

ARTICLES

 α -Terthiophene in Micellar Solutions: Influence of Micellar Size and Charge on the Terthiophene Photophysics and Photochemical Reactivity

Jan van Stam,^{†,||} Frank Imans,[†] Lucien Viaene,^{*,†} Frans C. De Schryver,[†] and Christopher H. Evans^{‡,§}

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, BE-3001 Heverlee, Belgium, and Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavík, Iceland

Received: October 8, 1998; In Final Form: February 24, 1999

The photophysics and photochemistry of α -terthiophene (α T) in one nonionic, three cationic, and one anionic micellar systems have been investigated. If the micelles are large enough, α T follows a Poissonian distribution among the micelles. The extinction coefficients and the fluorescence quantum yields are independent of the surfactant forming the host micelle. The survival probability of the α T triplet is dependent on the number of α T's per micelle; the lower this number is, the longer the triplet survives. The triplet decays multiexponentially at times close to the excitation event but monoexponentially at longer times. The triplet remains in its host micelle due to a substantially slower intermicellar migration as compared to that of the α T radical cation. Delayed fluorescence emission, due to triplet–triplet annihilation, was detected in all systems. The rate constant of the delayed fluorescence could be correlated to the micellar volume of the ionic surfactants. For the nonionic surfactant, it was assumed that the α T molecule can penetrate the hydrophilic shell between the hydrophobic core of the micelle and the aqueous bulk. The yield of formation of the α T radical cation is the highest in the anionic system and the lowest in the neutral one. For the cationic surfactant micelles, the yield is intermediary and approximately equal. The formation of the radical is found to be biphotonic. The formation of the radical coupling product α -hexathiophene occurred in all micellar systems, proving that the radical can leave its host micelle and migrate via the bulk. The α -hexathiophene yield was highest in the anionic micellar system.

1. Introduction

α -Terthiophene (2,2':5',2''-terthiophene, α T) is a compound of increasing interest, due to its potential applicability as a pesticide¹ and as an oligomeric model for conducting polythiophenes and for nonlinear optics materials.^{2–6} The photochemistry and photophysics of the α T chromophore have been investigated in both of these contexts, and emphasis has been put on the chromophore's ability to photosensitize singlet oxygen formation.⁷ Some effort has been made in exploring the nature of the α T singlet excited state,⁸ but much more interest has been paid to its triplet state^{9–17} and the α T radical cation.^{7,17–19}

The study of excited chromophores in organized media continues to be a thriving research field. In many ways, α T is an excellent choice of “guest” or “probe” molecule for such studies. It is a very hydrophobic molecule (aqueous solubility less than 10^{-7} M)²⁰ and a strongly absorbing chromophore that is readily observable even at very low concentrations (μ M level). Its photophysics and photochemistry have been extensively

studied, involving intermolecular energy transfer and electron donor reactions.^{8,9,15–18,21–26} Further, its dynamic photophysics in an organized medium can be probed by a variety of properties including absorbance, fluorescence, and delayed fluorescence.^{11,14,19,27–29}

Excited α T has been examined in a number of organized media, including micelles,¹⁹ zeolites,¹¹ proteins,¹³ and cyclodextrins.^{14,27} Recently, a preliminary study of the photophysics of α T in a nonionic micelle, Triton X-100, was reported.²⁹ It was found that the photophysical and photochemical properties of α T are determined by its Poisson distribution over the Triton X-100 micelles, that neither triplet α T nor the ground-state migrate between micelles while the radical cation does, and that the formation of the α T radical cation is biphotonic.

In the present contribution, the study has been extended to include ionic micelles of the anionic sodium dodecylsulfate (SDS), and the cationic dodecyltrimethylammonium chloride (DoTAC), tetradecyltrimethylammonium chloride (TTAC), and cetyltrimethylammonium chloride (CTAC), as well as to extend the data for the neutral surfactant Triton X-100. Assuming a Poissonian distribution of α T among the micelles, which is shown to also yield a Poissonian distribution of the transients,³⁰ allows the experimental conditions to be chosen so that a known amount of single, double, and multifold occupancy of α T per micelle is achieved.

* To whom correspondence should be addressed. E-mail: Lucien.Viaene@Chem.KULeuven.ac.be.

[†] Department of Chemistry.

[‡] Science Institute.

^{||} Present address: Department of Chemistry, Karlstad University, SE-651 88 Karlstad, Sweden.

[§] Present address: Department of Applied Chemical and Biological Sciences, Ryerson Polytechnic University, 350 Victoria St, Toronto, ON, Canada, M5B-2K3.

TABLE 1: Composition and Acronyms of the Different α T(micelle) Solutions Used in This Study^a

| sample | C_{surf} [mM] | C_{mic} [μ M] | \bar{n} | % _{mono} |
|--------|------------------------|-----------------------------|-----------|-------------------|
| Tx1 | 150 | 2000 | 0.02 | 98 |
| Tx2 | 27.5 | 364 | 0.11 | 90 |
| Tx3 | 8.5 | 111 | 0.34 | 71 |
| Tx4 | 4.4 | 56 | 0.67 | 52 |
| Tx5 | 2.6 | 32 | 1.16 | 32 |
| SDS1 | 128 | 2000 | 0.02 | 98 |
| SDS2 | 29.8 | 364 | 0.10 | 90 |
| DoTAC1 | 130 | 2000 | 0.02 | 98 |
| DoTAC2 | 40.0 | 364 | 0.10 | 90 |
| TTAC1 | 144 | 2000 | 0.02 | 98 |
| TTAC2 | 29.5 | 364 | 0.11 | 90 |
| TTAC3 | 11.8 | 111 | 0.34 | 71 |
| TTAC4 | 7.9 | 56 | 0.66 | 52 |
| CTAC1 | 221 | 2000 | 0.02 | 98 |
| CTAC2 | 41.3 | 364 | 0.11 | 90 |
| CTAC3 | 13.5 | 111 | 0.34 | 71 |
| CTAC4 | 7.5 | 56 | 0.68 | 51 |
| CTAC5 | 4.8 | 32 | 1.17 | 32 |

^a The α T concentration was $38 \pm 2 \mu\text{M}$ for all samples. C_{surf} and C_{mic} are the concentrations of the surfactant and micelles in the samples, while \bar{n} and %_{mono} are defined in the text.

2. Experimental Section

α -Terthiophene (α T, Aldrich), Triton X-100 (Tx-100, Janssen), sodium dodecylsulfate (SDS, BDH specially pure), cetyltrimethylammonium chloride (CTAC, TCI), tetradecyltrimethylammonium chloride (TTAC, TCI), and dodecyltrimethylammonium chloride (DoTAC, ACROS) were used as received. A known volume of a stock solution of α T in methanol was transferred to a volumetric flask and the solvent evaporated. Surfactant and water of Milli-Q quality were added to give the desired final concentrations. The solutions were allowed to stir for at least 24 h to ensure complete dissolution of α T. The composition of the samples is given in Table 1. The micelle concentrations varied within the range 30–2000 μM , while the α T concentration was about 38 μM in all cases.

The steady-state emission and excitation spectra were recorded in the front-face mode on a SPEX Fluorolog 1680 combined with a SPEX Spectroscopy Laboratory Coordinator DM1B, and the absorption spectra recorded on a Perkin-Elmer λ -6 spectrophotometer. The triplet–triplet absorption and annihilation measurements were made on deoxygenated samples (Ar bubbling). The transient absorption spectrometer has been described elsewhere.^{31,32} Gate widths of 10 and 100 ns were used. The excitation wavelength was 355 nm and the temperature 20 °C for all measurements.

The α -hexathiophene (α H) formation was estimated by measuring the decrease of α T absorption at the absorption maximum.

Compartmentalization of small hydrophobic molecules in a micellar solution results in a Poissonian distribution of the dissolved species.³³ If \bar{n} denotes the stoichiometric average of dissolved species per micelle, and assuming that α T follows a Poissonian distribution in the micelles, the probability P of finding i α T molecules in a micelle can be estimated by

$$P(i) = \frac{\bar{n}^i}{i!} \exp(-\bar{n}) \quad (1)$$

For simplicity, the α T distribution among the micelles, assuming a Poissonian distribution, will be given as the parameter %_{mono} in Table 1. %_{mono} is the percentage of all α T molecules yielding a single occupancy of the micelles, i.e.,

$$\%_{\text{mono}} = \bar{n} \exp(-\bar{n}) / \sum_i i P(i) \quad (2)$$

If assuming that the relative amount of all α T present as dimers or higher in the micelles, i.e., double or higher occupancy, can be taken together and be treated as double occupancy only, $100 - \%_{\text{mono}}$ equals the percentage of micelles with a double occupancy by α T. The error introduced by this sum of different aggregates is minor, as only an extremely low percentage of the α T will be present as trimers or higher, even at higher values of \bar{n} . For instance, for $\bar{n} = 1$, only 8% of the α T molecules are in micelles with triple occupancy or higher.

Surfactant micelles were used for the compartmentalization of α T. The characteristics of these micelles, i.e., the critical micelle concentration (cmc), aggregation number ($\langle a \rangle$), and the micellar hydrophobic volume ($V_{\text{h,mic}}$) are given in Table 2.

3. Results and Discussion

3.1. Emission and Absorption Measurements and α T Distribution. The emission of α T in the ionic micelles is similar to that reported earlier for the neutral Tx-100 micelles.²⁹ The emission intensity was constant within experimental error, as are also the extinction coefficients, for the different micellar environments, showing that the fluorescence quantum yield can be regarded as independent of the charge sign of the surfactant forming the micellar host for α T. It should also be mentioned that none of the micellar systems showed the emission attributed to the α T excited dimer that was found in inclusion complexes of α T with γ -cyclodextrin.²⁷

To determine the extinction coefficients of α T in the different micellar systems, absorption measurements were performed. For low \bar{n} , the α T absorption follows the Lambert–Beer law in all systems. But, for high \bar{n} , yielding low %_{mono}, deviations were found for the surfactants with the shortest hydrophobic tails, i.e., SDS and DoTAC. The micelles of these surfactants have a small volume, Table 2, evidently too small to allow double occupancy by α T. For the systems of surfactants with longer hydrophobic chains, two or more α Ts per micelle are possible. Scaling the absorption with %_{mono} for the SDS and DoTAC micelles yielded a constant extinction, further proving that these micelles hardly allow double occupancy by α T. To determine the extinction coefficient, stock solutions with a very low \bar{n} , i.e., $\bar{n} = 0.01$, were used. The extinction coefficients, Table 3, are close to identical for all systems studied and are similar to the extinction coefficient of α T in Tx-100 micelles reported by Reyftman et al.³⁴

One may argue, that more than one molecule of α T should be allowed to dissolve in an SDS or DoTAC micelle. Pyrene, for instance, does not have this restriction, even though its volume is larger than that of α T.^{35–37} One must remember two things, however, concerning α T: First, its length is larger than that of pyrene. Not only the volume, but also the length is a restricting factor for the solubility in micelles. Second, as has been shown earlier,²⁷ the solubility of α T is very sensitive to the volume of the hydrophobic environment. In a host γ -cyclodextrin molecule, it is possible to include two α T molecules, while this is not possible in the slightly smaller β -cyclodextrin cave. One reason for this behavior is that the α T molecule is twisted around its bonds and that this twisting changes upon excitation. The twisting also leads to a larger effective volume, which also may play an important role in the present investigation. Evidently, these factors, possibly together with others, lead to a solubility limit in the SDS and DoTAC micelles, which is smaller than that of micelles of the other surfactants used in this study, preventing double occupancy.

TABLE 2: Characteristics for the Surfactants Used in This Study and Their Micelles^a

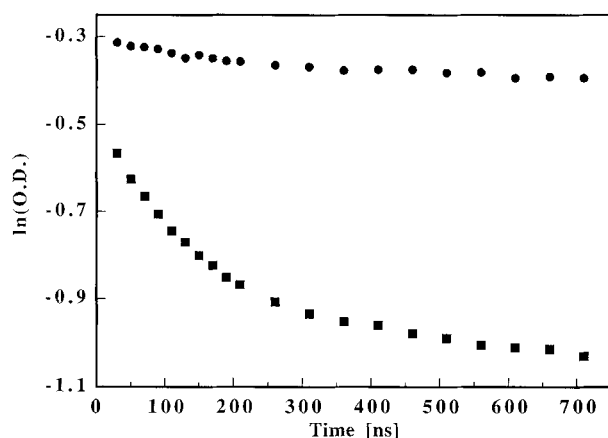
| surfactant | Tx-100 | SDS | DoTAC | TTAC | CTAC |
|--------------------------------------|---------------------------------|------------------|------------------|---------------------|-------------------|
| $\langle a \rangle$ | 75 ⁴⁵ | 60 ⁴⁶ | 55 ³⁶ | 65–70 ⁴⁷ | 110 ⁴⁸ |
| cmc [mM] | 0.2 ⁴⁹ | 8 ³⁶ | 20 ³⁶ | 4 ³⁶ | 1.3 ³⁶ |
| r_{mic} [Å] | 26 ^{b/43} ^c | 17 | 17 | 19 | 22 |
| V_{h} [Å ³] | 980 | 350 | 350 | 400 | 460 |
| $V_{\text{h,mic}}$ [Å ³] | 73600 ^b | 21000 | 19300 | 26300 | 50400 |
| | 333000 ^c | | | | |
| V_{rel} | 3.5–16 | 1 | 0.92 | 1.25 | 2.40 |

^a $\langle a \rangle$ is the micellar aggregation number and cmc the critical micelle concentration. The hydrophobic radius r_{mic} and the hydrophobic volume per surfactant V_{h} are calculated by Tanford's formulae⁴⁴ for the ionic surfactants, while the results of Robson and Dennis⁴⁰ are used for Tx-100. The micellar hydrophobic volume $V_{\text{h,mic}}$ is calculated by use of $\langle a \rangle$ and V_{h} . V_{rel} is the hydrophobic micellar volume relative to that of SDS. ^b Hydrophobic core. ^c Micelle.

TABLE 3: Molar Extinction Coefficients at the Absorption Maximum and the Absorption Maximum Wavelength of α T in Different Micellar Systems^a

| surfactant | $\epsilon_{\lambda_{\text{max}}}$ [M ⁻¹ cm ⁻¹] | λ_{max} [nm] |
|------------|---|-----------------------------|
| Tx-100 | 22700 | 357 |
| SDS | 23600 | 354 |
| DoTAC | 24400 | 360 |
| TTAC | 24100 | 362 |
| CTAC | 24100 | 361 |

^a The extinction coefficients were determined at low α T concentrations, yielding no double occupancy of the micelles.

**Figure 1.** Logarithm of the triplet–triplet optical density at 465 nm vs time, with a gate width of 10 ns. (●) Sample Tx2. (■) Sample Tx5.

3.2. α T Triplet Lifetime and Yield. The decay of the triplet state of α T, $^3\alpha$ T, was investigated by transient absorption measurements. For events close to the excitation moment, i.e., the first 200 ns, the triplet decay is multiexponential, Figure 1. This might at a first sight seem to contradict what was reported earlier for α T in Tx-100 micelles.²⁹ One must keep in mind, though, that, in the preceding study, the triplet decay was studied with a lower time resolution. In the present study, the decay close to the excitation event is better resolved and shows a clear multiexponential decay. For longer times, however, the decay tends to a monoexponential part in all investigated systems, Figure 1. The contribution of the initial decay increases with increasing \bar{n} , as well as with increasing excitation energy. This is due to triplet–triplet annihilation at higher α T occupancy of the micelles. For the nonmigrating $^3\alpha$ T (vide infra), triplet–triplet annihilation can only occur if two $^3\alpha$ T are created in the same micelle upon excitation, hence the dependency on \bar{n} and laser energy. For longer times, i.e., after 200 ns, when triplet–triplet annihilation becomes negligible because all multioccupied

TABLE 4: Triplet–Triplet Absorption at 465 nm, as a Function of Excitation Laser Energy, Measured 100 ns after the Excitation and with a Gate Width of 100 ns

| sample | 7 mJ/pulse | 17 mJ/pulse | 38 mJ/pulse |
|--------|------------|-------------|-------------|
| Tx2 | 0.51 | 0.84 | 0.88 |
| Tx3 | 0.47 | 0.72 | 0.77 |
| Tx4 | 0.41 | 0.65 | 0.66 |
| Tx5 | 0.37 | 0.49 | 0.50 |
| CTAC2 | 0.57 | 0.91 | 0.94 |
| CTAC3 | 0.54 | 0.84 | 0.85 |
| CTAC4 | 0.51 | 0.79 | 0.82 |
| CTAC5 | 0.49 | 0.76 | 0.79 |

TABLE 5: Decay Rates and Integrated Intensities of the Delayed Fluorescence from α T Triplet–Triplet Annihilation in Different Micellar Solutions^a

| sample | $k_{\text{DF}} \times 10^{-7}$ [s ⁻¹] | intensity ^b |
|--------|---|------------------------|
| Tx2 | 0.74 | 0.23 |
| Tx3 | 0.78 | 0.68 |
| Tx4 | 0.85 | 0.79 |
| Tx5 | 0.90 | 1 |
| SDS2 | 8.5 | 0.03 |
| DoTAC2 | 7.4 | 0.03 |
| TTAC2 | 4.5 | 0.06 |
| TTAC3 | 5.0 | 0.13 |
| TTAC4 | 5.3 | 0.19 |
| CTAC2 | 2.4 | 0.08 |
| CTAC3 | 2.6 | 0.18 |
| CTAC4 | 2.8 | 0.27 |
| CTAC5 | 3.0 | 0.32 |

^a The excitation laser energy was 17 mJ/pulse and the gate width 10 ns. ^b Relative to the intensity of Tx5.

micelles are fully quenched, the triplet decay is identical for the different samples. The decay time is 120 ± 20 μ s, in accordance with what has been reported for other compartmentalized systems¹⁴ and substantially longer than in homogeneous solutions.^{14,16} The dependence of $^3\alpha$ T formation on \bar{n} and excitation energy is also clear when comparing the triplet absorption 100–200 ns after excitation, Table 4. The absolute values of the triplet–triplet absorption decrease as \bar{n} increases, while they increase with increasing laser energy. At higher laser energies, a saturation limit is reached. The dependence on \bar{n} is due to the increased probability of triplet–triplet annihilation at higher \bar{n} , while the saturation limit is a consequence of the finite number of α T molecules, i.e., ground-state depopulation.

The wavelength of the absorption maximum of $^3\alpha$ T in the different micellar environments does not shift much, it varies between 463 nm for SDS and 467 nm for Tx-100. When comparing systems with equal \bar{n} , one finds that the absorption of $^3\alpha$ T in SDS, 100–200 ns after excitation, is significantly lower compared to the other micellar systems, while it is approximately equal in the systems of the other surfactants. This difference can, however, not unequivocally be ascribed to a lower triplet quantum yield in the anionic environment. The much more efficient radical formation in SDS, vide infra, will play a decisive role in this system.

3.3. Delayed Fluorescence. Delayed fluorescence, due to triplet–triplet annihilation, is observed in all samples. The intensity of the delayed fluorescence is proportional to the α T occupancy, Table 5. This is due to the immobility of $^3\alpha$ T triplet, which was shown earlier for Tx-100,²⁹ and also found for the ionic surfactant micelles in this study. Annihilation will only occur in micelles that initially contain more than one $^3\alpha$ T, and will thus be a function of both \bar{n} and excitation energy. From the absorption measurements, it was concluded that the SDS and DoTAC micelles on average are too small to host more than one α T molecule. The delayed fluorescence observed in

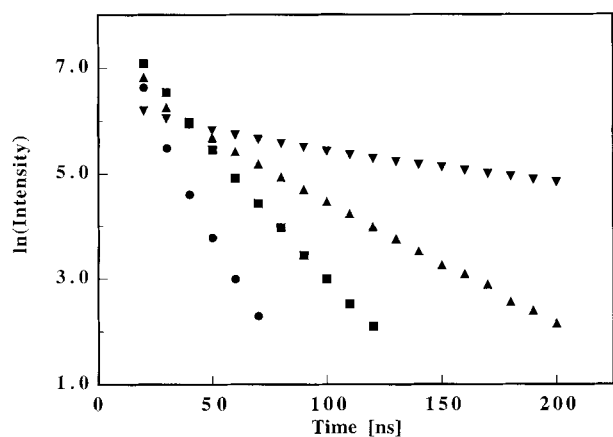


Figure 2. Logarithm of the delayed fluorescence intensity vs time, with a gate width of 10 ns. (●) Sample SDS2. (■) Sample TTAC2. (▲) Sample CTAC2. (▼) Sample Tx2.

these systems is indeed an order of magnitude weaker than that in TTAC and CTAC, Table 5, but significant. An explanation for the observed delayed fluorescence in these systems is that the presence of excess α T induces aggregation of small α T/surfactant aggregates (vide infra), from which the weak delayed fluorescence originates. One should also keep in mind that there is a certain distribution of the micellar sizes, allowing some SDS or DoTAC micelles to be large enough to host more than one α T.

Delayed fluorescence due to triplet-triplet annihilation has by nature a biexponential decay: a growth-in at shorter times and a decay at longer times. Due to experimental conditions, the delayed fluorescence was studied from 10 ns after the excitation event. Under these circumstances, the decay is monoexponential, and its rate is approximately independent of \bar{n} for micelles of the same surfactant, Table 5. The rate is, however, strongly dependent on the surfactant forming the micelle, Table 5 and Figure 2. To understand this difference, a comparison with fluorescence quenching in micelles can be made. It has been assumed that the pseudo-first-order quenching rate in micelles can be treated as inversely proportional to the micellar hydrophobic volume,³⁸ an approach successfully applied to complex micellar systems.³⁹ Applying this model to the delayed fluorescence, though different from fluorescence quenching but similarly originating from the diffusion of two species within a micelle, and use of the data in Table 2, allows control of the correlation between the decay rate and the micellar hydrophobic volume. From this control, it is evident that the hydrophobic volume of Tx-100 is by far too small to explain the low value of the delayed fluorescence decay rate in this surfactant micelle. Keeping in mind, however, that the hydrophilic headgroup of Tx-100 is a neutral ethylene oxide oligomer, allows the assumption that the α T molecule, excited or not, is not restricted to the hydrophobic core only in Tx-100 micelles, but can penetrate the hydrophilic corona as well. If so, the effective volume of the Tx-100 micelle, available to α T, will be larger.

Using the decay rate constants in Table 5 and the hydrophobic radii given in Table 2 makes it possible to calculate the effective radius, \bar{r}_{Tx} , of the sphere wherein α T is confined in a Tx-100 micelle by

$$\bar{r}_{Tx} = r_x \left(\frac{k_x}{k_{Tx}} \right)^{1/3} \quad (3)$$

where r_x is the radius of the hydrophobic core of one of the

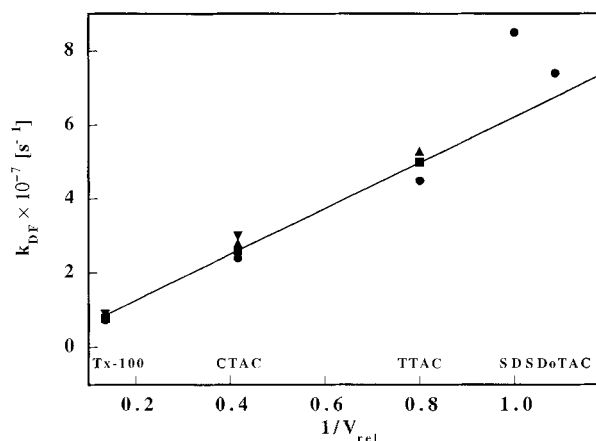


Figure 3. The decay rate of the delayed fluorescence as a function of the inverse effective micellar volume, relative to that of SDS, measured at different α T occupancy numbers: (●) $\bar{n} = 0.1$. (■) $\bar{n} = 0.3$. (▲) $\bar{n} = 0.7$. (▼) $\bar{n} = 1.1$. The inserted line serves as a guide for the eye only.

TABLE 6: Absorption, at 540 nm, of the α T Radical Cation, 10 μ s after Excitation^a

| sample | absorption |
|--------|------------|
| Tx1 | 0.03 |
| SDS1 | 0.24 |
| DoTAC1 | 0.06 |
| TTAC1 | 0.06 |
| CTAC1 | 0.05 |

^a The gate was 100 ns and the laser excitation energy 38 mJ/pulse.

other surfactant micelles and k_x and k_{Tx} are the decay rates of the delayed fluorescence in the other surfactant micelle and Tx-100, respectively. Using the values from Table 5 and calculating \bar{r}_{Tx} for the different \bar{n} , yields an average value of $\bar{r}_{Tx} = 32.5 \pm 0.4$ Å. This means, with the values for the radius of the hydrophobic core and the thickness of the hydrophilic corona taken from Robson and Dennis,⁴⁰ i.e., 26 and 17 Å, respectively, that the α T molecule can penetrate a substantial part of the hydrophilic shell of the Tx-100 micelle. The effective volume of the Tx-100 micelle can be calculated to be 7.4, relative to that of an SDS micelle. From Figure 3, where this value for the relative volume of the Tx-100 micelle is used, it can be seen that the estimated decay rates of the delayed fluorescence show a linear dependence with the inverse of the relative volume, as predicted. For two of the micellar systems, though, the decay rates deviate from the linear relation shown by the others; for SDS and DoTAC, the decay rates are higher than expected. As mentioned above, these surfactant micelles are not able to dissolve more than one α T molecule, while at least a double occupancy is a prerequisite for delayed fluorescence. Most probably, the presence of excess α T induces formation of small α T/surfactant aggregates with a volume of such an aggregate smaller than that of an ordinary micelle. This kind of aggregation causes the α T molecules to be much closer to each other and yields a faster decay of the delayed fluorescence.

3.4. α T Radical Cation Formation and Decay. The α T radical cation, αT^{*+} , was formed in all systems studied. The formation yield, however, is strongly dependent on the kind of micelle, Table 6.

Comparing the cationic surfactant micelles at the lowest \bar{n} , at which there is almost no double occupancy by α T in the micelles and, subsequently, annihilation processes do not occur to a significant extent, shows that the formation yield in these systems is equal within experimental error. The αT^{*+} formation

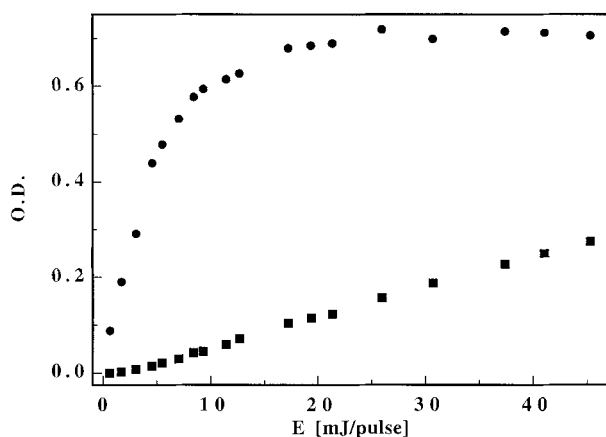


Figure 4. Amount of $^3\alpha\text{T}$ (●) and $\alpha\text{T}^{\bullet+}$ (■) as a function of laser excitation energy. The sample was SDS2. $^3\alpha\text{T}$ was measured at 465 nm, 100–200 ns after excitation, and $\alpha\text{T}^{\bullet+}$ at 540 nm, 10–10.1 μs after excitation.

in Tx-100 micelles is slightly less efficient than in the cationic ones, while it is about 5 times more efficient in SDS micelles, Table 6. These findings are what one would expect for the formation of a cationic species. First, the formation will be more efficient in a polar environment than in a nonpolar one, hence the lowest yield for Tx-100. Second, $\alpha\text{T}^{\bullet+}$ is formed by the extraction of an electron, which will be more efficiently transferred to a cationic bulk (SDS counterions) than to an anionic one (DoTAC, TTAC, and CTAC counterions). Finally, the anionic SDS/water interface can stabilize the cationic $\alpha\text{T}^{\bullet+}$. The two last arguments explain the much higher yield in SDS as compared to the cationic surfactant micelles. It should be mentioned that the same conclusion was made for the formation of a quinoline derivative radical in charged micelles.⁴¹ Another feature to keep in mind is that it was not possible to follow the $\alpha\text{T}^{\bullet+}$ for the first 10 μs after excitation, because of the high triplet–triplet absorption, even in samples that are not deoxygenated.

The decay of $\alpha\text{T}^{\bullet+}$ was measured in samples SDS1 and SDS2, and was found to be monoexponential in both cases. The monoexponential decay is due to the pseudo-first order reactions in a micellar environment. In these specific samples, where evidently no double occupancy by αT in the micelles occurs, the rate-determining step will be the exit rate of $\alpha\text{T}^{\bullet+}$ from the micelle into the bulk. Despite the similarities of the two samples, the estimated decay times were different: they were 3.3 ms and 7.5 ms in SDS1 and SDS2, respectively. This might at a first sight seem to be contradictory, because the initial αT concentration was approximately equal in both samples. There is, however, a large difference in ionic strength between the two samples; it is about 4 times higher in SDS1. For this sample, electrostatic effects will be less pronounced, leading to a faster exit of $\alpha\text{T}^{\bullet+}$ from the micelle to the bulk. The decay of the radical cation was faster in the cationic and neutral micellar systems, but because of the very low formation yield, rate constants could not be determined.

Finally, the formation of $\alpha\text{T}^{\bullet+}$ as a function of excitation laser energy was investigated for ionic micelles. It was reported that the formation of the radical occurred biphotonically in Tx-100 micelles,²⁹ contrary to what has been suggested for αT in homogeneous solutions, where a monophotonic creation is suggested.¹⁵ From Figure 4, it can be concluded that the formation of $\alpha\text{T}^{\bullet+}$ in SDS micelles is also a biphotonic process. Even at energies higher than that at which the triplet saturation limit is reached, the radical absorbance increases with excitation energy. At the point where the triplet formation is saturated,

TABLE 7: Rate of Formation of αH via Radical Coupling of $\alpha\text{T}^{\bullet+}$, Relative to the Rate Estimated for Sample SDS2

| sample | relative rate | sample | relative rate |
|--------|---------------|--------|---------------|
| Tx1 | 0.04 | TTAC1 | 0.30 |
| Tx2 | 0.10 | TTAC2 | 0.50 |
| Tx3 | 0.17 | TTAC3 | 0.65 |
| Tx4 | 0.23 | TTAC4 | 0.75 |
| Tx5 | 0.26 | CTAC1 | 0.32 |
| SDS1 | 0.63 | CTAC2 | 0.32 |
| SDS2 | 1 | CTAC3 | 0.33 |
| DoTAC1 | 0.26 | CTAC4 | 0.34 |
| DoTAC2 | 0.31 | CTAC5 | 0.36 |

all αT molecules are excited. If the radical yield increases at laser energies higher than this saturation energy, a second photon has to be absorbed by an excited αT and, hence, the radical formation is biphotonic. The same was found for the cationic micelles (data not shown). Furthermore, the triplet saturation limit is reached at 20 mJ/pulse, which is equal to what was found for αT in Tx-100 micelles.²⁹ This corroborates the assumption that the triplet yield is independent of the kind of surfactant forming the host micelle.

3.5. Formation of α -Hexathiophene. Wintgens et al. mentions radical coupling as a possible reaction path for the $\alpha\text{T}^{\bullet+}$ radical, leading to the formation of α -hexathiophene (αH).¹⁵ The formation of αH was reported earlier for Tx-100 micelles.²⁹ A more thorough study, taking \bar{n} as well as the kind of micelle into account as parameters, reveal striking differences between the micellar host systems, Table 7. αH was produced in all systems studied, which proves that the αT radical can exit all host micelles into the bulk, even when it is stabilized by the anionic micelle/bulk interface in the SDS systems. The SDS systems are also the ones with the highest reactivity, Table 7, which is as expected, as the formation yield of $\alpha\text{T}^{\bullet+}$ is the highest in this environment. Moreover, the decay time of $\alpha\text{T}^{\bullet+}$ is long for both SDS samples (vide supra), and longer than in the cationic and neutral systems. The longer decay time increases the probability of an $\alpha\text{T}^{\bullet+}$ to exit the host micelle into the bulk and to react with another αT , either a radical in the bulk or a ground- or triplet-state αT in a micelle. The higher yield for SDS2 as compared with SDS1 is a consequence of the longer radical decay time in the former, as discussed above.

Turning to the cationic micelles, some similarities and differences are found. At the lowest \bar{n} , where only singly occupied micelles are present and all αH formation has to be due to a migrating $\alpha\text{T}^{\bullet+}$, the formation rate is roughly equal for DoTAC, TTAC, and CTAC. For higher occupancies, however, differences are found. In DoTAC, a slight increase is found going from DoTAC1 to DoTAC2, for the same reason as for SDS1 and SDS2. For TTAC, where it is possible to go up to $\bar{n} = 0.66$, with only 50% of the αT in singly occupied micelles, a clear increase in αH formation is seen as a function of \bar{n} . This is due to the possibility of a radical coupling reaction within the micelle where the radical is formed as a complement to a bulk reaction and in competition with recombination. For CTAC, though, the reaction rate is nearly constant with \bar{n} . The CTAC micelles are quite large and also take a different shape than the other ionic micelles. The larger volume leads to an increased probability for $\alpha\text{T}^{\bullet+}$ to exit the micelle into the bulk before it reacts with another αT in the same micelle. The CTAC micelle has a lower curvature as compared to TTAC, which might influence the surface potential of the micelle and facilitate the exit. Because the αH formation rate remains almost equal to that estimated for CTAC1, the conclusion is that the radical coupling predominantly occurs in the aqueous bulk for the CTAC systems.

The nonionic Tx-100 shows a similar pattern as TTAC, i.e., an increase in αH formation with increasing \bar{n} , despite the large effective volume of Tx-100 micelles. One thing needs to be kept in mind for the Tx-100 systems: the radical yield is lower than what is found in the ionic systems. One should also keep in mind the influence of the rather thick hydrophilic shell on the charge separation following radical formation, as pointed out by others.^{42,43} Clearly, the αH formation in this nonionic system is not predominantly a bulk reaction but occurs in the micelle. Finally, it should be mentioned that adding a salt, NaCl, to a Tx-100 solution promotes the formation of αH . This is possibly due to either a higher $\alpha\text{T}^{+\bullet}$ yield or to a more efficient separation of the radical and the electron, leading to a longer decay time, with the latter possibility being more likely.

The influence of the laser excitation energy on αH formation was also investigated (data not shown). Increasing the excitation energy leads, as expected, to a higher αH yield, as reported earlier for Tx-100.²⁹ This result is consistent with a biphotonic creation of the radical cation.

4. Conclusions

The photophysics and photochemistry of α -terthiophene in anionic, cationic, and nonionic micellar systems were investigated. For the larger TTAC, CTAC, and Tx-100 micelles, αT was found to follow a Poissonian distribution among the micelles, which was used to alter the local αT concentrations. For the smaller SDS and DoTAC, however, it was found that they could host only one αT per micelle. As the extinction coefficients and the emission intensities are independent of the surfactant forming the host micelle, the fluorescence quantum yield must be independent of the kind of surfactant used in this study.

The detected amount of triplet $^3\alpha\text{T}$ is dependent on the micellar occupancy number \bar{n} : The lower the occupancy, the more $^3\alpha\text{T}$ is detected. This is due to the triplet–triplet annihilation process that consumes triplets formed in the same micelle upon excitation. The decay of $^3\alpha\text{T}$ is multiexponential, also due to the annihilation process, but has a monoexponential part at longer times, when annihilation becomes insignificant.

Delayed fluorescence emission is due to triplet–triplet annihilation, a process similar to fluorescence quenching in micellar systems. Because of this similarity, the rate constant of delayed fluorescence is thought to be inversely proportional to the micellar hydrophobic volume. This assumption turned out to be valid for the ionic surfactant micelles, while it yielded a discrepancy for the nonionic Tx-100. The assumption that even a part of the nonionic ethylene oxide oligomer hydrophilic shell should be taken into account for the effective volume yielded a consistent interpretation. When SDS and DoTAC, which are too small to host more than one αT , are employed as surfactants, small, micellar-like, aggregates are formed to dissolve αT aggregates, leading to high delayed fluorescence rates.

The yield of formation of the radical $\alpha\text{T}^{+\bullet}$ is the highest in the anionic SDS micelles, and the lowest in the nonionic Tx-100 micelles. For the cationic surfactant micelles, the yield is intermediary and approximately equal. The formation of $\alpha\text{T}^{+\bullet}$ is biphotonic.

The formation of the radical coupling product α -hexathiophene, αH , was detected in all micellar systems. The yield was highest in the SDS systems, and in the other systems studied, the yield was lower and of the same order of magnitude at low \bar{n} . The αH formation in the smaller SDS and DoTAC micelles has to occur in the bulk. For the samples with higher \bar{n} , the formation in TTAC and Tx-100 occurs predominantly in the host micelle,

while for CTAC, αH is formed in the bulk after exit of the radical from its host micelle.

Acknowledgment. J.v.S. is a guest scientist at the Laboratory for Photochemistry and Spectroscopy. F.I. thanks the IWT, Belgium, for a predoctoral grant. Financial support from the following sources is gratefully acknowledged: The Katholieke Universiteit Leuven, The Icelandic Research Council (Grant 961880096), The Research Fund of the University of Iceland, The University of Iceland Travel Fund (Sattmalasjodur), DWTC, Belgium, through Grant IUAP-IV/11, and NATO through Grant CRG951478 (J.v.S.).

References and Notes

- (1) Kagan, J. In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Grisebach, H., Kirby, G. W., Tamm, C., Eds.; Springer-Verlag: Wien, 1991; Vol. 56, p 87.
- (2) Greenham, N. C.; Friend, R. H. *Solide State Phys.* **1995**, 49, 1.
- (3) Zotti, G.; Zecchin, S. *Synth. Met.* **1997**, 87, 115.
- (4) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, 119, 5065.
- (5) Fréchet, M.; Belletête, M.; Bergeron, J.-Y.; Durocher, G.; Leclerc, M. *Synth. Met.* **1997**, 84, 223.
- (6) Fréchet, M.; Beletête, M.; Bergeron, J.-Y.; Durocher, G.; Leclerc, M. *Macromol. Chem. Phys.* **1997**, 198, 1709.
- (7) Boch, R.; Mehta, B.; Connolly, T.; Durst, T.; Arnason, J. T.; Redmond, R. W.; Scaiano, J. C. *J. Photochem. Photobiol. A* **1996**, 93, 39.
- (8) Rossi, R.; Ciofalo, M.; Carpita, A.; Ponterini, G. *J. Photochem. Photobiol. A* **1993**, 70, 59.
- (9) Scaiano, J. C.; Redmond, R. W.; Mehta, B.; Arnason, J. T. *Photochem. Photobiol.* **1990**, 52, 655.
- (10) Evans, D. F.; Ninham, B. W. *J. Phys. Chem.* **1986**, 90, 226.
- (11) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, 113, 600.
- (12) Liu, T.-L.; Parakka, J. P.; Cava, M. P.; Kim, Y.-T. *Langmuir* **1995**, 11, 4205.
- (13) Boch, R.; Mohtat, N.; Lear, Y.; Arnason, J. T.; Durst, T.; Scaiano, J. C. *Photochem. Photobiol.* **1996**, 64, 92.
- (14) Evans, C. H.; De Feyter, S.; Viaene, L.; van Stam, J.; De Schryver, F. C. *J. Phys. Chem.* **1996**, 100, 2129.
- (15) Wintgens, V.; Valat, P.; Garnier, F. *J. Phys. Chem.* **1994**, 98, 228.
- (16) Becker, R. S.; de Melo, J. S.; Maçanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, 100, 18683.
- (17) Garcia, P.; Pernaut, J. M.; Hapiot, Ph.; Wintgens, V.; Valat, P.; Garnier, F.; Delabouglise, D. *J. Phys. Chem.* **1993**, 97, 513.
- (18) Scaiano, J. C.; Evans, C. H.; Arnason, J. T. *J. Photochem. Photobiol. B* **1989**, 3, 411.
- (19) Evans, C. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, 112, 2694.
- (20) Downum, K. R.; Rodriguez, E. *J. Chem. Ecol.* **1986**, 12, 823.
- (21) Evans, C. H.; Weir, D.; Scaiano, J. C.; MacEachern, A.; Arnason, J. T.; Morand, P.; Hollebone, B.; Leitch, L. C.; Philogène, B. J. R. *Photochem. Photobiol.* **1986**, 44, 441.
- (22) Port, H.; Hartschuh, A.; Hirsch, T.; Wolf, H. C. *J. Lumin.* **1997**, 72–74, 75.
- (23) Bolívar-Marínez, L. E.; dos Santos, M. C.; Galvão, D. S. *Synth. Met.* **1997**, 85, 1117.
- (24) Bosisio, R.; Botta, C.; Colombo, A.; Destri, S.; Porzio, W.; Grilli, E.; Tubino, R.; Bongiovanni, G.; Mura, A.; Di Silvestro, G. *Synth. Met.* **1997**, 87, 23.
- (25) Demanze, F.; Cornil, J.; Garnier, F.; Horowitz, G.; Valat, P.; Yassar, A.; Lazzaroni, R.; Brédas, J.-L. *J. Phys. Chem. B* **1997**, 101, 4553.
- (26) Lap, D. V.; Grebner, D.; Rentsch, S. *J. Phys. Chem. A* **1997**, 101, 107.
- (27) De Feyter, S.; van Stam, J.; Imans, F.; Viaene, L.; De Schryver, F. C.; Evans, C. H. *Chem. Phys. Lett.* **1997**, 277, 44.
- (28) Botta, C.; Bosisio, R.; Bongiovanni, G.; Mura, A.; Tubino, R. *Synth. Met.* **1997**, 84, 535.
- (29) Viaene, L.; van Stam, J.; Imans, F.; Evans, C. H.; De Feyter, S.; De Schryver, F. C. *Chem. Phys. Lett.* **1998**, 286, 452.
- (30) Rothenberger, G.; Infelta, P. P.; Grätzel, M. *J. Phys. Chem.* **1981**, 85, 1850.
- (31) Van Haver, Ph.; Helsen, N.; Depaemelaere, S.; Van der Auweraer, M.; De Schryver, F. C. *J. Am. Chem. Soc.* **1991**, 113, 6849.
- (32) Van Haver, Ph.; Viaene, L.; Van der Auweraer, M.; De Schryver, F. C. *J. Photochem. Photobiol. A* **1992**, 63, 265.
- (33) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, 101, 279.

- (34) Reyftmann, J. P.; Kagan, J.; Santus, R.; Morliere, P. *Photochem. Photobiol.* **1985**, *41*, 1.
- (35) Almgren, M.; Löfroth, J.-E. *J. Chem. Phys.* **1982**, *76*, 2734.
- (36) Malliaris, A.; Le Moigne, J.; Sturm, J.; Zana, R. *J. Phys. Chem.* **1985**, *89*, 2709.
- (37) Winnik, F. M.; Winnik, M. A.; Tazuke, S. *J. Phys. Chem.* **1987**, *91*, 594.
- (38) Almgren, M. In *Kinetics and Catalysis in Microheterogeneous Systems*, Grätzel, M., Kalyanasundaram, K., Eds.; Marcel Dekker: Basel, 1991; p 63.
- (39) Almgren, M.; van Stam, J.; Lindblad, C.; Li, P.; Stilbs, P.; Bahadur, P. *J. Phys. Chem.* **1991**, *95*, 5677.
- (40) Robson, R. J.; Dennis, E. A. *J. Phys. Chem.* **1977**, *81*, 1075.
- (41) Nekipelova, T. D.; Pirogov, N. O.; Assovski, O. I. *J. Phys. Chem.* **1995**, *99*, 4976.
- (42) Weidemaier, K.; Tavernier, H. L.; Chu, K. T.; Fayer, M. D. *Chem. Phys. Lett.* **1997**, *276*, 309.
- (43) Weidemaier, K.; Tavernier, H. L.; Fayer, M. D. *J. Phys. Chem. B* **1997**, *101*, 9352.
- (44) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; Wiley: New York, 1973.
- (45) Brown, W.; Rymdén, R.; van Stam, J.; Almgren, M.; Svensk, G. *J. Phys. Chem.* **1989**, *93*, 3, 2512.
- (46) van Stam, J.; Lindblad, C.; Almgren, M. *Prog. Colloid. Polym. Sci.* **1991**, *84*, 8.
- (47) Roelants, E.; De Schryver, F. C. *Langmuir* **1987**, *3*, 209.
- (48) Almgren, M.; Hansson, P.; Mukhtar, E.; van Stam, J. *Langmuir* **1992**, *8*, 2405.
- (49) Perkowski, J.; Mayer, J.; Ledakowicz, S. *Colloids Surf. A* **1995**, *101*, 103.