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PHOTOCHEMICAL BEHAVIOR OF MICELLIZED 4-(4′-ALKYLSTYRYL)PYRIDINIUM SALTS

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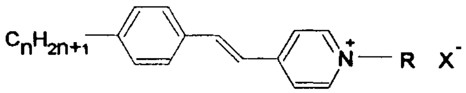
New photochromic surfactants, 1-alkyl-4-(4′-alkylstyryl)lpyridinium halides (C_nStzRX; $n = 0, 4, 6, 8$; R = Me, Et, CH_2CH_2OH, *n*-Bu, *n*-C_9H_{19}; X = Br, I), were synthesized and the photochemical behavior of their micellar aggregates in water was characterized in relation to non-micellizing 1-methyl-4-stilbazolium ions. Reversible *trans–cis* isomerization through a photothermal cycle was observed for the micellized C_nStzRX. Furthermore, photoreactions upon prolonged irradiation of C_nStzRX micelles resulted in a 3–31% formation of thermodynamically least stable *syn*-head-to-head and *ca.* 3% of *anti-* head-to-head dimers. These findings indicate that the self aggregation process of C_nStzRX may provide some topologically organized microenvironment affecting the steric and like-charge repulsions of the aggregate components.

INTRODUCTION

The photochemical behavior of amphiphilic photochromic compounds in solution,[1] in the solid state,[1a,c] solubilized in micelles[1c] and vesicles[2] and embedded in monolayer assemblies[1b,c,3] revealed that the microenvironment can play a major role in determining photoreactivity. The hydrophilic–hydrophobic nature of these molecules may modify their reactivity relative to non-surfactant analogs.[4] The ability of microheterogeneous media[5] to provide a restricted volume of hydrophobic space in an aqueous environment or to offer an interface between the aqueous exterior and a hydrocarbon-like interior, wherein the reactants can be aligned, suggests an opportunity to control or at least obtain some selectivity in photoinduced processes[6] such as *trans–cis* isomerization, dimerization or cyclization.

Derivatives of stilbene,[7] azobenzene,[8] diphenylazomethine,[8c] cinnamic acid[9] and 2-indenecarboxylic acid[9a] have been examined in surfactant systems but none of the cited reports deals with the photoreactions in the micellar aggregates containing exclusively molecules of the photochromic surfactants. In the literature there are also examples of photochemical studies of *N*-methyl and protonated stilbazolium salts in homogeneous solution,[10,11] reversed Aerosol OT micelles[10,11b] and clays.[11,12] The photochemistry and photophysics of amphiphilic *N*-octadecylstilbazolium salts were examined in homogeneous solution,[1a,c] micelles of hexadecyltrimethylammonium bromide,[1c] crystals[1a,c] and monolayer assemblies.[1b,c] It was found that in the solid state and in the monolayer assemblies



n	R	X
0	n - C_9H_{19}	Br
4	Me	Br
6	Me	Br
6	CH_2CH_2OH	Br
6	Et	Br
6	n - Bu	Br
8	Me	Br
6	Me	I

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excimer fluoresce and cyclodimerization are the dominant photoprocesses.[1c] In addition, non-reversible *trans*⟶*cis* isomerization occurs in monolayers. In contrast, for both micellar, and acetonitrile or chloroform solutions, reversible *trans–cis* photoisomerization and monomer fluorescence were the only observed photoreactions even at the solubility limits of surfactant octadecyl-4-stilbazole salts in the solvents.[1c]

In this present work, a new series of 1-alkyl-4-(4'-alkylstyryl)pyridinium halides (C_nStzRX) were designed and synthesized. The photochemical properties of their micellar aggregates in water are characterized in relation to the lengths of the flexible alkyl chain C_nH_{2n+1} and the character of the nitrogen substituent R. For the purpose of comparison, similar non-micellizing compounds, 1-methyl-4-stryrylpyridinium bromide and iodide, were also prepared.

RESULTS AND DISCUSSION

Amphiphilic *trans*-1-alkyl-4-(4'-alkylstyryl)pyridinum halides (C_nStzRX) were prepared in 25–55% yield from alkylbenzenes via formylation, coupling with 4-methylpyridine and quaternization. The products were identified on the basis of their ^{1}H, ^{13}C NMR and IR spectra.

The aqueous solutions of C_nStzRX are clear and non-viscoelastic at room temperature, exhibiting a long-wavelength absorption maximum at 350 nm with log $\varepsilon = 4{\cdot}2$—$4{\cdot}5$. The critical micelle (aggregate) concentration (cmc) values (Table 1) were extracted from electric conductivity measurements.

Dynamic light scattering studies revealed that transparent solutions of C_nStzRX at concentrations of 10 mM or lower but higher than the cmc value include molecular aggregates with a hydrodynamic radius (R_h) ranging from 38 to 50×10^{-10} m (the values of R_h for C_nStzRX are included in Table 1). According to the literature, simple micelles are characteristically spherical in shape with a diameter of $(20-100) \times 10^{-10}$ m,[13] hence it is reasonably assumed that the micellar aggregates of C_nStzRX may be spherical. For dilute solutions, i.e. at concentrations *ca.* five times lower than the cmc, premicellar aggregation has not been detected.

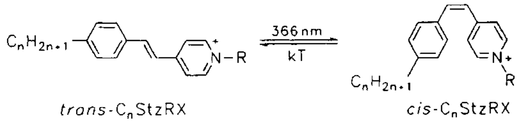
Table 1. Products distribution in the photolysis[a] of C_nStzRX

				Composition of products (%)				
				Alkene		Cyclobutanes[c]		
Compound[b]	Cmc (mM)	10^{10} R_h (m)	Concentration (mM)	*trans*	*cis*	*syn*-HH	*syn*-HT	*anti*-HH
Micellar aggregates								
C_0Stz*n*-C_9H_{19}Br	0·26	50·0	10	29	59	9	nd[c]	3
C_4StzMeBr	3·20	38·2	10	63	25	9	nd	3
C_6StzMeBr	0·88	42·0	2	62	25	10	nd	3
			10	61	25	11	nd	3
C_6StzEtBr	0·87	42·5	10	57	31	9	nd	3
C_6StzCH_2CH_2OHBr	0·83	42·8	10	46	18	31	nd	5
C_6Stz*n*-BuBr	0·54	40·3	10	46	49	3	nd	2
C_8StzMeBr	0·42	47·5	10	57	23	17	nd	3
C_6StzMeI	0·32	43·2	2	73	23	2	nd	2
			10	72	22	3	nd	3
Homogeneous media								
C_0StzMeBr			0·1	20	80	nd	nd	nd
			10	22	13	nd	65	nd
			100	15	9	nd	76	nd
C_0Stz*n*-C_9H_{19}Br			0·05	12	88	nd	nd	nd
C_4StzMeBr			0·64	36	64	nd	nd	nd
C_6StzMeBr			0·17	36	64	nd	nd	nd
C_6StzEtBr			0·17	32	68	nd	nd	nd
C_6StzCH_2CH_2OHBr			0·16	33	67	nd	nd	nd
C_6Stz*n*-BuBr			0·1	27	73	nd	nd	nd
C_8StzMeBr			0·08	39	61	nd	nd	nd
C_0StzMeI			0·2	15	85	nd	nd	nd
			10	23	13	nd	64	nd
			100	17	9	nd	74	nd
C_6StzMeI			0·08	21	79	nd	nd	nd

[a] Irradiation (366 nm) for 16 h at 25 ± 0·1 °C. Composition of products determined by means of 300 MHz ^{1}H NMR spectroscopy.
[b] Abbreviations according to Scheme 2.
[c] Not detected.

Micellar and homogeneous solutions of C_nStzRX were submitted to the UV treatment as described in the Experimental section. The details of irradiation conditions and products formed are summarized in Table 1. Photolysis of C_nStzRX in a micellar assembly resulted in *trans*⟶*cis* isomerization and a photostationary state of a mixture of *trans* and *cis* isomers was attained within 2–2·5 h. Also for homogeneous solutions of surfactants C_nStzRX and their non-micellizing analogs C_0StzMeX in water, the latter at concentrations of 0·2 mM or lower, direct irradiation resulted exclusively in photoisomerization with establishment of the photostationary state within 0·5–1 h. As shown in Scheme 1 this change can undergo a reversible process by heating at 40 °C for 6–8 h in the case of C_nStzRX micelles or for 2–3 h in homogeneous solutions. The NMR spectra showed that the *trans* isomer was recovered. A slight difference (*ca* 5%) between spectra of the starting material and the recovered *trans*-stilbazolium salt was observed in the first cycle. However, in the next four irradiation–thermal reversion cycles, the changes in the spectra were completely reproducible.

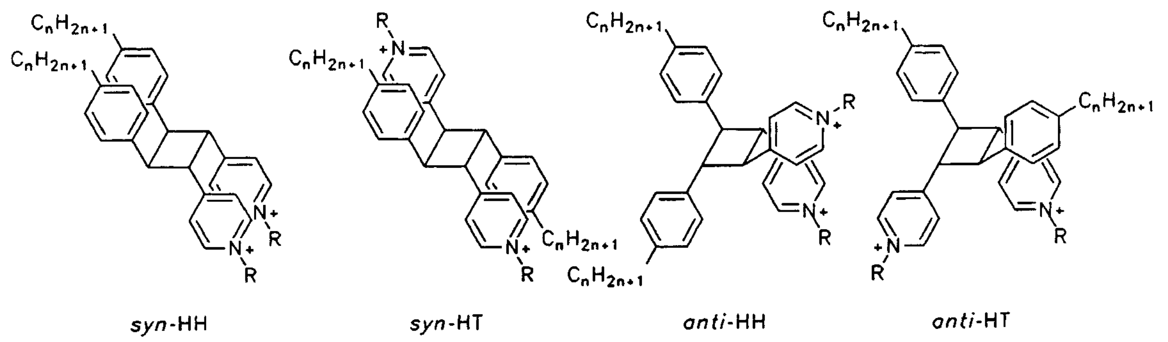
On successive irradiation for 16 h, the formation of three out of four possible structures (as depicted in Scheme 2) was detected in micellar C_nStzRX and concentrated non-surfactant analogs. The composition of the products was determined from the 300 MHz ^{1}H NMR spectra of the following protons: *trans*-olefinic (pair of doublets at δ7·7, 7·4; $J = 16$ Hz), *cis*-olefinic (pair of slightly broadened doublets at δ6·95, 6·75; $J = 9$ Hz), cyclobutane ring[14] [broad doublets at δ5·2, 4·8; $J = 6$ Hz were assigned to *syn*-head-to-head (*syn*-HH), a quartet at δ4·2; $J = 6·8$ Hz to *anti*-head-to-head (*anti*-HH) and doublets at δ5·17, 4·48; $J = 5·8$ Hz to *syn*-head-to-tail (*syn*-HT) photodimers]. Additionally, triplets at δ2·8–2·4 were assigned to the benzylic protons.



Scheme 1

The results obtained indicate that an increase in the nitrogen substituent alters the stereochemistry to the *cis*-olefin, which is the major product from the reaction of monomeric molecules. For the aggregated entities the *cis*/*trans* ratio was 0·41, 0·54 and 1·06, and in homogeneous solution 1·78, 2·13 and 2·70 for R = Me, Et and *n*-Bu, respectively, in C_nStzRX. The introduction of a long substituent at the 4′-position of the 4-stilbazolium ion had little effect on the *cis*/*trans* ratio, which was 0·40, 0·41, 0·40 in C_nStzRX micelles and 1·78, 1·78, 1·56 in homogeneous solutions for $n = 4$, 6 and 8 respectively. Additionally, as shown in Table 1, the formation of the thermodynamically least stable *syn*-HH dimers was achieved in aqueous micelles of C_nStzRX, especially *ca* 31% from C_6StzCH$_2$CH$_2$OHBr and 17% from C_8StzMeBr. The ease of the *anti*-HH alignment was also detected in *ca* 3%. On the other hand, the non-surfactant C_0StzMeX derivatives in concentrated aqueous (10 and 100 mM) solutions predominantly give rise to about 64–76% of the *syn*-HT photodimer products.

The dimerization of quaternary stilbazole salts in the solid state has been reported to yield almost exclusively head-to-head structures.[1c] For the C_0Stz $^+C_{18}H_{37}$ surfactant in crystals, the apparent favoring of a *syn*-HH alignment occurs,[1c] indicating that the electrical repulsion is overcome in these highly ordered systems. Efficient and selective formation of the *syn*-HH photodimer has also been found from irradiation of non-substituted 4-stilbazolium ions in reversed micelles, formed from hexane or heptane–Aerosol–water and characterized by low water-pool compositions.[10] The large change in the yield of dimers in the case of the 2-hydroxyethyl substituent is probably related to the tight packing of C_6StzCH$_2$CH$_2$OHBr molecules at the Stern layer of the micelle enhanced by the intermolecular hydrogen bonding. This effect is also shown by the *cis*/



Scheme 2

trans alkene ratio, which is the smallest among all the cases studied. The largest amount of *syn*-HH dimer for the C_8StzMeBr micelles in comparison with other 4′-alkyl-substituted 4-stilbazolium homologous surfactants proves that the aggregation process increases the local concentration of the photochromic group and enhances the photodimerization. The organized photodimerization in C_nStzMeBr ($n = 4, 6, 8$) micelles in relation to $C_0StzC_9H_{19}Br$ indicates that the former surfactants create a more rigid microenvironment than that of the 1-nonyl-substituted derivative. On the other hand, this microenvironment may become more loosened as the bulk of the surfactant head group [the C_6StzRBr (R = Me, Et, *n*-Bu) series] increases. The nature of the counterion (X = Br, I) introduces to the C_6StzMeX series photobehavior further coulombically unfavorable interactions as a consequence of an increased fraction of micelle surface covered by bromide in comparison with iodide ions.

The studied 1-alkyl-4-(4′-alkylstyryl)pyridinium bromides and iodides possessing distinct regions of hydrophilic–hydrophobic character may provide to some extent a topologically organized microenvironment of variable order and properties intermediate between those of a solid and solution. Their semi-rigid photochromic 4-stilbazolium segment has a small cross-sectional area,[1c] resides in both amphipatic zones of the molecule and is suggestive of a parallel alignment in the micellar self-assembly. Because of its cationic charge, which is responsible for intermolecular repulsion, the C_nStzRX amphiphiles in homogeneous aqueons solution are good candidates only for *trans*⟶*cis* photoisomerization. In this case, their photochemistry is similar in nature to that observed for low-concentration mobile non-micellizing C_0Stz^+Me ions. In the micellar state, the preferential association of the hydrophobic moiety may be important enough to offset unfavorable like-charge interactions in the hydrophilic microenvironment and may provide a successful interaction of an excited C_nStz^+R *with neighbouring* C_nStz^+R *in the aggregate* to induce also the *syn*-head-to-head and small amounts of *anti*-head-to-head alignments.

EXPERIMENTAL

Materials. Water used for all experiments was deionized, doubly glass distilled and degassed before measurements. Analytical-grade chloroform was distilled from P_2O_5 before use. Reagent-grade 2,6-di-*tert*-butyl-4-methylphenol (BHT) and benzaldehyde were not purified before use.

2-(4-Alkylphenyl)-1,3-dioxolanes were prepared by the procedure given below.[15] A stirred solution of alkylbenzene (0·36 mol) in $CHCl_3$ (200 ml) was treated dropwise with $TiCl_4$ (0·54 mol) at −22 °C, followed by the addition of CH_3OCHCl_2 (0·3 mol) at the same temperature over 20 min. The resulting mixture was stirred at the same temperature for 60 min and then poured into crushed ice. BHT (0·2 g) was added to the organic phase, which was separated, washed three times with water, dried over $MgSO_4$, evaporated *in vacuo* and crystallized three times from hexane at −40 °C. The resultant crude mixture of substrate, 2-alkylbenzaldehyde and 4-alkylbenzaldehyde (*ca* 21:4:75, GC control) was acetalized in boiling toluene (150 ml) with ethylene glycol (0·35 mol) and TsOH (0·5 g) for 12 h. Distillation at reduced pressure gave pure dioxolanes.

2-(4′-Butylphenyl)-1,3-dioxolane: yield 51%; b.p. 115–119 °C/0·8 Torr; ^{13}C NMR ($CDCl_3$), δ 141·5, 140·7, 128·3 126·9, 114·3, 65·2, 36·5, 33·5, 22·1, 15·2; IR (neat), 3090–3030, 2960–2930, 2856, 1865, 1750, 1604, 1496, 1414, 1108, 825 cm^{-1}; MS, *m*/*z* (relative intensity, %) 207 (M + 1, 3), 206 (M^+, 22), 205 (100), 161 (16), 149 (66), 119 (13), 91 (69), 73 (25); anal. calcd for $C_{13}H_{18}O_2$, C 75·69, H 8·79, found, C 75·90, H 8·9%.

2-(4′-Hexylphenyl)-1,3-dioxolane: yield 55%; b.p. 139–143 °C/1 Torr; ^{13}C NMR ($CDCl_3$) δ139·9, 139·5, 128·5·, 127·2, 114·2, 65·4, 37·2, 32·4, 31·8, 24·0, 20·0, 14·8; IR (neat), 3085–3030, 2960–2930, 2855, 1865, 1745, 1604, 1496, 1410, 1100, 830 cm^{-1}; MS, *m*/*z* (relative intensity, %) 235 (M + 1, 3), 234 (M^+, 21), 233 (100), 189 (16), 149 (70), 119 (13), 91 (68), 73 (25); anal. calcd for $C_{15}H_{22}O_2$, C 76·88, H 9·46; found, C 77·05, H 9·72%.

2-(4′-Octylphenyl)-1,3-dioxolane: yield 46%; b.p. 148–153 °C/1 Torr; ^{13}C NMR ($CDCl_3$) δ 141·0, 140·6, 128·0, 126·1, 113·8, 66·2, 39·0, 32·7, 32·3, 30·4, 29·7, 29·1, 20·5, 14·2; IR (neat), 3090–3030, 2960–2930, 2856, 1868, 1744, 1604, 1500, 1409, 1108, 830 c,$^{-1}$; MS, *m*/*z* (relative intensity, %) 263 (M + 1,4), 262 (M^+, 21), 261 (100), 217 (15), 149 (69), 119 (15), 91 (100), 73 (23); anal. calcd for $C_{17}H_{26}O_2$, C 77·82, H 9·99; found C 77·99, H 10·24%.

4-Alkylbenzaldehydes were obtained from the hydrolysis reaction of the corresponding dioxolanes. A mixture of dioxolane (0·15 mol), water (100 ml) and TsOH (1 g) was stirred under nitrogen for 4 h at 45 °C. After cooling to an ambient temperature the reaction mixture was extracted with diethyl ether. The organic fractions were washed three times with water, dried over $MgSO_4$ and evaporated *in vacuo* to afford alkylbenzaldehydes. The NMR and MS data were consistent with the structures.

4-(4′-Alkylstyryl)pyridines were synthesized on the 0·06 mol scale and worked up according to the Horwitz procedure.[16]

4-Styrylpyridine: yield 46%; ^1H NMR ($CDCl_3$), δ 8·54 (d, $J = 5·4$ Hz, 2H), 7·8–6·9 (m, 9H); anal. calcd for $C_{13}H_{11}N$, C 86·15, H 6·12, N 7·73; found, C 88·32, H 6·40, N 7·85%.

4-(4′-Butylstyryl)pyridine: yield 44%; ^1H NMR ($CDCl_3$), δ 8·54 (d, $J = 5·4$ Hz, 2H), 7·8–6.9 (m, 8H), 2·75 (t, *J* = 8·5 Hz, 2H), 1·45–1·0 (m, 4H), 0·9 (t, *J* = 5·5 Hz, 3H); anal. calcd for $C_{17}H_{19}N$, C 86·03, H, 8·07, N 5·90; found, C 86·30, H 7·91, N 6·01%.

4-(4′-Hexylstyryl)pyridine: yield 40%; ^{1}H NMR ($CDCl_3$), δ 8·57 (d, *J* = 5·4 Hz, 2H), 7·8–6·9 (m, 8H), 2·67 (t, *J* = 8·5 Hz, 2H), 1·65–0·85 (m, 11H); anal. calcd for $C_{19}H_{23}N$, C 85·99, H 8·73, N 5·28; found, C 86·11 H 9·05, N 5·33%.

4-(4′-Octylstyryl)pyridine: yield 46%; ^{1}H NMR ($CDCl_3$) δ 8·5 (d, *J* = 5·2 Hz, 2H), 7·8–6·9 (m, 8H), 2·7 (t, *J* = 8·5 Hz, 2H), 1·65–0·75 (m, 15H); anal. calcd for $C_{21}H_{27}N$, C 85·95, H 9·27, N 4·77; found, C 86·09, H 9·40, N 4·93%.

4-(4′-Alkylstyryl)-1-methylpyridinium bromides were prepared by the following procedure. A mixture of 4-(4′-alkylstyryl)pyridine (0·05 mol), methyl bromide (0·1 mol) and diethyl ether (50 ml) was placed in a stainless-steel vessel and heated for 10 h at 60 °C. After cooling to −30 °C, the diethyl ether was filtered off and the solid residue was dissolved in methanol (15 ml), precipitated with diethyl ether (150 ml), allowed to stand at −30 °C for 3 h, then the precipitate was filtered off at the same temperature. This procedure was repeated several times to afford pure compounds.

1-Methyl-4-styrylpyridinium bromide: yield 55%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·18 (d, *J* = 6·5 Hz, 2H), 8·5 (d, *J* = 6·5 Hz, 2H), 7·9–7·15 (m, 7H), 2·96 (s, 3H); ^{13}CNMR [water–dioxane-d_8 (10:1)], δ 158·5, 146·7, 135·4, 129·5, 129·0, 127·4, 127·0, 124·5, 124·4, 40·3; IR (KBr), 3028, 2958, 2860, 1642, 1622, 1604, 1588, 1502, 1465, 1452, 1181, 1052, 883, 750, 700 cm^{-1}; UW (water), λ_{max}350 nm (log ε 4·35); anal. calcd for $C_{14}H_{14}BrN$, C 60·89, H 5·11, N 5·07; found, C 60·85, H 5·36, N 5·22%.

4-(4′-Butylstyryl)-1-methylpyridinium bromide: yield 54%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·18 (d, *J* = 6·5 Hz, 2H), 8·5 (d, *J* = 6·5 Hz, 2H), 7·88 (d, *J* = 8·5 Hz, 2H), 7·7 (d, *J* = 16·5 Hz, 1H), 7·42 (d, *J* = 16·5 Hz, 1H), 7·15 (d, *J* = 8·5 Hz, 2H), 2·96 (s, 3H), 2·7 (t, *J* = 8 Hz, 2H), 1·55–1·0 (m, 4H), 0·93 (t, 3H); ^{13}C NMR [water–dioxane-d_8 (10:1), δ 158·5, 146·7, 140·7, 133·2, 129·5, 128·0, 126·7, 124·5, 124·4, 40·3, 36·7, 33·5, 22·0, 15·1; IR (KBr), 3024, 2955, 2857, 1642, 1622, 1604, 1567, 1518, 1465, 1420, 1181, 1052, 883, 837 cm^{-1}; W (water), λ_{max} 352 nm (log ε 4·30); anal. calcd for $C_{18}H_{22}BrN$, C, 65·06, H, 6·67, N 4·22; found,C, 65·27, H 6·81, N 4·32%.

4-(4′-Hexylstyryl)-1-methylpyridinium bromide: yield 51%; ^{1}H NMR [D_2O–acetone-δ_6 (10:1)], δ 9·22 (d, *J* = 6·4 Hz, 2H), 8·47 (d, *J* = 6·4 Hz, 2H), 7·85 (d, *J* = 8·5 Hz, 2H), 7·71 (d, *J* = 16 Hz, 1H), 7·4 (d, *J* = 16·0 Hz, 1H), 7·17 (d, *J* = 8·3 Hz, 2H), 3·1 (s, 3H), 2 73 (t, *J* = 8 Hz, 2H), 1·75–0·85 (m, 11H); ^{13}C NMR [water–dioxane-d_8 (10:1)], δ 161·0, 146·9, 140·3, 133·1, 129·5, 128·4, 128·0, 124·6, 124·4, 41·0, 38·0, 32·0, 31·9, 23·7, 20·1, 12·5; IR (KBr), 3030, 2952, 2855, 1640, 1623, 1604, 1570, 1520, 1465, 1420, 1184, 1052, 1018, 875, 840 cm^{-1}; W (water), λ_{max} 352·5 nm (log ε 4·27); anal. calcd for $C_{20}h_{26}$ BrN C 66·67, H 7·27, N 3·89; found, C 66·90, H 7·45, N 4·01%.

1-Methyl-4-(4′-octylstyryl)pyridinium bromide: yield 51%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·15 (d, *J* = 6·6 Hz, 2H), 8·5 (d, *J* = 6·6 Hz, 2H), 7·89 (d, *J* = 8·5 Hz, 2H), 7·69 (d, *J* = 16 Hz, 1H), 7·39 (d, *J* = 16·0 Hz, 1H), 7·2 (d, *J* = 8·0 Hz, 2H), 3·03 (s, 3H), 2·68 (t, *J* = 8 Hz, 2H), 1·75–0·85 (m, 15H); ^{13}C NMR [water–dioxane-d_8 (10:1)], δ 159·0, 146·5, 140·4, 133·1, 127·9, 127·1, 126·8, 124·5, 124·4, 39·9, 38·1, 32·0, 31·8, 29·4, 29·2, 20·1, 14·2; IR (KBr), 3028, 2957, 2857, 1641, 1622, 1604, 1572, 1515, 1466, 1422, 1180, 1050, 1018, 873, 840 cm^{-1}; UV (water), λ_{max} 352·5 nm (log ε 4·28); anal. calcd for $C_{22}H_{30}BrN$, C 68·04, H 7·79, N 3·61; found, C 68·31, H 8·09, N 3·75%.

4-(4′-Hexylstyryl)-1-(2-hydroxyethyl)pyridinium bromide was prepared as follows. To a stirred solution of 4-(4′-hexylstyryl)pyridine (0·05 mol) in diethyl ether (100 ml), 2-bromoethanol (0·053 mol) was added at room temperature and the mixture was allowed to stand for 72 h at the same temperature. Subsequent isolation was performed as described for C_4StzMeBr to afford $C_6StzCH_2CH_{20}HBr$: yield 42%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·2 (d, *J* = 6·6 Hz, 2H), 8·55 (d, *J* = 6·6 Hz, 2H), 7·68 (d, *J* = 8·5 Hz, 2H), 7·68 (d, *J* = 16·5 Hz, 1H), 7·41 (d, *J* = 16·0 Hz, 1H), 7·19 (d, *J* = 8·5 Hz, 2H), 3·91 (t, 2H), 3·65 (t, 2H), 2·75 (t, *J* = 8 Hz, 2H), 1·7–0·8 (m, 11H); ^{13}C NMR [water–ioxane-d_8 (10:1)], δ 158·9, 146·8, 141·7, 133·2, 128·5, 128·3, 127·8, 124·5, 124·4, 62·7, 44·1, 38·2, 32·2, 30·3, 23·7, 14·5; IR (KBr), 3045, 2926, 2853, 1640, 1624, 1604, 1567, 1505, 1465, 1419, 1337, 1181, 1089, 1050, 1018, 875, 824 cm^{-1} UV (water), λ_{max} 347 nm (log ε 4·45); anal· calcd for $C_{21}H_{28}BrNO$ C 64·61, H 7·23 N 3·59; found, C 64·85, H 7·40, N 3·78%.

1-Ethyl-4-(4′-hexylstyryl)pyridinium, 1-butyl-4-(4′-hexylstylyl)pyridinium and 1-nonyl-4-styrylpyridinium bromides were prepared as follows. To a stirred solution of 4-(4′-hexylstyryl)pyridine or 4-styrylpyridine (0·05 mol) in diethyl ether–methanol (1:1) (100 ml), the corresponding bromoalkane (0·053 mol) was added at room temperature. The resulting mixture was heated at 34·5 °C for 72 h, cooled to ambient temperature and diluted with diethyl ether (200 ml). Subsequent isolation was performed by means of the procedure for C_4StzMeBr.

1-Ethyl-4-(4′-hexylstyryl)pyridinium bromide: yield 30%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·26 (d,*J* = 6·5Hz, 2H), 8·58 (d, *J* = 6·5 Hz, 2H), 7·78 (d, *J* = 8·1 Hz, 2H), 7·70 (d, *J* = 16·2 Hz, 1H), 7·39 (d, *J* = 16·2 Hz, 1H), 7·13 (d, *J* = 8·1 Hz, 2H), 3·43 (q, 2H), 2·65 (t, *J* = 8·5 Hz, 2H), 1·85–0·8 (m, 14H); ^{13}C

NMR [water–dioxane-d_8 (10:1)] δ 157·7, 150·0, 141·0, 132·8, 128·3, 128·0,,126·9, 124·2, 124·1, 41·5, 38·2, 32·1, 31·8, 23·5, 20·2, 15·8, 12·6; 1R (KBr), 3045, 2930, 2855, 1642, 1622, 1604, 1567, 1502, 1465, 1420, 1337, 1181, 1090, 1050, 1028, 870, 820 cm^{-1}; W (water), λ_{max}352 nm (log ε 4·30); anal. calcd for $C_{21}H_{28}BrN$, C 67·38, H, 7·54, N 3·74; Found: C 67·40, H 7·59, N 3·70%.

1-Butyl-4-(4′-hexylstyryl)pyridinium bromide: yield 28%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·24 (d, J = 6·5 Hz, 2H), 8·51 (d, J = 6·5 Hz, 2H), 7·75 (d, J = 8·2 Hz, 2H), 7·68 (d, J = 16·0 Hz, 1H), 7·41 (d, J = 16·0 Hz, 1H), 7·18 (d, J = 8·2 Hz, 2H), 3·41 (t, 2H), 2·69 (t, J = 8·5 Hz, 2H), 1·85–0·8 (m, 18H); ^{13}C NMR [water-dioxane-d_8 (10:1)], δ 158·6, 149·6, 140·9, 133·1, 128·1, 127·9, 126·8, 124·6, 124·4, 42·5, 39·0, 33·2, 32·3, 32·1, 30·8, 28·7, 24·1, 15·2, 13·5; IR (KBr), 3045, 2926, 2853, 1640, 1624, 1604, 1567, 1505, 1465, 1419, 1337, 1181, 1089, 1050, 1018, 875, 824 cm^{-1} (water), λ_{max} 351·5 nm (log ε 4·25); anal· calcd for $C_{23}H_{32}BrN$, C 68·65, H 8·02, N 3·48; found: C 68·81, H 8·17; N, 3·09%.

1-Nonyl-4-styrylpyridinium bromide: yield 30%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·27 (d, J = 6·5 Hz, 2H), 8·55 (d,J = 6·5 Hz, 2H), 7·8–7·1 (m, 7H), 3·35 (t, 2H), 1·85–0·8 (m, 17H); ^{13}CNMR [water–dioxane-d_8 10:1)], δ 158·6, 149·6, 136·1, 129·2, 128·3, 127·9, 126·8, 124·6, 124·4, 41·5, 30·3, 30·1, 30·0, 28·2, 25·6, 23·2, 14·7; IR (KBr) 3020, 2963, 2858, 1642, 1622, 1603, 1585, 1500, 1464, 1452, 1181, 1052, 883, 752, 697 cm^{-1}; UV (water), λ_{max} 351·5 nm (log ε 4·22); anal· calcd for $C_{22}H_{30}BrN$ C 68·03, H 7·79, N 3·61; Found, C 68·25, H 8·11, N 3·72%.

Syntheses and isolation of the 1-alkyl-4-(4′-alkylstyryl)pyridinium iodides C_nStzRI were performed as for $C_6StzCH_2CH_2OHBr$.

1-Methyl-4-styrylpyridinium iodide: yield 50%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·22 (d, J = 6·4 Hz, 2H), 8·47 (d, J = 6·4 Hz, 2H), 7·85–7·1 (m, 7H), 3·1 (s, 3H); ^{13}C NMR [water–dioxane-d_8 (10:1)], δ 159·4, 146·3, 136·0, 129·5, 129·0, 127·5, 126·9, 124·5, 124·2, 41·0; IR (KBr), 3025, 2958, 2860, 1642, 1622, 1602, 1588, 1497, 1465, 1452, 1180, 1052, 886, 740, 702 cm^{-1}; UV (water), λ_{max} 350·5 nm (log ε 4·25); anal· calcd for $C_{14}H_{14}IN$, C 52·03, H 4·37, N 4·34; found C 52·30, H 4·58, N 4·39%.

4-(4′-Hexylstyryl)-1-methylpyridinium iodide: yield 48%; ^{1}H NMR [D_2O–acetone-d_6 (10:1)], δ 9·22 (d, J = 6·4 Hz, 2H), 8·47 (d, J = 6·4 Hz, 2H), 7·85 (d, J = 8·5 Hz, 2H), 7·71 (d, J = 16 Hz, 1H), 7·4 (d, J = 16·0 Hz, 1H), 7·17 (d, J = 8·5 Hz, 2H), 3·1 (s, 3H), 2·73 (t, J = 8 Hz, 2H), 1·75–0·85 (m, 11H); ^{13}C NMR [water–dioxaned-d_8 (10:1)] δ 161·0, 146·9, 140·3, 133·1, 129·5, 128·4, 127·5, 124·6, 124·4, 41·0, 38·0, 32·0, 31·9, 23·7, 20·1, 12·5; 1R (KBr), 3030, 2952, 2855, 1640, 1623, 1604, 1570, 1520, 1465, 1420, 1184, 1052, 1018, 875, 840 cm^{-1}; UV(water), λ_{max} 351 nm (log ε 4·27); anal. calcd for $C_{20}H_{26}IN$, C 58·97, H 6·43, N 3·44; found, C 59·11, H 6·68, N 3·53%.

Equipment. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker DRX-300 spectrometer and ^{13}C NMR spectra at 25·14 MHz on a Tesla BS-567A spectrometer. ^{1}H chemical shifts are referenced in acetone-d_6 and $CDCl_3$ to residual protons of acetone-d_6 (2·05 ppm) and $CDCl_3$, (7·27 ppm). $_{13}$C NMR spectra are referenced to the solvent [$CDCl_3$, 76·9 ppm; water–dioxane-d_8 (10:1), 67·4 ppm]. GC–MS analyses were carried out using a Hewlett-Packard Model 5971A electron impact (70 eV) mass spectrometer with an HP 5890A gas chromatograph, equipped with a 25 m × 0·2 mm id HP-1 column. IR spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrometer. UV–visible spectra were taken on a Varian Cary 3E double-beam spectrophotometer. Elemental analyses was performed on a Perkin-Elmer CHN Analyser. The critical micelle concentrations (cmcs) of stilbazolium salts (C_nStzRX) were determined by electric conductivity measurements on a Tesla bridge voltmeter connected to a thermostated cell capable of regulating the sample temperature at 25 ± 0.05 °C. The conductivity was plotted against the surfactant concentration and the cmcs were determined from the break point of the plots. Dynamic light scattering was performed using a Carl Zeiss Jena light-scattering apparatus operating at 488 nm with an output power of 0·8 W, Thorn EMI 9130 BO3100 photomultiplier, ALV/PM—PD preamplifier/discriminator (ALV, Germany) and multi-tau ALV500 digital correlator (ALV) at 25 ± 0·2 °C. Micellar solutions of studied surfactants containing a fixed 0·02 M concentration of NaBr or NaI were filtered through 0·2 μm Millpore membranes directly into the dust-free scattering cells.

Irradiation procedure and analysis of photoproducts. Degassed water solutions of C_nStzRX were irradiated by stirring at 25 ± 0·1 °C for 16 h in 200 ml immersion-type quartz vessel (Photochemical Reactors) equipped with a 80 W medium-pressure mercury lamp and 366 nm liquid filter. After irradiation, 0·2–10 ml aliquots were taken, water was azeotropically removed with butan-2-one at 32 °C/30 Torr, traces of the solvents were purged at high vacuum, then the dry samples were dissolved in acetone-d_6–D_2O (3:2). The number of FID accumulations was 128 and the resolution was 0·2 Hz.

Thermal reisomerization. Irradiation was stopped after reaching the photostationary state and the sample was moved to a temperature—controlled sample holder. Solutions of C_nStzRX were stirred in the dark at 40 ± 0·1 °C and 0·2–10 ml aliquots were taken at ever 0·5 h up to 8 h, worked up and analysed as described above.

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