Bimolecular Electron Transfer

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Direct Femtosecond Observation of Tight and Loose Ion Pairs upon Photoinduced Bimolecular Electron Transfer**

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It is often assumed that in photoinduced bimolecular electron transfer (ET),[1–4] in which charge separation (CS) between donor and acceptor units occurs (Figure 1), tight ion pairs (TIPs; also named contact or intimate ion pairs) and loose ion pairs (LIPs; also dubbed solvent-separated or solvent-shared ion pairs) are produced, depending on polarity of the solvent and exergonicity of the ET reaction. Subsequently, TIPs and LIPs may interchange by solvent rearrangement, undergo dissociation into free ions, or reach the neutral ground state by charge recombination (CR). Although details such as characteristic timescales have been uncovered by ultrafast electronic spectroscopy,[3–7] a clear experimental distinction between TIPs and LIPs has till now not been demonstrated, because the typical strong broadening of electronic transitions in liquid solution masks structural differences between these different ion pairs. Hence, the exact microscopic geometries of TIPs and LIPs have remained essentially unknown. Whereas theoretical models assume spherical symmetry, that is, reaction probabilities having equal magnitude regardless of the mutual orientation, one can argue that TIPs composed of quasiplanar aromatic molecules would rather arrange in sandwichlike fashion with contact distances of about 3.5 Å that result in substantial molecular orbital overlap.[1] Indeed, TIPs can directly be formed by photoexcitation of charge-transfer (CT) transitions of donor–acceptor complexes.[3] Different views exist on the nature of LIPs, for which either a larger and yet precise interionic distance of 7–8 Å is assumed (with specific formation, dissociation, and CR rates),[2] or a distribution of interionic distances ranging from 7 to about 12 Å is invoked to describe the two diffusing ions.[8,9]

Herein we show that polarization-resolved ultrafast infrared spectroscopy[10] can distinguish signal contributions of TIPs and LIPs, and thus we can distinctly identify the characteristic timescales for photoinduced CS and CR reactions of these ion-pair reaction pathways. Moreover, we obtain structural insight from the anisotropic distribution of

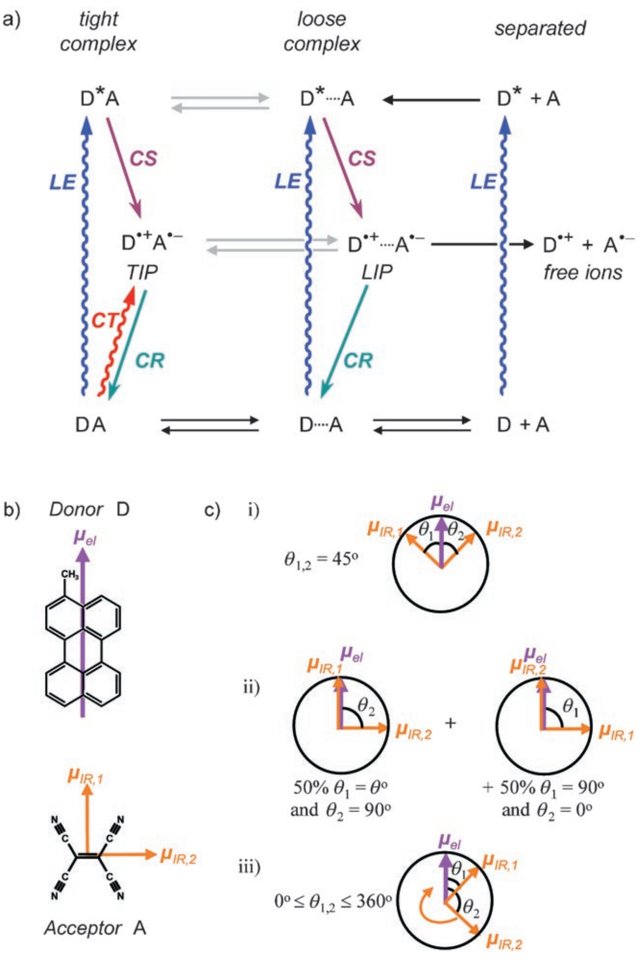

Figure 1. a) General scheme for bimolecular ET between donor D and acceptor A. Solid arrows indicate charge separation (CS), charge recombination (CR), and molecular diffusion. Photoinduced local excitation (LE) to the S_1 state of the donor D* and charge-transfer (CT) excitation of a ground-state complex DA to TIPs are indicated by wavy lines. The gray solid lines indicate solvation or desolvation, which according to the standard model should take place in polar solution between tight and loose complexes, and between TIPs and LIPs. These solvation/desolvation routes are not observed in this work with donor MePe and acceptor TCNE. b) Molecular structures and electronic and IR transition dipole moments ($\boldsymbol{\mu}_{el}$, $\boldsymbol{\mu}_{IR,1}$, and $\boldsymbol{\mu}_{IR,2}$). c) Three possible cases for which both IR-active vibrations show an anisotropy value of $r = 0.1$, as discussed in the text.

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relative orientations of the constituents of TIPs that should stimulate refinement of existing theories.

To study ion-pair formation on photoinduced CS (Figure 1), we used the electron donor 3-methylperylene (MePe) and the strong electron acceptor tetracyanoethene (TCNE), for which the driving force for CS is large ($\Delta G_{CS} = -2.25$ eV). We used both polar acetonitrile (ACN) and weakly polar dichloromethane (CH_2Cl_2) as solvents. Solvent reorganization is important for ACN, as opposed to CH_2Cl_2. Photoexcitation with an ultrashort pump pulse gives MePe in the electronically excited S_1 state (Figure 2; local excitation (LE) at 400 nm, 3.10 eV), after which an encounter with a TCNE molecule leads to CS. At low quencher concentration, the observed transient signals are dominated by slow diffusional dynamics between donor and acceptor, with typical timescales of 0.1–1 ns.[11] At higher quencher concentrations, however, prompt CS dynamics generating ion pairs is expected to contribute at early pulse delays without being masked by the slower diffusional motion. According to conventional models,[12–14] CS in ACN is expected to proceed to LIPs (even if tight encounter pairs are initially locally excited), whereas in CH_2Cl_2 formation of TIPs should be the dominant pathway. In addition, in ACN a fraction of LIPs can slowly dissociate into free ions (on a timescale of ca. 0.25 ns),[11] whereas in CH_2Cl_2 all ion pairs ultimately relax to the ground state by CR. For comparison, we also studied the charge-transfer (CT) excitation of MePe–TCNE complexes preformed in the electronic ground state in ACN and CH_2Cl_2 (by pumping at 800 nm, 1.55 eV). Here TIPs are directly generated by optical excitation.[15] Transient response of these TIPs is governed by ultrafast CR to the ground state. In the case of CT excitation, rearrangements into LIPs and effects of slower diffusional motions can be discarded.

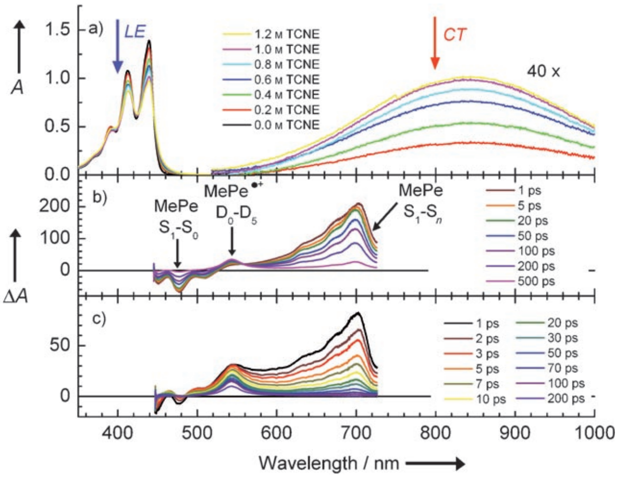

Figure 2. a) Electronic absorption spectra of 4 mM MePe and TCNE in ACN solution (thickness 100 µm). The arrows indicate the spectral positions of the pump pulses for the LE and CT transitions (the latter has been multiplied by a factor of 40 for clarity). Transient UV/Vis difference absorbance spectra ΔA measured at different pulse delays after local excitation and plotted for TCNE quencher concentrations of b) 0.1 and c) 0.9 M show the substantial spectral overlap of the excited-state absorption and stimulated emission bands, and the absorbance of the radical cation.

Figure 2 shows electronic absorption spectra of the MePe + TCNE system and transient spectra obtained after local excitation probing the electronic transitions of MePe in the S_1 state and of MePe$^{\bullet+}$. Fitting the time profiles of the spectrally broad and substantially overlapping MePe (S_1) and MePe$^{\bullet+}$ (D_0–D_5) bands at 700 and 543 nm requires at least three exponential functions with characteristic timescales ranging from femtoseconds to hundreds of picoseconds (see Table S1, Supporting Information). The observed complex dynamics points to the occurrence of a multitude of types of ion pairs with different associated couplings.

More structural detail is revealed by transient infrared absorption spectra obtained by probing with 150 fs infrared pulses tuned to the $C\equiv N$ stretching-mode range of TCNE$^{\bullet-}$. Two transient bands, measured after local excitation of MePe in ACN, are located around 2150 and 2190 cm^{-1}, that is, the frequency positions of the IR-active $C\equiv N$ stretching vibrations of TCNE$^{\bullet-}$.[16] Figure 3 b–d show how the transient spectra depend on the applied quencher concentration. With 0.2 M TCNE (Figure 3 c), the spectral changes originate from two distinct spectral components, rather than from a continuous variation of the band shape.[17] Two $C\equiv N$ stretching vibrational bands appear within time resolution and subsequently decay in the first 20 ps. This is followed by the appearance of spectrally narrower $C\equiv N$ stretching vibrations, blueshifted by 4–5 cm^{-1}, in the time range between 50 and 200 ps, after which the signals remain essentially constant up

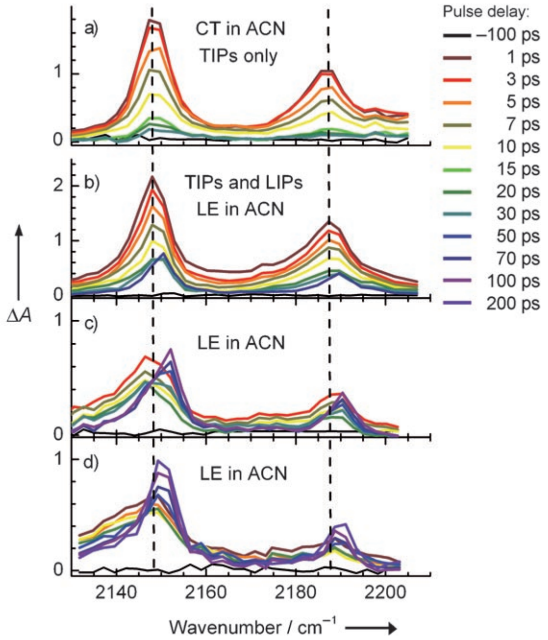

Figure 3. Transient absorbance ΔA [mOD] spectra of the $C\equiv N$ stretching-mode region of the TCNE radical anion in ACN after local excitation of MePe for three different quencher concentrations: 0.9 (b), 0.2 (c), and 0.1 M (d), clearly showing the early and late spectral components assigned to TIPs and LIPs, respectively. CT excitation of MePe in ACN (a; 0.9 M TCNE) only shows the redshifted component assigned to TIPs. The dotted line indicates the frequency position for TIPs.

to 1 ns (the maximum pulse delay in the experiment). Comparison of the transient spectra recorded for different quencher concentrations (0.05–0.9 M TCNE) shows that these two components are always present, whereby the spectral component at early pulse delay dominates at high quencher concentration, and vice versa for low quencher concentration.[18]

Insight into the origin of the two spectral components for MePe + TCNE in ACN was obtained by comparing the results with those measured with CT excitation of MePe + TCNE in ACN (Figure 3 a) as well as local and CT excitation in CH_2Cl_2 (Figure S2, Supporting Information). Here only the redshifted spectral component is observed. The time resolution of these transient IR experiments is 200 fs. Transient UV/Vis experiments show that the CR of TIPs in ACN can be reproduced with a biexponential decay with two time constants: 0.2 ps (major component) and 7 ps (minor component).[19] The signals observed in the transient IR experiment, where limited time resolution and broadband absorption induced in the solvent mask early-time dynamics, thus only show a fraction of the total response induced by CT excitation.

Figure 4 a shows the time evolution of the integrated area of the early $C\equiv N$ stretching spectral component at 2150 cm^{-1}, estimated by fitting a Lorentzian line shape to the experimental data (to subtract the underlying broad featureless contribution), measured at various TCNE concentrations. The amplitude of the spectral component at early times scales with quencher concentration, whereas the dynamics remains essentially the same. The dynamics of the blueshifted spectral component, however, strongly varies with TCNE concentration. This shows that the signal at early pulse delays (less than 20 ps) originates from ions at close distance, whereas the signal at longer pulse delays is caused by diffusional quenching. The temporal behavior of the two distinctly different spectral components of the $C\equiv N$ stretching band matches closely the fitting parameters obtained by multiexponential analysis of the transient UV/Vis measurements, and thus provides key evidence that the early-time dynamics in the UV/Vis results is dictated by these two components.

Thus, TIPs and LIPs can be distinguished by their respective frequency positions of the $C\equiv N$ stretching bands for $TCNE^{\bullet -}$, that is, the component on the red side originates from TIPs, and the component on the blue side from LIPs. A frequency redshift at early times does not a priori indicate a different species, as local excitation of MePe in acetonitrile, wherein 2.25 eV of energy is released on ET, may cause redistribution of excess energy into vibrational modes that may potentially contribute to lowering of transient frequencies.[20] Subsequent vibrational cooling would then also cause similar frequency upshifting on a timescale of tens of picoseconds. In contrast, CT excitation generates a $TCNE^{\bullet -}$ radical anion without significant excess energy. Local excitation of MePe in CH_2Cl_2, where only TIPs can contribute to the observed signals, results in a minor frequency shift in the $C\equiv N$ stretching bands of $TCNE^{\bullet -}$ of about 1 cm^{-1} (with a time constant of around 20 ps, typical for cooling rates in CH_2Cl_2). We thus conclude that the relaxation of excess energy in the case of local excitation is channeled mainly through intramolecular vibrational redistribution in $MePe^{\bullet +}$ and dissipation to the solvent, whereas transient vibrational heating of $TCNE^{\bullet -}$ is only a minor pathway (likely caused by the much smaller spectral density of high-frequency accepting modes in TCNE).

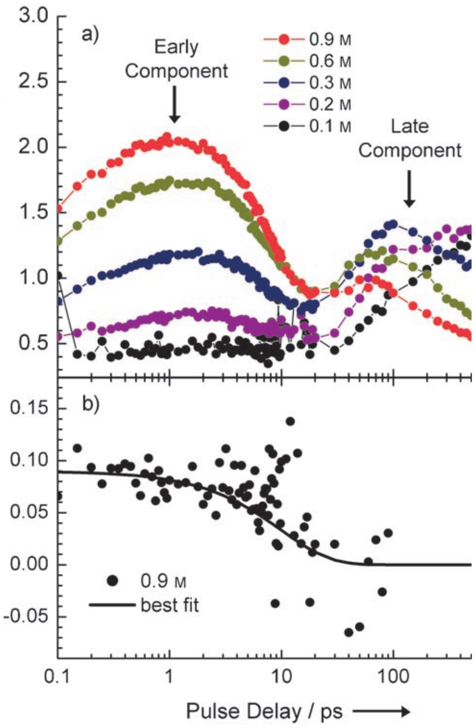

Figure 4. a) The time-dependent magnitude *I* of the $C\equiv N$ stretching band at 2150 cm^{-1} of $TCNE^{\bullet -}$ in ACN, obtained by analyzing the transient spectra at different quencher concentrations, clearly shows an early component dominated by TIPs, and a late component of LIPs governed by diffusional dynamics. b) The anisotropy *r* of this band, measured for 0.9 M TCNE (dots), decays on a similar timescale to the early time component, as indicated by a single-exponential fit with a time constant of 10 ps (solid line).

The fact that the redshifted spectral component is found at the same spectral position, regardless of whether the TIPs are generated by local excitation of MePe or by direct CT excitation of the donor–acceptor complex, suggests that the redshift is due to a significantly different charge distribution in the $TCNE^{\bullet -}$ radical anion. In addition, the early dynamics is essentially the same for LE and CT excitation. On local excitation in ACN, TIPs result from quasistatic quenching of the fraction of MePe (S_1) with a TCNE molecule at optimal position for ultrafast CS, which guarantees strong electronic coupling. Such a situation is favored at higher quencher concentration. Quantum chemical calculations suggest that, in the case of TIPs, the vibrational redshift points to a stronger coupling of $TCNE^{\bullet -}$ with $MePe^{\bullet +}$. However, solvent-induced frequency shifts are of similar magnitude, and the underlying reasons for the frequency shifts may be more intricate.

We now address the question whether TIPs have preferred geometries, or are just generated by a statistical distribution of donor–acceptor complexes at close range. Polarization-sensitive ultrafast infrared spectroscopy[10] can provide insight into this. From the measured value of the anisotropy $r=(S_{\parallel}-S_{\perp})/(S_{\parallel}+2S_{\perp})$, where $S_{\parallel}$ and $S_{\perp}$ are the signals measured for respective parallel and perpendicular polarization of pump and probe pulses, one can calculate the relative angle θ between the electronic and IR transition dipole moments (e.g., $r=0.4$ for $\theta=0$, and $r=-0.2$ for $\theta=90°$). The electronic transition dipole moment for the LE transition is directed along the in-plane long axis of MePe. The IR transition dipole moments are aligned in the plane of TCNE, parallel and perpendicular to the ethylenic bond, for the bands at 2190 and 2150 cm^{-1}, respectively. We measured the anisotropy for both transient bands at early pulse delay times to be $r=0.09\pm0.03$, that is, an average angle of 45° exists between the electronic transition dipole moment $\boldsymbol{\mu}_{\text{el}}$ of MePe and the IR transition dipole moments of the two vibrations $\boldsymbol{\mu}_{\text{IR},1}$ and $\boldsymbol{\mu}_{\text{IR},2}$ (see Figure 1). We note here that we only probe the $v=0\rightarrow v=1$ transition of TCNE$^{\bullet-}$, and corrections for overlapping bleach, stimulated emission and excited-state absorption, typically necessary in UV/Vis experiments, are not necessary in our case. The IR transition dipole moments of these two vibrations $\boldsymbol{\mu}_{\text{IR},1}$ and $\boldsymbol{\mu}_{\text{IR},2}$ are orthogonal (90° angle) to each other. This finding implies that the electronic transition dipole moment of MePe, directed along the long axis of MePe, must be parallel to the plane of the TCNE molecule. Furthermore, within this plane it can be oriented in three different fashions (see Figure 1c): 1) with an angle of 45° with respect to the C=C axis for all TIPs ($\theta=45°$ for both IR transitions), 2) in a statistical distribution of 50% MePe with the long axis oriented parallel and 50% perpendicular to the TCNE C=C axis ($\theta=0°$ and $\theta=90°$ for both IR transitions in equal proportion), and 3) completely random within the plane (θ values for both bands are uniformly distributed between 0 and 360°). Based on these geometric facts and the fact that ultrafast electron transfer rates are found for TIPs, we conclude that MePe and TCNE are aligned in a sandwich-type fashion that maximizes orbital overlap and electronic coupling. Further support for this is provided by our quantum chemical calculations showing equilibrium configurations of MePe-TCNE complexes in the electronic ground state with TCNE aligned either parallel or perpendicular to the MePe long axis (see Figure S3, Supporting Information). Such detailed structural information cannot be obtained from the spectral component of the LIPs appearing at times later than 20 ps, as anisotropy decay due to rotational motions of the ions is by then almost complete.[21]

From our experimental observations we conclude that two types of ion pairs exist: TIPs, most likely with face-to-face alignment of the ions and strong couplings that lead to fast formation and decay rates on subpicosecond timescales, and LIPs in which the CS and CR reaction rates typically lie in the picosecond range. Considering these distinctly different orders of magnitude for the timescales for CS and CR in the case of tight and loose reaction pathways, as well as the fact that diffusional motions are slow, we conclude that rearrangement of tight reactant pairs into loose reactant pairs does not occur before CS proceeds. In addition, CR of TIPs prevents any diffusional motions into LIPs. On the other hand, CR in the weakly coupled LIPs is slow enough to allow separation of the ions to compete. Therefore, these ion pairs are the unique source of free ions. The crucial parameter governing the nature of the primary CS products, TIPs or LIPs, is the distribution of neutral reaction pairs in the ground state. This distribution strongly depends on the quencher concentration, and on the magnitude of interaction between the reactants.

Our finding that the primary reaction products of highly exergonic CS quenching consist of both TIPs (dominant at high quencher concentration and showing dynamics at early times), and LIPs (dominant for lower quencher concentration with formation dynamics at later times) is in strong disagreement with the conventional model invoking a driving-force-dependent ET distance[22] to explain the absence of the inverted regime in bimolecular photoinduced ET.[23] Moreover, current ET theories cannot account for both CS and CR being of ultrafast nature. Considering the sum of the driving forces of the two processes $\Delta G_{\text{CS}}+\Delta G_{\text{CR}}$ to be as large as -3 eV implies that either one of the CS or CR processes should be in the inverted regime. Because of its anisotropic nature, the electronic coupling V at contact distance is much larger than assumed in models with spherical symmetry, where the couplings are averaged over all mutual orientations of the reactants. This means that even if CS at contact distance is in the inverted regime, the couplings are large enough to guarantee ultrafast ET reaction rates, much faster than diffusion. Furthermore, because of the anisotropy, the decrease of V with distance (when TIPs rearrange into LIPs) is much steeper than that assumed for spheres. Then CS always slows down with increasing distance, independent of the magnitude of the driving force. As a consequence, non-Markovian unified theories of CS and CR,[9,24,25] which take the time dependence of the distribution of distances between the reactants into account, should be refined to include orientational degrees of freedom in V.

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