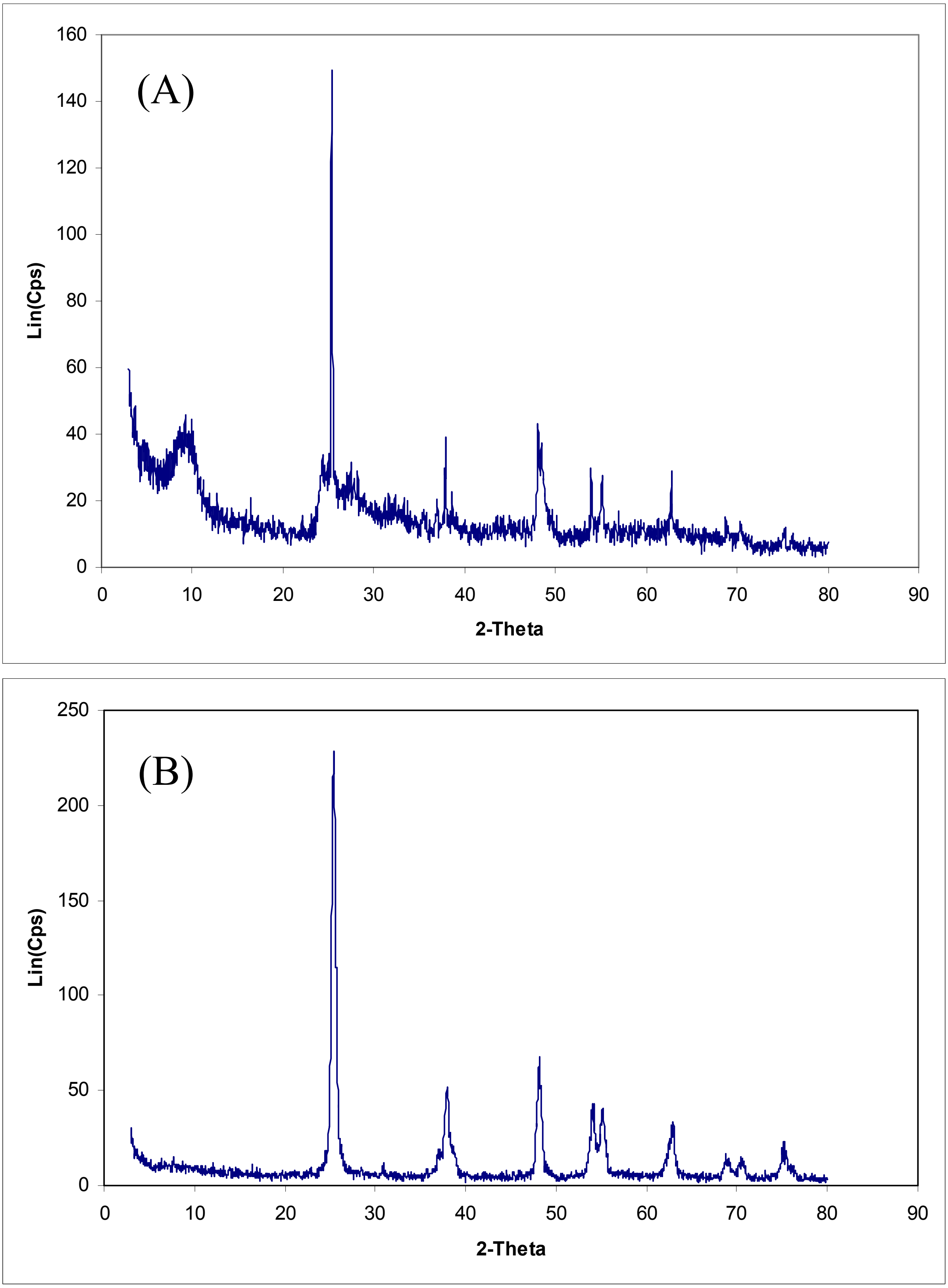


Figure S1. XRD spectrum of titania nanotubes (A) and anatase nanorods (B)

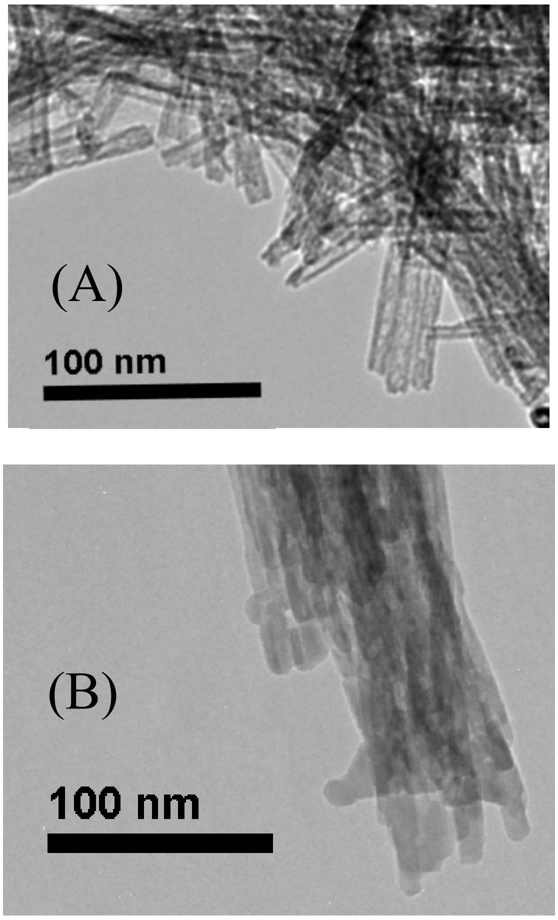


Fig. S2. TEM image of titania nanotubes (A) and anatase nanorods (B)

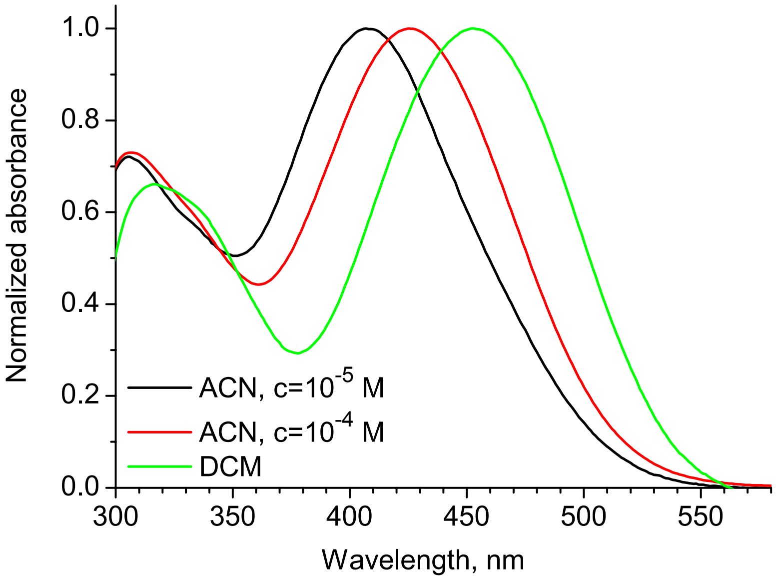


Fig. S3. Uv-visible absorption spectrum of TPC1 normalized to 1 in the maximum of long-wavelength band taken at indicated concentration and in the indicated solvents. The spectrum in DCM is the same for both c=10^{-4} M and c=10^{-5} M.

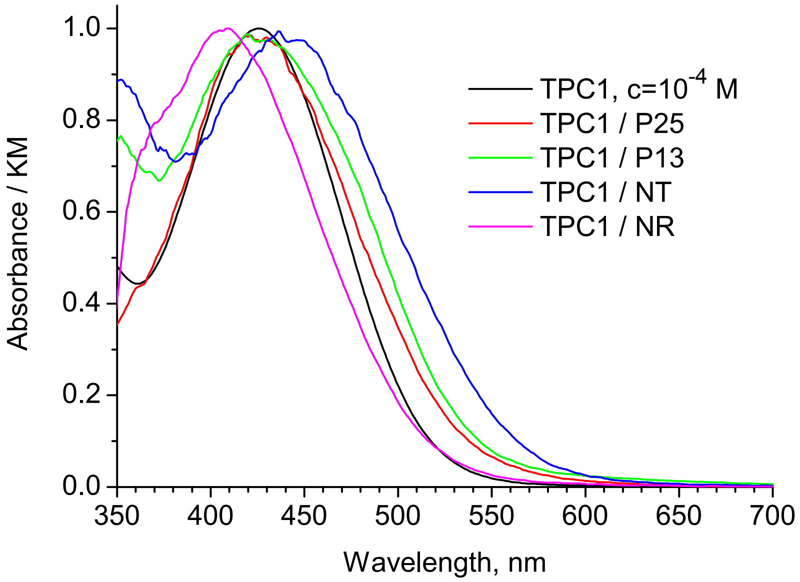


Fig. S4. Uv-visible absorption spectrum of TPC1 in ACN and Uv-visible diffuse absorption spectra of different indicated complexes of TPC1 with titania, all normalized to 1 in the maximum of long-wavelength band. The intensities below 400 nm are strongly influenced by the absorption of titania itself.

Femtosecond time-resolved emission studies of TPC1in ACN at high concentration

To have more fs data on the free dye in solution, we did additional measurements of TPC1 in ACN for a higher concentration (c=10^{-4} M, not reported previously [1]) since this concentration was used for preparing samples with titania. The emission transients, and the results of the multi-exponential fits are given in Figure S5 and Table S1, respectively. Similarly as for lower concentration (c=10^{-5} M), the average lifetime of the ultrafast decay component (<1ps) increases with increasing observation wavelength [1]. We observed an additional 40 ps decay component for gating at 650 and 700 nm, apart from long-decay component (constant in the measured 200 ps window) that was present at lower concentration and assigned to the lifetime of the anion structure (2.6 ns). At higher concentration (c=10^{-4} M) the contribution of TPC1 neutral form should be dominant having the fluorescence band shifted to the red as compared to that of the anion structure. Therefore, the 40 ps time constant should be assigned to the lifetime of the relaxed neutral structure, and this value is more precise than the previously obtained lifetime (80 ps) from TCSPC measurements in long 25-ns time window [1].

Table S1.

Values of time constants (τ_i) and their fractional amplitudes (A_i, normalized to 1) obtained from three-exponential functions used to fit the fs transient emission (convoluted with an IRF of 200 fs) at the indicated emission wavelengths (λ_{em}) of: (A) TPC1 in ACN (c=10^{-4} M) solution. 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	0.84	0.05	0.14	0.54	0.02	700
550	0.73	0.05	0.18	0.70	0.09	700
600	0.53	0.07	0.31	0.53	0.16	700
650	0.71	0.40	0.13	40	0.16	2500
700	0.53	0.66	0.26	40	0.21	2500

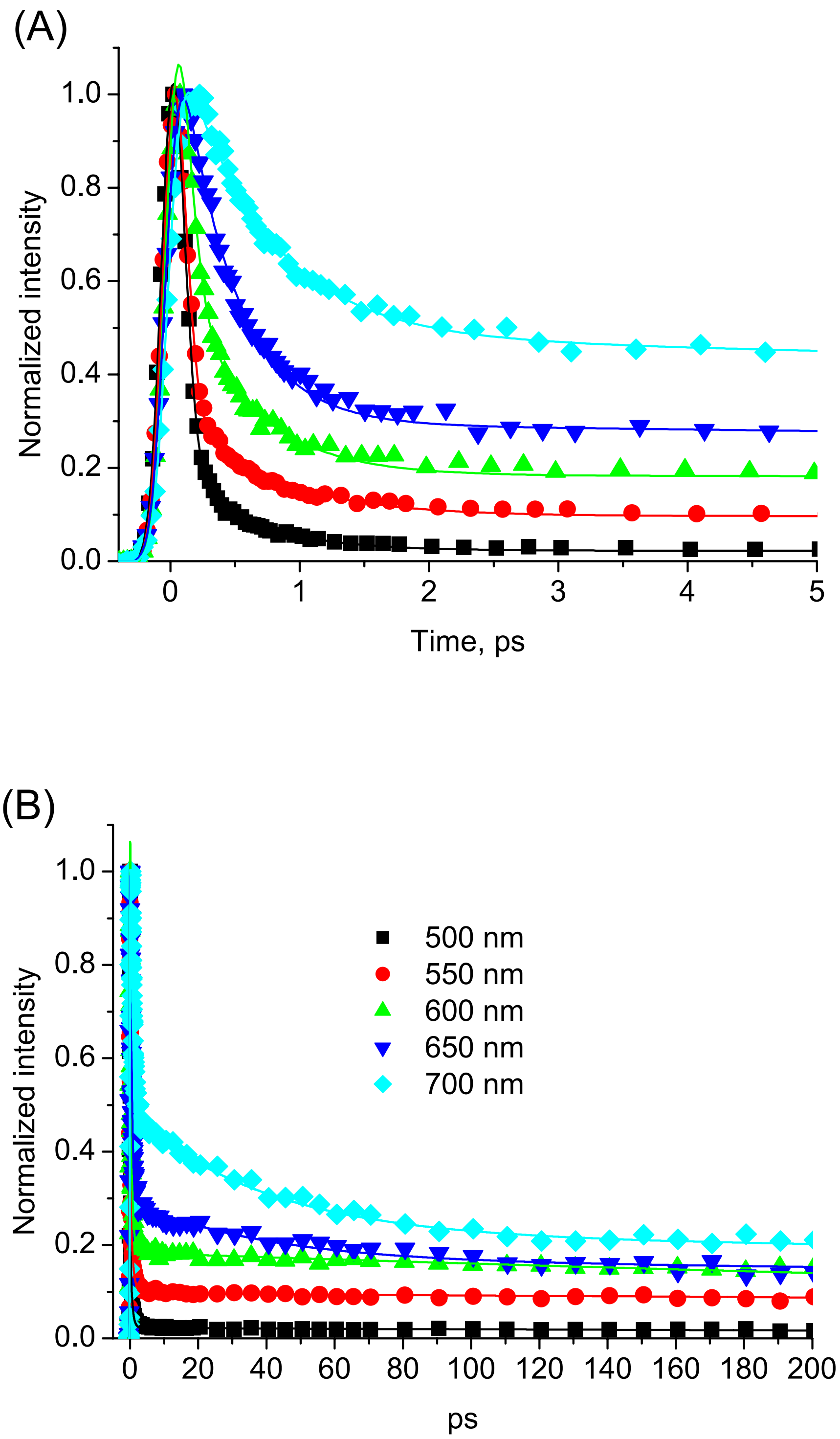


Fig. S5. Femtosecond (fs) emission transients of TPC1 in ACN (c=10^{-4} M) at the indicated wavelengths of observation, and upon excitation at 400 nm in (A) shorter and (B) longer time window. The solid lines are from the best fit. See Table S1 for the obtained data from the fit.

Table S2.

Values of time constants (τ_i) and their fractional amplitudes (A_i, normalized to 1) obtained from three-exponential functions used to fit the fs transient emission (convoluted with an IRF of 200 fs) at the indicated emission wavelengths (λ_{em}) of TPC1/P25 in DCM solution. The excitation wavelength was 400 nm. We observed a small contribution (<6%) of long component (1 ns), which is probably due to a small fraction of molecules not attached to titania, and it should not significantly influence the observed kinetics.

λ_{em} /nm	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3 / ps
475	0.89	0.05	0.11	0.94		
550	0.73	0.05	0.26	0.34	0.01	1000
650	0.52	0.15	0.44	0.97	0.05	1000
700	0.75	0.47	0.19	3.3	0.06	1000

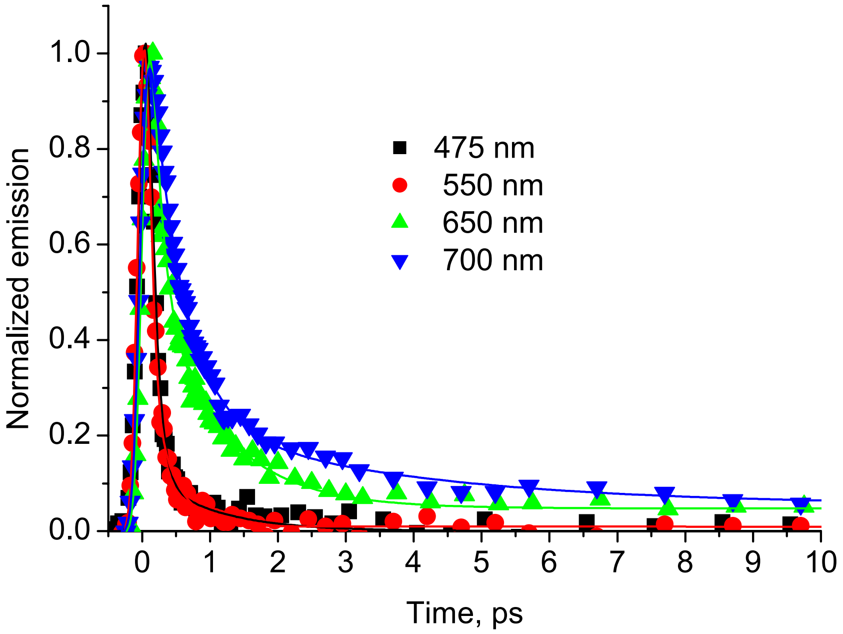


Fig. S6. Fs emission transients of TPC1 / P25 in DCM solution at the indicated wavelengths of observation, and upon excitation at 400 nm. The solid lines are from the best fit. See Table S2 for the obtained data from the fit.

Table S3.

Values of time constants (τ_i) and their fractional amplitudes (A_i, normalized to 1) obtained from three-exponential functions used to fit the fs transient emission (convoluted with an IRF of 200 fs) at the indicated emission wavelengths (λ_{em}) of TPC1/NT in DCM solution. The excitation wavelength was 400 nm. We observed a small contribution (<6%) of long component (1 ns), which is probably due to a small fraction of molecules not attached to titania, and it should not significantly influence the observed kinetics.

λ_{em} /nm	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3 / ps
475	0.68	0.05	0.27	0.60	0.05	1000
650	0.67	0.15	0.26	0.69	0.06	1000
700	0.80	0.21	0.18	1.2	0.02	1000

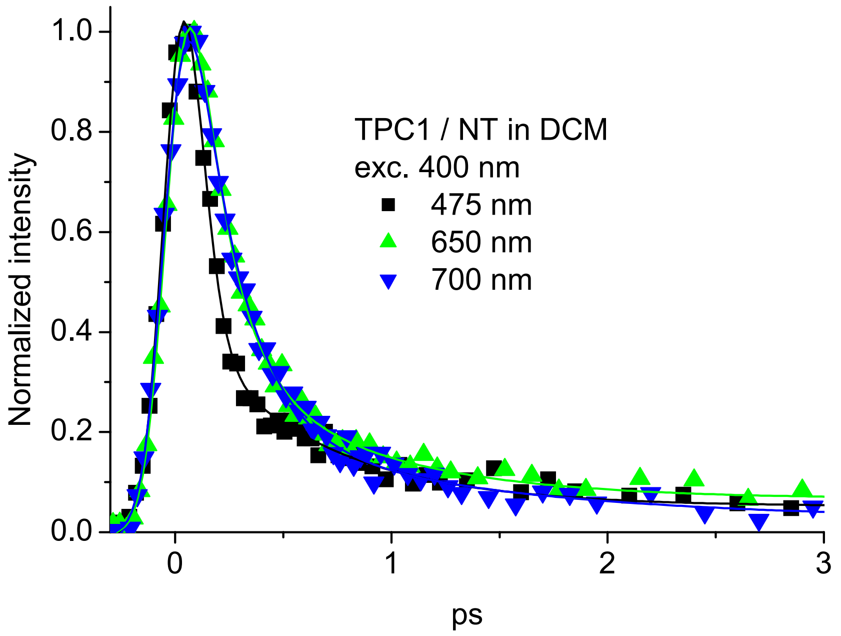


Fig. S7. Fs emission transients of TPC1 / NT in DCM at the indicated wavelengths of observation, and upon excitation at 400 nm. The solid lines are from the best fit. See Table S3 for the obtained data from the fit.

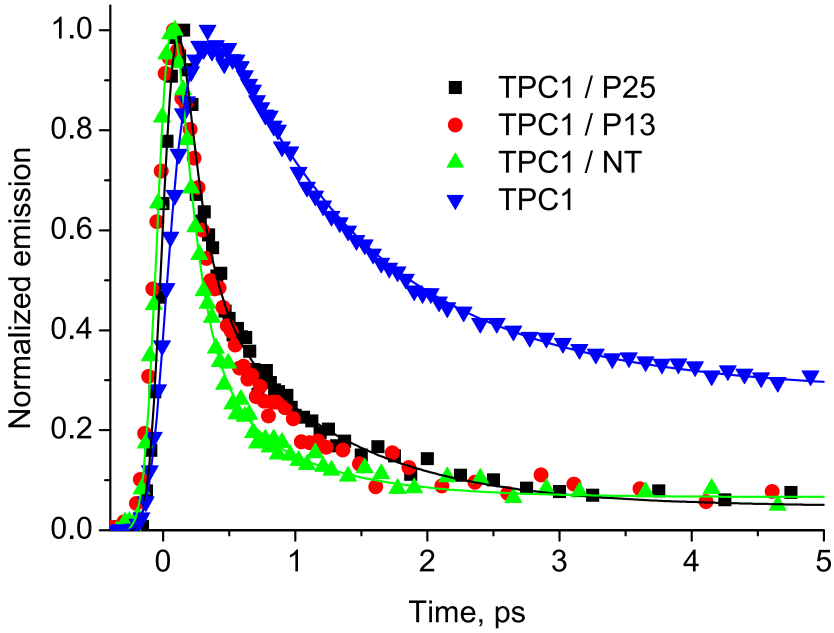
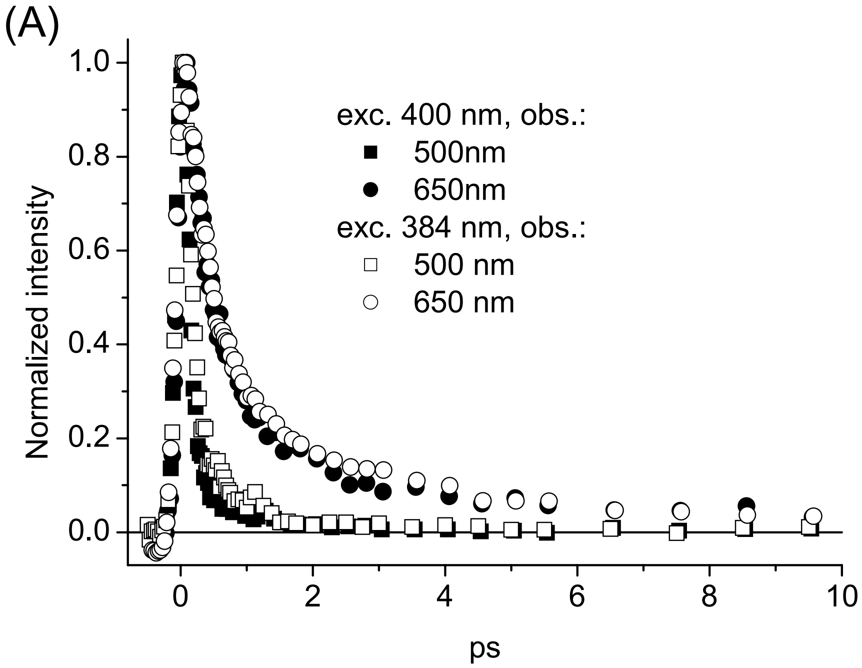


Fig. S8. Comparison of the fs emission transients of TPC1 in DCM solvent and interacting with the P13, P25 and NT of titania upon excitation at 400 nm and observation at 650 nm. The solid lines are from the best fit. See Tables S2 and S3 for the obtained data from the fit.



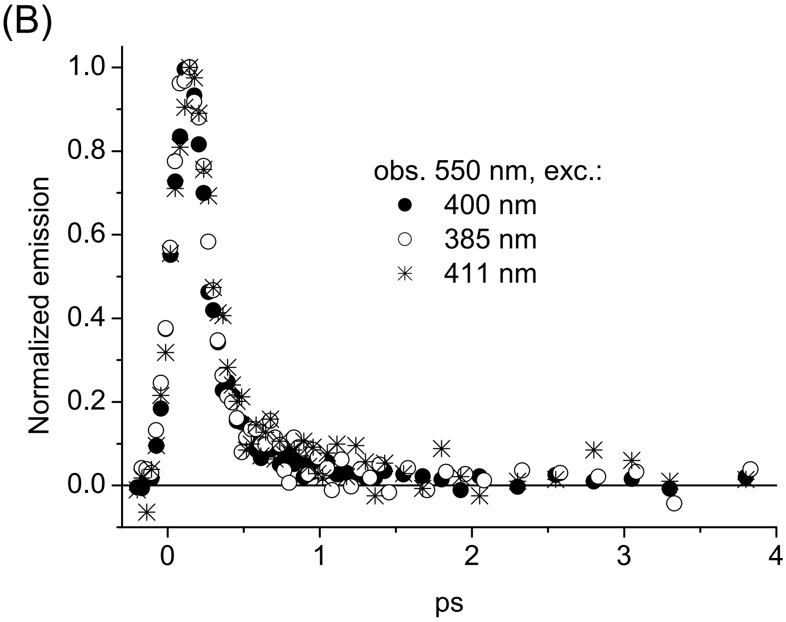


Fig. S9. Comparison of fs emission transients of TPC1 / P25 in (A) ACN and (B) DCM solutions upon different indicated excitation and observation wavelength. For the transients observed at 650 nm and excited at 385 nm in Fig. B a negative vertical offset was added to account for the small contribution of the long-living free dye present in solution.

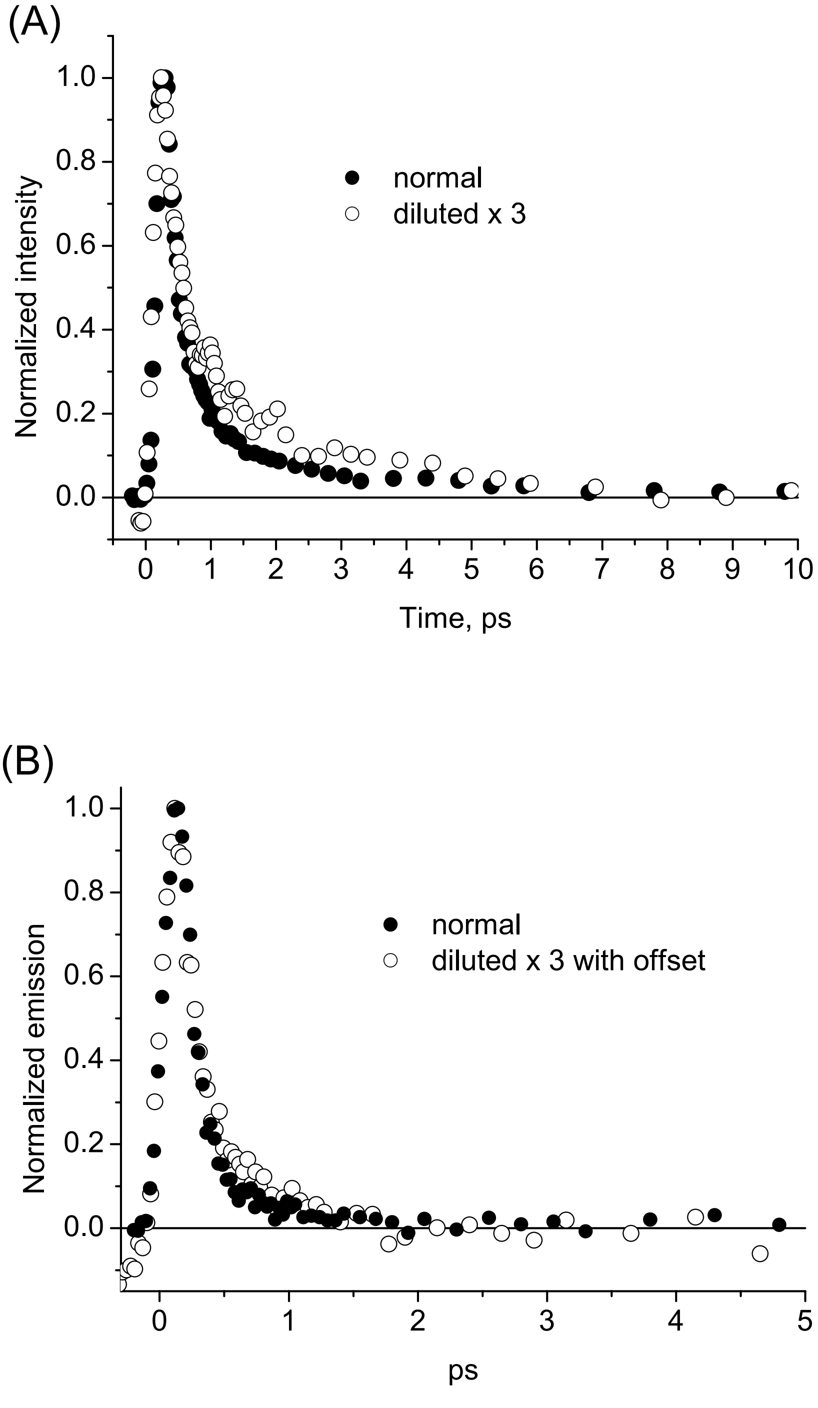


Figure S10. Comparison of femtosecond emission transients of TPC1 / P25 complexes prepared from the initial solutions of different concentration of the dye in: (A) ACN solution at observation wavelength 600 nm, and (B) DCM solution at observation wavelength 550 nm, both upon excitation at 400 nm. For the transients of diluted samples a negative vertical offset was added to account for the small contribution of the long-living free dye present in solution.

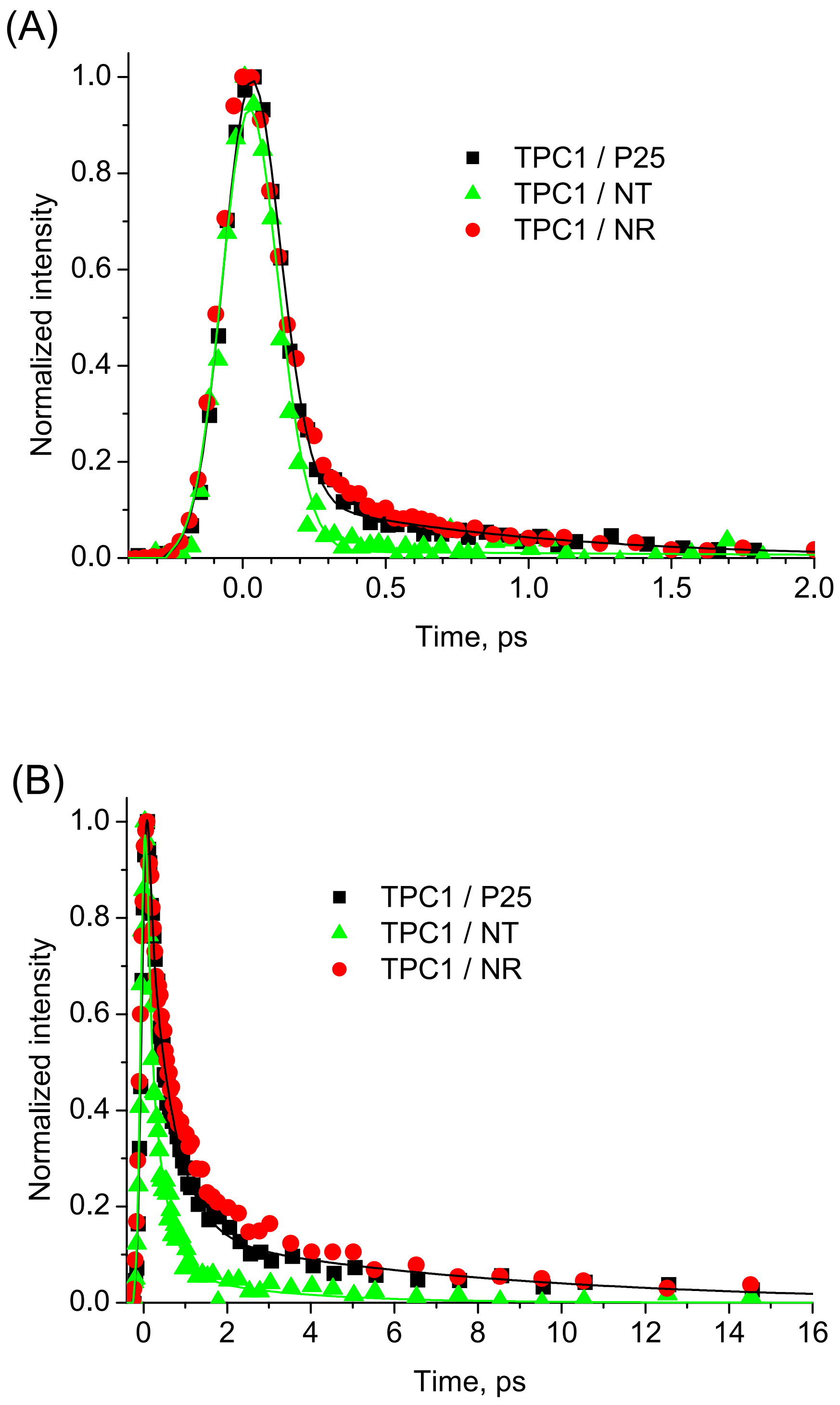


Fig. S11. Comparison of the femtosecond emission transients of TPC1 and interacting with the P25, NT and NR in ACN solvent, upon excitation at 400 nm, and observation at: (A) 500 and (B) 650 nm. The solid lines are from the best fit. See Table 1 and Table S1 for the obtained data from the fit.

Global analysis of femtosecond transient absorption studies of free TPC1 in ACN

Singular Value Decomposition (SVD) analysis for TPC1 in ACN solution predicts the existence of 4 transient species in the overall transient absorption changes. This is because the first 4 values in Table S4 (3.212, 0.418, 0.223, 0.103) differ significantly from the rest (0.047, 0.029, 0.023, etc), which can be regarded as a noise in the analysis. A global multi-exponential fit gives the time constants of these four components as <100 fs, 400 fs, 40 ps and >1ns, respectively. Figure S12 shows the pre-exponential spectra (also called decay-associated spectra) of these components. It should be noted that a negative value indicates a rising component, while a positive one is for a decay component. The validity of the time constants obtained by the global fit is further checked by examining the kinetics at representative wavelengths fitted using the above time constants and presented in Figure 5A (in the parent article).

Two comments should be given related to the limitation of the use of SVD and global fit. First, in the global fit procedure the convolution of IRF with multi-exponential functions is done for IRF function of the same duration at all interrogated wavelengths. Since the effect of an increase in its duration with an increasing probe wavelength is not included, the pre-exponential factor spectra of the fastest component (<100 fs) in Figure S12 might be slightly distorted. Second, in principle, if the bands change their shape (because of a shift in peak position due to the solvation or a spectral narrowing due to thermalization), the SVD analysis can fail, since it gives a series of many decreasing singular values instead of one. However, it was often reported that the "hot" state can act as one separate transient species, and it adds only one more singular value greater than the noise in SVD analysis [2,3]. Also, in the present case the kinetic changes due to the solvation process of TPC1 in ACN can be satisfactory modeled at particular wavelengths by one averaged time constant of 400 fs obtained from the global fit (Figure 5A and Table 2A), and this time constant can be regarded as a characteristic average solvent response time of ACN, in agreement with other works [4,5].

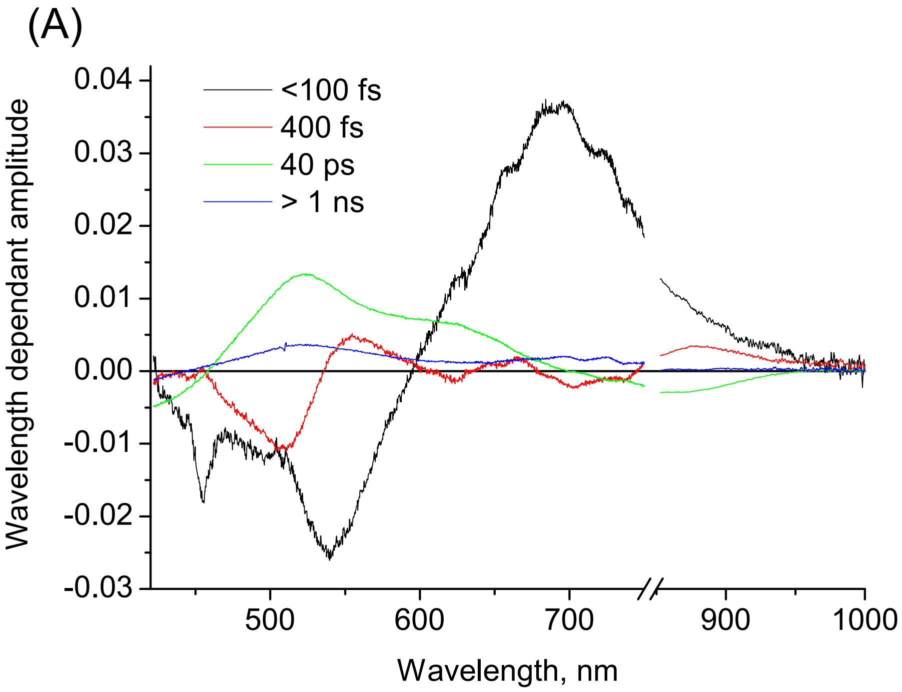
Table S4.

First 10 singular values obtained by global SVD analysis of the transient absorption spectra of free TPC1 and TPC1 interacting with P13 measured in the visible range (420-750 nm) under 400 nm excitation. The values that are considered as different from the noise are indicated in bold, for the rest values the differences between the neighboring values is less than 2 times.

SVD no.	TPC1 in ACN	TPC1 / P13 in ACN	TPC1 in DCM
1	**3.212**	**3.224**	**9.896**
2	**0.418**	**0.360**	**0.937**
3	**0.223**	**0.252**	**0.810**
4	**0.103**	**0.174**	**0.250**
5	0.047	**0.127**	**0.108**
6	0.029	0.049	0.051
7	0.023	0.040	0.040
8	0.023	0.037	0.028
9	0.021	0.037	0.027
10	0.019	0.029	0.023

Concentration effect on femtosecond transient absorption studies of free TPC1 in ACN

A small residual transient absorption (maximum around 520 nm) and bleaching signals stay constant in the temporal window of the experiment (200 fs). We suggest that they originate from a weak contribution of the anion structure (2.6 ns lifetime in ACN [1]) and this assignment is further confirmed by the experiments at different concentrations of TPC1 in ACN (Figure S12). At [TPC1]=0.3 x 10^{-4} M the contribution of the anion signal to the total signal at 520 nm is 20 %, while at 1.0 x 10^{-4} M, it drops to 10 %, as the equilibrium shifts towards neutral form when increasing the concentration of the dye [1]. The presence of the anion signal implicates that the transient absorption spectra of the LE and CT states before solvation also include a contribution of the related states of the anion. However, except for the residual contribution, the results are similar for both TPC1 concentration meaning that both the spectra and the dynamics on short time scale of the anion are similar to those of the neutral structure. A similar conclusion related to the solvation dynamics was reached from the time-resolved emission spectra of the two forms in DCM [1].



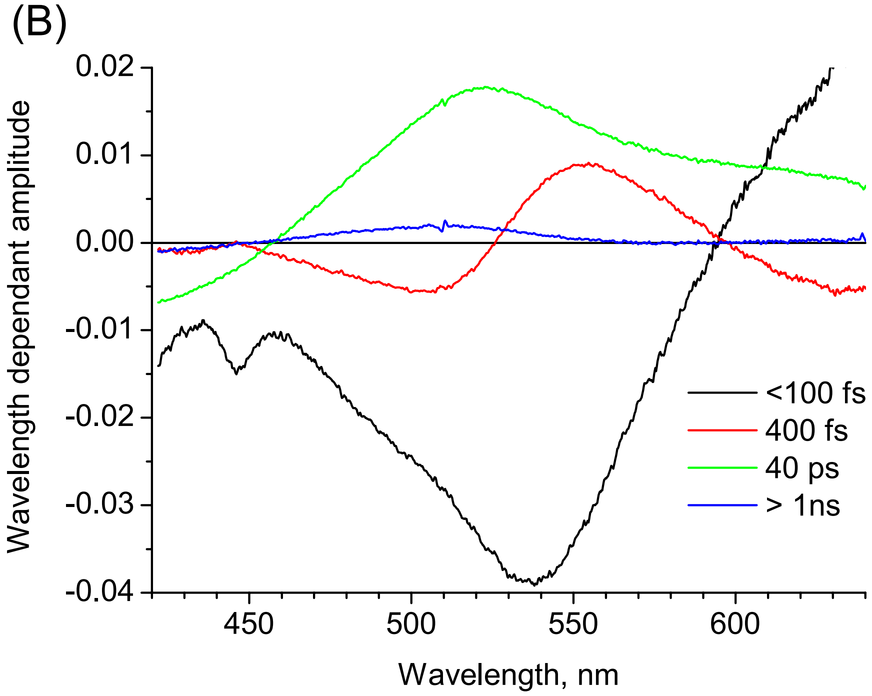


Fig. S12. Pre-exponential spectra obtained from global analysis of transient absorption spectra of free TPC1 in ACN solutions at different concentrations: (A) c=0.3 x 10^{-4} M and (A) c=1.0 x 10^{-5} M. The negative values indicate a rising component, while the positive values – a decay component. The fitted time components are indicated in the figures.

Femtosecond transient absorption studies of free TPC1 in DCM

To understand the solvent nature effect on the TPC1 dynamics in solution, we performed also transient absorption studies of TPC1 in DCM (a less polar solvent than ACN). Figure S13 shows the transient spectra, while Table S4 gives the results of the SVD analysis, and Figure S14 exhibits the results of the global fit. Moreover, Figure S15 shows the kinetic traces at selected wavelengths in short-time window (10 ps), and the results of the multi-exponential fits for these wavelengths are presented in Table S5. Because of smaller extinction coefficient of stationary absorption (at the pump wavelength 400 nm) of TPC1 in DCM than in ACN, we have used a 2-mm sample cell for DCM instead of 0.8-mm (to have comparable transient absorption signals at the same concentration). The drawback was that the temporal resolution for the probe wavelength far from that of the pump was not as good as using ACN (Table S5). Because the lifetime of the neutral structure of TPC1 in DCM is longer (800 ps [1]) than in ACN (40 ps) experiments, the transient spectra were collected for larger time windows, up to 1 ns.

The main differences in the transient absorption spectra in DCM when compared to those in ACN are the following. Firstly, the bleaching band is more shifted to the red region (the negative signal to 480 nm). This is because the stationary absorption band of TPC1 in DCM is also shifted to the red in comparison to that in ACN (Figure S3). Secondly, the negative band of the stimulated emission is shifted to the blue in DCM and it is visible already for wavelengths longer than 680 nm. The reason for this is a lower emission Stokes shift in DCM, and the fluorescence band maximum (715 nm) is shifted to the blue when compared with that of the neutral form in ACN solution (estimated 825 nm). Now, we discuss the time domain result. The main averaged time component connected with the solvation dynamics in DCM is longer and equals to 1.3 ps (very similar to the characteristic DCM response time 1.4 ps found previously from TRES analysis [1]). In this case one more component of several hundreds of fs is necessary in the global fit to properly describe the solvation kinetics in some spectral regions (Figure S14). Because of that, the SVD analysis also gives one more singular value (greater than the noise) when compared to the results using ACN (Table S4). The necessity of the second component is well visualized in the fits of the traces at 575 nm (Figure S15), for which a rise-time of 440 fs and a decay of 1.8 ps are were obtained.

Table S5.

Values of time constants (τ_i) and their fractional amplitudes (A_i, a negative value indicates a rise time) obtained from three-exponential functions used to fit the fs absorption transients at the indicated probed wavelengths (λ) of TPC1 in DCM solution measured in the short time window (0-20 ps). The excitation wavelength was 400 nm. The full width at half maximum (FWHM) of intensity of fitted IRF is also indicated.

λ /nm	FWHM/ fs	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3=const / ps
425	50	-0.010	0.05			-0.017	500
450	100	-0.009	0.10	0.005	0.60	-0.015	500
530	200			-0.037	0.91	0.059	500
575	250	-0.055	0.44	0.026	1.82	0.045	500
650	300	0.026	0.15	-0.015	1.83	0.015	500
720	350			0.034	0.60	-0.017	500
880	450	0.002	0.23	0.007	1.47	-0.005	500

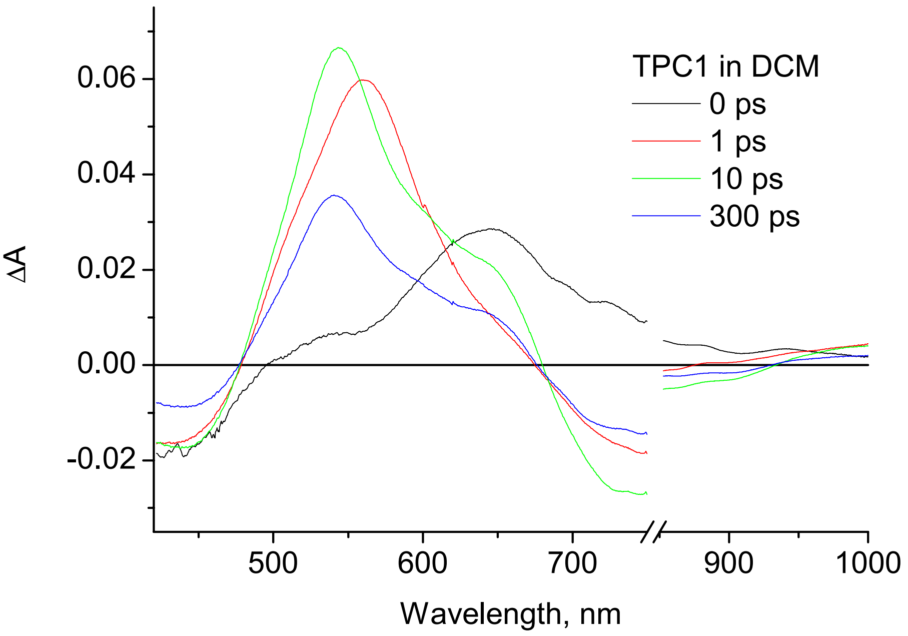


Fig. S13. Representative transient absorption spectra (ΔA is the difference between the absorbance of the probe and reference pulse) of TPC1 (c=0.5 x 10^{-4} M) in DCM solution, at selected time delays between pump (400 nm) and probe pulses.

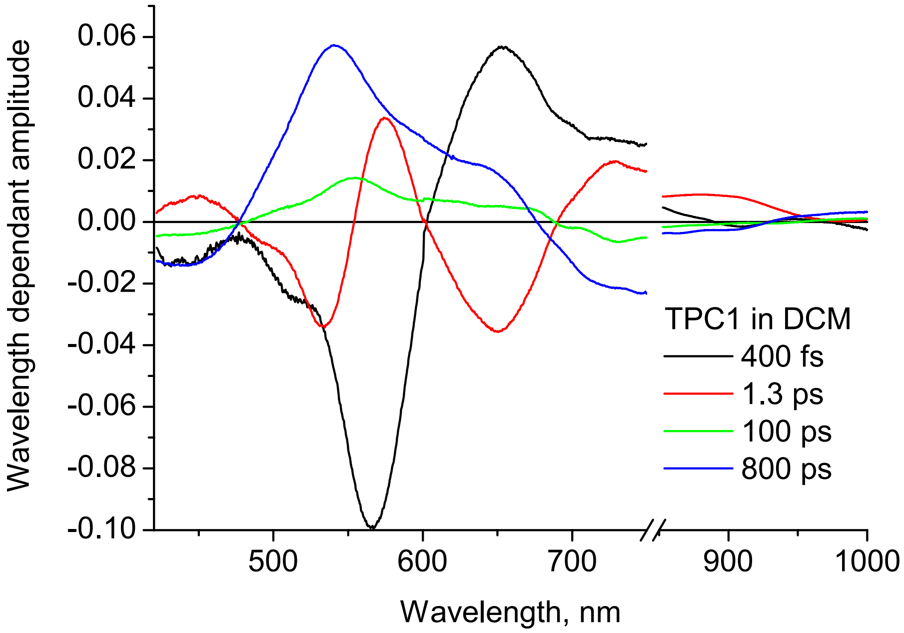


Fig. S14. Pre-exponential spectra for indicated decay times obtained from global analysis of transient absorption spectra of TPC1 in DCM (c=0.5 x 10^{-4} M) solution. The long-time decay due to a relaxed charge-transfer state was fitted by 800 ps component, in agreement with the fluorescence lifetime value. There is also a small contribution (15%) of an additional decay component of 100 ps duration, and with pre-exponential spectrum very similar to that of 800 ps component. Its contribution does not change with 4 time variation in the concentration as well as with the pump pulse intensity (also 4 times change). Its origin is not clear but due to its small contribution we believe that its presence do not influence the interpretation of the results in DCM.

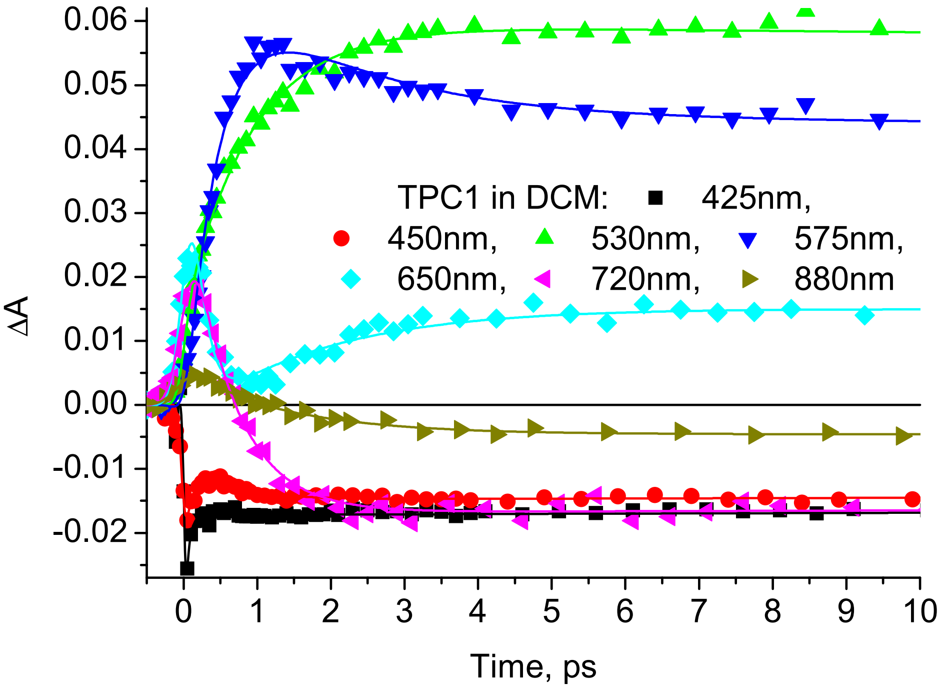


Fig. S15. Representative transient absorption kinetics of TPC1 in DCM (c=0.5 x 10^{-4} M) solution, upon excitation at 400 nm and at the indicated probe wavelengths. The solid lines are from the best fit. See Table S5 for the obtained data from the fit.

Principal SVD component analysis

We also present yet another global approach to analyze the transient absorption spectra with the help of singular value matrix decomposition, particularly useful for data with large noise. As stated in the experimental part, the number of singular values (from SVD analysis) greater than the noise suggests the number of species participating in the measured dynamics. As it was previously shown for the DSSC systems, if only one singular value dominates, then the spectral and time vectors associated with this value reproduce very well the spectrum and the kinetics of the main, single chemical species dominating the observed transient absorption signals [6]. These vectors are much filtrated from the noise and can be often more reliable fitted. It should be noted that it only operates for one principal SVD component – if there are more than one dominant singular values, then their corresponding spectral and time vectors do not have so straightforward interpretations. They can be linear combinations of the spectra and kinetics of each species and need to be further extracted.

The principal SVD components of TPC1 and TPC1-titania transient absorption data were computed and analyzed separately in the visible (420-750 nm) and near IR (850-1000 nm) regions. In all cases, the first singular values are about 10 times larger than the next (Table S4), so we can take their base vectors as the spectra and the kinetics, both associated with the species that dominates over all transients. For the reference - free TPC1 in ACN - it is the relaxed charge-transfer state of the normal form that decays in the visible range with a 40 ps time constant (together with the decrease of the bleaching band intensity), while in the near IR region its stimulated emission rises with 400 fs and decays with 40 ps time constants (shown in Figure S16). As it can be seen in Figure S17, for TPC1 interacting with titania nanoparticles the dominant features consist of dye bleach, absorption of the radical cation and absorption of the electrons. The feature decays with 1 ns in the near IR (where only the contribution of free electrons in the conduction band is present), while in the visible part it can be satisfactory fitted with a 3-exponential decay function with the time constant of 1 ps, 15 ps and 1 ns (the same as obtained in the global analysis). After 1 ns, the residual signal left is 20-30% of the initial, which is in the agreements with the findings from the single-wavelength analysis in the maximum of the bleaching band (Figure 6 in the parent article). However, this principal SVD component analysis allows also to extract more noisy kinetics for the TPC1-NT complexes up to 1 ns delay (Figure S18), which was not possibly by tracking the decays at a single wavelength. As it can be seen, the back electron recombination dynamics is very similar in nanotubes and nanoparticles.

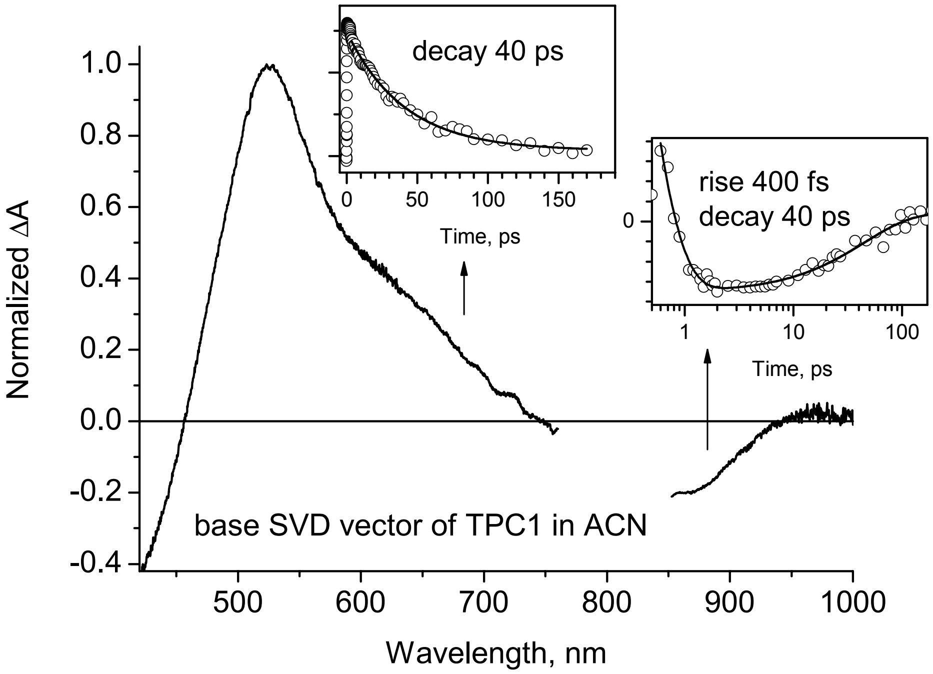


Fig. S16. The spectrum of principal SVD component obtained from transient absorption spectra of free TPC1 in ACN (c=0.3 x 10^{-4} M). The insets show the kinetics associated with the base SVD kinetic vector in visible and near IR ranges together with the results of the fit.

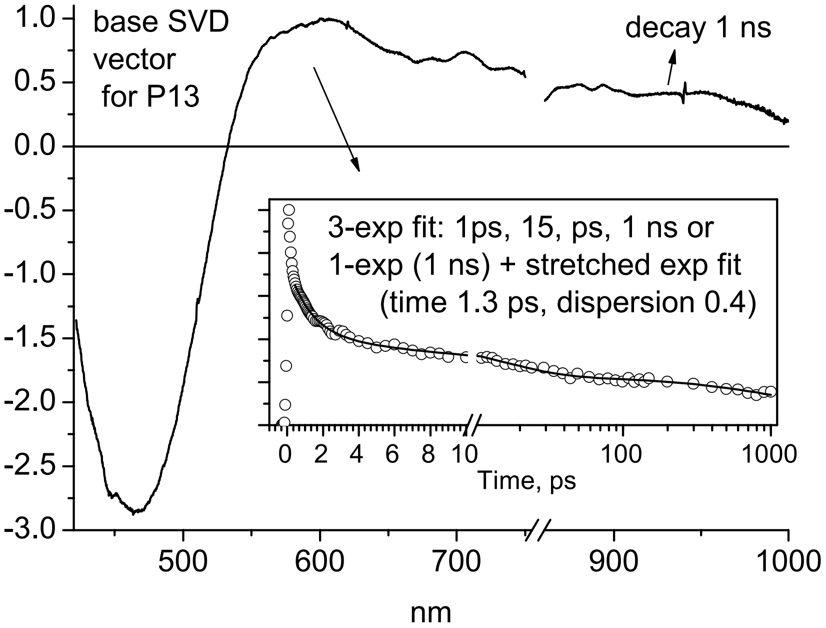


Fig. S17. The spectrum of principal SVD component obtained from transient absorption spectra of TPC1 / P13 in ACN. The inset shows the kinetics associated with the base SVD kinetic vector in visible range together with the results of the fit.

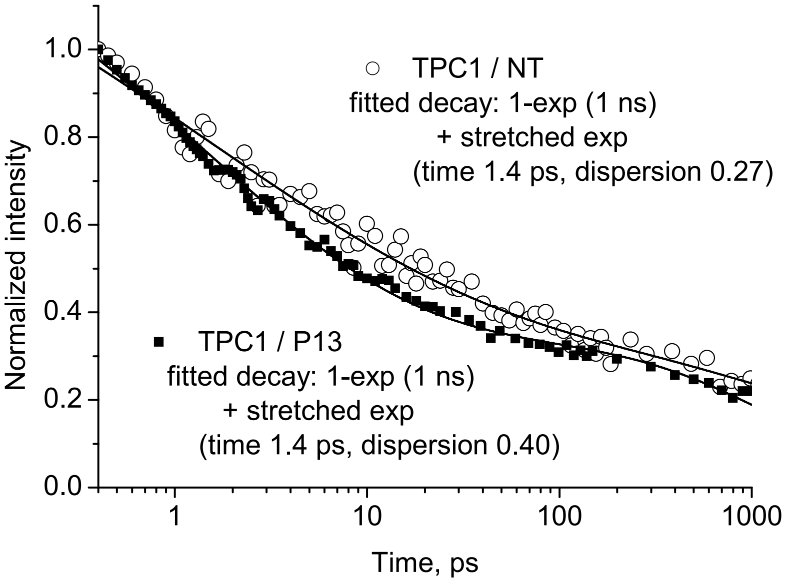


Fig. S18. Comparison of the base SVD kinetic vector for TPC1 / P13 and TPC1 / NT in ACN. The figures also present the fitted function in the form of the sum of 1-exponential function and stretched exponential function.

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