Photoinduced Electron Transfer In Naphthalimide-pyridine Systems: Effect Of Proton Transfer On Charge Recombination Efficiencies

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INTRODUCTION

Achieving long-lived charge separation (LLCS) is crucial for solar energy utilization. In natural photosynthetic organisms, LLCS is accomplished by a series of electron transfer steps to spatially separate radical ions.1 Within less than a nanosecond, oxidized and reduced species are separated by almost 30 Å. Because electron transfer rates fall off exponentially with distance, spatial separation of radical ions reduces drastically the rate of charge recombination, which is demonstrated by a nearly 100% quantum efficiency of charge separation in photosynthetic reaction centers. Inspired by the efficiency of photosynthetic organisms, chemists have developed many artificial donor–acceptor dyads and triads that achieve LLCS by spatially separating the charges.2–4 Most commonly used components for artificial photosynthetic triads include porphyrins as light absorbers, quinones or methyl-viologens as electron acceptors, and carotenoids or amines as electron donors. The lifetimes of charge separated states in these systems extend even to the millisecond time scale.

Another interesting approach to LLCS is to decrease the reorganization energy required for electron transfer. If reorganization energy $\lambda$ is small, the charge recombination will occur deeply in the Marcus inverted region,5 which drastically increases lifetimes of charge separated ions. The efficiency of this approach has been demonstrated by using fullerene as electron acceptors.6,7 Due to the high symmetry and rigid structure of fullerenes, the accepted electron is highly delocalized, leading to small solvent and nuclear reorganization energy required to accommodate the newly produced charge (for example, $\lambda = 0.66$ eV for Zn-porphyrin/C60 dyad6). In organic photovoltaics, the use of C60 as an electron acceptor has significantly increased the solar conversion efficiency of a device.8,9

A third approach to LLCS involves a chemical modification of radical ions formed upon electron transfer. For example, $I^-/I_3^-$ couple was shown to be an excellent redox mediator in dye-sensitized solar cells (DSSC).10 The iodide/triiodide couple is used for the reduction of the oxidized Ru dye (iodide is oxidized in this process: $2I^- \rightarrow I_3^- + e^-$. The $I_3^-$ ion is unstable and undergoes disproportionation reaction to form triiodide ion ($2I_3^- \rightarrow I_5^- + I^-$).11 Thanks to this chemical step, the recombination of electrons in TiO$_2$ and I$_2^-$ does not occur to a large extent and contributes to a large conversion efficiency of DSSCs (11.1%).12 The main disadvantage of the chemical modification approach is the loss of electron energy (voltage) that can be extracted from the device ($\sim 0.75$ V loss in DSSC).

Much less explored approach toward chemical modification of radical ions involves a simple protonation/deprotonation of radical ions. It is known that the acidic/basic properties of radical ions change relative to their neutral analogs: once oxidized, the compound becomes more acidic, while the reduced compound usually becomes more basic. These changes in acid/base properties of radical ions can be used to neutralize the charges formed upon photoinduced electron transfer and achieve LLCS.

ABSTRACT: We studied the effect of proton-coupled electron transfer on lifetimes of the charge-separated radicals produced upon light irradiation of the thiomethyl-naphthalimide donor SMe-NI-H in the presence of nitro-cyano-pyridine acceptor (NO2-CN-PYR). The dynamics of electron and proton transfer were studied using femtosecond pump–probe spectroscopy in the UV/vis range. We find that the photoinduced electron transfer between excited SMe-NI-H and NO2-CN-PYR occurs with a rate of $1.1 \times 10^9$ s$^{-1}$ to produce radical ions SMe-NI-H$^+$ and NO2-CN-PYR$^-$. These initially produced radical ions in a solvent cage do not undergo a proton transfer, possibly due to unfavorable geometry between N–H proton of the naphthalimide and aromatic N-atom of the pyridine. Some of the radical ions in the solvent cage recombine with a rate of $2.3 \times 10^{10}$ s$^{-1}$, while some escape the solvent cage and recombine at a lower rate ($k = 4.27 \times 10^8$ s$^{-1}$). The radical ions that escape the solvent cage undergo proton transfer to produce neutral radicals SMe-NI$^+$ and NO2-CN-PYR-H. Because neutral radicals are not attracted to each other by electrostatic interactions, their recombination is slower that the recombination of the radical ions formed in model compounds that can undergo only electron transfer (SMe-NI-Me and NO2-CN-PYR, $k = 1.2 \times 10^8$ s$^{-1}$). The results of our study demonstrate that proton-coupled electron transfer can be used as an efficient method to achieve long-lived charge separation in light-driven processes.

Photoinduced Electron Transfer in Naphthalimide-Pyridine Systems: Effect of Proton Transfer on Charge Recombination Efficiencies

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For example, Gust and Moore studied photoinduced charge separation in carotenoid/porphyrin/quinone (CPQ) triads to form long-lived C"PQ" radical ions. The authors found that the protonation of the reduced quinone radical anion to form C"PQH" drastically increases radical lifetimes (from 62 ns in nonprotonated to 2.5 μs in the protonated system). An example for LLCS using deprotonation of the oxidized donor has been reported by Hamachi and co-workers, who studied photoinduced electron transfer in a synthetic heme/Ru(bpy)₃/viologen triad incorporated in the myoglobin protein network. The authors found that the lifetime of charge separated state increases 10² to 10³ times if the oxidation of Fe-hydroxyl complex is accompanied by the deprotonation of the hydroxyl group (Fe³⁺—OH → Fe⁴⁺—O).

In this study, we wish to expand on our understanding of proton-mediated electron transfer for achieving LLCS. As model compounds, we chose simple naphthalimide/pyridine donor/acceptor systems presented in Scheme 1. To ensure that the electron transfer flows from the naphthalimide to the pyridine, we incorporated electron-donating groups on naphthalimides (SMe-NI-H and SMe-NI-Me) and electron withdrawing groups on the pyridine (NO₂-CN-PYR). Based on pKₐ values of pyridines and naphthalimides, photoinduced electron transfer from SMe-NI-H to NO₂-CN-PYR is expected to be accompanied by the deprotonation of the hydroxyl group (Fen³⁺—OH → Fe⁴⁺—O).

The Journal of Physical Chemistry A

EXPERIMENTAL SECTION

Synthesis. 2-Cyano-4-nitro-pyridine was purchased from Sigma-Aldrich. All solvents were purchased from Fischer Scientific and used without further purification. Synthesis of SMe-NI-H was reported previously. 1 Ha n d 13 C NMR spectra were recorded using Bruker Avance 300 MHz spectrometer. GC-MS spectra were measured using Shimadzu GC-MS-Q5050A spectrometer.

N-Methyl-4-thiomethyl-naphthalimide (SMe-NI-Me). SMe-NI-Me was prepared from 4-thiomethyl naphthalic anhydride in a reaction with methylamine. Syntheses of 4-thiomethyl naphthalic anhydride were described previously. 17 To a stirred solution of 4-thiomethyl naphthalic anhydride (0.2104 g, 0.8623 mmol) in 100 mL of methanol was added 5 mL of 37% solution of methylamine in ethanol. The mixture was heated for 3 h, cooled down and excess solvent was evaporated. The precipitate was collected and dried in the vacuum. Yield: 70%. MS-EL: m/z 257 [M⁺] calcd
for C\textsubscript{14}H\textsubscript{14}O\textsubscript{2}NS\textsuperscript{+}. \textsuperscript{1}H NMR (300 MHz, DMSO-d\textsubscript{6}), \(\delta\) ppm: 8.54 (dd, \(J_{a,b} = 8.7\) Hz, \(J_{g,b} = 7.5\) Hz, 2H), 8.39 (d, \(J_{a,d} = 7.8\) Hz, 1H), 7.91 (dd, \(J_{g,d} = 7.5\) Hz, \(J_{g,b} = 8.7\) Hz, 1H), 7.67 (d, \(J_{a,d} = 7.8\) Hz, 1H), 3.38 (s, 3H, -SCH\textsubscript{3}), 2.74 (s, 3H, \(-N=CH\textsubscript{3}\)). \textsuperscript{13}C NMR (75 MHz, DMSO-d\textsubscript{6}) \(\delta\) ppm: 161.2, 161.0, 141.3, 131.4 (3-C), 130.9, 129.6, 126.6, 127.7, 127.6, 121.9, 118.6, 14.6 (SCH\textsubscript{3}), 12.1 (\(-N=CH\textsubscript{3}\)).

**Steady-State Spectroscopy.** Absorption spectra were recorded on Agilent 8453 UV spectrometer in a 2 mm quartz cell. Fluorescence spectra were recorded on Edinburg Instruments Fluorimeter equipped with Xe900 lamp in 1 cm quartz cell. For fluorescence measurements, naphthalimide solutions were prepared with absorption of 0.05–0.1 at the excitation wavelength. SMe-NI-H and SMe-NI-Me were excited at 356 nm.

**Binding Constant Determination.** We evaluated the binding constant between SMe-NI-H and deuterated pyridine in CDCl\textsubscript{3} using \(^1\)H NMR spectroscopy. A shift of the SMe-NI-H N-H peak was monitored as a function of varying concentrations of deuterated pyridine. Stock solutions of SMe-NI-H (\(c = 1.23\) mM) and deuterated pyridine (\(c = 1.4\) mM) in CDCl\textsubscript{3} were mixed in several different ratios and the shift of the N–H peak was plotted as a function of pyridine concentration. The binding constant was obtained using the following equation:

\[
\frac{1}{\Delta\delta} = \frac{1}{K \cdot \Delta\delta_{\text{max}}} \cdot \frac{1}{[\text{PYR-d}]} + \frac{1}{\Delta\delta_{\text{max}}}
\]

where [PYR-d] is the concentration of deuterated pyridine, \(\Delta\delta\) is a difference in the N–H chemical shift between SMe-NI-H in the presence and absence of PYR-d, \(\Delta\delta_{\text{max}}\) is the difference in the N–H chemical shift between SMe-NI-H in chloroform and in pure PYR-d. The binding constant of \(K = 3 \pm 1\) M\(^{-1}\) was obtained for SMe-NI-H/pyridine complexation in chloroform.

**Electrochemistry.** Cyclic voltammograms were obtained at room temperature using a BAS Epsilon electrochemistry setup equipped with Pt-working electrode, nonaqueous Ag/Ag\textsuperscript{+} reference electrode (0.01 M AgNO\textsubscript{3} in 0.1 M N(C\textsubscript{4}H\textsubscript{9})\textsubscript{4}ClO\textsubscript{4} nonaqueous Ag\textsuperscript{+}/Ag electrode. The changes in the absorption spectra were recorded using Agilent 8453 UV spectrometer.

**Excited-State Behavior of Nahpthalimides.** In the previous study, we investigated the excited state behavior of a series of naphthalimide derivatives, including SMe-NI-H.\textsuperscript{17} We found that the photophysics of SMe-NI-H are dictated by two closely-lying excited states: (i) \(^1\)n,\textit{\(\pi\)}* (S\textsubscript{1}) state in which the nonbonding oxygen electrons of the imide moiety are promoted to the \(\pi^*\) orbital of the naphthalimide, and (ii) \(\pi,\textit{\(\pi\)}^*\) (S\textsubscript{2}) state with a significant charge transfer character (SMe group acts as an electron donor). Pump–probe experiments showed that the initially produced S\textsubscript{2} (\(^1\)n,\textit{\(\pi\)}*) state quickly decays to form a long-lived S\textsubscript{1} (\(\pi,\textit{\(\pi\)}^*\)) state with charge transfer character.

For our current studies of photoinduced electron transfer between naphthalimides and NO\textsubscript{2}-CN-PYR, it is important to show that methylated and protonated naphthalimides exhibit the same excited-state behavior. This assures that the only difference in the electron transfer dynamics of methylated and protonated naphthalimides is caused by the proton motion in the case of protonated systems. Thus, we present here a careful comparison of the photophysics of the methylated naphthalimide SMe-NI-Me with the previously studied protonated analog SMe-NI-H.

**RESULTS AND DISCUSSION**

**Spectroelectrochemistry was performed to obtain the absorption spectrum of NO\textsubscript{2}-CN-PYR\textsuperscript{+}.** The reduction of NO\textsubscript{2}-CN-PYR (\(c = 2\) mM) in chloroform containing 0.1 M N(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}ClO\textsubscript{4} was performed at the controlled potential of \(-1.22\) V versus Fc (using Epsilon potentiotstat). Electrodes used were as follows: working, gold mesh electrode; counter, Pt wire; reference, nonaqueous Ag\textsuperscript{+}/Ag electrode. The changes in the absorption spectra were recorded using Agilent 8453 UV spectrometer.

**Pump–Probe Measurements.** The laser system for the ultrafast transient absorption measurements was described elsewhere.\textsuperscript{19} The 800 nm pulse was generated by a mode-locked Ti:Sapphire laser (Hurricane, Spectra-Physics) at 1 kHz frequency. The pulse width (\(\sim 110\) fs) was determined by autocorrelator (Positive Light). The beam output from Hurricane was split into pump (85%) and probe (8%) beams. The pump beam was sent through second harmonics generator (Super Tripler, CSK) to obtain a 400 nm excitation source (pump). The energy of the pump was 2 mJ/pulse. The probe beam was sent through the delay stage (MM 4000, Newport) and then focused into a CaF\textsubscript{2} crystal for white light continuum generation between 350 and 770 nm. The sample concentrations were 0.4–0.5 mM in chloroform (HPLC grade, stabilized by amylene). The flow cell (Spectrocell Inc., 0.7 mL volume with 2 mm path length), pumped by a Fluid Metering R51106 Y Lab pump (Scientific Support Inc.), was used to prevent photodegradation. Transient absorption spectra were collected using a CCD camera (Ocean Optics, S2000).

**Data Processing and Analysis.** (i) Chirp correction was determined using nonresonant optical Kerr effect (OKE) measurements;\textsuperscript{20} (ii) Noise was reduced using a singular value decomposition (SVD) method using a code written in Matlab 7.1; (iii) Transient absorption data were analyzed using SPECFIT/32 Global Analysis System (Spectrum Software Associates, MA, U.S.A.). This program allows a decomposition of transient absorption data using kinetic models. The analysis is achieved by a global analysis method that uses singular value decomposition method to reduce the size of the fitted data.\textsuperscript{21} First, we performed global analysis of the data to determine the sufficient number of decay components and obtain the decay-associated difference spectra (DADS). Once we obtained the decay lifetimes, we applied a series of models and the goodness of the fit was judged using the value of root-mean-square error. This procedure provided species-associated difference spectra (SADS) presented in this manuscript.

**DFT Calculations.** All computations were performed at the Ohio Supercomputer Center. Geometry optimizations were performed using Gaussian 03\textsuperscript{22} with Becke’s three-parameter hybrid exchange functional with Lee–Yang–Parr correlation functional (B3LYP).\textsuperscript{23} We used 6-31+G* basis set\textsuperscript{24} and the solvent effect (chloroform) was calculated using polarizable continuum model (PCM).\textsuperscript{25–28} All stationary points were confirmed to be energy minima using vibrational frequency calculations (B3LYP/6-31+G*), which showed that all of the computed vibrational frequencies were nonimaginary. Vertical transition energies and difference density plots were then calculated at the TD-B3LYP/6-31+G* level of theory.\textsuperscript{29}
naphthalimides. The absorption (fluorescence) of −SMe derivatives appear at 390 nm (445 nm), and the methylated and protonated derivatives exhibit almost identical spectral features.

To assign the excited-state character of the methylated derivative, we performed time-dependent density functional theory (TD DFT) calculations for SMe-NI-Me using B3LYP/6-31 +G* (PCM model for chloroform) methodology. Atom labels: carbon (gray); oxygen (red); nitrogen (blue); sulfur (yellow); hydrogen (white). Red color represents the depletion of the electron density in the excited state, while green represents accumulation of the electronic density in the excited state.

Figure 1. Normalized absorption and fluorescence spectra of SMe-NI-Me and SMe-NI-H in CH2Cl2 (c = 60 μM). Excitation wavelengths for fluorescence spectra was $\lambda = 390$ nm for SMe-NI-H and SMe-NI-Me.

Figure 2. $S_1-S_0$ and $S_2-S_0$ difference density plots for SMe-NI-Me obtained using B3LYP/6-31+G* (PCM model for chloroform) methodology. Atom labels: carbon (gray); oxygen (red); nitrogen (blue); sulfur (yellow); hydrogen (white). Red color represents the depletion of the electron density in the excited state, while green represents accumulation of the electronic density in the excited state.

Figure 3. (a) Transient absorption spectra for SMe-NI-Me at 510 nm recorded for the S2 state. The absorption maximum shifts to lower wavelength (450 nm) within 10 ps after the 400 nm excitation. (b) Transient absorption spectra for SMe-NI-H at 510 nm recorded for the S2 state. The absorption maximum shifts to lower wavelength (450 nm) within 10 ps after the 400 nm excitation. (c) Transient absorption spectra for SMe-NI-Me at 510 nm recorded for the S1 state. The absorption maximum shifts to lower wavelength (450 nm) within 10 ps after the 400 nm excitation.

Electrochemistry. The driving force for photoinduced electron transfer between naphthalimides and NO2-CN-PYR was evaluated using oxidation and reduction potentials obtained using cyclic voltammetry. As can be seen from Figure 4A, cyclic
Figure 3. (a) Transient absorption spectra of SMe-NI-Me in chloroform (c = 0.4 mM) obtained at 0–10 ps delays after the 400 nm excitation pulse; (b) spectra and lifetimes of two SMe-NI-Me components obtained using global analysis; (c) decays at 500 nm obtained for SMe-NI-H (red) and SMe-NI-Me (black).

Figure 4. (A) Cyclic voltammograms of SMe-NI-H (red) and SMe-NI-Me (black) in chloroform (c = 1 mM). (B) Cyclic voltammograms for NO2-CN-PYR (c = 2 mM) in chloroform (black) and acetonitrile (blue). Tetrabutyl-ammonium perchlorate was used as a supporting electrolyte. Sweep rate: 100 mV/s. Working electrode: platinum; counter electrode: platinum wire; reference electrode: Ag/Ag+ (nonaqueous).

Table 1. Estimates of the Driving Force for Photoinduced Electron Transfer and Geminate Recombination between Naphthalimides and NO2-CN-PYR

<table>
<thead>
<tr>
<th></th>
<th>( \Delta G_0^\ddagger ) (eV)</th>
<th>( \Delta G_{e^0}^\ddagger ) (eV)</th>
<th>( \Delta G_{f^\ddagger}^\ddagger ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMe-NI-H</td>
<td>1.95</td>
<td>2.98</td>
<td>2.59</td>
</tr>
<tr>
<td>SMe-NI-Me</td>
<td>1.95</td>
<td>2.98</td>
<td>2.59</td>
</tr>
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*Because the oxidation potential is chemically irreversible, we tabulated the potentials of anodic peaks from cyclic voltammograms. \( S_1-S_0 \) energy gap (\( E_{\text{red}} \)) was calculated as a half point between absorption and fluorescence maxima (Figure 1). Calculated using Rehm–Weller equation: \( \Delta G_i = (E_{\text{ox}} - E_{\text{red}}) - E_{\text{f}} \), where \( E_{\text{ox}} = 0.64 \) V (reduction potential of NO2-CN-PYR). d Calculated using \( \Delta G_0 = E_{\text{red}} - E_{\text{f}} \).

Spectroelectrochemistry was performed to determine the spectral features of radicals involved in the electron transfer. Figure 5 shows the spectrum of NO2-CN-PYR radical anion obtained upon reduction of NO2-CN-PYR at −1.0 V versus NHE. Before electrolysis, the absorption spectrum of NO2-CN-PYR consists of a band with a maximum at 280 nm. During electrolysis, we observe the growth of new absorption bands with maxima at 270, 325, and 480 nm, which we assign to the absorption of NO2-CN-PYR radical anion (NO2-CN-PYR−). Thus, in our studies of photoinduced electron transfer using transient absorption, we expect to observe the growth of an absorption band at 480 nm. In our studies of PCET, we expect the formation of neutral NO2-CN-PYR radical (NO2-CN-PYR-H), whose spectrum is not known. However, we expect that the spectrum of neutral radical is similar to the spectrum of radical anion presented in Figure 7. For example, the absorption spectrum of...
4-carbamylpyridinyl radical anion (∼390 nm) is slightly blue-shifted relative to the absorption spectrum of its conjugate acid (410 nm). We also attempted to obtain the spectrum of radical cations of naphthalimides by performing spectroelectrochemical measurements during anodic oxidation of SMe-NI-H. However, we were unable to record the absorption spectra due to chemical instability of these radical cations. Based on the previous studies with naphthalene radical cation, we expect the radical cations of naphthalimides to exhibit very weak absorption in the visible range. Therefore, we do not anticipate to observe these transients in our transient absorption measurements.

**Photoinduced Electron Transfer.** Photoinduced electron transfer between SMe-NI-H and NO$_2$-CN-PYR was studied using pump–probe spectroscopy (Figure 6C,D). In the presence of NO$_2$-CN-PYR, transient absorption signal of SMe-NI-H decays faster at all probe wavelengths, which is consistent with the electron transfer process from excited SMe-NI-H to NO$_2$-CN-PYR. The most drastic change is observed at 500 nm, where SMe-NI-H in the absence of NO$_2$-CN-PYR exhibits stimulated emission (Figure 6D, black curve). In the presence of NO$_2$-CN-PYR, the stimulated emission signal does not appear, and instead a positive signal persists for ∼20 ps (Figure 6D, red curve). Based on spectroelectrochemical measurements (Figure 5), we assign the transient signal at 500 nm to the NO$_2$-CN-PYR radical. To confirm that the photoinduced electron transfer to NO$_2$-CN-PYR is responsible for changes in the SMe-NI-H signal, we performed pump–probe experiments on SMe-NI-H in the presence of pyridine. Pyridine is similar in structure to NO$_2$-CN-PYR, but its reduction potential is too negative for photoinduced electron transfer from excited SMe-NI-H to take place (the reduction potential of pyridine is −2.76 V, the driving force for the electron transfer between excited SMe-NI-H/SMe-NI-Me and pyridine is ΔG = +1.73 eV). As expected, the excited-state behavior of SMe-NI-H does not change if pyridine is added to the solution (Figure 6A,B). These results confirm that the deactivation of SMe-NI-H excited state in the presence of NO$_2$-CN-PYR is caused by photoinduced electron transfer and not some other deactivation pathway, such as excited-state deprotonation of the N–H proton in SMe-NI-H.

We investigated the electron transfer dynamics at several NO$_2$-CN-PYR concentrations (Figure 7). The rate of electron transfer is concentration-dependent, suggesting that the process is diffusion-controlled. This result suggests that the hydrogen-bonded complex between SMe-NI-H and NO$_2$-CN-PYR does not form at the appreciable degree, and is consistent with the low association constant for the formation of SMe-NI-H/pyridine complex (K = 3 M$^{-1}$) determined using $^1$H NMR spectroscopy (see Experimental Section for more information). We were not able to determine the association constant for SMe-NI-H/NO$_2$-CN-PYR complex due to the overlap of the N–H proton signal of SMe-NI-H with the proton signals of NO$_2$-CN-PYR. However, due to the electron-withdrawing nature of nitro and cyano substituents of NO$_2$-CN-PYR, we predict that this binding constant is even lower than the K = 3 M$^{-1}$ we obtained in the case of pyridine. Thus, the electron transfer process studied here does not involve the electron transfer of the preassociated complex.

The occurrence of PCET in SMe-NI-H/NO$_2$-CN-PYR was investigated by comparing the dynamics of SMe-NI-H decay with those of SMe-NI-Me. In contrast to SMe-NI-H, which can undergo PCET, the methylated SMe-NI-Me does not have acidic protons and can perform only an electron transfer process. Figure 8 compares the decays of SMe-NI-H and SMe-NI-Me transient absorption signals in the presence of high concentration of NO$_2$-CN-PYR. At 625 nm, the only absorbing species is the excited SMe-NI-H (or SMe-NI-Me). Thus, the decay at this wavelength is associated with the rate of the forward electron transfer. As can be seen from Figure 8A, the decays of SMe-NI-H and SMe-NI-Me are similar, with a slightly faster decay in the case of SMe-NI-Me. Both decays were fit to a biexponential function: lifetimes for SMe-NI-H were τ$_1$ = 40 ps and τ$_2$ = 903 ps, while those for SMe-NI-Me were τ$_1$ = 40 ps and τ$_2$ = 667 ps. The 40 ps component is present in all SMe-NI-H samples and was discussed previously. The lifetimes τ$_2$ are associated with the diffusion-controlled photoinduced electron transfer between SMe-NI-H (or SMe-NI-Me) and NO$_2$-CN-PYR, and show that the rate is similar, but slightly faster in the case of SMe-NI-Me.
Given the similarity in the decay dynamics ($k_f = 1.1 \times 10^9$ s$^{-1}$ for SMe-NI-H and $k_f = 1.5 \times 10^9$ s$^{-1}$ for SMe-NI-Me, Table 2), we conclude that both processes involve only a transfer of the electron, without the accompanying proton transfer. The small difference in the electron transfer rates between SMe-NI-Me and NO$_2$-CN-PYR can be assigned to a larger electronic coupling constant for electron transfer between SMe-NI-Me and NO$_2$-CN-PYR.

The charge recombination rates were obtained from the decays of SMe-NI-H/SMe-NI-Me signals at 500 nm (Figure 8B). The transient absorption at this wavelength arises due to three signals: (i) excited-state absorption due to $S_2$ state of SMe-NI-H (or SMe-NI-Me); (ii) stimulated emission due to $S_1$ state of SMe-NI-H (or SMe-NI-Me); (iii) the absorption due to NO$_2$-CN-PYR radical (or radical anion). The absorption by radical cation of SMe-NI-H (or SMe-NI-Me) is not expected to be detectable via transient absorption, as illustrated in previous studies of radical cations of similar naphthalimide derivatives. 40,41 We extracted the contribution due to NO$_2$-CN-PYR radical by subtracting the contribution from $S_1$ and $S_2$ states of SMe-NI-H/SMe-NI-Me.

For this purpose, we assumed that the decay at 625 nm arises purely due to SMe-NI-H excited state. We scaled and subtracted this contribution from the decay at 500 nm, and the NO$_2$-CN-PYR radical signal obtained using this approach is presented in Figure 9. We used this approach in previous studies of photoinduced electron transfer in micelles and liquids to extract the dynamics of the Rhodamine B radical. 41,42 As can be seen from Figure 9, the decays of NO$_2$-CN-PYR$^*$ (formed in the presence of SMe-NI-Me) and neutral NO$_2$-CN-PYRH$^*$ (formed in the presence of SMe-NI-H) are different. Both signals decay biexponentially with lifetimes of $\tau_1 = 44$ ps and $\tau_2 = 2340$ ps in the case of SMe-NI-Me and of $\tau_1 = 75$ ps and $\tau_2 = 835$ ps in the case of SMe-NI-Me. We assign the shorter $\tau_1$ component to recombination of radical pairs at a contact distance (in the solvent cage), while the longer-lived component $\tau_2$ possibly arises due to the diffusion-limited recombination of the solvent-separated radicals. The values for charge recombination in the solvent cage for SMe-NI-H and SMe-NI-Me are similar ($k_{b2}$ values in Table 2). Thus, we assign this process to the electron recombination between radical ions, without the accompanying proton transfer. On the other hand, the recombination of solvent-separated radical pairs exhibits and opposite trend: $\tau_2$ component is longer-lived in the case of SMe-NI-H, which we assign to be due to proton-coupled electron transfer.

Scheme 2 outlines electron transfer and proton-coupled electron transfer processes that occur in our study. We postulate

that the photoinduced electron transfer between excited SMe−NI-H (or SMe-NI-Me) and NO2−CN-PYR forms solvent-caged radical ion pairs with a rate of $k_f \sim 1 \times 10^{10}$ s$^{-1}$. Even though SMe-NI-H offers the possibility of the proton-coupled process, we conclude that the proton transfer does not occur during this early charge-transfer process. This conclusion is based on the similarity between $k_f$ values in SMe-NI-H and SMe-NI-Me model compounds. The possible reason for the lack of proton transfer during the initial electron transfer process is the unfavorable orientation of the imide N−H group relative to the pyridine N-atom. For efficient electron transfer, the donor/acceptor aromatic moieties are oriented in the π-stacked geometry. At this geometry, the proton transfer will not be favored, due to large distance and unfavorable orientation between N−H moiety of SMe-NI-H and aromatic N-atom of NO2-CN-PYR. Once the solvent-caged radical ions are formed, some of them recombine with the rate of $k_{b1} \sim 1−2 \times 10^{10}$ s$^{-1}$. Some radical ions escape the solvent cage and their recombination occurs at a lower rate $k_{b2}$. In this case, we observe an interesting reversal of rates constant values: the recombination rate becomes slower in the case of SMe-NI-H, suggesting that the solvent-separated ion-pairs undergo proton transfer process to produce neutral radicals. Because the neutral radicals formed upon proton transfer are not attracted to each other by electrostatic interactions, their recombination is slower than the recombination of the charged radical ions produced from SMe-NI-Me. This results in a significant reduction of the $k_{b2}$ values in the case of SMe-NI-H ($k_{b2} = 4.3 \times 10^9$ s$^{-1}$) relative to that of SMe-NI-Me ($k_{b2} = 1.2 \times 10^9$ s$^{-1}$).

**CONCLUSIONS**

We compared the recombination rates of radicals produced in two model systems: (i) SMe-NI-Me and NO2-CN-PYR, where photoinduced electron transfer produces charged radical ions, and (ii) SMe-NI-H and NO2-CN-PYR, where proton-coupled electron transfer produces neutral radicals. We initially compared the electronic properties of SMe-NI-H and SMe-NI-Me to demonstrate that the two derivatives exhibit very similar electrochemical and excited-state behavior. Based on their similar electronic properties, we conclude that SMe-NI-H and SMe-NI-Me can be used to study the effect of proton transfer on the rates of radical recombination. Using ultrafast pump–probe spectroscopy, we obtained the rates of forward and back electron transfer in the two model systems. We found that the initial charge separation involves electron transfer to produce radical ion pairs in the solvent cage (with a rate of $\sim 1 \times 10^{10}$ s$^{-1}$). A portion of solvent-caged radical ions quickly recombine (with a rate of $\sim 1 \times 10^{10}$ s$^{-1}$). We postulate that the proton transfer does not occur during these early time events, possibly due to unfavorable orientation of SMe-NI-H and NO2-CN-PYR. However, a portion of radical ions manage to escape the solvent cage and they recombine at the longer time scale. This process appears to be accompanied by the proton transfer in the case of SMe-NI-H, producing neutral radical pairs. We find that the recombination rate is slower in the case of SMe-NI-H ($4.27 \times 10^9$ s$^{-1}$) than in the case of SMe-NI-Me ($1.2 \times 10^9$ s$^{-1}$), and we attribute this difference to the lack of electrostatic attraction between the neutral radicals in the case of SMe-NI-H. Our results demonstrate that the proton-coupled electron transfer can be successfully used to achieve long-lived charge separation in the light-driven donor−acceptor systems.

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