indole ring would give a protonated intermediate **1**, which then loses a deuteron (path a) or a proton (path b) to yield nondeuterated Trp and original Trp-*4*-d_1.[12] Unfortunately, the quantum efficiency of the latter process (path b) cannot be obtained experimentally. However, it is obvious that the quantum yield for path b may well exceed 0.09 since the rate of lighter hydrogen loss from **1** by deprotonation would be much faster than that of the deuteron loss ($\phi = 0.09$). Thus, the quantum yield of proton transfer to the C-4 position of singlet Trp-*4*-d_1 leading to **1** may reach to more than 0.18, i.e., 0.18 ± α.[13] Our results strongly suggest that the reaction of the singlet indole ring with the α-ammonium group leading to the protonated species **2** constitutes one major route for nonradiative decay of singlet Trp at neutral pH.[14] Irradiation of 1-methyltryptophan (18 mM) in D_2O (pD 5.5) gave 4-deuterated 1-methytryptophan (22% D at 30 min) regiospecifically, indicating that the photodeprotonation[3b,15] of N-1 hydrogen of Trp is not responsible for the hydrogen–deuterium exchange reaction. Irradiation of L-tryptophyl-L-tyrosine in D_2O resulted in a selective deuteration at the C-4 position of Trp with no incorporation into the tyrosine moiety.

In summary, we found an efficient and highly selective photosubstitution of C-4 hydrogen of Trp with deuterium in D_2O. Intramolecular proton transfer from the α-ammonium group giving rise to formation of the protonated species **2** has been suggested to play an important role in nonradiative decay of singlet Trp at neutral pH. In light of this finding, mechanistic studies on fluorescence of Trp and indole derivatives should be reinvestigated.

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Registry No. trp, 73-22-3; trp-*4*-d_1, 90697-20-4.

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[12] The calculation of indole by CNDO/S method indicates that the C-4 position displays a considerable increase in electron density on excitation to the ^1L_b state: Evleth, E. M.; Chalvet, O.; Bamière, P. *J. Phys. Chem.* **1977**, *81*, 1913.

[13] If one assumes that the kinetic isotope effect (k_H/k_D) for path a and path b is 2.0, then the quantum yield for the formation of 1 would be 0.27.

[14] Quantum efficiencies for the processes occurring from singlet Trp in light water at pH 7 are as follows: $\phi_f = 0.14$;[3b] $\phi_{isc} \sim 0.27$[8c] (0.10[3e]); $\phi_{ion} \sim 0.08$.[8c] ϕ_f in D_2O is reported to be 0.32.[3b]

[15] Song, P. S.; Kurtin, W. E. *Photochem. Photobiol.* **1969**, *9*, 175.

Thermochromism of Charge-Transfer Complexes between a Vesiculating Paraquat Derivative and Benzidine

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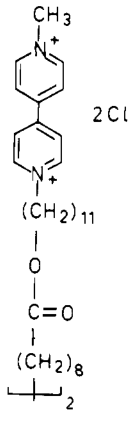
We have recently described the bolaamphiphile **1** with two paraquat head groups, which is readily soluble in water. **1** does, however, form large aggregates (micelles, vesicles, monolayered crystals) if the chloride counterions are partly or fully replaced by perchlorate or if the paraquat dication is reduced to the viologen monocation radical.[1] Further experiments indicated that the reversible aggregation of the tetrachloride **1** can also be induced by cooling of a relatively concentrated aqueous solution (≥10^{-3} M) to 10 °C. A ^1H NMR probe of **1** in D_2O, for example, gives a well-resolved spectrum at 30 °C and very broad bands at 0 °C.



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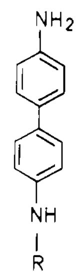

2a: R = H

2b: R = n-$C_{18}H_{37}$

A more dramatic effect of the temperature-dependent aggregation is the reversible formation of a colored polymeric molecular complex ("Scheibe complex"[2]). If benzidine (**2a**) (2 mM) is added to the paraquat tetrachloride **1** (1 mM) at room temperature a slightly reddish colorization of the aqueous solution is observed.[3] On cooling to 15 °C the color turns to bluish, at 5 °C it is dark blue. A new, relatively broad band with a maximum at 615 nm at 15 °C and 630 nm at 5 and 0 °C (OD = 1.9) is observed (Figure 1). On warming to 30 °C the blue color disappears. This cycle can be repeated several times without indications of decomposition of the components. The blue solution is stable against oxygen, gives no ESR signal (no formation of viologen radicals), and produces a blue precipitate after some hours or days. The composition of the precipitate is benzidine–**1**, 4:1,[3,4] i.e., two benzidine molecules per bipyridinium head group. Under the assumption that in solution a 1:1 complex is first formed, we determined a complex formation constant of $K = 250 \pm 100\ M^{-1}$ following Drago's procedure.[5] This compares to a literature value for a dimethylviologen–benzidine complex of $K = 10.5\ M^{-1}$ in ethanol–water, 1:1.[3] An extinction coefficient $\epsilon = 6500 \pm 1400$ was also determined. If sodium perchlorate (1 mM) was added to the solution at 40 °C, a blue complex was formed at once (λ_{max} = 650 nm). On heating this solution, precipitation was first observed, but above 70 °C a clear, slightly yellow solution was obtained. With *N*-octadecylbenzidine (**2b**), no charge-transfer complex was formed with **1**. Indole gave a yellow molecular complex (λ_{max} = 388 nm) but no effect of temperature (0–30 °C) was observed.

The complex formation is pH dependent, since protonated benzidine is not an efficient electron donor and does not bind to paraquat cations. At 0 °C we determined the pH at which half of the blue complex that was present at pH = 6.5 had disappeared. We found this to be the case at pH = 4.6, which is identical with the pK_a = 4.66 reported for the first protonation of benzidine.[6] From this finding it can be concluded that one amino group of benzidine cannot be in contact with the paraquat heat groups, since it is known that the pK_a of bases that are surrounded by positive charges is lowered by at least one unit.[7] We propose a structure in which a positive center of the paraquat head groups binds to one of the electron-rich aniline groups of benzidine. The second aniline ring would be in the aqueous phase (Figure 2).

This structures is in accordance with several crystal structures of charge-transfer complexes, which show the aromatic rings of both components to be shifted by half a ring diameter against each other.[8] The model also explains why the N-alkylated benzidine derivative **2b** gives no charge-transfer complex. It would disturb the aggregation of **1** and its aniline rings could be forced into a position relative to the bipyridinium head groups, where no charge

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[1] Fuhrhop, J.-H.; Fritsch, D.; Tesche, B.; Schmiady, H. *J. Am. Chem. Soc.* **1984**, *105*, 1998.

[2] Scheibe, G. *Angew. Chem.* **1937**, *50*, 212. Zimmermann, H.; Scheibe, G. *Z. Elektrochem.* **1956**, *60*, 566.

[3] Murthy, A. S. N.; Bhardwaj, A. P. *Spectrochim. Acta, Part A* **1982**, *38A*, 207.

[4] White, B. G. *Trans. Faraday Soc.* **1969**, *65*, 2000.

[5] Rose, N. J.; *Drago*, R. S. *J. Am. Chem. Soc.* **1959**, *81*, 6138.

[6] Weast, R. C., *Ed.* "Handbook of Chemistry and Physics", 55th ed.; CRC Press: Cleveland, OH, 1974-1975.

[7] Fuhrhop, J.-H.; Mathieu, J. *Angew. Chem.* **1984**, *96*, 124.

[8] Prout, C. K.; Wright, J. D. *Angew. Chem.* **1968**, *80*, 688.

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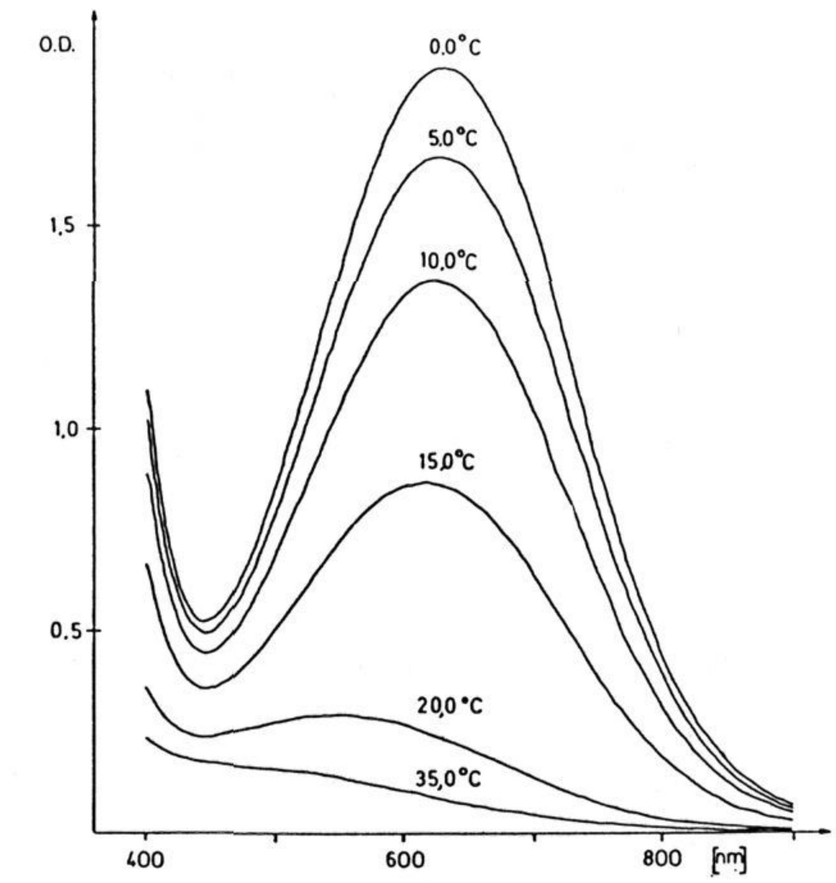

Figure 1. Electronic spectra of a mixture of **1** (1 mM) and **2a** (2 mM) in water (pH 6.5) at different temperatures.

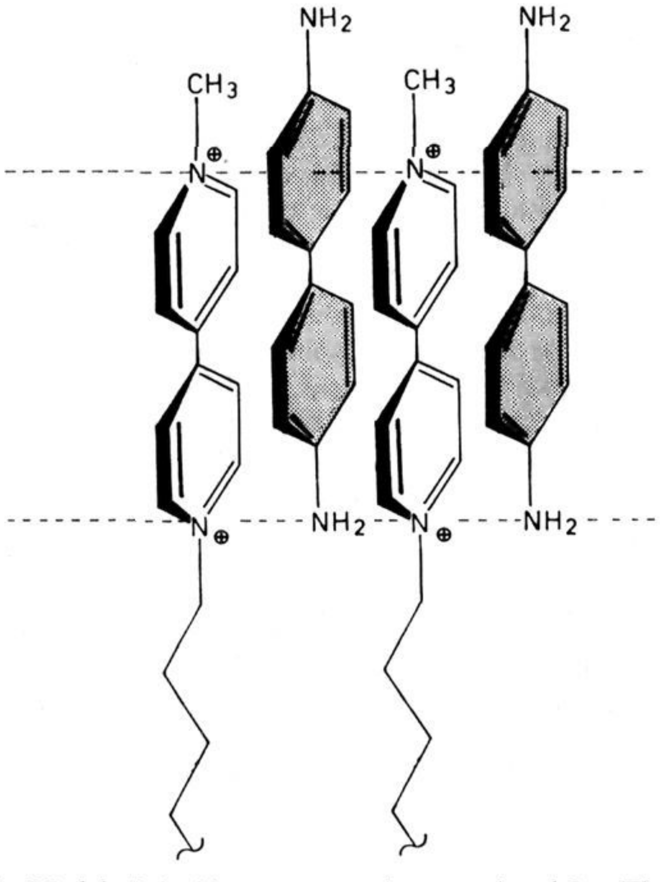

Figure 2. Model of the blue aggregate between **1** and **2a**. The broken lines connect the supposed electron-donating and -accepting centers.

transfer occurs. Less dramatic reversible spectroscopic shifts have been observed earlier.[9] They occur around the phase transition temperature of the hydrophobic membrane. This is not the case with the molecular complex of Figure 2. The temperature at which the color change is observed rather depends on counterions, solubility, and surface charges of guest vesicles. A vesicular charge-transfer complex has also has been desribed earlier,[10] but its absorption spectrum does not change significantly with temperature.

The formation of the blue complex of aggregated paraquat amphiphiles is also useful for the proof of domain formation in host vesicle membranes. **1** was dissolved in dipalmitoyl phosphatidylcholine vesicles in a molar ratio of 1:10. Addition of benzidine gave no blue color at room temperature or 0 °C. After addition of sodium perchlorate at 35 °C and short sonication to circumvent precipitation, however, a strong 615-nm absorption band was again observed at room temperature, which disappeared at 70 °C.

The appearance of long-wavelength bands in vesicular systems is probably not limited to membranes having bipyridinium head groups. We expect similar phenomena with analogous systems, e.g., benzidine head groups and paraquat monomers, hydrophilic quinone head groups and hydroquinone monomers, etc. Work along this line is in progress.

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(9) (a) Russell, J. C.; Costa, S. B.; Seiders, R. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5678. (b) Nakashima, N.; Kunitake, T. *J. Am. Chem. Soc.* **1982**, *104*, 4261.

(10) Murakami, Y.; Nakano, A. *J. Am. Chem. Soc.* **1982**, *104*, 2937.

Controlled Modification of Organic Polymer Surfaces by Continuous Wave Far-Ultraviolet (185 nm) and Pulsed-Laser (193 nm) Radiation: XPS Studies

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Modification of polymer surfaces to improve adhesion or biocompatibility or to provide functionalities for further reaction is an attractive goal.[1,2] Of the various techniques[3,4] that have been considered so far for this purpose, photochemistry has received little attention.[2,5,6] IR and XPS studies of polymer surface oxidation brought about by radiation of wavelength greater than 200 nm have been reported,[7,8] but these were mainly concerned with the photostability of the polymers.

In contrast to radiation >200 nm, far-ultraviolet offers several attractive features for the modification of polymer surfaces: (i) Nearly all polymers absorb intensely and penetration of the radiation (95% absorption) is limited to a depth of 3000 Å.[9] Therefore, the absorption of the photons in the polymer is confined to the diffusion depth of the gas molecules, resulting in high efficiency for the reaction. (ii) The high quantum yield for bond breaking results in short exposure times: upon exposure to 2.5 mW/cm^2 at 185 nm from a mercury resnance lamp, the maximum change in surface composition as monitored by XPS occurs in just a few minutes. Modification of the polymer surface by ablative photodecomposition[9] with a pulsed 193-nm ArF laser results in the creation of a fresh surface with a novel composition.

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(1) Mittal, K. L. "Physicochemical Aspects of Polymer Surfaces"; New York: Plenum Press, 1983. Lyman, D. J. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 108.

(2) Tazuke, S.; Kimura, H. *Makromol. Chem.* **1978**, *179*, 2603.

(3) Chromic acid etching, see: (a) Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4782. (b) Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *Ibid.* **1977**, *99*, 4740.

(4) Plasma treatments, see: (a) Briggs, D.; Rauce, D. G.; Kendall, C. R.; Blythe, A. R. *Polymer* **1980**, *21*, 895. (b) Clark, D. T. In "Polymer Surfaces"; Clark, D. T., Feast, W. J., Eds.; Wiley: London, 1978. (c) Yasuda, H.; Marsh, H. C.; Brandt, S.; Reilley, C. N. *J. Polym. Sci.* **1977**, *15*, 991. (d) Amouroux, J.; Goldman, M.; Revoil, M. F. *J. Polym. Sci.* **1982**, *19*, 1373.

(5) Owens, D. K. *J. Appl. Polym. Sci.* **1975**, *19*, 3315.

(6) (a) Peeling, J.; Clark, D. T. *J. Appl. Polym. Sci.* **1981**, *26*, 3761; *J. Polym. Sci.* **1984**, *22*, 419.

(7) Blais, P.; Day, M.; Wiles, D. M. *J. Appl. Polym. Sci.* **1973**, *17*, 1895.

(8) Peeling, J.; Clark, D. T. *Polymer Degradation Stab.* **1981**, *3*, 92, 177.

(9) Srinivasan, R.; Leigh, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 6784.

0002-7863/84/1506-4288$01.50/0