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Photochemically Removable Protecting Groups Based on Covalently Linked Electron Donor−Acceptor Systems

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Abstract: Photoremovable protecting groups based on intramolecular electron transfer have been synthesized and studied. One molecule contains a *N,N*-dimethylaniline chromophore covalently linked to a phenacyl ester of acetic acid. UV photolysis of this molecule results in the release of acetic acid. Laser flash photolysis experiments show that photolysis creates an intramolecular charge-transfer state that has a lifetime of approximately 500 ns. This charge-transfer state partitions between a bond scission pathway leading to elimination of acetic acid and a charge-recombination pathway leading back to ground-state reactants. An analogous system, using an anthracene chromophore, was also synthesized. This did not release the carboxylic acid upon UV photolysis. Instead, laser flash photolysis experiments showed rapid formation of an anthracene-localized triplet excited state.

Technological advances in areas such as photolithographic fabrication of DNA-chip sensors,[1−5] photomodulation of cellular functions,[6−9] and time-resolved X-ray crystallography[10] have increased demand for photoremovable protecting groups (PRPGs) with improved properties. Recent advances include new PRPGs based on phenacyl photochemistry, [11−13] benzophenone photochemistry,[14] and coherent two-photon absorption.[15]

In previous work we identified a novel approach based on photochemically induced electron transfer.[16−19] Specifically, we showed that irradiation of an excited-state electron donor molecule (sensitizer) in the presence of a phenacyl ester could effect release of the corresponding carboxylic acid in excellent isolated yields. The initial photochemical step leading to release is one-electron transfer from the excited sensitizer molecule to the phenacyl group. It was further demonstrated that the wavelengths required to initiate release could be controlled through judicious choice of the sensitizer. For example, 2-aminoanthracence allowed for photorelease with visible (>400 nm) light.[18] Thus this approach allows for modular design of PRPGs where the light-absorption step and the bond-breaking step can be optimized separately. In the previous examples the sensitizer was included as a separate additive. Therefore, the rate (and thus quantum yield) of photorelease is limited by the probability of encounter between the electronically excited sensitizer and the phenacyl ester substrate.

Although the two-component approach may be desirable in certain applications, we also anticipated a need for a single-component PRPG. For example, when photorelease in vivo is desired it may not be possible to introduce both the sensitizer and masked molecule in sufficiently high concentrations to effect photorelease in reasonable exposure times. Complex matrixes might also contain other redox-sensitive molecules, which would also be susceptible to undesired electron transfer from the sensitizer. For these reasons we have begun to examine covalently linked electron donor−acceptor systems that are designed to release carboxylic acids upon absorption of a photon. There are several challenges in designing such systems. First, the photolysis must lead to efficient charge separation. Second, the charge-separated state should be sufficiently energetic to break the desired bond. Third, this bond-breaking event must occur more rapidly than the competing back electron-transfer processes.

Compounds **1a** and **2a** (Chart 1) were prepared, and their photochemical and photophysical behaviors in CH_3CN were examined. The dimethylaniline-based system (**1a**) successfully releases acetic acid upon photolysis. Laser flash photolysis (LFP) experiments show that the desired charge-transfer state is

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(1) Fodor, S. P. A.; Read, J. L.; Pirrung, M. C.; Stryer, L.; Lu, A. T.; Solas, D. *Science (Washington, DC)* **1991**, *251*, 767−773.

(2) Gallop, M. A.; Barrett, R. W.; Dower, W. J.; Fodor, S. P. A.; Gordon, E. M. *J. Med. Chem.* **1994**, *37*, 1233−1251.

(3) McGall, G.; Labadie, J.; Brock, P.; Wallraff, G.; Nguyen, T.; Hinsberg, W. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 13555−13560.

(4) McGall, G. H.; Barone, A. D.; Diggelmann, M.; Fodor, S. P. A.; Gentalen, E.; Ngo, N. *J. Am. Chem. Soc.* **1997**, *119*, 5081−5090.

(5) Pirrung, M. C.; Fallon, L.; McGall, G. *J. Org. Chem.* **1998**, *63*, 3, 241−246.

(6) Corrie, J. E. T.; Trentham, D. R. *Caged Nucleotides and Neurotransmitters*; Morrison, H., Ed.; Wiley: New York, 1993; pp 243−304.

(7) Gee, K. R.; Kueper, L. W.; Barnes, J.; Dudley, G.; Givens, R. S. *J. Org. Chem.* **1996**, *61*, 1228−1233.

(8) Rossi, F. M.; Margulis, M.; Tang, C.-M.; Kao, J. P.-Y. *J. Biol. Chem.* **1997**, *272*, 32933−32939.

(9) Hess, G. P.; Grewer, C. *Methods Enzymol.* **1998**, *291*, 443−473.

(10) Schlichting, I.; Almo, S. C.; Rapp, G.; Wilson, K.; Petratos, K.; Lentfer, A.; Wittinghofer, A.; Kabsch, W.; Pai, E. F.; Petsko, G.; Goody, R. S. *Nature* **1990**, *345*, 309−315.

(11) Pirrung, M. C.; Bradley, J.-C. *J. Org. Chem.* **1995**, *60*, 1116−1117.

(12) Givens, R. S.; Jung, A.; Park, C.-H.; Weber, J.; Bartlett, W. *J. Am. Chem. Soc.* **1997**, *119*, 8369−8370.

(13) Klán, P.; Zabadel, M.; Heger, D. *Org. Lett.* **2000**, *2*, 1569−1571.

(14) Jones, P. B.; Pollastri, M. P.; Porter, N. A. *J. Org. Chem.* **1996**, *61*, 9455−9461.

(15) Furuta, T.; Wang, S. S.-H.; Dantzker, J. L.; Dore, T.; Bybee, e. J.; Callaway, E. M.; Denk, W.; Tsien, R. Y. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 1193−2000.

(16) Banerjee, A.; Falvey, D. E. *J. Org. Chem.* **1997**, *62*, 6245−6251.

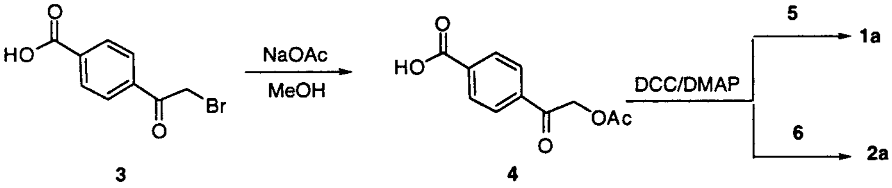
(17) Banerjee, A.; Falvey, D. E. *J. Am. Chem. Soc.* **1998**, *120*, 2965−2966.

(18) Banerjee, A.; Lee, K.; Yu, Q.; Fang, A. G.; Falvey, D. E. *Tetrahedron Lett.* **1998**, *39*, 4635−4638.

(19) Banerjee, A.; Lee, K.; Falvey, D. E. *Tetrahedron* **1999**, *55*, 12699−12710.

10.1021/ja9939441 CCC: $19.00

Scheme 1



Scheme 2

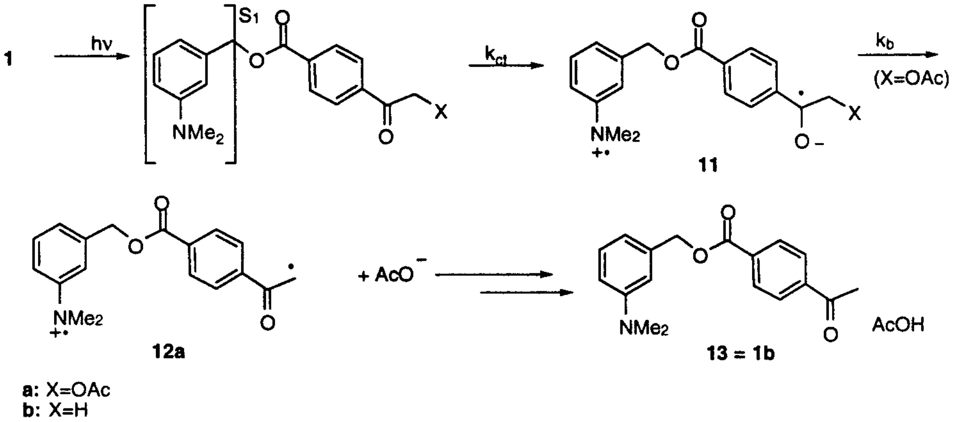
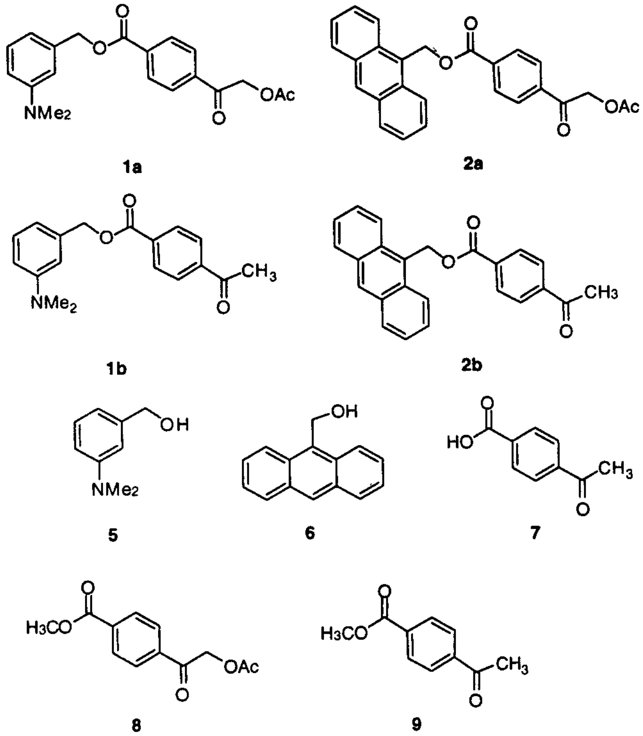


Chart 1



efficiently created and lives for ca. 500 ns. The quantum yield for carboxylate release is limited by the rate of C−O bond scission, which is somewhat slower in the linked system than it is in the parent phenacyl system. The anthracene-based system **2a** shows no release of the carboxylate anion, even after prolonged irradiation. This is attributed to efficient formation of an anthracene-based excited triplet state (2^{T1} , see Scheme 3, below) through efficient back electron transfer.

Results and Discussion

The linked donor−acceptor compounds **1a** and **2a** were synthesized via the routes depicted in Scheme 1. In brief, 4-(α-bromoacetyl)benzoic acid (**3**) was combined with sodium acetate to give 4-(α-acetoxyacetyl)benzoic acid (**4**). The latter was coupled with either 3-hydroxymethyl-*N*,*N*-dimethylaniline (**5** in the case of **1a**) or 9-hydroxymethylanthracene (**6,** in the case of **2a**) using *N*,*N*-dicyclohexylcarbodiimide (DCC) to give the linked systems. Two model compounds, **1b** and **2b**, were also synthesized by coupling 4-acetylbenzoic acid **7** with the corresponding alcohols (**5** or **6**). Model compounds **1b** and **2b** were designed to undergo the same electron-transfer reaction as **1a** and **2a**, but were incapable of releasing a carboxylate anion.

The UV absorption spectrum of **1a** corresponds to the sum of the spectra of the two chromophores in this linked system, namely the *N*,*N*-dimethylaniline group and the 4-carboxyacetophenone group. This is illustrated in Figure 1, which shows the spectrum for **1a** along with that for two molecular models for the isolated chromophores, 3-(*N*, *N*-dimethyl)benzyl alcohol **5** and 4-carbomethoxyphenacyl acetate **8**. The singlet energy of the chromophores is estimated from the absorption onset of the two models. For **5** this is 335 nm, corresponding to an energy of 84 kcal/mol for the aniline antenna. For **8** this corresponds to 315 nm or 91 kcal/mol. Thus, the first excited singlet state (S_1) of **1a** is considered to be localized on the antenna group and the next highest singlet excited state (S_2) is considered to be localized on the acetophenone group. This is illustrated in Figure 2 along with the projected triplet energies of the individual chromophores. The latter were estimated from available literature data for *N*,*N*-dimethylaniline and acetophenone.[24] The two triplet states are very close in energy (ca. 1 kcal/mol). Thus it is not certain which chromophore possesses the lower energy triplet state.

Also shown in Figure 2a is the energy level of the charge-transfer state (CT depicted as **11** in Scheme 2) resulting from

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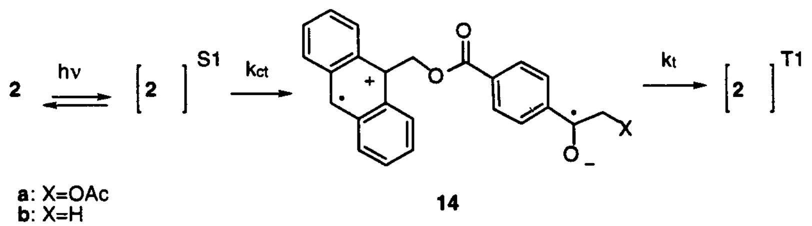
(20) Zhang, X.; Yeh, S.-R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211−4220.

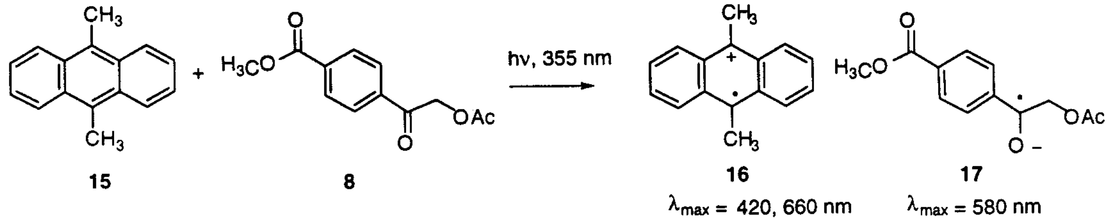
(21) Lutz, H.; Bréhéret, E.; Lindqvist, L. *J. Phys. Chem.* **1973**, *77*, 1758−1762.

(22) Compound **1b** is photolyzed, but much more slowly than **1a**. Its decomposition rate is therefore assumed to be negligible relative to the rate of back electron transfer.

Scheme 3



Scheme 4



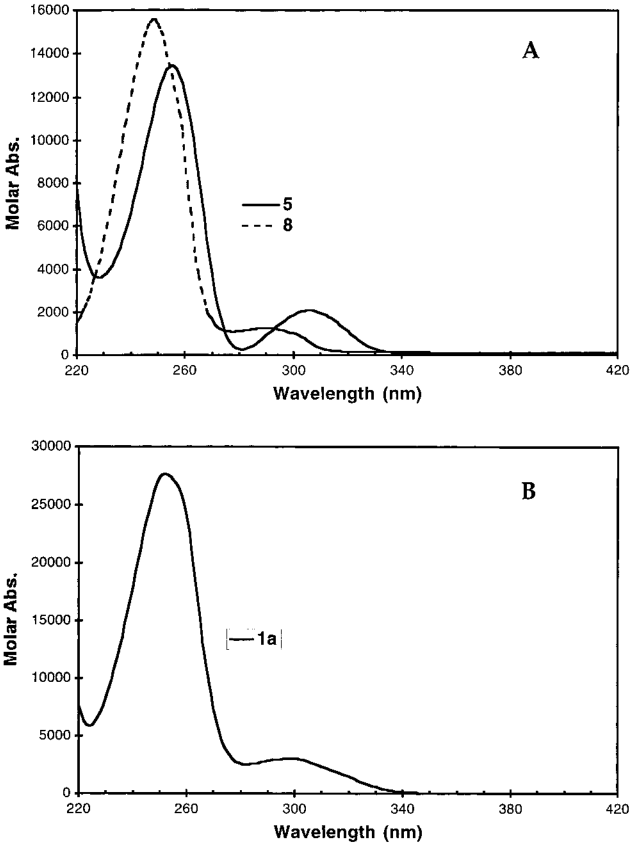


Figure 1. UV–vis absorption spectra (CH_3CN) for model chromophores **5** and **8** (panel A, solid and dashed lines, respectively) and linked PRPG **1a** (panel B).

electron-transfer from the aniline chromophore to the acetophenone chromophore. This energy was calculated from eq 1 using the literature oxidation potential of *N*,*N*-dimethylaniline (E_{ox}) and the reduction potential (E_{red}) 4-carbomethoxyacetophenone **9**. We measured the latter as −1.58 V [vs saturated calomel electrode (SCE)] using cyclic voltammetry.

$$\Delta G_{ct} = 23.06(E_{ox} - E_{red}) \tag{1}$$

Figure 2b shows the corresponding potential energy diagram for **2a**, which was constructed in the same way as that for **1a**. The energies of S_1 and T_1 were estimated from energies of the corresponding excited states of 9-methylanthracene. The acetophenone-localized excited states (S_2 and T_2) were considerably higher in energy. For **2a** the charge-transfer state (**14** in Scheme 3) is higher in energy than T_1. The significance of this will become apparent below.

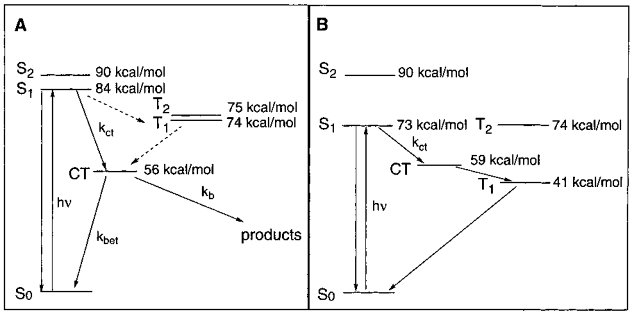


Figure 2. State energy level diagram for linked aniline-phenacyl compounds **1** (A) and linked anthracene-phenacyl compounds **2** (B).

The photochemical behavior of the linked systems is summarized in Schemes 2 and 3. Photolysis of these molecules creates a dimethylaniline- or anthracene-localized singlet excited state (S_1). The latter partition between fluorescence and formation of charge-transfer states (**11** in the case of **1** and **14** in the case of **2**) through the process labeled k_{ct}.

That electron transfer occurs upon excitation of the chromophores in **1** and **2** can be inferred from two observations. First, the free energy change for electron transfer from the excited-state chromophores to the phenacyl group is calculated to be exergonic (−35.3 kcal/mol for **1** and −15.9 kcal/mol for **2**).[16] Second, both linked systems show a substantial diminishment of their fluorescence intensity relative to that of their parent chromophores as illustrated in Table 1. The fluorescence yield of **1a** is only 11% compared with **5**, and the fluorescence yield of the model compound **1b** is only 9%. The fluorescence yield of **2a** is 4% relative to **6**, and the value for the model system **2b** is 0.8%. The quantum efficiency of charge transfer ϕ_{ct} can be estimated using eq 2, where the second term is the ratio of fluorescence intensities. The values of ϕ_{ct} are thus 0.89 for **1a**, 0.91 for **1b**, 0.96 for **2a**, and 0.99 for **2b.** In no case was exciplex emission observed.

$$\phi_{ct} = 1 - \frac{I_{\text{linked compound}}}{I_{\text{parent chromophore}}} \tag{2}$$

Table 1. Relative Fluorescence Quantum Yields Φ_{fl} and Charge-Transfer Quantum Efficiencies ϕ_{ct} for Linked Donor−Acceptor Compounds

compound	Φ_{fl}	ϕ_{ct}
1a	0.11[a]	0.89
1b	0.09[a]	0.91
5	1.00	n/a
2a	0.04[b]	0.96
2b	0.008[b]	0.99
6	1.00	n/a

[a] Relative to model compound **5**. [b] Relative to model compound **6**.

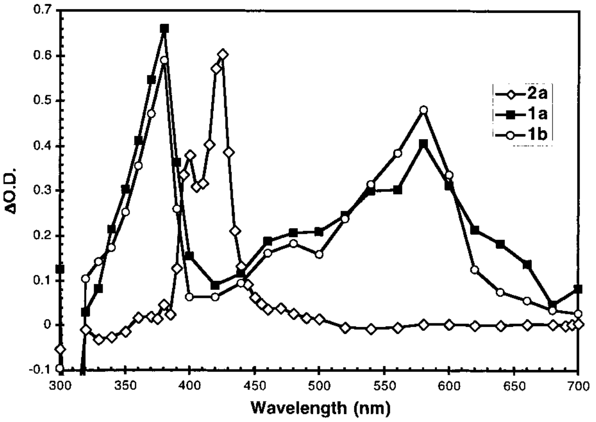


Figure 3. Transient absorption spectra obtained from LFP (308 nm, 50 mJ/pulse, 10 ns) of **1a** (filled squares), **1b** (open circles), and **2a** (open diamonds) in N_2-purged CH_3CN.

For **1a** and **1b**, electron transfer was verified further by the observation of a charge-transfer state by LFP. Pulsed laser photolysis (308 nm, 50−80 mJ, 10 ns) of **1a** and **1b** gives the transient spectra shown in Figure 3. Immediately after the laser pulse, bands at 380, 480, and 580 nm are observed. The shoulder at 480 nm matches the well-characterized spectrum of the *N,N*-dimethylaniline cation radical.[20] The peaks at 380 and 580 nm are assigned to the phenacyl-localized anion radical. These assignments were confirmed by three further experiments. First, addition of O_2 (a quencher of anion radicals) to the LFP solution abolishes the absorbances at 380 and 580 nm, but leaves the peak at 480 nm. Second, the anion radical of **9** was generated independently by LFP. In this experiment a mixture of *N,N*-dimethylaniline and 4-carbomethoxyacetophenone (**9**) was photolyzed. Similar transient absorption bands were detected in this experiment (data not shown).

Also considered was the possibility that the 380 and 580 nm peaks were due to a phenacyl-localized triplet state. To test for this, the triplet state of model compound **9** was generated by LFP (266 nm) of a CH_3CN solution containing **9** (but no electron donor). This creates a transient absorption with a strong $\lambda_{\max}$ at 325 nm, a weaker shoulder at ca. 380 nm, and no absorption in the 580 nm region (see Supporting Information). The spectrum is similar to those reported for the triplet state of acetophenone and several derivatives.[21] The lack of a strong band at 325 nm in linked system **1a** and the lack of a 580 nm band in the triplet spectrum of model compound **9** leads us to reject the possibility that significant amounts of the phenacyl-localized triplet state is formed in the photolysis of **1a** and **1b**.

The decay kinetics for the charge-transfer state of model system **1b** are fairly simple. The transient signals decay in a first-order fashion showing a rate constant (k_{obs}) of $(6.0 \pm 0.5) \times 10^6$ s^{-1}. The ester **1a** shows more complex behavior. For example, the absorbance at 480 nm decays in a biexponential fashion. The more rapid component (k_1) fits to a rate constant of 3×10^6 s^{-1} and the slower component (k_2) to 8×10^4 s^{-1}. For **1a** the reduced signal-to-noise and the increased complexity of the kinetic model reduces the accuracy of the fit parameters. Thus k_1 for **1a** is in fact indistinguishable from k_{obs} for model system **1b**. The biphasic decay behavior for **1a** can be attributed to the sequential decays of the charge-transfer state (**11a**) and the diradical cation (**12a**), both of which absorb at that wavelength. Intermediate **12a** arises from the C−O bond scission (pathway k_{b} in Scheme 2).

Photoproduct analysis also supports the mechanism in Scheme 2. Irradiation of **1a** in CH_3CN with a 350-W Xe lamp filtered through a 320 nm cutoff filter gives CH_3CO_2H and the byproduct **1b**. Quantitative ^{1}H NMR analysis of the reaction mixtures at moderate (70%) conversion shows that the carboxylic acid is formed in quantitative yield and **1b** in 85% yield (based on consumed starting material). The identity of product **1b** was also confirmed by gas chromatography/mass spectrometry (GC/MS). It was noted that the yields of **1b** were significantly lower when the photolysis was performed to complete conversion and/or when anhydrous CH_3CN was used as the solvent. The reduced yield at high conversion is most likely caused by secondary photolysis. In fact control experiments on **1b** show that it decomposes upon photolysis, albeit much more slowly than **1a**. The effect of trace amounts of water has not yet been fully explored.[16]

Trapping experiments show that the C−O bond scission step leading to deprotection is clearly due to the formation of the phenacyl-localized anion radical. When a similar photolysis of **1a** was performed under 1 atm of O_2 (a quencher of anion radicals), no acetic acid was formed. However, several decomposition products were detected.

The quantum yield for the decomposition of **1a**, Φ, was determined to be 0.02. This is consistent with the observation of a similar rate of decay for the model system **1b** ($k_{\mathrm{obs}} = k_{\mathrm{bet}}$) and **1a** ($k_1 = k_{\mathrm{bet}} + k_{\mathrm{b}}$).[22] In other words, the decay of the charge-transfer state is dominated by the back electron transfer giving unreacted starting material. From the quantum yield we can estimate rate of bond scission as $k_{\mathrm{b}} \sim 1.3 \times 10^5$ s^{-1}. The overall photolysis quantum yield, Φ, is the product of the quantum efficiencies of the charge-transfer step, ϕ_{ct} (eq 2), and the bond scission step, $\phi_{\mathrm{b}} = k_{\mathrm{b}}/(k_{\mathrm{b}} + k_{\mathrm{bet}})$. Given the assumption that k_{bet} is the same for **1a** and the nonreactive model **1b**, solving eq 3 gives $k_{\mathrm{b}} \sim 10^5$ s^{-1}.

$$\Phi = \phi_{\mathrm{ct}} \frac{k_{\mathrm{b}}}{k_{\mathrm{b}} + k_{\mathrm{bet}}} \tag{3}$$

Earlier success with a two-component, anthracene-sensitized deprotection system encouraged us to examine the corresponding linked system **2a**. However, in this case exhaustive irradiation fails to produce detectable amounts of acetic acid. LFP studies on both **2a** (Figure 3) and **2b** show efficient formation of an anthracene-localized triplet state $\mathbf{2}^{\mathbf{T1}}$. LFP of **2a** results in the immediate (<20 ns) appearance of transient absorption bands at 400 and 430 nm, which decayed in a first-order manner with a lifetime of 6 μs. Assignment of this transient species to the anthracene-localized triplet state is based on the similarity of the observed spectral profile to that of the excited triplet state of anthracene[23] and the observation that is it quenched by O_2.

The anthracene-localized triplet state lies approximately 41 kcal/mol above the ground state,[24] placing it 18 kcal/mol lower

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(23) Compton, R. H.; Grattan, K. T. V.; Morrow, T. *J. Photochem.* **1980**, *14*, 61−66.

(24) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2 ed.; Marcel Dekker: New York, 1993.

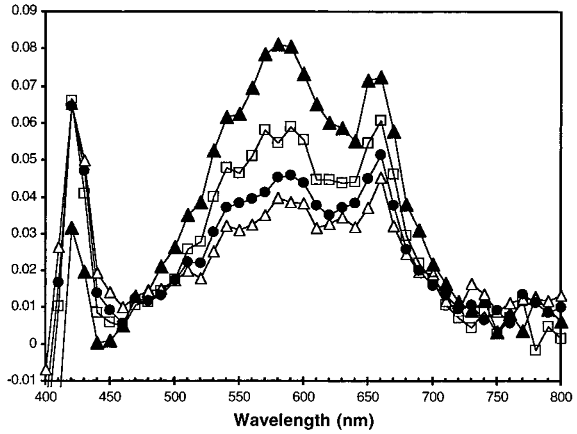

Figure 4. Transient absorption spectra obtained from LFP (355 nm, 4−10 mJ/pulse, 6 ns) of a mixture of compounds **8** and **15** in CH_3CN taken at 200 (filled triangles), 350 (open squares), 600 (filled circles), and 1000 (open triangles) ns after the excitation pulse.

in energy than the charge-transfer state. The lack of photoproducts and the rapid appearance of the aforementioned triplet state lead to the conclusion that charge-transfer state **14** is rapidly deactivated to form the localized triplet state (k_t) rather than bond scission (k_c). No signals attributable to charge-transfer state **14** were detected, but its formation is inferred from several facts. First, fluorescence from S_1 is substantially quenched relative to the parent chromophore (Table 1). Second, the formation of the charge-transfer state is calculated to be exothermic by 16 kcal/mol (Figure 2b). Finally, experiments, described below, on unlinked analogues show that these chromophores are competent toward photoinduced electron transfer.

For comparison purposes we conducted LFP experiments on an analogous unlinked system, specifically, a mixture of 9,10-dimethylanthracene **15** and 4-carbomethoxyphenacyl acetate **8** in CH_3CN. This experiment produces the transient spectra shown in Figure 4. The sharper peaks at 420 and 660 nm correspond to the cation radical of 9,10-dimethylanthracene **16**. This assignment is based on a comparison with the literature spectrum[25] and our observation that these signals are not affected significantly upon purging with O_2.[26] The broad peak at 580 nm is assigned to the anion radical of the 4-carbomethoxyphenacyl acetate **17**. This assignment is based on the observation that the peak is quenched by O_2 and its similarity to the spectrum of a similar species, namely 4-acetyl-α-phenoxyacetophenone anion radical.[27] No transient absorptions attributable to the triplet state of anthracene were detected in this unlinked system. The formation of the anthracene-localized triplet state thus apparently requires covalent linkage.

Population of an excited triplet state through back electron transfer is a relatively rare occurrence. Such events have been seen in some photosynthetic models and more recently in a smaller linked system consisting of a piperdinylnaphthyl donor group and a naphthalene diimide acceptor.[28] In the aniline system, **1**, the corresponding 4-carboxyacetophenone-localized triplet state is 18 kcal/mol higher in energy than the charge-transfer state, making triplet formation energetically irrelevant in this case. (There is also an *N*,*N*-dimethylaniline-localized triplet state that is 19 kcal/mol above the charge-transfer state.)

These experiments with **1** demonstrate the feasibility of photoreleasable protecting groups based on linked donor−acceptor molecules. Through synthetically straightforward tethering of the donor and acceptor molecules, charge-transfer state lifetimes of several hundred nanoseconds can be achieved. These lifetimes are comparable with bond scission rates for anion radicals of phenacyl esters, and measurable amounts of bond scission can be observed. The anthracene-based systems, **2**, demonstrate the importance of avoiding chromophores with localized triplet states that are lower in energy than the charge-transfer state. In that latter case, rapid nonradiative relaxation via the triplet state will prevent the desired bond scission process. We are currently designing improved systems based on these considerations.

Experimental Section

General Procedures. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Acetonitrile was distilled from CaH_2 under N_2 atmosphere through a vacuum-sealed column (30 cm) packed with glass helices. Tetrahydrofuran (THF) and ethyl ether (Et_2O) were distilled from sodium/benzophenone ketyl. ^1H NMR spectra were run at either 200- or 400-MHz NMR spectrometer. ^{13}C NMR spectra were run at 55.1 MHz. High-resolution mass spectrometry was performed using a VG 707e magnetic sector mass spectrometer. Electron ionization (EI) and fast atom bombardment (FAB) were used alternately depending on compound structure. UV−Visible Spectral were recorded in a 1-cm quartz cell by using a Perkin-Elmer Lambda 2S spectrometer. Freshly distilled MeCN was used as the solvent for all the photophysical studies.

Laser Flash Photolysis. LFP experiments were performed using both an excimer laser and an Nd:YAG laser as the excitation source. An Oriel CW 350-W Xe arc lamp was used as the probe light source. The excimer laser using Xe/HCl reagent gas in He buffer supplies 308 nm pulses of 10-ns duration. The Nd:YAG laser used was a Continuum Surelite II-10 with 355 nm pulses of between 4- and 6-ns duration. Kinetic waveforms were captured using a LeCroy 9420 350-MHz digital oscilloscope. MATLAB 4.2 and LabView 5.0 software were used in processing the waveform data obtained. Samples for LFP were prepared such that their optical densities (OD) at the excitation wavelength used (either 308 or 355 nm) were 2−2.5 cm^{-1}. All samples were placed sealed quartz cuvettes, purged with N_2 (or O_2 for control experiment) for 15 min, and stirred continuously throughout the experiments.

Quantum Yields. The output from a 1000-W Hg−Xe arc lamp was passed through a spectral Energy GM 252 monochromator set to 300 ± 10 nm and directed onto a 1-cm quartz cell containing 3 mL of **1a** in CH_3CN (10^{-4} mol/L). Rates of linked ester disappearance were monitored after 0, 2, 4, 6, 10, 20, 30, and 60 min of photolysis and were acquired from the peak areas obtained from the high-performance liquid chromatography (HPLC) analysis. The yield is an average from four independent runs. Light intensities were measured using an International Light Research radiometer model IL 1700.

Cyclic Voltammetry. All electrochemical experiments were conducted on a BAS-50 cyclic voltammetry (CV) with $[Bu_4N][PF_6]$ as the supporting electrolyte. In all experiments, the electrodes were a carbon working, platinum auxiliary, and Ag/AgCl reference. All CV data were taken after purging samples with N_2 in spectroscopic grade CH_3CN, where the ferrocene/ferrocenium couple was found at 458 mV. Scan speed for CV data were 100 mV/s.

Relative Fluorescence Quantum Yields. Relative fluorescence quantum yields were measured using a Gilford Fluoro IV fluorimeter. Samples were prepared in sealed, N_2-purged, quartz cuvettes. For cases in which relative intensities were compared, the concentrations of the two solutions were adjusted such that they had identical optical densities at the excitation wavelength or else the relative fluoresence yields were corrected. For **1a**, **1b**, and **5** the excitation wavelength was 320 nm. For **2a**, **2b**, 9-methylanthracene, and **6**, the excitation wavelength was 386 nm.

Photoproduct Analysis. Preparative photolysis of **1a** and **2a** was performed using a 350-W Xe arc lamp whose output was filtered

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(25) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(26) Lee, K.; Falvey, D. E. **2000**, Manuscript in preparation.

(27) Mathivanan, N.; Johnston, L. J.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 8190−8195.

(28) Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R.; Galili, T.; Levanon, H. *J. Am. Chem. Soc.* **1999**, *121*, 7726−7727.

through a 320 nm cutoff filter in **1a** and a 395 nm cutoff filter in **2a**. Solutions of 10−15 mg of the reactants were dissolved in 1.5 mL of CD_3CN which contained 0.5 equiv of hexamethyldisiloxane as an internal standard. The sample solutions were purged with N_2. The yield of released CH_3CO_2H was determined at various photolysis times by ^1H NMR peak integration (δ 1.98 ppm) relative to the starting material (using the peak at 5.34 ppm) and the internal standard. Formation of **1b** from photolysis of **1a** was also quantified by ^1H NMR through integration of its peak at δ 2.59. The identity of this product was further verified by GC/MS analysis of the photoproduct mixtures [Shimadzu QP-5000 system with XTI-5, 30 M 5% phenyl column and electron-impact mass spectrometry (EIMS) detection]. **1b** was the only product detected with this method. **1b** was also isolated using preparative thin-layer chromatograpy (TLC) in 60% yield from a preparative photolysis of **1a**.

4-Carbo-(3-*N,N*-dimethylaminobenzyloxy)phenacyl acetate (1a). Compound **1a** was prepared from 4-(α-acetoxyacetyl)benzoic acid **4** and 3-(*N,N*-dimethylamino)benzyl alcohol **5**. DCC (0.72 g, 3.15 mmol) and **4** (0.70 g, 3.15 mmol, see Supporting Information) were dissolved in 7 mL of dry THF. After 15 min of stirring, **5** (0.52 g, 3.47 mmol, see Supporting Information) and a catalytic amount of *N,N*-(dimethylamino)pyridine (DMAP) (38.5 mg, 0.32 mmol) were added to the reaction flask. A yellow byproduct, dicyclohexylurea, began to precipitate out after 1 h. The solution was allowed to stand at room temperature for 48 h. The reaction was not complete at this point by TLC, but a workup was performed. The precipitate was removed by filtration, and filtrates were washed with saturated NH_4Cl, and then water. The aqueous layer was extracted with ether. Organic layers were combined, washed with water, and dried over $MgSO_4$. The resulting solution was concentrated under vacuum. Purification with flash column chromatography using 65:35 hexane/ethyl acetate solvent system gave **1a** as a yellow solid (0.14 g, 21%); mp 86−88 °C; UV λ_{max} (MeCN), 252 nm (log ϵ = 4.45), 300 nm (log ϵ = 3.48); ^1H NMR (CD_3CN) δ 2.13 (s, 3H), 2.91 (s, 6H), 5.29 (s, 2H), 5.34 (s, 2H), 6.73 (m, 2H), 6.82 (d, J = 2 Hz, 1H), 7.21 (t, J = 8 Hz, 1H), 7.99 (d, J = 8 Hz, 2H), 8.12 (d, J = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 191.9, 170.3, 165.4, 150.7, 137.3, 136.3, 134.8, 130.1, 129.4, 127.7, 116.4, 112.5, 112.3, 67.9, 66.1, 40.5, 20.5; HRMS (FAB) calcd for $C_{20}H_{22}O_5N$ $[M + H]^+$ 356.1498; found, 356.1518.

4-(Carbo-3-*N,N*-dimethylaminobenzyloxy)acetophenone (1b). A solution of 3-(*N,N*-dimethylamino)benzyl alcohol, **5** in pyridine (2.63 mL) at 0 °C was treated with 4-acetyl benzoyl chloride (0.6789 g, 3.72 mmol, see Supporting Information). The solution was heated at 60 °C for 1 h 20 min. The dark brown crude mixture was then poured into 20 mL H_2O, and the aqueous solution was extracted with three 15-mL portions of ether. The organic layers were combined and washed with 10% aqueous HCl solution, saturated. $NaHCO_3$, and then H_2O. The resulting solution was concentrated under vacuum. The resulting crude brown oil was purified using flash column chromatography with 3:2 hexane/ethyl acetate as the elutant. A yellow oil was obtained which solidified upon standing. 0.606 g, 62%; mp 61−62 °C; ^1H NMR ($CDCl_3$) δ 2.62 (s, 3H), 2.95 (s, 6H), 5.32 (s, 2H), 6.77 (m, 3H), 7.23 (t, J = 8 Hz, 1H), 8.13 (d, J = 7 Hz, 2H), 8.15 (d, J = 7 Hz, 2H) ^{13}C NMR ($CDCl_3$) δ 197.6, 165.6 150.7, 140.2, 136.4, 134.1, 129.9, 129.4, 128.2, 116.4, 112.5, 112.3, 67.8, 40.5, 26.9; HRMS calcd for $C_{18}H_{19}O_3N$ 297.1365; found, 297.1360.

4-Carbo-(9-anthrylmethoxy)phenacyl Acetate (2a). Compound **2a** was prepared from 4-(α-Acetoxyacetyl)benzoic acid, (**4**, 0.70 g) and 9-hydroxymethylanthracene (**6**) using the procedure for **1a**. This provides 0.36 g (30%) of **2a** as a dark yellow solid; mp 184−186 °C; ^1H NMR ($CDCl_3$) δ 2.18 (s, 3H), 5.25 (s, 2H), 6.41 (s, 2H), 7.54 (m, 4H), 7. 84 (d, J = 8 Hz, 2H), 8.05 (t, J = 9 Hz, 4H), 8.41 (d, J = 9 Hz, 2H), 8.53 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 191.8, 170.8, 165.7, 137.9, 134.5, 131.4, 131.2, 130.2, 129.5, 129.2, 127.6, 126.8, 125.7, 125.2, 123.8, 66.1, 59.9, 20.5; HRMS (FAB) calcd for $C_{26}H_{21}O_5$ $[M + H]^+$ 413.1389; found, 413.1414.

4-Carbo-(9-anthrylmethoxy)acetophenone (2b). Compound **2b** was prepared from **6** and 4-acetylbenzoic acid (**7**, 0.637 g, 3.89 mmol) using the procedure for **1a**. This provides 0.520 g (49%) of **2b** as a yellow solid: mp 118−120 °C; ^{1} H NMR ($CDCl_3$) δ 2.57 (s, 3H), 6.41 (s, 2H), 7.52 (t, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 7.90 (d, J = 9 Hz, 2H), 8.05 (m, 4 H), 8.41 (d, J = 9 Hz, 2H), 8.53 (s, 1H); ^{13}C NMR (CD_3CN) δ 197.5, 165.5, 140.3, 133.7, 131.4, 130. 9, 129.5, 129.3, 129.0, 128.2, 126.8, 126.3, 125.3, 124.0, 59.6, 26.2; HRMS calcd for $C_{24}H_{18}O_3$ 354.1256; found, 354.1228.

4-Carbomethoxyphenacyl acetate (8). First 4-carbomethoxyacetophenone (**9**) was prepared by combining CH_2N_2 and 4-acetylbenzoic acid **7** (1.64 g) using Smissman's procedure.[29] This provides **9** (1.69 g, 95%) as silky needles: mp 94−95 °C (lit[27] mp 95.0−95.5 °C). Compound **9** was then brominated using a published procedure[30] to give α-bromo-4-(carbomethoxy)acetophenone as fine light orange powder in 91% yield: mp 134−136 °C; ^1H NMR ($CDCl_3$) δ 3.95 (s, 3H), 4.46 (s, 2H), 8.03 (d, J = 9 Hz, 2H), 8.14 (d, J = 9 Hz, 2H); ^{13}C NMR (CD_3CN) δ 191.3, 165.8, 137.5, 134.5, 129.6, 128.8, 52.1, 32.9; HRMS calcd for $C_{10}H_9O_3{}^{79}Br$ 255.9735; found, 255.9727. This latter compound (0.64 g) was combined with NaOAc in absolute MeOH to give **8** (see the preparation of **4** in the Supporting Information). Compund **8** was obtained as white crystals (0.92 g, 64%): mp 150−152 °C dec; UV (λ_{max} MeCN), 248 nm (logϵ = 4.20), 290 nm (log ϵ = 3.11); ^1H NMR ($CDCl_3$) δ 2.21 (s, 3H), 3.94 (s, 3H), 5.32 (s, 2H), 7.94 (d, J = 9 Hz, 2H). 8.13 (d, J = 9 Hz, 2H); ^{13}C NMR (CD_3CN) δ 193.5, 171.0, 166.7, 138.4, 135.5, 130.6, 128.8, 67.3, 53.0, 20.6; HRMS calcd for $C_{12}H_{12}O_5$ 236.0685; found, 236.0690.

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Supporting Information Available: ^1H NMR spectra for **1a**, **1b**, **2a**, **2b**, and **8**. Transient spectrum from direct excitation of **9**. Preparation procedures and characterization data for synthetic intermediates **3**, **4**, **5**, and 4-acetylbenzoyl chloride (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Smissman, E. E.; Li, J. P.; Israili, Z. H. *J. Org. Chem.* **1968**, *33*, 4231−4235.

(30) Rather, J. B.; Reid, E. E. *J. Am. Chem. Soc.* **1919**, *41*, 77−83.