

Photoinduced Charge Migration in the Picosecond Regime for Thianthrene-Linked Acridinium Ions

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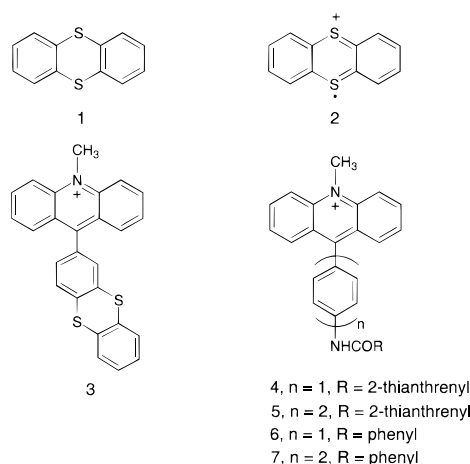
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The thianthrene ring system (**1**) has a novel redox chemistry that has been the subject of study for three decades. The sulfur heterocycle undergoes a reversible one-electron oxidation ($E_{1/2} = 1.23$ vs SCE, CH_3CN),¹ yielding a radical cation species (**2**) that is stable enough to be isolated for independent investigation;² magnetic resonance studies on the cation have included ESR, ENDOR, and CIDEP measurements.³ Photoinduced electron transfer involving thianthrene (TH) as an electron donor has been studied, including a report of trapping of the radical cation.⁴ As part of a study of linked donor–acceptor systems that employ the acridinium ion as electron acceptor,⁵ we have prepared the first linked thianthrenes appropriate for investigation of intramolecular electron transfer involving TH as an electron donor. Structures such as **3–5** are of special interest, since 1-e oxidation of the TH moiety should be accompanied by a significant geometry change. According to a variety of studies, including X-ray crystallography, NMR, and photoelectron spectroscopy,⁶ TH is non-planar with a bond angle of 130° – 140° between ring planes, whereas the radical cation, $\text{TH}^{+\bullet}$, is a nearly planar species (e.g., an interplanar angle of 174° is reported for the AlCl_4^- salt).⁷ Interest in electron-transfer systems that display large internal reorganization energies has been recently renewed in a number of papers, including reports on conformationally distorted porphyrins.⁸

Our principal findings include the observation of very fast forward and back electron transfer (charge shift, CSH) in the picosecond time domain involving TH and acridinium subunits. The issue for **4** and **5** had to do with whether the cationic site created in a donor benzamide would migrate to the distal TH and develop an electron-transfer triad.^{9,10} Comparison with model compounds **6** and **7** showed that, for **4** and **5**, the addition of the



TH moiety resulted in alterations in both spectral features and the rate of overall decay of picosecond transients. Also, the amidophenyl bridges for **4** and **5** are effective in providing electronic coupling between subunits; reverse charge shift from more distant TH moieties can proceed on a very rapid time scale.

The absorption spectra for acridiniums **3–7** (PF_6^- salts)¹¹ displayed principal transitions that are typical of the acridinium chromophore (bands at 360 and 430–450 nm, with 19 000 and 8000 $\text{M}^{-1} \text{cm}^{-1}$, respectively).^{5,12} The longer wavelength absorption band was more sensitive to substituent pattern and to solvent (e.g., slight red-shifts for the less polar solvent, CH_2Cl_2), consistent with the perturbation by a low-lying CSH state (Figure 1).^{5,12} Comparison of long-wavelength maxima showed that the perturbation due to the CSH transition is similar for **3** and for the amidoaryl links **4–7** (e.g., for CH_2Cl_2 solutions, $\lambda_{\text{max}} = 434$ nm, $\epsilon = 8300$; and 454 nm, $\epsilon = 8100$, for **3** and **7**, respectively). On excitation of the acridinium chromophores at 360 nm, emission appears either as a fluorescence associated with local excitation of the acridinium ring (LE emission, 490–500 nm) or as a red-shifted emission associated with the CSH state.^{5,12} Fluorescence occurs principally from the LE state for acridinium ions in a more polar medium (CH_3CN), whereas lower polarity solvents generally favor CSH fluorescence.^{13,14} For ions modified with the TH group, fluorescence was generally weak (quantum yields $< 10^{-3}$); in some solvents, the emission is shifted noticeably to the red (Figure 1), consistent with the appearance of a lower-lying CSH state that involves charge migration to TH moieties.

Transients associated with photoinduced electron transfer were examined using pump–probe techniques that employed a Ti:sapphire laser capable of producing 70 fs pulses ($1 \mu\text{J}$ at 1.3 kHz) at the frequency-doubled wavelength of 417 nm.¹⁰ The important species that have been previously identified are the acridinyl

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(11) Acridinium **3** was prepared by reaction of diphenylamine and thianthrene-2-carboxylic acid, followed by quaternization.^{5,12} **4–7** were prepared by reaction of 9-(4-aminophenyl)-10-methylacridinium¹² or the aminobiphenyl analogue^{3a} with either thianthrene-2-carbonyl chloride or benzoyl chloride. The structures of new compounds were confirmed by NMR and by high-resolution MS.

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(13) As has been argued separately,^{5,12} the red-shift of CSH transitions is consistent with a greater relative stabilization of a less polar (less charge localized) excited state vs the ground state in media of lower polarity.

(14) Moderately red-shifted CSH emission bands appear for **6** and **7**, oxidation potentials for which are $E_{1/2} = 1.86$ and 1.68 V vs SCE (CH_3CN), respectively; phototransient behavior for these derivatives is reported separately.^{3c}

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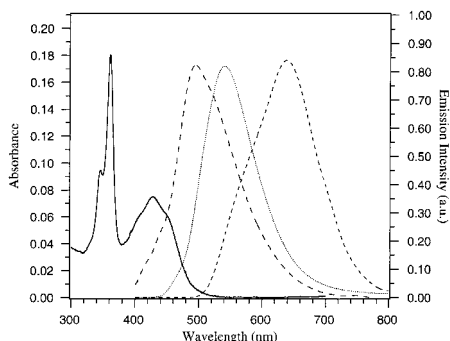


Figure 1. For **3**, the absorption spectrum in CH_2Cl_2 and emission spectra for acetonitrile (---), dichloromethane (···), and hexane (—) solutions ($10\text{--}20\ \mu\text{M}$; $\lambda_{\text{exc}} = 360\ \text{nm}$).

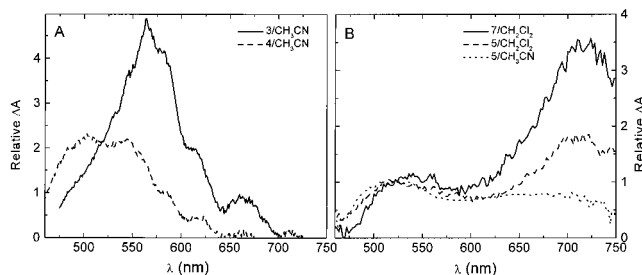
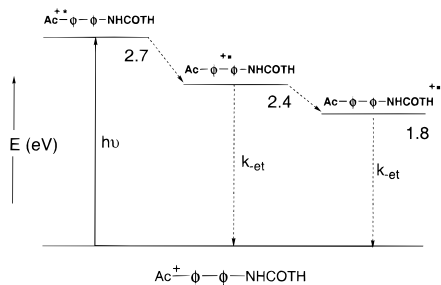


Figure 2. Phototransients observed on flash photolysis at $400\ \text{nm}$ for (A) **3** and **4** and (B) **5** and **7** at $5\ \text{ps}$ following the laser pulse ($30\ \mu\text{M}$ dye in indicated solvent).

Scheme 1



neutral radical ($\lambda_{\text{max}} = 500\ \text{nm}$), the radical cations associated with substituted biphenyls ($\lambda_{\text{max}} = 700\ \text{nm}$),^{5,12,15,16} and the familiar $\text{TH}^{+\bullet}$ radical ion (**2**, $\lambda_{\text{max}} = 545\ \text{nm}$).² On excitation, **3** provided a strong transient that developed within $1\ \text{ps}$ and peaked at $560\ \text{nm}$ (indicative of the $\text{TH}^{+\bullet}$ species having a modest spectral shift due to mutual perturbation by the linked acridine) (Figure 2a). Flash photolysis of **4** led to a broader transient at $500\text{--}550\ \text{nm}$, indicative of more segregated contributions from the acridine radical and the remotely positioned thianthrene radical ion. For **5**, the behavior contrasted noticeably in that spectra contained contributions from the strongly absorbing $680\ \text{nm}$ biphenyl radical ion (Figure 2b).^{5c} However, in a comparison of spectra obtained for the model compound **7** (and a biphenyl derivative^{5a,c}) not having the TH moiety, transient absorbances of acridinyl and biphenyl species (for **5**) on the $1\text{--}10\ \text{ps}$ time scale revealed a faster depletion of the $700\ \text{nm}$ band relative to the feature at $500\text{--}550\ \text{nm}$ (Figure 2b). The pattern of results is consistent with sequential electron transfer involving, alternately, the anilide donor in an ultrafast electron transfer followed by competition between return electron transfer (conversion to the ground state) and the transfer of the photogenerated hole to TH (Scheme 1, for **5**).

Transient decays that obeyed first-order kinetics are reported in Table 1. The notable features of the data are (1) the short decay times observed for directly linked **3**; (2) the decrease in decay

Table 1. Phototransient Decay Times from Laser Flash Photolysis of Acridinium Derivatives^a

	τ_{CSH} (ps) (CH_3CN)	$k_{\text{-et}}$ ($\times 10^{10}\ \text{s}^{-1}$)	τ_{CSH} (ps) (CH_2Cl_2)	$k_{\text{-et}}$ ($\times 10^{10}\ \text{s}^{-1}$)
3	1.1	91.0	19.0	5.3
4	1.2 (12.0) ^b	83.0	14.	7.1
5	2.6	38.0	36.0 ^c (48.0) ^d	2.8
6	21.0	4.8	615.0	0.16
7	1.9	53.0	71.0	1.4

^a Deaerated $30\ \mu\text{M}$ solution; τ_{CSH} values ($\pm 10\%$) for decay of radical (ion) absorption transients ($500\text{--}550$ or $675\text{--}700\ \text{nm}$, see text).

^b Biexponential decay ($52:48$ ratio of components). ^c Decay monitored at $675\ \text{nm}$. ^d Decay monitored at $550\ \text{nm}$.

time for amide-linked **4** vs **6**, indicating clearly the participation by the TH moiety in a second electron-transfer step; (3) measurable differences in decay times for the pair, **5** and **7**, that depended in a subtle way on the selected solvent (and for **5**, a distinction on monitoring at 555 and $675\ \text{nm}$); (4) the lengthening of decay times for the less polar solvent, CH_2Cl_2 , a pattern that has been previously associated with reverse electron-transfer processes (inverted region behavior).^{18,19} The role of the less polar solvent principally involves the lengthening of the lifetime of the first charge-shift state, so that transfer of the hole to the appended TH moiety (most noticeable for **4** vs **6**, Table 1) can compete with charge return, yielding the ground state (Scheme 1).⁹ The triad arrays thus engage in an adiabatic forward electron-transfer step involving directly linked amidoaryl groups and the acridinium ring, followed by a slower charge migration to a TH moiety.

The $3\text{--}10$ -fold acceleration for return electron transfer observed for the TH-substituted ions vs previously reported dyads composed of the acridinium moiety linked with phenol or aniline donors¹⁸ is unexpected and points to an effective mechanism that employs thianthrene ring motion in promoting nonradiative decay. Vibrational (acceptor) modes potentially involved are those associated with neutral TH that are shifted in frequency upon TH oxidation, including 1118 (ring C—S—C stretch) and $419\ \text{cm}^{-1}$ (C—S—C skeletal deformation) vibrations.²⁰ The picosecond electron-transfer findings are not supportive of the proposal that rates of fluorescence quenching for $\text{TH}^{+\bullet}$ are compromised by a sizable energetic requirement for structural reorganization²¹ but are more consistent with the high (diffusion-limited) rate of self-exchange for $\text{TH}^{+\bullet}$ and TH that has been reported.²² We note also the effective electronic coupling that is exhibited by the bridging anilide groups for **4** and **5** that contribute to fast rates of reverse charge shift and a very modest falloff with distance that is observed on comparing $k_{\text{-et}}$ for **3–5**.²³ In conclusion, the linkage of the thianthrene ring to an acridinium electron acceptor leads to rapid (ps) reversible electron transfer, despite restrictions that might have been imposed due to internal reorganization of the TH heterocyclic frame.

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(16) Reported extinction coefficients for the 10-methylacridinyl radical and the biphenyl radical cation¹⁷ are $\epsilon_{515} = 7400$ and $\epsilon_{700} = 14\ 500\ \text{M}^{-1}\ \text{cm}^{-1}$.

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(19) Rate constants ($k_{\text{-et}}$) are 6.7×10^9 and $16.0 \times 10^9\ \text{s}^{-1}$ (CH_2Cl_2 solvent) for 9-hydroxyphenyl or 9-aminophenyl acridiniums, for which $\Delta G^\circ = -1.9$ and $-1.4\ \text{eV}$, respectively, compared to $\Delta G^\circ = -1.8\ \text{eV}$ for **3**.

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