

Supporting Information:

**Real-Time Observation of the Formation of
Excited Radical Ions in Bimolecular
Photoinduced Charge Separation: Absence of the
Marcus Inverted Region Explained**

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1 Experimental

1.1 Chemicals

Acetonitrile (Roth, Rotidry, $\geq 99.9\%$, ≤ 10 ppm H₂O) was used as received. 1,1,2,2-Tetracyanoethylene, TCNE, (Aldrich, 98%) and 1,2-dicyanoethylene, DCE (Acros, 98%) were sublimed under reduced pressure and stored in the dark in a dry atmosphere. 9,10-dicyanoanthracene, DCA, (Kodak) was recrystallized and 9,10-diphenylanthracene, DPA, (Aldrich, 97%) was used as received. 3-Cyanoperylene, CNPe, and 3-methylperylene, MePe, were synthesized according to the literature¹ and purified by column chromatography. Sulfuric acid (Carlo Erba reagents, 96%) was used as received.

1.2 Ultrafast Spectroscopy

1.2.1 Fluorescence Up-Conversion

Femtosecond time-resolved fluorescence measurements were performed using a fluorescence up-conversion set-up described in references 2 and 3. Excitation was performed at wavelengths between 400 and 430 nm using the frequency-doubled output of a tunable Kerr lens mode-locked Ti:Sapphire laser (Mai Tai, Spectra-Physics). Excitation of the sample was performed after adjusting the angle between the pump and gate pulses to magic angle. The

sample was placed in a spinning cell in order to avoid decomposition. The up-converted signal was focussed into a monochromator equipped with a photomultiplier tube (Hamamatsu R1527P) working in single photon counting mode. The full width at half maximum of the overall instrument response function amounted to 250 fs.

The fluorescence time-traces were analyzed using an analytical expression for the convolution of the gaussian instrument response function with a multiexponential model function.⁴

1.2.2 Vis-Pump / UVVis Probe Transient Absorption

Femtosecond visible transient absorption spectra were obtained using an apparatus described in references 5,6. The instrument response function has a full width at half maximum of approximately 200 fs as obtained from measurements of the optical Kerr effect in acetonitrile. The pump power at 400 nm was in the order of 1 μ J per pulse. The sample absorbance at 400 nm was of the order of 0.5 in a 1 mm quartz cuvette. Samples were bubbled with nitrogen during the experiment to constantly refresh the excitation volume, thus avoiding sample decomposition. Changes in the sample concentration due to degradation and / or solvent evaporation were negligible as judged from absorption spectra recorded before and after the experiments.

1.2.3 Vis-Pump / IR Probe Transient Absorption

All measurements on the CN-stretch region were initially performed at the Max-Born Institut (MBI). All these experiments were repeated in Geneva and complemented with the remaining experiments for consistency.

MBI Set-up. Femtosecond mid-infrared experiments were performed using 20 mL solutions consisting of either MePe, CNPe, DCA or DPA and different concentrations of TCNE in acetonitrile. The sample absorbance at 400 nm was about 1.0 independent of the TCNE concentration. UV-visible absorption spectra of the samples were recorded before and after

the measurements in order to verify that no sample degradation occurred throughout the experiment.

Local excitation of MePe, CNPe, DCA and DPA was achieved with pulses (400 nm, $3.5\ \mu\text{J}$, 55 fs) generated by the frequency doubling of a fraction of the output of a standard 1 kHz amplified Ti:Sapphire laser (Spitfire, Spectra Physics). After passing an optical delay line, the pump pulses, polarized at magic angle, were focused onto the sample with a beam diameter of approximately $250\ \mu\text{m}$. Horizontally polarized mid-infrared pulses, with their center frequency tuned to $4.6\ \mu\text{m}$, were generated using double-pass collinear optical parametric amplification followed by difference frequency mixing of signal and idler.⁷ The probe and reference pulses were obtained using reflections from a ZnSe wedge, and focused onto the sample by means of an off-axis parabolic mirror (focal diameter $150\ \mu\text{m}$). The probe and reference pulses were dispersed in a polychromator ($2.4\ \text{cm}^{-1}$ resolution), and spectrally resolved absorbance changes were recorded simultaneously for each shot using a liquid-nitrogen-cooled HgCdTe double array detector (2×31 pixels). The polychromator was not tuned during measurements to avoid repositioning error effects (on the order of $2.4\ \text{cm}^{-1}$). The time resolution was determined to be 200 fs, based on the cross-correlation between the UV pump and IR-probe pulses measured in a ZnSe semiconductor placed at the sample position. A peristaltic pump was used to circulate the sample through a flow cell (1-mm-thick BaF₂ windows separated by a $200\ \mu\text{m}$ -thick Teflon spacer) to guarantee that a new sample volume was excited for every laser shot. All experiments were performed at room temperature ($22.5 \pm 1^\circ\text{C}$).

Geneva Set-up. The experimental setup for fs UV pump/mid-IR probe experiments was based on a Ti:Sapphire amplified system (Spectra Physics Solstice) producing 100 fs pulses at 800 nm at 1 kHz. Excitation was performed with a $2\ \mu\text{J}$ pulse energy at 400 nm produced by frequency doubling a fraction of the amplifier output. These pulses were focussed onto the sample to a $300\ \mu\text{m}$ diameter spot, resulting in an irradiance of $2.8\ \text{mJ}/\text{cm}^2$.

Mid-IR probe pulses at around $4.6\text{ }\mu\text{m}$ ($\text{C}\equiv\text{N}$) and $6.6\text{--}7\text{ }\mu\text{m}$ ($\text{C}=\text{C}$) were generated by difference frequency mixing the output of an optical parametric amplifier (Light Conversion, TOPAS-C with NDFG module) pumped at 800 nm . The polarization of the IR beam was controlled using a wire-grid polarizer. Two horizontally polarized beams were produced by means of a CaF_2 wedge and focussed onto the sample to a $140\text{ }\mu\text{m}$ diameter spot.⁸ One of the beams was overlapped with the pump beam, polarized at magic angle with respect to the pump beam, whereas the second was used as a reference beam. Both IR beams were focussed onto the entrance slit of an imaging spectrograph (Horiba, Triax 190, 150 lines/mm) equipped with a liquid nitrogen cooled 2×64 element MCT array (Infrared Systems Development), giving a resolution of $3\text{--}4\text{ cm}^{-1}$ ($\text{C}\equiv\text{N}$) and $1\text{--}2\text{ cm}^{-1}$ ($\text{C}=\text{C}$).

The sample area and the detection system were located in a box that was purged with dry air for at least 45 minutes before each experiment. The average of 8000 signal shots was taken to collect one data point. At least 15 measurements for each system were averaged to reconstruct the spectra. To provide a new sample solution for each shot, a flow cell as described in reference 8 was used. The absorbance at 400 nm was always below 0.6 on a $400\text{ }\mu\text{m}$ ($\text{C}\equiv\text{N}$) and $200\text{ }\mu\text{m}$ ($\text{C}=\text{C}$) optical pathlength.

The wavenumber axis was calibrated by comparing the bleach of the used donors ($\text{C}=\text{C}$) and the bleach of 9-cyanoanthracene and 9,10-dicyanoanthracene ($\text{C}\equiv\text{N}$) with the FTIR. No sample degradation was observed throughout the experiment.

2 Calculations

2.1 Calculations of transient IR spectra of the cyano stretching modes of TCNE

Vibrational spectra have been calculated for TCNE using density functional theory (B3LYP/aug-cc-pvdz) as implemented in Gaussian 03.⁹ A complete cubic and semidiagonal quartic force field was numerically calculated from analytical second order derivatives applying a finite procedure as described previously.^{10–12} Anharmonicity constants x_{ij} were derived from the cubic and semidiagonal quartic force constants according to standard procedures.^{13–16} Anharmonic frequency shifts and the shape of absorption lines for the two IR active cyano stretching vibrations (modes 23 and 24) were calculated as described in reference 17 (Eqs. 2a and 3b).

Anharmonic frequency shifts of vibrational modes are temperature dependent, because they depend on the level of excitation of all modes. The calculated absorption bands include all possible transition frequencies weighted by the product of population factors of all levels. To determine the number of possible transitions contributing to the absorption spectra for a given temperature, a thermal Boltzmann population distribution for all levels and all modes was calculated first. Maximum levels of excitation for each mode were then defined by considering all levels up to a maximum level, for which the population factor is still larger than 20% of the maximum value.

Temperatures up to 1100 K corresponding to an excess internal energy of about 1.2 eV have been considered. Higher internal energies or temperatures, respectively, were neglected, because the numerical problem quickly becomes unmanageable and the absorption band for this temperature is already considerably broadened with a correspondingly weak maximum intensity (see below).

Examples of maximum levels v of excitation of 1-24:

T = 0 K: [1,0,...]

$T = 100 \text{ K:}$ $[1,1,0,\dots]$
 $T = 300 \text{ K:}$ $[4,3,2,2,2,1,1,0,\dots]$
 $T = 500 \text{ K:}$ $[7,5,4,3,3,2,2,1,0,\dots]$
 $T = 1100 \text{ K:}$ $[16,11,10,8,8,4,4,3,2,2,2,2,2,1,1,1,1,0,\dots]$

Up to these maximum levels of excitation of the modes, all permutations of excitation level distributions were calculated leading to a number of 1, 4, 2160, 1.105.920, and 212.009.529.600 relevant transitions for the temperatures given above. The intensity of each absorption line and thus its contribution to the spectrum is proportional to the population factor given as the product of thermal Boltzmann population factors of each level that is excited in the particular transition. It is seen that the number of possible transitions quickly grows. For the highest temperature of 1100K considered here the processing of all transitions is already too expensive and thus unmanageable. For this temperature a truncated set has been considered, which means that the resulting absorption curve is not fully converged, i.e. it should be even further shifted and broadened. Each transition line was convoluted with a Gaussian function of $\text{FWHM} = 4 \text{ cm}^{-1}$. Results are shown in Figure 4 of the main manuscript. Anharmonic shifts are plotted relative to the anharmonic frequencies calculated for $T = 0 \text{ K}$ (mode 23: 2301 cm^{-1} ; mode 24: 2311 cm^{-1}).

2.2 Estimation of the Vibrational Temperature

The vibrational temperature, T , of the ground state D/A pair upon CS and subsequent CR was estimated from the following equation:¹⁸

$$E = \sum_i^{3N-6} \frac{h\nu_i}{\exp\left(\frac{h\nu_i}{k_{\text{B}}T}\right) - 1} \quad (1)$$

where E is the amount of energy stored in the vibrational modes of the molecule, N is the number of atoms, ν_i is the frequency of the vibrational mode i , and k_{B} is the Boltzmann

constant. The vibrational frequencies were determined from DFT calculations with the B3LYP functional and the 6-31G basis set, as implemented in Gaussian09.¹⁹ Eq. (1) was first used to calculate the vibrational energy of the molecules at 300 K, E_{RT} . The energy dumped into the vibrational modes of the D/A pair, E_{DA} , was then added to this value and the total vibrational temperature was then calculated using the vibration frequencies of D+A together. The obtained temperature was taken as the vibrational temperature of TCNE, T_{A} . For CS^0 , E_{DA} was taken as $-(\Delta G_{\text{CS}} + \Delta G_{\text{CR}})/2 = E_{00}(\text{D}/2)$, where $E_{00}(\text{D})$ is the 0-0 transition energy of D. Even if CS^0 is operative, the vibrational temperature of D, T_{D} , is, in most cases, larger than T_{A} because the excitation energy (3.1 eV, 400 nm) is larger than $E_{00}(\text{D})$ by an amount E_{ee} , the excess excitation energy. To determine T_{D} , T_{A} was inserted again in eq. (1) with the vibration frequencies of D alone. This allowed to determine the amount of vibrational energy stored in D, E_{D} . T_{D} was then calculated using eq. (1) with the vibration frequencies of D and with $E = E_{\text{ee}} + E_{\text{D}}$.

For CS^* , a similar procedure was used. T_{A} was calculated as above (with $E = E_{\text{RT}} + E_{\text{DA}}$) but with $E_{\text{DA}} = -(\Delta G_{\text{CS}^*} + \Delta G_{\text{CR}})/2$. T_{D} was calculated with $E = E_{\text{ee}} + E_{\text{D}} + E_{00}(\text{D}^{\bullet+})$, where $E_{00}(\text{D}^{\bullet+})$ is the 0-0 transition energy from the ground state to the first excited state of the cation.

The so-calculated vibrational temperatures in K are listed in the Table below:

D/A	CS^0		CS^*	
	T_{D} (K)	T_{A} (K)	T_{D} (K)	T_{A} (K)
DCA/TCNE	690	635	-	-
PeCN/TCNE	660	565	800	435
DPA/TCNE	565	565	690	475
MePe/TCNE	640	585	805	460

3 Data Treatment

In order to obtain transient absorption spectra (visible as well as IR), which only correspond to the ionic products, $P(t, \lambda)$, all spectral contributions pertaining to the locally excited state of the donor, D, were subtracted. To this end, we applied a procedure similar to the one described in reference 20 and recently applied in reference 3. The spectrotemporal behavior of the ion pair, $P(t, \lambda)$ can be obtained as¹

$$P(t, \lambda) = A_{\text{D,TCNE}}(t, \lambda) - A_{\text{D}}(t, \lambda) \frac{I_{\text{D,TCNE}}(t, \lambda_{\text{em}})}{I_{\text{D}}(t, \lambda_{\text{em}})} S, \quad (2)$$

where $A_x(t, \lambda)$ are the transient absorption spectra of the D-TCNE pair (D, TCNE) and the pure electron donor (D). $I_{\text{D,TCNE}}(t, \lambda_{\text{em}})$ and $I_{\text{D}}(t, \lambda_{\text{em}})$ denote the emission decays of the locally-excited fluorophore obtained from the fluorescence up-conversion experiment at a given emission wavelength, λ_{em} , in the presence and absence of TCNE, respectively. S denotes a scaling factor, which accounts for drifts in the laser intensity and changes in the sample absorbance at the excitation wavelength in the experiments for $A_{\text{D,TCNE}}$ and A_{D} . Obviously this method can only be applied for time delays larger than the instrument response function, as the convolution is not accounted for.

In case of the visible transient absorption spectra, we applied an additional modification: In order to improve the quality of the resulting spectra, which are the product of 3 subtractions of experimental spectra, we decided to perform global multiexponential fits to the experimental transient absorption spectra. Basically the fitting is only used to eliminate the experimental noise and scattering in the data. Sufficient experimental components were used to obtain homogeneously distributed residuals. The so obtained "noise-reduced" experimental spectra are used as input in equation (2).

¹Excitation of a solution containing only 1 M TCNE yielded weak spectra in both Vis and IR-TA experiments. However, given their low intensity, we did not attempt to also correct for their contribution to the overall spectra.

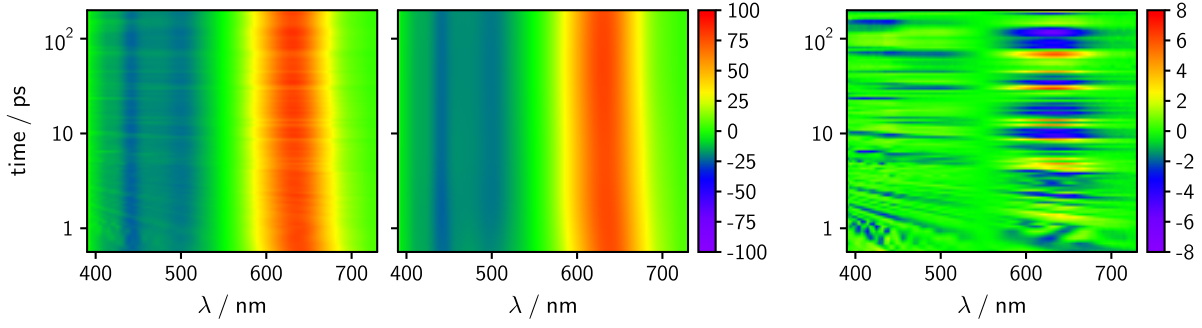


Figure S1: Transient absorption spectrum measured with CNPe in acetonitrile (left) and the global multiexponential fit to it (middle). The residuals (right) are found to be less than 10% of the signal. The color coded absorption scales are given in mOD.

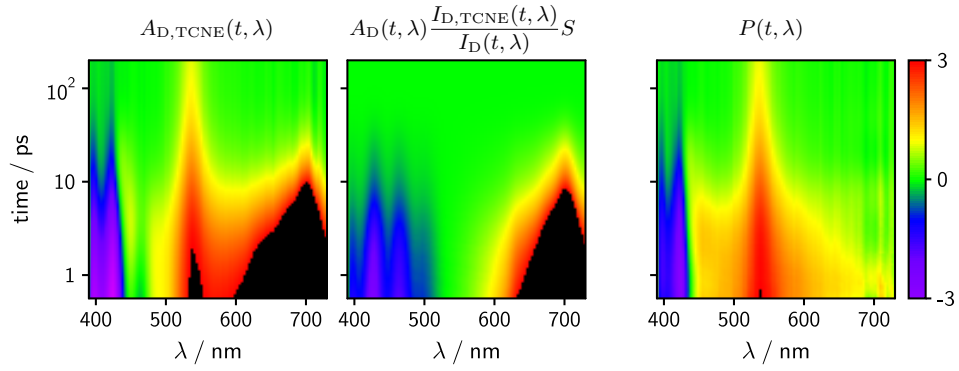


Figure S2: Graphical representation showing the effect of applying equation (2) to the quenching data of MePe with TCNE. The black areas are outside the absorption scale (in mOD), which was chosen rather narrow to show the low intensity hot ground state feature.

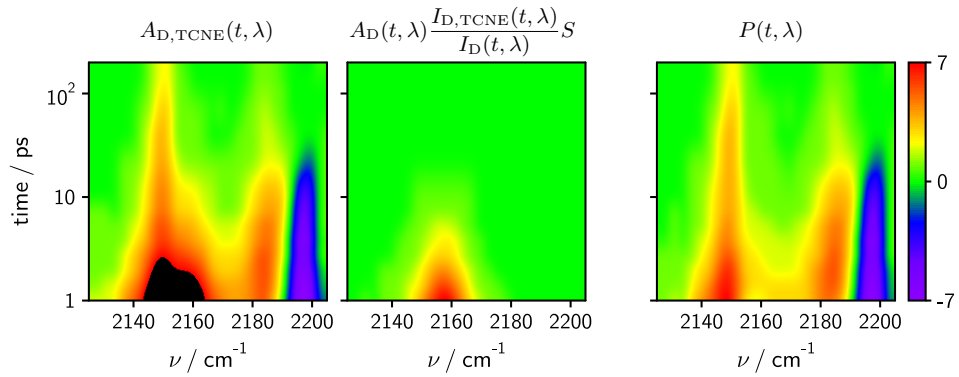


Figure S3: Graphical representation showing the effect of applying equation (2) to the quenching data of CNPe with TCNE in the region of the CN-stretch vibration. The absorption scale is given in 0.1 mOD.

4 Experimental Data

4.1 Fluorescence Up-Conversion

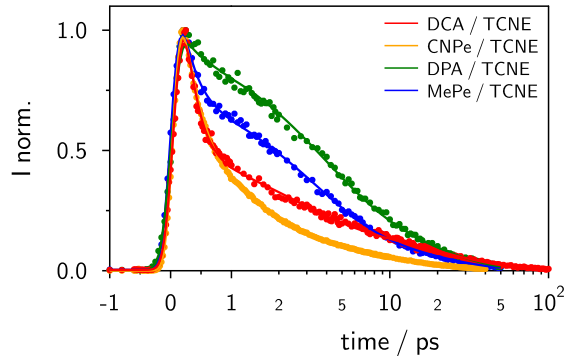


Figure S4: Fluorescence up-conversion traces measured with the four donors with 1 M TCNE. Lines depict the multiexponential fits to the data used for the decomposition described in Section 3.

Table S 1: Summary of multiexponential fits to the FU-traces shown in Figure S 4.

system	λ_{exc} (nm)	λ_{em} (nm)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)
MePe / TCNE	413	500	0.45	0.2	0.42	3.1	0.13	16.4
DPA / TCNE	400	460	0.67	3.2	0.33	15.9	—	—
CNPe / TCNE	430	500	0.66	0.4	0.26	1.7	0.08	13.5
DCA / TCNE	420	500	0.69	0.2	0.19	2.3	0.12	21.5

4.2 Vis TA Spectra

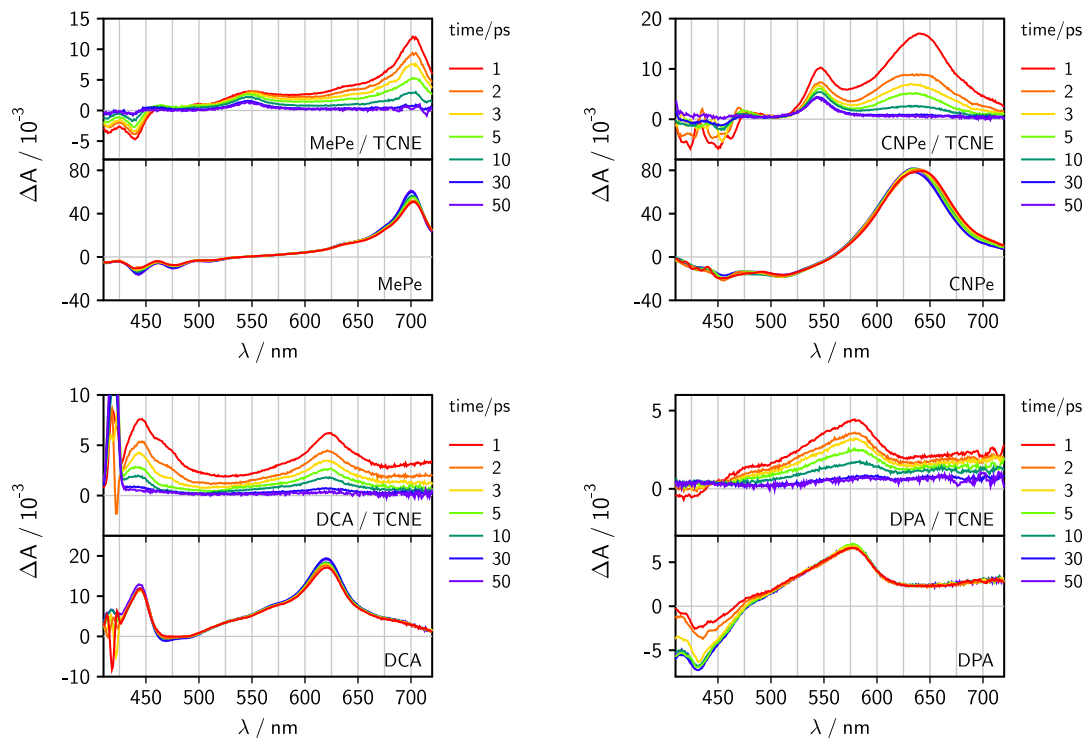


Figure S5: Vis transient absorption spectra measured with the four systems studied in the absence and presence of 1 M TCNE. The noise at 420 nm in the DCA data is due to scattering, as this sample was excited at 420 nm.

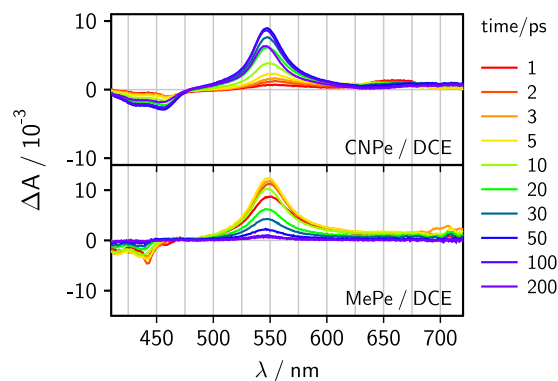


Figure S6: Vis transient absorption spectra measured with MePe and CNPe in the presence of DCE. All the contributions from the donor excited state (absorption, stimulated emission, corresponding ground state bleach) have been subtracted, leaving the ion and hot ground state bands as well as the ground state bleach corresponding to the ion population. The recombination is in the range of hundreds of ps in these cases, thus no hot ground state features are observed.

4.3 IR TA Spectra

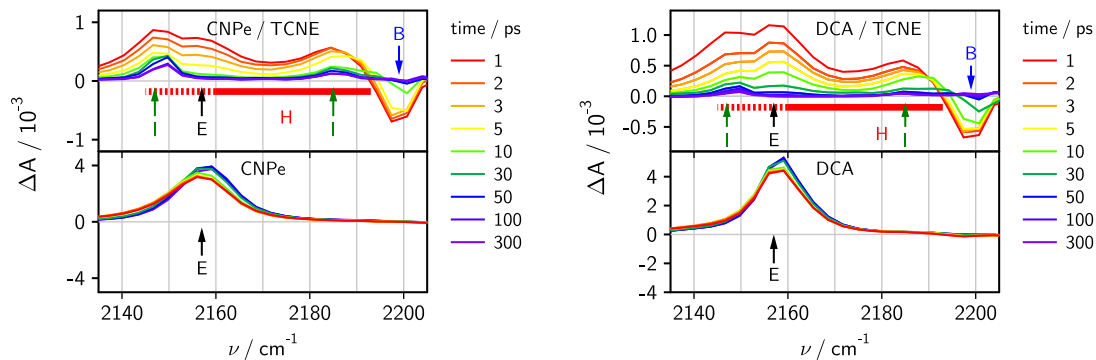


Figure S7: IR transient spectra measured with CNPe (left) and DCA (right) with and without 1 M TCNE in the CN region. E...excited state absorption; B...ground state bleach; l...ion; H...hot ground state

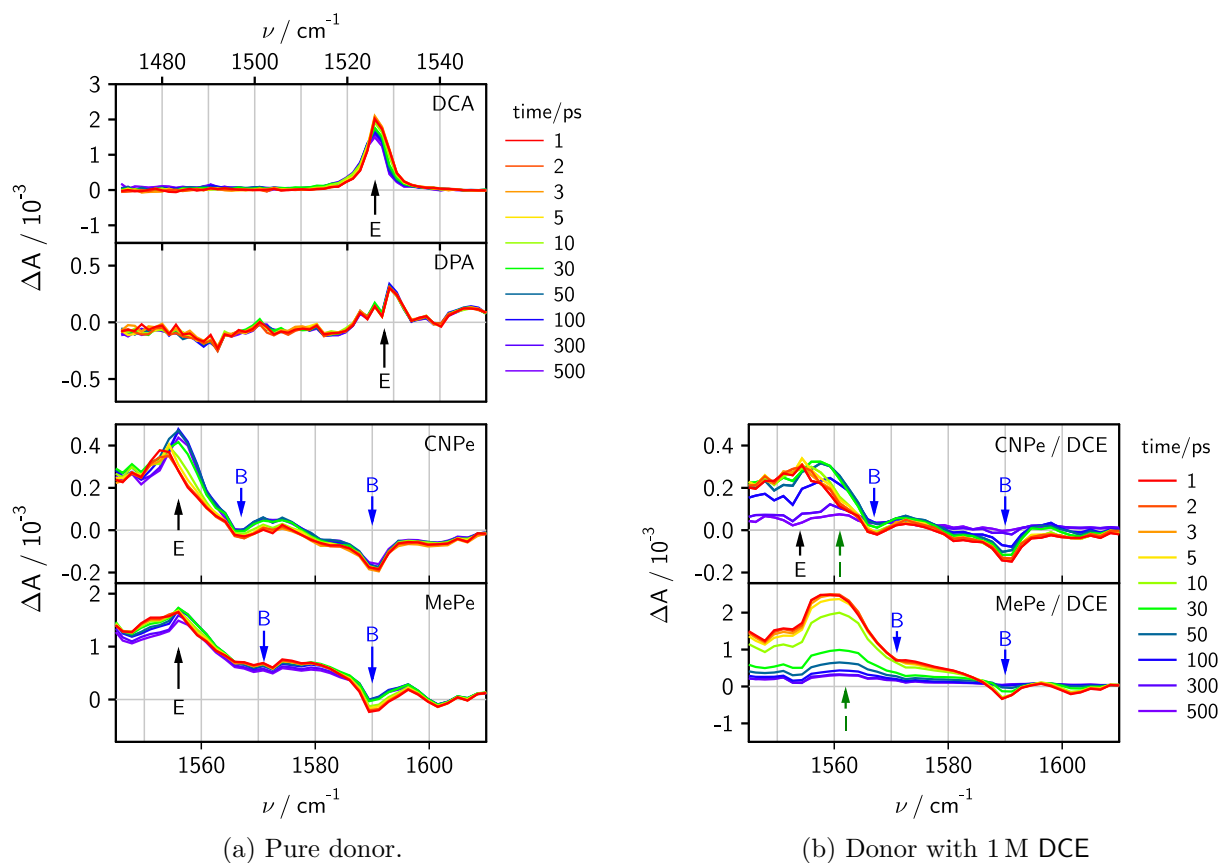


Figure S8: IR transient absorption spectra measured with the pure donors alone (a) and in the presence of 1 M DCE (b), where no hot ground state features are observable, in the region of the C=C stretch. E...excited state absorption; B...ground state bleach; l...ion.

4.4 Visible Absorption Spectra of the Cations in H₂SO₄

Figure S9 shows the electronic absorption spectra of the cations of the four donors used, recorded in concentrated H₂SO₄. As we are lacking the corresponding emission spectra the 0-0 transition energy, E_{00} , was estimated as the energy at half the absorption of the lowest energy absorption peak (see arrows indicating our estimation of E_{00}). In the case of **MePe**, where we seem to have a residual protonation or a follow-up product as well, we estimated E_{00} as being at the same position as for perylene, but displaced by the small shift observable from a comparison of both absorption spectra (0.05 eV). The low intensity absorption bands observed for perylene can also be found in frozen matrix absorption spectra of the perylene cation in reference 21. The absorption spectrum of **DPA**⁺ closely resembles the one observed by Workentin *et al.* using laser-induced photoionization in acetonitrile.²² Similarly, the weak absorption of **DCA**⁺, due to only partial formation of the cation, is very similar to the published cation spectrum of the 9-cyanoanthracene cation obtained electrochemically.²³ The cation spectrum for **CNPe** is also slightly “contaminated“ by residual non-oxidized precursor **CNPe**.

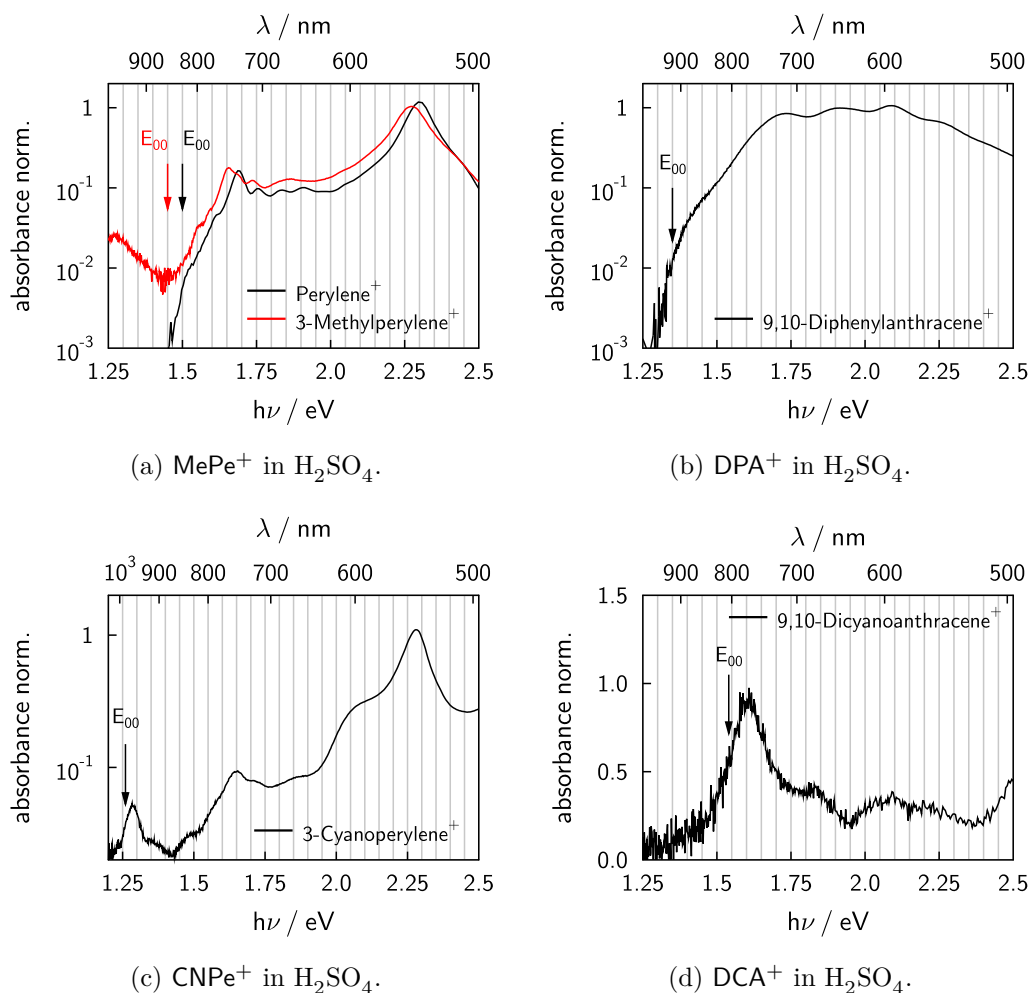


Figure S9: Radical cation spectra of the four donors obtained in conc. H_2SO_4 . Note that the broad peak in (a) above 900 nm is most probably a protonation product. The intensity of this peak increases with time, while the remaining spectrum changes its shape, most probably forming follow-up products.

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