strand breaks within a certain period of time is higher than that of brown (or green) Co^{III}–BLM used in previous reports.[3,6] Details of the DNA cleavage reaction will appear elsewhere.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra (300 MHz, 298 K) (Figure S1) and ^1H–^{13}C (J = 140 Hz) COSY spectrum (Figure S2) of **4** in $(CD_3)_2SO$, plasmid DNA cleavage experiment with **3** and **4** in Tris-borate buffer (Figure S3), and tables of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances and bond angles, and the H-atom coordinates for **4** (9 pages); table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Efficient Charge-Transfer Photochemistry via Fragmentable Cation Radicals with Variable Lifetimes. Direct Comparison with Chloranil Sensitization

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Electron transfer from various donors (D) to different acceptors (A) occurs upon the specific irradiation of the charge-transfer band ($h\nu_{CT}$) of the EDA precursor complex, i.e.[1,2]

$$D + A \overset{K}{\rightleftharpoons} [D, A] \underset{k_2}{\overset{h\nu_{CT}}{\rightleftharpoons}} [D^{\bullet+}, A^{\bullet-}] \xrightarrow{k_1} \text{products} \qquad (1)$$

Although such a direct process for photoinduced electron transfer does not depend on diffusional quenching that complicates the kinetics analysis of the more conventional sensitization methods,[3,4] its exploitation is often frustrated by an efficient back electron transfer (k_2).[5,6] This limitation can be addressed with labile acceptor moieties ($A^{\bullet-}$) such as that from tetranitromethane[7] and donor cations ($D^{\bullet+}$) derived from strained hydrocarbons,[8] which undergo unimolecular decomposition with rate constants comparable to k_2. Indeed the latter underscores the need for a related series of highly labile donor cations to enhance the efficiency of charge-transfer photochemistry. Accordingly, we report the use of arene donors derived from p-methoxytoluene (MT)[7c] in which the presence of the common chromophore also allows the direct comparison of charge-transfer and sensitized photochemistry as described by Jones, Farid, and co-workers.[9,10]

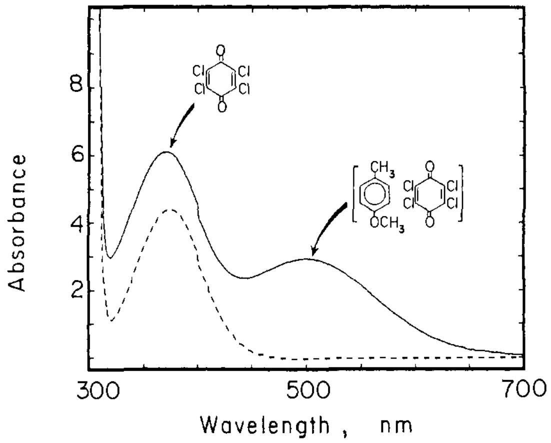
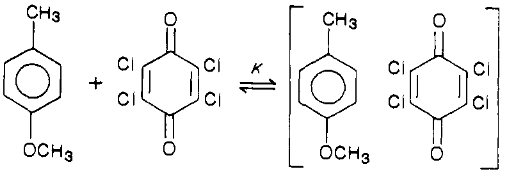


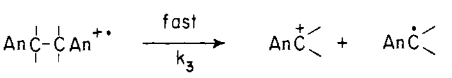
Figure 1. Absorption spectra of 2.0×10^{-3} M CA alone (- - -) and with 0.4 M MT (—) in dichloromethane.

The absorption spectrum in Figure 1 shows the simultaneous appearance of two resolved bands—one arising from the local excitation of the chloranil acceptor (CA) and the other from the CT excitation of the 1:1 EDA complex, i.e.



(2)

The spectrophotometric determination of the formation constant in eq 2 according to the Benesi–Hildebrand procedure[11] indicated $K = 0.3\ M^{-1}$ in dichloromethane.[12] In such weak EDA complexes, the previous photophysical and photochemical studies by time-resolved spectroscopy[13] as well as Mulliken theory[14] point to $[MT^{\bullet+}, CA^{\bullet-}]$ as the pertinent ion-radical pair in eq 1. In order to promote the CT photochemistry in eq 1, we utilize the methoxytoluene chromophore in various dimeric structures DMT that are known to yield highly unstable cation radicals,[15-18] i.e.



$$\mathrm{An\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}An^{+\bullet}} \xrightarrow[k_3]{\text{fast}} \mathrm{An\overset{+}{C}\lt} + \mathrm{An\overset{\bullet}{C}\lt} \qquad (3)$$

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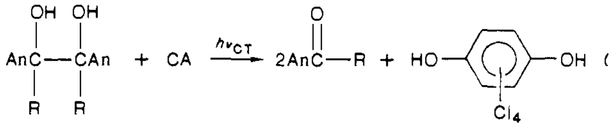
Table I. Charge-Transfer and Sensitized Photochemistry of Methoxytoluene Donors with Chloranil[a]

DMT donor[b]	$h\nu_{CT}$,[c] eV	Φ_{CT}[d]	Φ_{sens}[e]	τ, 10^{-10} s	products[f]
$[An_2COH]_2$	2.58	0.27	0.98	0.66	An_2CO, H_2CA
$[AnCMeOT]_2$	2.56	0.12	0.77	1.8	AnCOMe, T_2CA
$[AnCHOH]_2$	2.58	0.03	0.84	7.9	AnCHO, H_2CA
$[AnCHOT]_2$	2.56	0.01	0.77	24	AnCHO, T_2CA
$[AnCMe_2]_2$	2.51	<0.001	0.25	>200	$AnC(Me){=}CH_2$, H_2CA
$[AnCH_2]_2$	2.49	0	0.01		$(AnCH)_2$, H_2CA

[a] In dichloromethane containing 0.04 M anisyl donor and 0.02 M chloranil. [b] T = $(CH_3)_3Si$. [c] MT, 2.46 eV. [d] At λ 505 ± 5 nm. [e] At λ 405 ± 5 nm. [f] High yields (>90%) based on stoichiometry in eq 4.

where An = p-$MeOC_6H_4$. It is important to emphasize that the donor property of every DMT listed in Table I is essentially the same as that of the parent (MT), as quantitatively judged by the invariant positions of the CT bands (see column 2).[12]

Electron-transfer photochemistry resulting from the selective irradiation of only the charge-transfer band[19] is strongly dependent on the side-chain substitution pattern on the DMT donor. Thus the pinacols are quantitatively cleaved in the presence of 1 equiv of chloranil according to the stoichiometry



(4)

where R = An, Me, and H. Moreover, the bis(trimethylsilyl) ethers of the pinacols are similarly cleaved to 2 mol of dianisyl ketone, anisyl methyl ketone, or anisaldehyde and 1 mol of the bis(trimethylsilyl) ether of tetrachlorohydroquinone,[20] as listed in Table I. In strong contrast, the bibenzyl derivatives $[AnCH_2]_2$ and $[AnC(Me)_2]_2$ remain singularly unchanged, even upon prolonged irradiation (2 days) of the CT absorption band.

The quantum yields Φ_{CT} for charge-transfer photochemistry as listed in column 3[21] lead to the lifetimes (τ) of the cation radicals in column 5 when the measured rate constant $k_2 = 4.1 \times 10^{10}$ s^{-1} is used to evaluate the back electron transfer.[22] Thus the lifetime of 66 ps for $[An_2COH]_2^{\bullet +}$ is sufficient to ensure its unimolecular fragmentation within the caged ion pair (see eq 1),[8] followed by intracage proton transfer to yield the products in eq 4, i.e.[24]

$$\{[An_2COH]_2^{\bullet +}, CA^{\bullet -}\} \xrightarrow{66\ ps} \{An_2C^{+}OH, An_2\dot{C}OH, CA^{\bullet -}\} \rightarrow 2An_2CO + H_2CA \quad (5)$$

The lifetime of $[AnCHOH]_2^{\bullet +}$, which is an order of magnitude longer than that of $[An_2COH]_2^{\bullet +}$, accords with the expected difference in driving force for secondary/tertiary benzylic scissions.[17a,18] Furthermore, the absence of CT photochemistry from the bibenzyl analogues indicates that the fragmentation rates of their cation radicals are too slow to effectively compete with back electron transfer.[16a,17b]

The clean spectral separation of the chloranil absorption (λ_{max} 375 nm) from the CT absorption in Figure 1 also allows the separate evaluation of the efficacy of pinacolic cleavage via the diffusional quenching of the locally excited acceptor, i.e.[26]

$$CA \underset{}{\overset{h\nu_A}{\rightleftharpoons}} CA^{*} \overset{D}{\rightleftharpoons} [D^{\bullet +}, CA^{\bullet -}] \xrightarrow{k_1} \text{products} \quad (6)$$

The latter ($h\nu_A$) is achieved with a narrow-band-pass interference filter (λ 405 ± 5 nm) for the specific excitation of only chloranil.[27] The results in column 4 show consistently high efficiencies (Φ_{sens}) for the sensitized photochemistry of the pinacols and their silyl derivatives. Importantly, complete product analysis established the stoichiometry to be *identical* with that obtained by CT photochemistry. Moreover, the bibenzyl analogues $[AnCMe_2]_2$ and $[AnCH_2]_2$ undergo photofragmentation and elimination according to the following stoichiometries:

$$[AnCMe_2]_2 + CA \xrightarrow{h\nu_A} 2AnC(CH_3){=}CH_2 + H_2CA \quad (7)$$

$$[AnCH_2]_2 + CA \xrightarrow{h\nu_A} AnCH{=}CHAn + H_2CA \quad (8)$$

In both cases, the products of the sensitized photochemistry accord with prior electron transfer followed by the known fragmentation (eq 7) or proton transfer (eq 8) of the cation radical ($DMT^{\bullet +}$).[17,18,28]

The significantly enhanced values of Φ_{sens} for sensitized photofragmentation compared to Φ_{CT} for CT activation are undoubtedly related to the longer lifetimes of the donor cation radical ($DMT^{\bullet +}$). Part of the difference in their lifetimes can be attributed to the change in spin multiplicity required for back electron transfer from the triplet ion radical pair $^3[DMT^{\bullet +}, CA^{\bullet -}]$.[29,30] However, there are other complicating factors introduced by diffusional quenching, especially the ambiguity in the distance dependence of electron transfer[33] to generate solvent-separated and contact ion pairs.[34] As such, we believe that the series of labile $DMT^{\bullet +}$ with variable lifetimes evaluated by the CT process will prove to be invaluable aids as "chemical clocks"[35] to unravel the complex photochemical kinetics stemming from different types of ion pairs.

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(22) (a) The time-resolved picosecond spectrum obtained from the laser flash photolysis of a solution of 0.02 M CA and 0.4 M MT in dichloromethane with a 30-ps pulse at 532 nm consisted of a partially resolved absorption (λ_{max} = 460 and 440 nm) of $CA^{\bullet -}$ and $MT^{\bullet +}$, respectively.[7c,23] Both bands disappeared simultaneously to the base line with a first-order rate constant of (4.1 ± 0.7) × 10^{10} s^{-1} that is readily assigned to k_2 since no CT photochemistry occurred. (b) The same value of k_2 can be used for all the DMTs owing to their common donor properties (see Table I, column 2).

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(24) Although the fragmentation in eq 3 may be reversible (for k_{-3}, see ref 16 a,b), it is kinetically unimportant for Φ_{CT} since the subsequent proton transfer (k_4) from An_2COH^{+} is very fast.[25] Oxidation of $An_2\dot{C}OH$ by $HCA^{\bullet}$ is also probably fast.

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