Long-lived Charge-Transfer States in 9-Aryl-Acrnidinium Ions; A Critical Reinvestigation

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Abstract. In the recent literature a simple 9-aryl-acridinium ion was claimed to undergo an intramolecular, photoinduced charge shift to produce an extremely long-lived and very high energy charge-transfer state. The possible consequences of this observation are discussed and the tenability of the claims made is investigated via time resolved spectroscopy of a closely related system with spectroscopic characteristics allowing more solid identification of the actual photophysical events taking place. From the results obtained it appears likely that the long-lived species observed earlier in solution cannot be charge transfer in nature but must instead be identified as the lowest triplet state of the acridinium chromophore.

1. INTRODUCTION
Storage of light energy in a long-lived molecular charge-transfer state is a much pursued goal. Such molecular systems would be of importance for energy conversion analogous to natural photosynthesis and might also be applied in the construction of molecular photomechanical and photo-electric devices.

Crucial in photosynthetic energy conversion is the occurrence of a number of relatively fast short-range electron-transfer steps leading to a large overall charge separation distance which prevents the loss of the photoinduced redox potential as a result of rapid back electron transfer. Mimicking this has been achieved after decades of scientific effort but evidently requires quite complex and large multi-chromophoric systems ranging from triads to pentads [1–8].

Alternatively, attempts have been made to design simple and small dyad systems (“compact dyads”) in such a way that not only photoinduced charge separation occurs rapidly and quantitatively but, at the same time, charge recombination is somehow impeded. The most successful of such systems seem to be those in which “spin control” is applied by populating a charge-transfer state which is of different spin multiplicity (e.g., a triplet) than the ground state (usually a singlet) whereby charge recombination becomes a spin forbidden process [9–12].

While earlier results thus indicated that creation of a long-lived charge-transfer (CT) state is a complex issue, a very simple and compact dyad was recently reported in which a long-lived CT state was claimed to be populated without the need for long distance charge migration nor for spin restrictions [13]. The longevity was attributed to a high thermal barrier for decay of the CT state. This barrier was assigned to a pronounced and unprecedented inverted region effect. Below we will discuss those claims and present an alternative explanation that puts serious doubts on their validity.

2. LONG LIVED CHARGE MIGRATION IN A SIMPLE ARYL-ACRIDINIUM DYAD?
An amazing example of a long-lived CT state in a very simple and compact dyad was recently reported in the form of the 9-mesityl-10-methylacridinium ion 1 (see Figure 1) [13]. This system contains a directly linked donor/acceptor pair comprising a mesitylene moiety as a relatively weak electron donor and an acridinium ion as a rather strong electron acceptor that can be excited with visible light. It was reported that excitation of the acridinium acceptor chromophore leads to population of an intramolecular CT state which was reported to undergo photoinduced charge shift in ≥98% quantum yield. Very surprising, however, is the fact that the CT state thus populated was claimed to have an extremely long lifetime ranging from many microseconds in solution to many hours and even years at lower temperatures in a solid matrix [13]. Based on these observations 1 was explicitly claimed to constitute a system that surpasses natural photosynthesis both regarding the amount of energy
stored and the storage time. More recently these properties were also reported to allow 1 to act as a useful photoredox sensitizer [14, 15]. The long lifetime of the CT state in 1 was attributed to a high barrier for back electron transfer under the inverted region conditions caused by the high energy (2.37 eV) of the CT state in 1 [13]. This reasoning was especially based upon the strong temperature dependence of the very slow, first order decay kinetics of the CT state detected by EPR spectroscopy (no spectra shown) in a solid matrix between 203 and 243 K. The identification of this CT state was, however, mainly based upon its transient absorption spectrum measured by flash photolysis in liquid solution at higher temperatures.

While we comment on the low temperature photo-EPR experiments reported for 1 in a separate paper [16], in the present publication we concentrate specifically on the identification of its long-lived CT state by flash photolysis in solution.

We realized that the long lifetime of the CT state in 1 cannot be attributed to an eventual triplet character of this state because in 1 the lowest triplet state is not CT in nature but according to well documented literature data must be localized on the acridinium chromophore ($E_T \sim 2.0$ eV) [17, 18]. Furthermore we noted that in the visible region the transient absorption spectrum to be expected for the CT state of 1 is somewhat similar to that to be expected for the $T_1$-$T_n$ absorption of the acridinium chromophore [19]. This might make it difficult to discriminate between these species. We therefore now (re-)investigated the properties of 2 (see Figure 1), which is closely related to 1 but has the advantage that the transient absorption spectra of its CT state and its lowest triplet state are very different (see later). The only significant difference between 1 and 2 is that in the latter the CT state is at slightly lower energy (at ca. 2.14 eV) but—importantly in this context—still above the local acridinium triplet.

2.1. Steady state absorption and fluorescence. The absorption and fluorescence spectra of 2 are shown in Figure 2. As expected the visible and near UV absorption of 2 is dominated by the acridinium chromophore with no clear indication for interaction with the naphthyl moiety orientated almost perpendicular to it. Such interaction is, however, very evident in the fluorescence spectrum.

Whereas the isolated acridinium ion is known to display a strong and structured green fluorescence (maximum around 495 nm) [17, 20], this is fully quenched in 2 and substituted by a weak, broad and structureless emission in the far red region (maximum 675 nm in acetonitrile). This behaviour has been observed before and can safely be attributed to CT-fluorescence, i.e. emissive back electron transfer from a $1^{CT}$ state populated by electron transfer from the naphthyl donor to the acridinium ion [21–23]. From the measured decay of the CT fluorescence, the lifetime of the CT state in 2 could be determined directly as 3.0 ns. This value is in excellent agreement with earlier reports [22, 23].

2.2. Femtosecond transient absorption. In order to study the rise and decay pathways for the CT state in 2 in more detail laser flash photolysis measurements were performed with respectively subpicosecond and nanosecond temporal resolution.

Figure 3 shows the transient absorption spectra which evolve after femtosecond laser excitation (430 nm, fwhm 130 fs) of the acridinium chromophore in 2. Immediately after the laser pulse spectrum-1 is observed, with a maximum at 480 nm and a shoulder at $\sim$ 580 nm, which may be attributed to $S_1 \rightarrow S_0$ absorption of the acridinium chromophore. This is substituted on a subpicosecond time scale (risetime $\sim$ 0.4 ps, see Figure 4) by the spectrum of the CT state (spectrum-3), which remains stable over the observation period of the measurements ($\lesssim$ 1 ns) as expected from its lifetime of 3 ns determined from CT fluorescence (see above).

The spectrum of the CT state (i.e. spectrum-3 in Figure 3) displays features characteristic of both the neutral acridiny1 radical [24], and the naphthalene...
The resulting increased twist angle is part of the internal reorganization as previously [22], may indicate that a reduction in the absorption around 560 nm, which must be a result of interaction between the two constituent moieties. The dashed arrow indicates an extra band resulting from CT type interaction between these moieties (see text).

Figure 3. Transient absorption spectra of 2 observed at the delay times indicated in Figure 4 after femtosecond laser excitation at 430 nm (fwhm 130 fs) in acetonitrile (pathlength 2 mm). Spectral features attributable to the acridinyl radical (Acr*) and the naphthalene radical cation (Napht**) moieties have been indicated by solid arrows. The transient absorption due to the CT excited state of 2 will lead to a higher excited state, presumably localized on the naphthalene donor moiety as predicted from a simple MO diagram (see Figure 5).

2.3. Nano-microsecond transient absorption. Within the time window of the femtosecond transient absorption measurements (≤1 ns) the absorption spectrum of the CT state of 2, shown in Figure 3, undergoes only minor changes. The only real change is a slight decay in intensity, as expected on the basis of the 3 ns lifetime found for the CT fluorescence. However, on a longer time scale as observed via nanosecond flash photolysis, this spectrum is replaced by the much simpler spectral profile shown in Figure 6.

This spectrum displays a single maximum in the visible region at 490 nm and a pronounced shoulder around 550 nm. There is also a small but significant rise in absorption towards the red end of the spectral region (≤800 nm). By comparison with literature data, this spectrum can safely be assigned to the local acridinium triplet state [18, 19]. As concluded before by others, this species arises from the CT state by intersystem crossing and back electron transfer [23]. This local triplet has a microsecond lifetime in deoxygenated solution at room temperature. Its triplet nature is further confirmed by the observation that addition of iodomethane, as a heavy atom containing co-solvent, up to 10% (v/v) enhances the yield by a factor up to sevenfold (see Figure 7) and, at the same, time strongly quenches the CT fluorescence. These findings indicate that intersystem crossing to the local triplet state must occur with a quantum yield ≤14% in pure acetonitrile.

The observations described above for 2 fully agree with and augment earlier reports, especially regarding formation of the local acridinium T1 triplet as the only long-lived. However, these findings are in marked contrast with the claimed formation of a comparably long-lived CT state in 1. This enigma is further pronounced by the observation that the transient absorption spectrum of the local acridinium triplet clearly observed for 2 (see Figures 6 and 7) is virtually identical to the spectrum attributed in the literature to the long-lived CT state of 1, even including the weak absorbance in the near infrared [13].

2.4. Reaction of the long-lived transient with anthracene. A property of the long-lived species derived from 1 and claimed to support its CT nature is that it reacts with anthracene to produce the...
Figure 5. Simplified MO diagram to show how excitation of the CT state of a D/A system can lead to the locally excited state of the donor.

Figure 6. Long-lived transient absorption recorded for 2 in deoxygenated acetonitrile (conc. 0.5 mM, pathlength 1 cm) at room temperature. Curves from top to bottom represent spectra observed with a delay time of 200 ns, 600 ns, 1000 ns and 1400 ns respectively after laser excitation (450 nm, fwhm 2.7 ns, 2 mJ per pulse).

Figure 7. Transient absorption spectrum (delay 20 ns) obtained for 2 under identical conditions as in Figure 6 except for the addition of iodomethane (10% v/v). Note the ca. sevenfold increase in maximum absorbance.

It should be noted that the strongly oxidizing properties of the acridinium triplet may also well explain other photoredox processes reported for 1 and (again) thought to require a long-lived CT state as the active species [14, 15].

3. CONCLUDING REMARKS

Based on the results obtained herein for 2 we tentatively conclude that, not only in 2 but in all likelihood also in 1, photoexcitation produces a CT state with
a lifetime in the nanosecond domain. Furthermore, the long-lived species observed for 1 by flash photolysis in solution is in fact the local triplet of its acridinium chromophore, as shown above for 2.

Whether the very persistent EPR signals reported [13] for 1 after illumination in a solid matrix at low temperature are also attributable to such a local triplet state seems unlikely in view of what is known about the EPR behaviour of 2 under such conditions [23] as well as on the basis of photo-EPR results obtained by us with 1 [16]. We therefore feel the urgent need to re-investigate the photophysical and photochemical properties of 1 in solution. Such re-investigations are underway at the time of writing and will be reported separately.

4. EXPERIMENTAL

4.1. Materials. Spectrograde acetonitrile was used as a solvent. All solutions used in time resolved spectroscopy were deoxygenated by bubbling with argon. The 9-(1-naphthyl)-10-methylacridinium chloride 2 was available from earlier investigations [21], and was synthesized according to the method of Bernhisen [28] by heating diphenyl amine (13 mmol), 1-naphthoic acid (19.2 mmol) and zinc chloride (29 mmol) in methanol/ether. 1H-NMR (200 MHz; CD3OD): δ 5.05 (s, 3H, N+CH3), 7.00 (d, 1H, naphthyl), 7.33 (t, 1H, naphthyl), 7.59 (t, 1H, naphthyl), 7.65 (d, 1H, naphthyl), 7.7-7.9 (m, 5H, acridinium-H2,7; acridinium-H1,8; naphthyl-H), 8.14 (d, 1H, naphthyl), 8.30 (d, 1H, naphthyl), 8.42 (t, 2H, acridinium-H3,6), 8.84 (d, 2H, acridinium-H4,5).

4.2. Instrumentation. Continuous electronic absorption and emission spectra were measured on a Hewlett-Packard 8543 diode spectrophotometer and a SPEX Fluorolog III spectrofluorimeter with a GaAs photomultiplier. The fluorescence lifetime of 2 was determined using a Hamamatsu C5680-21 streak camera coupled to a Chromex IS250 spectrograph for detection and a Coherent Infinity-XPO laser for excitation at 450 nm (fwhm 2.7 ns). The same laser was also used as the excitation source in the nanosecond transient absorption measurements using a set-up slightly modified with respect to that described earlier [29]. As before a small microsecond flash lamp (EG & G, FX504) was used as the source of white probe light and spectrally resolved detection was done with a Princeton Instruments gated (minimum gatewidth 5 ns) intensified CCD camera (ICCD-576-G/RR-EM) coupled to a spectrograph. While alternating shots with laser-on and laser-off as usual provided the I and I0 signals, an additional beam splitter was now placed in the probe light beam before it enters the sample to generate on a separate stripe of the detection CCD a reference spectrum of the white light for every shot, which allows for better compensation in fluctuations of the spectral output of the probe flash.

For femtosecond transient absorption measurements a set-up was used nearly identical to one described before [30]. Excitation pulses (fwhm 130 fs, rep. rate 1 kHz) were derived from a Spectra-Physics Hurricane Titanium:Sapphire regenerative amplifier system via an optical parametric amplifier (Spectra Physics OPA 800). White probe light was generated using the residual fundamental light of the OPA focused on sapphire. The probe light was delayed using a motorized delay line (Physik Instrumente M-531DD). The excitation and probe beams pass through the stirred sample cell (pathlength 2 mm) at an angle of ca. 8 degrees. The probe beam emerging from the sample is fiber coupled into a CCD spectrometer (Ocean Optics, PC 2000). A chopper placed in the excitation beam provided I and I0 depending on the status of the chopper (open or closed). Experiments were performed under magic angle condition to circumvent the possible influence on the transient absorption of the solute molecule.

REFERENCES
