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Squarilium Dyes, their Infrared and Resonance Raman Spectra and Possible Use in Redox Reactions for Solar-energy Conversion†

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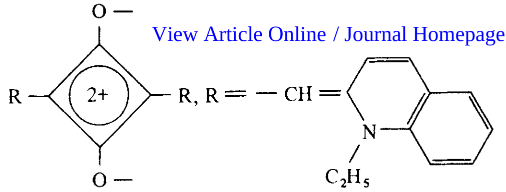
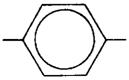
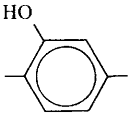
Infrared and resonance Raman spectra of squarilium dyes I-VI of the type



(I),



(II),



(III),

$—N(C_6H_5)_2$ (IV), $—NHC_6H_4$ (V), $—NHC_6H_4SO_3^-H_2\overset{+}{N}(CH_3)_2$ (VI)

are presented and some vibrational modes of the central 4-membered ring are assigned. Methyl viologen dication (MV^{2+}) is reduced photocatalytically by IV in DMSO+H_2O (95/5, v/v) with a quantum yield ϕ of $(1.8 \pm 0.4) \times 10^{-3}$ at 406.7 nm, if EDTA is present. Oxidation products of MV^{2+} behave similarly with $\phi = (4.7 \pm 0.6) \times 10^{-2}$ at 457.9 nm in DMF+H_2O (2/1, v/v). $IV^{\cdot+}$ seems to oxidize H_2O nearly reversibly.

The search for photochemical systems for the conversion and storage of solar energy has become intense in the past few years. One is the photolytic splitting of water into H_2 and O_2, a problem which has been tackled in various ways. Restricting ourselves to redox reactions in solution, two general reaction schemes have been proposed,[1] where the electronically excited state S* of a sensitizer S acts either as a reducing agent (scheme 1) or as an oxidizing agent (scheme 2):

scheme 1:

$$S \xrightarrow{h\nu} S^*$$

$$S^* + A \rightarrow S^{\cdot+} + A^{\cdot-}$$

$$A^{\cdot-} + H_2O \xrightarrow[\text{cat 1}]{} A + \tfrac{1}{2}H_2 + OH^-$$

$$S^{\cdot+} + \tfrac{1}{2}H_2O \xrightarrow[\text{cat 2}]{} S + \tfrac{1}{4}O_2 + H^+$$

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† A preliminary account of this work has been presented previously, *cf.* M. Forster and R. E. Hester, *Proc. 3rd Int. Conf. Photochem. Conversion Storage Solar Energy*, Boulder 1980 (SERI, Golden, Colorado, 1980).

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scheme 2:

$$S \xrightarrow{h\nu} S^*$$

$$S^* + D \rightarrow S^{\cdot -} + D^{\cdot +}$$

$$S^{\cdot -} + H_2O \xrightarrow[\text{cat 1}]{} S + \tfrac{1}{2}H_2 + OH^-$$

$$D^{\cdot +} + \tfrac{1}{2}H_2O \xrightarrow[\text{cat 2}]{} D + \tfrac{1}{4}O_2 + H^+$$

A and D are electron acceptors and donors, respectively, and cat 1 and cat 2 are catalysts for the promotion of water reduction or oxidation, respectively. In order to make the reactions in schemes 1 and 2 efficient, S, A, D, cat 1 and cat 2 have to fulfil a large number of conditions,[1-4] the most important of which are: (i) $\lambda_{\max}$ of S is in the visible region, (ii) the lifetime of S* is as long as possible, (iii) the redox potentials of S, S*, A and D match those of water at pH 7, *viz.* $E_0(O_2/H_2O) = +0.82$ V, $E_0(H_2O/H_2) = -0.41$ V, (iv) there is efficient separation of the ion pairs $S^{\cdot +} + A^{\cdot -}$ or $S^{\cdot -} + D^{\cdot +}$ and (v) the specific activity of cat 1 (*e.g.* colloidal noble metals[1,3]) and cat 2 (*e.g.* RuO_2[4]) must be right for the desired reactions.

In the search for new organic sensitizers S we have investigated squarilium dyes of the type shown in fig. 1. Squarilium dyes have the following properties: (*a*) they can easily be prepared by the condensation of squaric acid with the appropriate RH,[5] (*b*) they are stable even at temperatures $T > 200$ °C and in concentrated H_2SO_4,[5] (*c*) they have extinction coefficients up to 4×10^5 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$[16-11] and (*d*) their $\lambda_{\max}$ can be shifted over the whole range of 400–800 nm by varying R.

For dye IV in fig. 1 [R = —$N(C_6H_5)_2$] the redox potentials of the excited state S* can be calculated using $E_0(S^{\cdot +}/S) = +1.37$ V, $E_0(S/S^{\cdot -}) = -1.23$ V[12] and $\lambda_{\max} = 571$ nm for emission (instead of the 0–0 transition) by adopting a formalism originally proposed for metal complexes.[2]

Fig. 2 shows the redox levels for S = IV, which lie very close to those of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine)[13-15] and which fulfil criterion (iii). $Ru(bpy)_3^{2+}$ has already been established as an efficient sensitizer for the photolytic decomposition of water.[1,4,16-18]

Some vibrational modes belonging mainly to the central part of dyes I-VI have been derived for infrared (i.r.) and resonance Raman (r.R.) spectra. The behaviour of dyes IV and VI in photoredox reactions according to scheme 1 and fig. 2(*a*) will be reported. Oxidation products of MV^{2+} dichloride (MV^{2+} = methyl viologen or 1,1′-dimethyl-4,4′-bipyridinium dication) are shown to be even better photosensitizers than IV. The chemical oxidation of dye IV in aqueous solution was also investigated.

EXPERIMENTAL

EDTA (ethylenediamine tetra-acetic acid disodium salt), $Ce(SO_4)_2 \cdot 4H_2O$ and PtO_2 (all from B.D.H.) were analytical grade and used as received. NaLS (sodium laurylsulphate) (Aldrich) was twice recrystallized from ethanol. MV^{2+} dichloride from I.C.I. Ltd was recrystallized from methanol + acetone five times.[19] All solvents were analytical grade; DMSO (dimethylsulphoxide) was twice vacuum distilled and H_2O was doubly distilled. Prepurified N_2 gas was further O_2-scrubbed by bubbling through a solution consisting of 8 g pyrogallol and 24 g KOH in 200 $\mathrm{cm^3}$ H_2O before being dried at 77 K. Dye I (Aldrich) was used as received. Dyes II-V were prepared according to ref. (20) by refluxing one equivalent of squaric acid and two equivalents of the appropriate compound RH in benzene n-butyl alcohol (1:2.5, v/v) with concomittant azeotropic removal of the H_2O formed. For dye VI a mixture of benzene + n-butyl

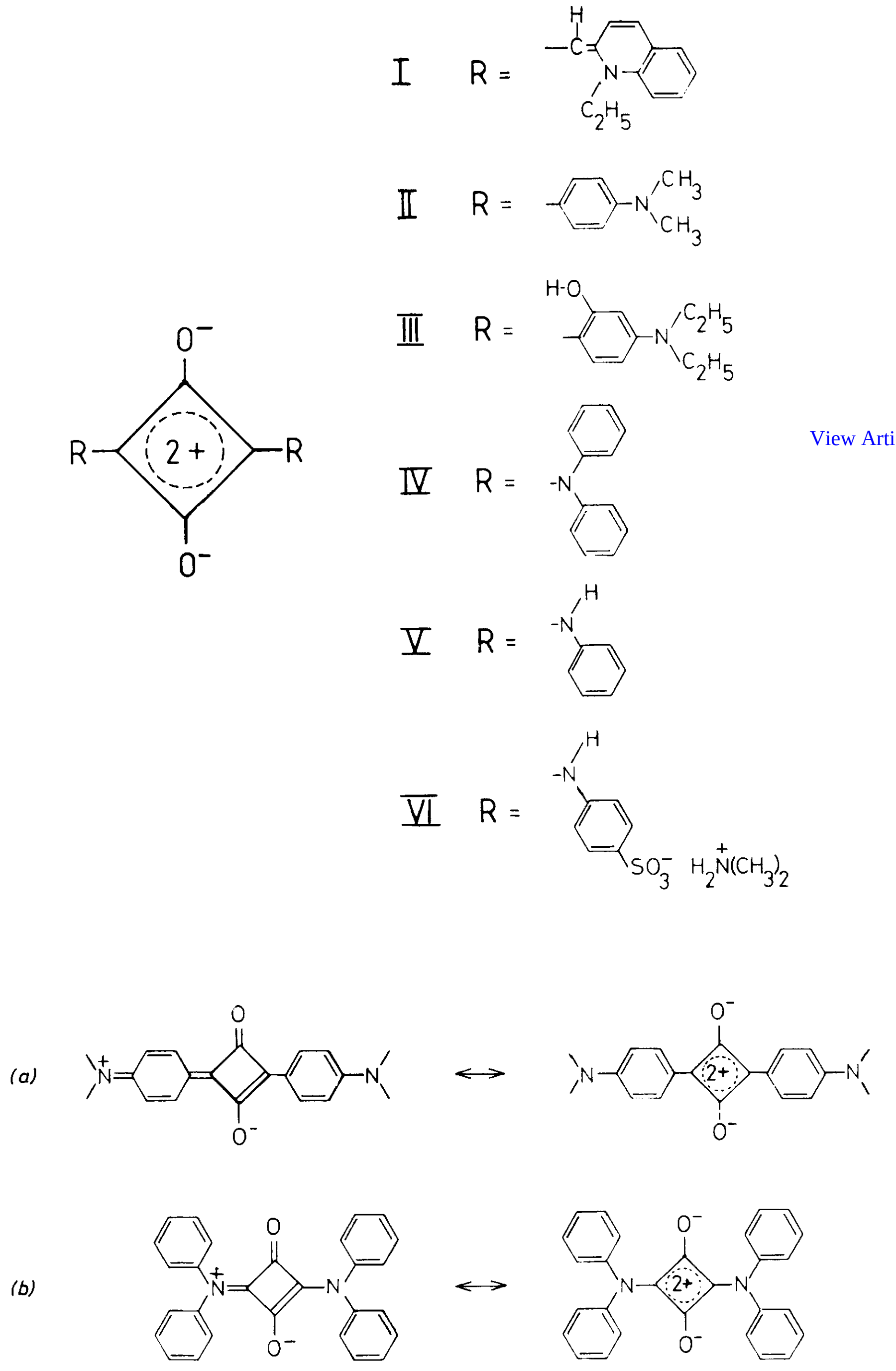


FIG. 1.—Investigated squarilium dyes I-VI; (*a*) and (*b*) are possible mesomeric structures.

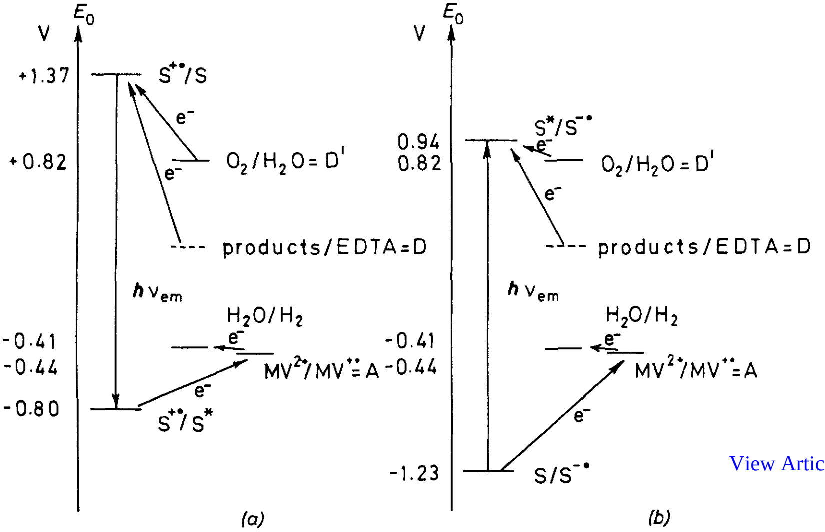
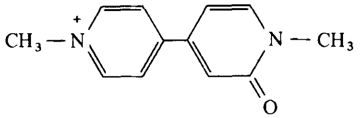


FIG. 2.—Redox levels of dye IV as sensitizer S in reactions according to scheme 1 or 2. (*a*) S* as reducing agent; (*b*) S* as oxidizing agent. MV^{2+} = methyl viologen = 1,1′-dimethyl-4,4′-bipyridinium dication; EDTA = ethylenediaminetetra-acetic acid disodium salt; A = electron acceptor; D,D′ = electron donors. Normal potentials of S calculated from ref. (12).

alcohol + dimethylformamide (DMF) was used as solvent, yielding the salt VI, due to the decomposition of DMF into $(CH_3)_2NH$ and CO at elevated temperatures.[21] Dye IV was recrystallized once from DMF + DMSO to remove an impurity with λ_{max} = 375 nm in DMSO (probably the 1,2-isomer of dye IV). Analytically pure dyes II-VI were obtained following these procedures. Table 1 gives the analytical and spectroscopic data for dyes I-VI. Elemental analysis data of dye VI were: C/H/N = 46.68/5.09/10.89 (theor.), 45.96/5.02/10.79 (found). A colloidal dispersion of dye IV was produced by adding an aqueous solution of 5×10^{-2} mol dm^{-3} Na LS, buffered at pH 6.2, to dye IV dissolved in concentrated H_2SO_4.

Mixtures of yellow oxidation products of MV^{2+} dichloride (named X for convenience) could be obtained reproducibly by stirring for 6 h at 80 °C a solution of 70 mg MV^{2+} dichloride and 1 g K_2CO_3 in 200 cm^3 DMF + H_2O (1/1, v/v) with admission of air. *Ca.* $\frac{1}{3}$ of the solvent was then removed with a vacuum rotary evaporator. After neutralization with H_2SO_4 the solution was evaporated to dryness *in vacuo* and the residues extracted with methanol. The methanolic solution was concentrated to 10 cm^3, 40 cm^3 acetone were added and the filtered solution then contained X for further use. X absorbs at 408 and 422 nm in DMF + H_2O (2/1, v/v) and emits intense yellow light upon irradiation with $\lambda_{exc} < 500$ nm. Thin layer chromatography of X on cellulose with n-butyl alcohol + acetic acid + H_2O (4/1/2, v/v/v)[22] showed that X contained at least 14 components. The main component with intense yellow emission when irradiated with λ = 366 nm had an r_f value of 0.63, which agrees well with r_f = 0.64 for the monopyridinone VII:[22]



VII.

Resonance Raman spectra were taken using the spinning cell technique[23, 24] on a Jobin Yvon Ramanor spectrometer, linked to a PDP 11/10 computer and a Nicolet 1074 data handling system.[25] A Cassegrain light collecting optic was used[26] and for solid samples plasma lines were rejected by a focusing-lens–pinhole system.[27] Excitation at 406.7, 457.9, 472.8, 488.0, 514.5, 632.8 and 647.1 nm was provided by Spectra Physics models 170 Kr^+ and 125 HeNe and

TABLE 1.—ANALYTICAL AND SPECTROSCOPIC DATA FOR DYES I-VI

dye	yield (%)	m.p./°C	λ_{max}/nm, (ε/dm^3 mol^{-1} cm^{-1}), solvent
I	—	> 300 (> 320[c])	670, 615, $CHCl_3$; ~ 720, 655, 420, NaLS[d]
II	52 (60[a])	> 335 (276[a])	626, $CHCl_3$
III	93	263	647, $CHCl_3$; 647, NaLS[d]
IV	71 (66[b])	> 320 (360[b])	408, (4.0×10^4), $CHCl_3$; 387, (3.5×10^4), concentrated H_2SO_4
V	41 (87[b])	> 330 (> 360[b])	401, (4.7×10^4), DMF
VI	72	> 330	385, (3.8×10^4), H_2O

[a] Ref. (20); [b] ref. (5); [c] ref. (7); [d] [NaLS] = 5×10^{-2} mol dm^{-3}.

Coherent Radiation model CR4 Ar^+ lasers. Emission spectra, corrected for spectrometer sensitivity, were recorded using the same instrumentation.

Emission lifetimes were measured using a homebuilt fluoroscope[28] with a mechanically chopped excitation beam. The decay times were calculated from the phase shift between exciting and emitted light.[29]

I.r. spectra of samples in KBr pellets were taken with a Perkin-Elmer PE-580 i.r. spectrometer. The backgrounds of the digitized spectra were artificially flattened and the peaks were determined numerically after the spectra had been smoothed by a seven point parabolic function.[30] U.v.–visible spectra were taken on a Unicam SP8000 u.v.–visible spectrometer.

For continuous irradiations and quantum-yield determinations solutions in 1 cm u.v. cells had N_2 bubbled through them for 15 min followed by irradiation with a laser beam expanded to *ca.* 0.5 cm diameter. The solutions were stirred and held under slight N_2 overpressure during irradiation. Aqueous solutions of MV^{2+} dichloride containing DMF or DMSO were prepared by mixing aqueous MV^{2+} dichloride with DMF + H_2O or DMSO + H_2O solutions, which had been cooled to 0 °C. The solutions were then used immediately for the irradiation experiments. This procedure prevented the formation of the oxidation products X of MV^{2+} dichloride.

By placing a silica lens in the laser beam before the u.v. cell, the photon flux density could be locally enhanced by a factor of 160, calculated according to ref. (31) for a laser beam with a Gaussian intensity distribution. Laser powers were measured with a calibrated Spectra Physics power meter, model 401 C.

RESULTS

INFRARED, RESONANCE RAMAN AND VISIBLE ABSORPTION AND EMISSION SPECTRA

Table 2 lists the vibrational frequencies of all the dyes I-VI. R.R. spectra of dyes IV-VI could be made in solution. Since dyes I-III fluoresce strongly in solution, r.R. spectra from dyes I-III could be obtained only as 1% (w/w) mixtures in KBr. For dye III the excitation had to be to the blue side of the absorption band in order to escape its high emission. Representative of the other dyes, fig. 3 shows the r.R. spectrum of dye IV in $CHCl_3$, taken with $\lambda_{exc} = 406.7$ nm. Intense r.R. bands, which are common to dyes I-VI, are collected in table 3. The assignments were made by comparing table 2 with i.r. data from other squarilium dyes[6, 8, 32, 33] and using the fact that the r.R. bands of dye IV shift when going from $CHCl_3$ to concentrated H_2SO_4 as solvent. The measured depolarization ratios ρ of the r.R. bands of dye IV all were *ca.* $\frac{1}{3}$. Dyes I-III absorb in the range 615-670 nm in $CHCl_3$ and dyes IV-VI in the range 385-408 nm. Only dyes I and III were weakly soluble in micellar NaLS solution. Dye

TABLE 2.—INFRARED AND RESONANCE RAMAN DATA FOR DYES I–VI

dye I

i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[a] $\tilde{\nu}/\mathrm{cm}^{-1}$	i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[a] $\tilde{\nu}/\mathrm{cm}^{-1}$
3077 vvw	—	1172 s	—
3060 vw	—	1153 w, sh	—
2982 vw	—	1140 w	—
2965 vw	—	1112 w, sh	—
2930 w	—	1090 vs	—
2860 vw	—	1082 s	—
1869 vvw	—	993 w	—
1825 vvw	—	978 vw	—
1790 vvw	—	882 vw	—
1758 vw	—	—	872 w
—	1722 m	845 w	
1620 m	1623 s	820 m	
1578 m	—	805 vvw	
—	1569 m	780 m	—
1564 s	—	753 m	—
1512 w	1515 m	740 vvw	—
1481 vs	—	702 vw	—
1457 m, sh	—	—	680 w
1448 s	1441 w	659 w	—
1436 vs	—	—	651 m
—	1415 m	599 vw	—
1409 w	—	567 w	—
1388 w	—	546 vw	541 m
1367 w	1367 s	526 vw	—
—	1350 vs	—	492 w
1338 vw	—	483 vvw	—
1323 vs	—	470 vw	—
1277 w	1271 w	—	457 w
1260 vs	—	439 vw	—
1247 vw, sh	1245 m	410 vvw	—
1230 w	1231 s	380 vvw	—
1189 m	—		157 w
			105 m

dye II

i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[b] $\tilde{\nu}/\mathrm{cm}^{-1}$	i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[b] $\tilde{\nu}/\mathrm{cm}^{-1}$
2975 vvw	—	1500 m	—
2930 vw	—	1460 w, br	—
2860 vvw	—	—	1440 m
—	1736 s	1395 m	1392 m
1700 vvw	—	1384 vw	—
1608 s	—	1350 vs	1356 w
—	1602 m	1318 vw	—
1588 vs	—	1250 m	—
—	1570 vs	—	1202 m

TABLE 2.—(*cont.*)

i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[b] $\tilde{\nu}/\mathrm{cm}^{-1}$	i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[b] $\tilde{\nu}/\mathrm{cm}^{-1}$
1182 m	—	782 s	—
1160 vs	—	—	752 vs
—	1154 m	619 vw	—
1128 s	—	—	572 vs
—	1062 m	501 w	—
—	1036 m	—	486 s
—	992 s	402 w	—
948 m	—	—	176 vs
832 m	—	—	90 vs
799 vvw	—		

dye III

i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[c] $\tilde{\nu}/\mathrm{cm}^{-1}$	i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[c] $\tilde{\nu}/\mathrm{cm}^{-1}$
3078 vw		—	1115 vs
2980 w	—	1077 s	—
2940 w	—	—	1069 w
2900 w	—	—	1038 vs
2703 w	—	1011 m	1009 w
2640 vw	—	960 s	962 m
2587 vw	—	928 vw	—
2240 vw	—	862 m	862 w
2178 w	—	816 m	814 w
2090 vw	—	—	793 m
—	1730 m	786 w	—
—	1628 s	746 s	747 w
1609 vs	1609 m	723 vw	—
1561 vw	1559 m	—	699 vs
1533 w	1528 vs	674 m	673 w
1493 w	1497 w	652 vw	654 vw
1446 vw	—	—	584 vs
1421 vw	1421 vs	555 w	559 w
1390 vs	—	522 vvw	521 w
—	1355 s	511 vw	—
1336 vs	—	500 vw	502 vw
1298 w	1300 w	484 vw	482 vw
—	1285 m	464 vw	462 w
1276 m	—	452 vw	—
1246 vs	1252 m	410 m	—
—	1229 m	—	341 m
1213 vs	1218 m	334 vw	—
1187 s, sh	1188 m	—	281 m
1174 vs	—	—	261 m
1153 s	1153 w	—	178 vs
1140 w, sh	—	—	158 w, sh
1121 m	—		

TABLE 2.—(*cont.*)

dye IV

i.r.	r.R.[d]		r.R.[e]
$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	ρ	$\tilde{\nu}$/cm^{-1}
3092 vvw	—	—	—
3062 vw	—	—	—
3038 vvw	—	—	—
3017 vvw	—	—	—
2927 vvw	—	—	—
2858 vvw	—	—	—
1952 vvw	1954 w	—	—
—	—	—	1908 w
1790 vvw	1790 w	0.28	1812 w
—	1704 w	0.40	1692 w
1631 vs	—	—	—
—	1614 w	—	—
—	1598 m	0.39	1596 s
—	1570 s	0.36	1522 s
1497 w, sh	—	—	—
1490 s	1494 m	0.33	1492 m
1462 s	—	—	—
—	—	—	1432 vw
1418 s, sh	1420 w	—	—
1406 vs	—	—	—
1398 s, sh	—	—	—
1362 w, sh	1360 w	—	—
1337 w	1334 w	—	—
1326 vw	—	—	—
1318 m	—	—	—
1290 vw	—	—	—
1270 w	—	—	—
—	1262 w	0.36	—
1214 w	—	—	—
—	1198 vs	0.34	1196 s
1182 vw	1178 m	0.33	1184 s
1174 vw	—	—	—
1162 vw	—	—	—
1154 vw	—	—	—
1140 w	—	—	—
1110 vw	—	—	—
1082 w	—	—	—
1073 w	—	—	—
1044 w	—	—	—
1032 w	—	—	—
1023 w	—	—	—
1002 vw	1006 m	0.40	996 m
990 vvw	—	—	—
968 vw	—	—	—
923 vw	928 w	0.38	—
902 vw	—	—	—
886 w	888 m	0.39	—
853 vvw	—	—	—

TABLE 2.—(*cont.*)

i.r.	r.R.[d]		r.R.[e]
$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	ρ	$\tilde{\nu}$/cm^{-1}
826 vvw	826 w	—	832 m
780 w	—	—	—
778 w	—	—	—
766 m	—	—	—
759 m	—	—	762 w
718 w	—	—	—
—	—	—	714 s
701 w, sh	—	—	—
697 m	696 w	0.33	694 w
690 m	—	—	—
—	650 w	—	624 vw
609 vw	—	—	—
574 m-s	—	—	—
—	—	—	554 m
533 w	—	—	—
—	504 s	0.36	494 m
459 w	—	—	—
447 w	—	—	—
413 vw	414 w	—	408 m
—	—	—	374 w
315 vw	—	—	—
—	—	—	244 w
—	218 w	0.40	—
—	—	—	88 w

dye V

i.r. $\tilde{\nu}$/cm^{-1}	r.R.[f] $\tilde{\nu}$/cm^{-1}	i.r. $\tilde{\nu}$/cm^{-1}	r.R.[f] $\tilde{\nu}$/cm^{-1}
3245 w	—	1868 vw	—
3180 m	—	1795 vw	1792 w
3130 m	—	1740 vw	—
3090 w	—	1680 vw	—
3060 w	—	—	1660 m
2998 vw	—	1615 vs	—
2970 s	—	1604 s	1602 vs
2937 vs	—	1587 vs	1584 s
2890 vw	—	1550 vs	—
2780 vw	—	—	1506 m
2750 vw	—	1499 s	—
2680 vw	—	1448 vs	—
2650 vw	—	1421 vs	—
2590 vw	—	1409 vs	—
2545 vw	—	1337 w	—
2470 vw	—	1293 vw	—
2390 vw	—	1245 m	—
1937 vw	—	—	1232 vs

TABLE 2.—(*cont.*)

i.r. $\tilde{\nu}$/cm^{-1}	r.R.[f] $\tilde{\nu}$/cm^{-1}	i.r. $\tilde{\nu}$/cm^{-1}	r.R.[f] $\tilde{\nu}$/cm^{-1}
1183 m	1188 m	—	720 w
1164 w	1164 w	688 s	694 w
1145 w	—	—	656 s
—	1094 w	621 m	—
1079 w	—	—	614 w
1037 w	—	601 m	—
1023 w	—	—	584 w
998 vw	1000 m	570 w	—
974 vvw	—	—	556 w
968 w	—	510 m	—
899 m	—	463 s	—
853 m	—	412 vw	408 w
—	842 s	—	358 w
824 s	—	322 w	318 w
794 m	—	305 vw	—
763 m	768 w	—	264 w
750 s	—		

dye VI

i.r. $\tilde{\nu}$/cm^{-1}	r.R.[g] $\tilde{\nu}$/cm^{-1}	i.r. $\tilde{\nu}$/cm^{-1}	r.R.[g] $\tilde{\nu}$/cm^{-1}
3240 vw	—	1315 w	1316 w
3195 w	—	1298 vw	—
3122 w	—	1245 w, sh	1246 s
3062 w	—	1215 s, sh	—
3025 vw	—	1192 vs	1192 w
2983 s	—	—	1154 w
2900 w, sh	—	1125 vs	1128 m
2844 w	—	1039 vs	—
2800 w, sh	—	1012 vs	—
2780 s	—	972 vw	—
2510 vw	—	950 vw	—
2422 m	—	890 vw	—
1912 w	—	866 w	—
—	1806 w	865 vw, sh	—
1790 w	—	—	852 m
—	1654 w	837 s	—
1615 vs	—	810 w, sh	—
—	1602 s	764 w	—
1590 vs	—	744 vw	740 m
—	1578 m	722 m	—
1547 s	—	696 vs	—
1503 m	1502 w-m	637 s	—
1470 m	—	—	622 m
1460 w	—	612 s	—
1425 vs	—	586 vw	—
1410 vs	—	569 s	570 w
1340 vw	—	523 w	—

TABLE 2.—(*cont.*)

i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[g] $\tilde{\nu}/\mathrm{cm}^{-1}$	i.r. $\tilde{\nu}/\mathrm{cm}^{-1}$	r.R.[g] $\tilde{\nu}/\mathrm{cm}^{-1}$
497 m	—	333 m	—
448 vw	—	298 vw	—
407 vw	—	—	260 w
378 w	—		

[a] 1% (w/w) in KBr, $\lambda_{\mathrm{exc}} = 632.8$ nm; [b] 1% (w/w) in KBr, $\lambda_{\mathrm{exc}} = 647.1$ nm; [c] 1% (w/w) in KBr, $\lambda_{\mathrm{exc}} = 514.5$ nm; [d] 4×10^{-4} mol dm^{-3} in $CHCl_3$, $\lambda_{\mathrm{exc}} = 406.7$ nm; [e] 1.1×10^{-3} mol dm^{-3} in concentrated H_2SO_4, $\lambda_{\mathrm{exc}} = 406.7$ nm; [f] 2.2×10^{-4} mol dm^{-3} in DMF, $\lambda_{\mathrm{exc}} = 406.7$ nm; [g] 1×10^{-3} mol dm^{-3} in H_2O, $\lambda_{\mathrm{exc}} = 406.7$ nm; s = strong, m = medium, w = weak, v = very, sh = shoulder, ρ = depolarization ratio.

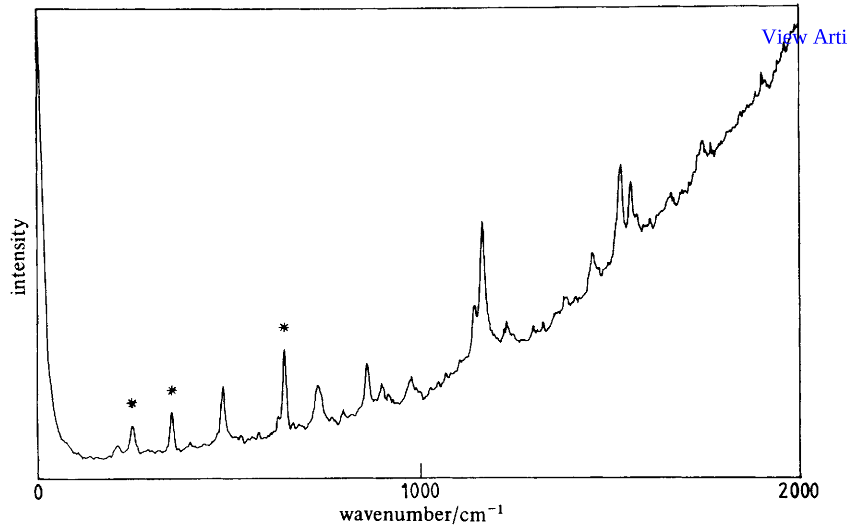


FIG. 3.—Resonance Raman spectrum of 4×10^{-4} mol dm^{-3} dye IV in $CHCl_3$, $\lambda_{\mathrm{exc}} = 406.7$ nm. Bands marked with an asterisk are due to $CHCl_3$.

IV could be obtained in colloidal form in aqueous NaLS solution at pH *ca.* 6.0. Solutions of dyes I-III in $CHCl_3$ fluoresce so strongly that they appear red in room light due to their red emission. Interestingly, the emission from dyes I-III in $CHCl_3$ could be efficiently quenched by adding solvents with OH groups, *e.g.* H_2O or EtOH (direct observation by eye). Dye IV emits only very weakly in the vicinity of its absorption band, as shown in fig. 3 and 4. Dyes V and VI must behave similarly, since r.R. spectra of these compounds could also be obtained in solution. A high Stokes shift of *ca.* 6700 cm^{-1} occurs for the emission of dye IV (band maxima taken instead of 0–0 transitions[34]). The decay time of the emission at 571 nm was $\tau < 3.6$ μs (lower time resolution limit of our fluoroscope).

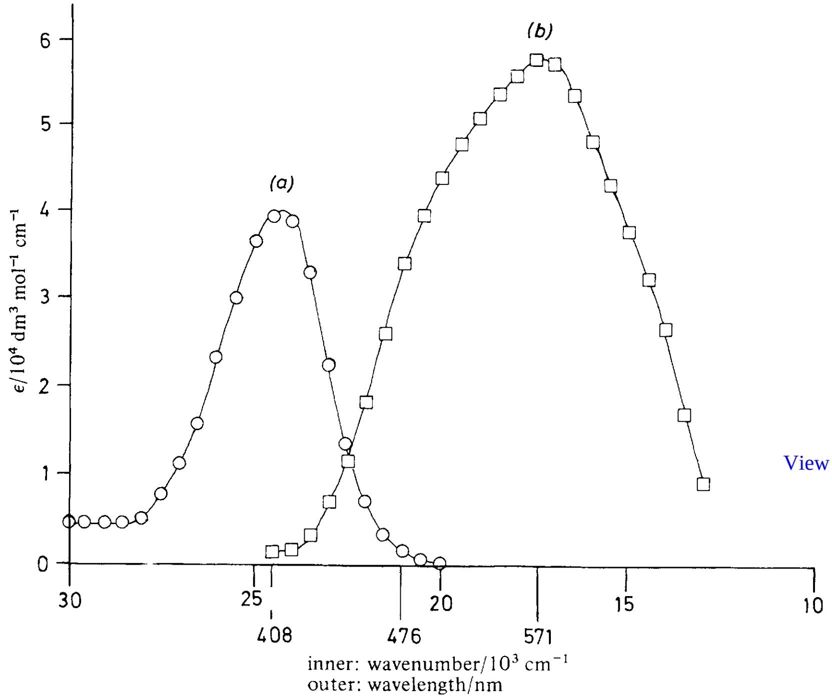


FIG. 4.—Absorption and emission spectrum (λ_{exc} = 406.7 nm) of dye IV in $CHCl_3$: (*a*) absorption, 1.6×10^{-4} mol dm^{-3}; (*b*) emission, 1.0×10^{-5} mol dm^{-3}, corrected for spectrometer sensitivity.

CONTINUOUS IRRADIATION EXPERIMENTS

In order to test the ability of dye IV to act in photoreactions as shown in schemes 1 and 2 and fig. 2, N_2-purged solutions containing 4.4×10^{-5} mol dm^{-3} dye IV + 5×10^{-4} mol dm^{-3} MV^{2+} dichloride + 1.3×10^{-3} mol dm^{-3} EDTA + phosphate buffer (pH 6.5) in DMF + H_2O (2/1, v/v) were irradiated with light of λ = 457.9 nm. Similar solutions in DMSO + H_2O (95/5, v/v)* were irradiated with λ = 406.7 nm. Using laser powers of 30-140 mW the solutions were turned dark blue within minutes of starting the irradiation. U.v.–visible spectra revealed the formation of $MV^{\cdot +}$ (methyl viologen radical cation).[19]

In an extensive first series of experiments with systematic omission of one or more of the constituents of the solutions, and varying the way in which the solutions were prepared, it was discovered that prolonged heating of the solutions prior to irradiation was mainly responsible for efficient $MV^{\cdot +}$ formation upon irradiation. In a second series, the formation of oxidation products X of MV^{2+} dichloride in DMF + H_2O or DMSO + H_2O upon heating could then be established. A third series of experiments, carried out with ice-cooled solutions, yielded reproducible results which are collected in table 4 (average of 3 or 4 experiments, 15 min irradiation time, laser power 30-140 mW). Direct excitation of MV^{2+} dichloride with subsequent $MV^{\cdot +}$ formation is obviously possible, as can be seen from table 4. For experiments with dye IV, the amount of $MV^{+\cdot}$ formed by this direct excitation process has been subtracted according to the method described in the Appendix.

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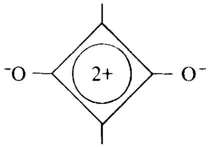
* We thank Dr T. Tanno, Riken Co. Ltd, Tokyo, Japan, for suggesting this solvent mixture.

TABLE 3.—PROMINENT INFRARED AND RESONANCE RAMAN BANDS (cm^{-1}) OF DYES I–VI ASSIGNED TO THE CENTRAL PART



I		II		III		IV			V		VI		
i.r.[a]	r.R.[a]	i.r.[a]	r.R.[a]	i.r.[a]	r.R.[a]	i.r.[a]	r.R.[b]	r.R.[c]	i.r.[a]	r.R.[d]	i.r.[a]	r.R.[e]	assignment
—	1722	—	1736	—	1730	—	1790	1812	—	1792	—	1806	ν_s(C=C)
1620	—	1630	—	1609	—	1631	—	—	1615	—	1615	—	ν_{as}(C—O)
—	1569	—	1570	—	1559	—	1570	1522	—	1584	—	1578	ν_s(C—O)
—	541	—	572	—	584	—	650	624	—	656	—	622	benzene?
—	157	—	176	—	178	—	218	244	—	264	—	260	ring modes?

[a] In KBr; [b] in $CHCl_3$; [c] in concentrated H_2SO_4; [d] in DMF; [e] in H_2O. ν = stretching mode; s = symmetric; as = asymmetric.

TABLE 4.—QUANTUM YIELDS, ϕ, AND NORMALIZED RATES OF $MV^{\cdot+}$ FORMATION, F, AND OPTICAL ABSORBANCES, A OF NON-IRRADIATED SOLUTIONS AT λ_{exc}

	λ_{exc} = 457.9 nm			λ_{exc} = 406.7 nm			
	H_2O with or without EDTA	DMF + H_2O (2/1 v/v)		DMSO + H_2O (95/5, v/v)			
		with EDTA		without EDTA		with EDTA	
	without S	without S	with S[a]	without S	with S[a]	without S	with S[a]
ϕ[b]	0	$3.8\times10^{-2}\pm4.5\times10^{-2}$	$7.9\times10^{-4}\pm5.4\times10^{-4}$	$1.1\times10^{-3}\pm0.5\times10^{-3}$	$1.0\times10^{-4}\pm0.7\times10^{-4}$	$4.6\times10^{-2}\pm4.0\times10^{-2}$	$1.8\times10^{-3}\pm0.4\times10^{-3}$
F[c]	0	$5.7\times10^{-10}\pm1.3\times10^{-10}$	$5.5\times10^{-10}\pm1.3\times10^{-10}$	$1.6\times10^{-10}\pm0.4\times10^{-10}$	$3.4\times10^{-10}\pm0.6\times10^{-10}$	$5.8\times10^{-9}\pm0.1\times10^{-9}$	$5.9\times10^{-9}\pm0.3\times10^{-9}$
A[d]	$2.0\times10^{-3}\pm1.4\times10^{-3}$	$1.8\times10^{-3}\pm2.9\times10^{-4}$	$9.2\times10^{-2}\pm5.0\times10^{-3}$	$1.9\times10^{-2}\pm3.6\times10^{-3}$	$2.68\pm1\times10^{-2}$	$1.8\times10^{-2}\pm4.2\times10^{-3}$	$2.70\pm1\times10^{-2}$

[a] Contribution from direct MV^{2+} excitation subtracted; [b] r.m.s. errors with 95% statistical significance;[35] [c] mol $MV^{\cdot+}$ produced/[W(light)s(irradiation time)] in 3.1 cm^3 solution with r.m.s. errors; [d] 1 cm path length, with r.m.s. errors.

TABLE 5.—QUANTUM YIELDS ϕ FOR $MV^{\cdot +}$ FORMATION USING OXIDATION PRODUCTS OF MV^{2+} DICHLORIDE AS PHOTOSENSITIZERS, IRRADIATED WITH $\lambda_{exc} = 457.9$ nm[a]

solvent	v/v	viscosity/cP	ϕ
$CH_3CN + H_2O$	2/1	< 1.0	3.0×10^{-4}
H_2O	— —	1.0	3.2×10^{-3}
glycerol + H_2O	1/1	5.0	3.7×10^{-3}
ethanediol + H_2O	2/1	6.3	1.8×10^{-2}
DMF + H_2O	2/1	2.3	$4.7 \pm 0.6 \times 10^{-2}$[b]
DMF + H_2O	2/1	2.3	4.7×10^{-2}[c]
DMF + H_2O	2/1	2.3	$8.0 \pm 1.2 \times 10^{-3}$[d]
DMF + H_2O	2/1	2.3	3.5×10^{-3}[e]

[a] 0.18 g dm^{-3} X + 1×10^{-3} mol dm^{-3} MV^{2+} dichloride + 1×10^{-2} mol dm^{-3} EDTA at pH 6.5; laser beam diameter ≈ 5 mm; [b] as (*a*); [c] focused laser beam, local photon flux density enhanced by a factor of 160 compared with (*b*); [d] using compound with $r_f = 0.63$ only as sensitizer, see text; [e] as (*b*) but without EDTA.

TABLE 6.—OXIDATION OF DYE IV WITH Ce^{4+}[a]

equivalents IV:oxidant[b]	solvent	oxidant reduced (%)	IV decomposed (%)	oxidant
1:1.1	1 mol dm^{-3} H_2SO_4 in H_2O	100	3.6 ± 1.7	[c]
1:20	1 mol dm^{-3} H_2SO_4 in H_2O	55	100	[c]
1:1.1	CH_3CN[e]	100	4.1	[d]

[a] E_0 (Ce^{4+}/Ce^{3+}) = + 1.44 V in 1 mol dm^{-3} H_2SO_4; [b] 2×10^{-4} mol dm^{-3} dye IV, max. solubility is 5×10^{-4} mol dm^{-3} in 1 mol dm^{-3} H_2SO_4; [c] $Ce(SO_4)_2$; [d] $Ce(NO_3)_6(NH_4)_2$; [e] contains traces of H_2O.

For solutions containing MV^{2+} dichloride + EDTA and colloidal dye IV in 5×10^{-2} mol dm^{-3} NaLS or dye VI in H_2O, no $MV^{\cdot +}$ was formed even after prolonged irradiation with $\lambda_{exc} = 406.7$ nm. Table 5 contains the quantum yields ϕ for $MV^{\cdot +}$ formation when the yellow oxidation products of MV^{2+} dichloride are used instead of dye IV in different solvents. Results for different photon flux densities and for reactions using only the compound with $r_f = 0.63$ instead of the whole mixture X are also presented in table 5. When PtO_2 was added to similar solutions containing X, MV^{2+} dichloride and an excess of EDTA at pH 6.5, irradiation with $\lambda_{exc} = 457.9$ nm produced only a low steady-state concentration of $MV^{\cdot +}$ (due to reduction of H_2O by $MV^{\cdot +}$ *via* PtO_2[16]). No depletion ($\pm 2\%$) of X could be observed after 5 h irradiation time, corresponding to *ca.* 20 h AM2 solar irradiation for the given experimental conditions.[36]

OXIDATION OF DYE IV BY Ce^{4+}

In the reactions of fig. 2(*a*) the intermediate $S^{\cdot +} = IV^{\cdot +}$ should occur. In order to detect $IV^{\cdot +}$ in such photoreactions, we tried to generate this species by oxidizing dye IV in different ways, as shown in table 6. When solutions of dye IV were mixed with Ce^{4+} solutions, the colour changed instantaneously to pale orange and then to blue.

By rapidly scanning the u.v.–visible spectra during the oxidation an intermediate absorption at 475 nm could be established. To our surprise the *ca.* 1:1 oxidised solutions were still found to contain dye IV ($\lambda_{\text{max}} = 408$ nm), apparently decomposed only by 3.6% (table 6), although all the Ce^{4+} was reduced. Furthermore, the oxidized solution showed a broad absorption with $\lambda_{\text{max}} = 570$ nm, $\varepsilon = 1.1 \times 10^5$ $dm^3 mol^{-1} cm^{-1}$ (calculated with the assumption that all decomposed dye IV has been transformed into the substance with λ_{max} at 570 nm). In 1 mol dm^{-3} H_2SO_4 in $CH_3CN + H_2O$ (8/2, v/v), the half-life of $\lambda_{\text{max}} = 570$ nm was 2 h.

DISCUSSION

SOLUBILITY, ABSORPTION AND EMISSION

Squarilium dyes I-V are insoluble in water. For the purpose of solar-energy conversion, water solubility would be a great advantage. We tried, therefore, to dissolve dyes I-V in 0.1 mol dm^{-3} aqueous micellar NaLS solution, which is known to dissolve aromatic substances. But only dyes I and III, which contain C_2H_5 groups, could be dissolved in this medium. Obviously, squarilium dyes with their unusual charged central part do not behave like normal aromatic systems with respect to solubility. Only those dyes containing aliphatic chains, which can immerse in the aliphatic core of a micelle, could be solubilized. The red shift of the absorption of dye I upon micellization indicates strong interactions of dye I with either water itself or with the charged surface of the micelle.

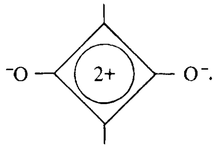
Dye VI represents the first known water-soluble squarilium dye. The yellow colour of the aqueous solution, however, faded within some weeks. Obviously dye VI decomposes in H_2O, probably *via* OH^- attack on the central 4-membered ring.[5]

Dyes I-III absorb in the red, whereas dyes IV-VI absorb in the blue. This blue shift indicates a much shorter chromophore in the latter cases, which can also be seen from fig. 1(*a*) and (*b*); in dyes IV-VI the conjugated system extends at most over one R group and the central part, whereas in dyes I-III both R groups are included for the different mesomeric structures.

The emission spectrum of dye IV given in fig. 4 shows a shoulder at 476 nm and a peak at 571 nm. No mirror image relation between absorption and emission exists. At first sight one might assign the 476 nm band to monomer and the 571 nm band to excimer emission. However, for the low concentrations used here (1×10^{-5} mol dm^{-3}) excimer formation is unlikely.[37] Another interpretation would be that dye IV behaves as a donor–aromatic-acceptor (DArA) molecule with the $N(C_6H_5)_2$ substituents as electron donors and the central ring, which is doubly positively charged, as the aromatic system and as electron acceptor. DArA molecules with an NR_2 group as electron donor are known to relax from the first excited singlet state S_1 into a twisted internal charge-transfer (t.i.c.t.) state,[38-40] which then emits with a large red shift compared with S_1. The formation of such t.i.c.t. states is strongly solvent dependent. Since dye IV is soluble only in a small number of similar solvents, no detailed study was possible and the explanation for the 571 nm emissions has to be taken as a mere hypothesis.

INFRARED AND RESONANCE RAMAN SPECTRA

The main purpose of the investigation of the vibrational spectra of dyes I-VI was to identify the vibrational modes of the central part



With the substituents R assumed to be point masses, the central part has local symmetry D_{2h}. Four totally symmetric r.R. and seven i.r. bands should be observable for dyes I-VI. However, since the chromophores extend also over the substituents R (fig. 1), r.R. bands of the R groups also are expected to show up.

For the r.R. band in the range 1720-1812 cm^{-1} no combination or overtone could be assigned and this is believed to be the fundamental symmetric stretching mode $\nu_S(C{=}C)$. For rectangular cyclobutadiene (CB), the same mode has been calculated at 1785[41] or 1744 cm^{-1} [42] and at 1632 cm^{-1} for perdeuterated CB.[41] Although the masses of the oxygens and the substituents R in the dyes I-VI are much higher than H or D in CB, a very high $\nu(C{=}C)$ can be expected in the former since the central part is doubly positively charged and is presumably highly strained. This assignment, however, supposes a central part with partially single and partially double bonds.

When dye IV is dissolved in concentrated H_2SO_4 the O^- are likely to be protonated and $\nu(C{-}O)$ is expected to decrease. A frequency shift of -48 cm^{-1} is observed for the band of dye II at 1570 cm^{-1} when $CHCl_3$ is replaced by concentrated H_2SO_4. This frequency is therefore assigned to the $\nu_S(C{-}O)$, and the corresponding asymmetric mode is observed in the i.r. at *ca.* 1609-1630 cm^{-1}. Likewise, the band at 650 cm^{-1} moves to 624 cm^{-1} and the band at 218 cm^{-1} moves to 244 cm^{-1}. Both are r.R. bands which occur in the same frequency region in all dyes I-VI, but their assignment is not yet clear. Since a protonation of the phenyl rings in dye IV is unlikely, these bands also appear to belong to the central part. Common to most i.r. and r.R. spectra, bands around 1600 and 1200 cm^{-1} are believed to originate from phenyl ring vibrations.

The depolarization ratios ρ of all the r.R. bands of dye IV indicate totally symmetric modes. The value $\rho \approx \frac{1}{3}$ indicates that the excited state of dye IV is non-degenerate.[43]

CONTINUOUS IRRADIATION EXPERIMENTS

SQUARILIUM DYES IV AND VI

Table 4 shows that $MV^{\cdot+}$ can be formed *via* direct excitation of MV^{2+} even if no EDTA is present (in DMSO + H_2O). According to the oxidation potential of DMSO ($E_0 \lesssim 1.0$ V[44]) water would be the electron donor [$E_0(O_2/H_2O) = 0.82$ V]. However, the exact oxidation potential of DMSO does not seem to be known.[45] Furthermore, with H_2O as the reducing agent for electronically excited MV^{2+}, O_2 would also be formed. If no efficient catalyst for H_2O reduction is present,[3] O_2 would oxidize $MV^{\cdot+}$ back to MV^{2+}, thereby resulting in no net formation of $MV^{\cdot+}$. No reduction took place either with dye IV as a colloid or with dye VI, both in water. For the former case the excited-state lifetime is probably too short to allow efficient quenching by MV^{2+}. That the latter shows no photoactivity might be due either to unfavourable redox potentials or to the solvent water: for analogous photoredox reactions with the sensitizer X or with phthalocyanines[46] in mixtures of DMF + H_2O or DMSO + H_2O, much higher quantum yields were obtained for $MV^{\cdot +}$ formation than for reactions in H_2O alone.

According to table 4 dye IV can act in photoredox reactions as shown in fig. 2. Although the direct excitation of MV^{2+} exhibits a higher quantum yield ϕ for $MV^{\cdot +}$ formation than by excitation *via* dye IV, the $MV^{\cdot +}$ concentrations after irradiation were higher when dye IV was present. For solutions with EDTA the quantum yield for $MV^{\cdot +}$ formation is 18 times higher than for solutions without EDTA. Obviously EDTA is the electron source in this case. Similar sacrificial systems have been proposed for practical use.[47] However, the quantum yield for the $MV^{\cdot +}$ formation found here is too low for a practical application, although it demonstrates that the excited state of dye IV, with a lifetime τ probably much shorter than 3.6 μs (τ_{S_1} of dye I is 0.28 ns[48]), is able to reduce MV^{2+}. Since squarilium dyes can be prepared with almost any desired substituents R and any colour, the chances for finding squarilium dyes better suited for solar-energy conversion in solution are high.

MIXTURE X

Although no complete analysis of all the components of X is available, the presence of mono- and bi-pyridinones in this mixture seems to be obvious: the reaction conditions for formation of X are very similar to those for pyridinone formation[22] and the t.l.c. results agree with ref. (22) for the monopyridinone VII.

On the one hand, VII does not appear to be the substance with the highest photocatalytic activity for formation of $MV^{\cdot +}$ upon irradiation, as table 5 shows. On the other hand, for practical purposes this is not important since the solutions designed for solar-energy conversion could be produced by a single vessel reaction: MV^{2+} dichloride is heated in basic DMF + H_2O, then neutralized and more MV^{2+} dichloride is added. This solution then could be used for reactions as described by Krasna.[47] The preliminary stability test of X looks promising and the experiments with variable photon flux densities show that a monophotonic reaction drives the reduction of MV^{2+}.

Table 5 indicates a drastic solvent effect on the quantum yield for formation of $MV^{+\cdot}$. Viscosity alone can not explain the results and the highly dipolar character of DMF + H_2O may also have an influence.

The quantum yield $\phi = 4.7 \times 10^{-2}$ for the formation of $MV^{\cdot +}$ with X as photosensitizer in DMF + H_2O (2/1, v/v) compares favourably with $Ru(bpy)_3^{2+}$ as sensitizer. The latter system, also with EDTA as electron source, had $\phi = 2 \times 10^{-2}$ in H_2O.[49] X promotes the photoreduction of MV^{2+} even in the absence of EDTA in DMF + H_2O (2/1, v/v). Probably $(CH_3)_2NH$, which is always present in small quantities in DMF,[21] acts as the electron source $\{E_p[(CH_3)_2NH^{\cdot +}/(CH_3)_2NH] = 1.03$ V *vs.* SCE at pH 11.9[50]$\}$, or otherwise H_2O, with the same uncertainty as outlined in above.

Finally, the photoactivity of X indicates that photoredox reactions of MV^{2+} dichloride carried out in DMF + H_2O or DMSO + H_2O can lead to spurious results (*via* X formation) if no precautions such as cooling and rapid use of the solutions are taken.

OXIDATION OF DYE IV WITH Ce^{4+}

The intermediate absorption at 475 nm indicates the occurrence of a short-lived transient in the oxidation of dye IV with Ce^{4+} We assume this transient to be $IV^{\cdot +}$. The structure of the compound with $\lambda_{max} = 570$ nm is not yet clear. R.R. spectra of the dark blue solutions, obtained by oxidation of dye IV by a 9-fold excess of $Ce(SO_4)_2$ in 1 mol dm^{-3} H_2SO_4 in $CH_3CN + H_2O$ (8/2, v/v) yielded intense bands at 1585, 1573, 1451, 1422, 1233, 1208 and 1180 cm^{-1} and weaker bands at 878, 816, 726, 707, 689, 538, 513, 431 and 411 cm^{-1}. No bands below 300 cm^{-1}, which would indicate radical dimers,[51-56] where observed.

The decomposition of Ce^{4+} by dye IV seems to be partially catalytic: only 3.6% of dye IV was decomposed in reducing 100% of the Ce^{4+}. With a 19-fold excess of Ce^{4+}, 55% of the Ce^{4+} was reduced and 100% of dye IV decomposed. Although Ce^{4+} can oxidize water when catalysts such as RuO_2 are present,[57] we do not believe that a reaction with no chemical change of the catalyst can explain the results obtained here. With RuO_2 as the catalyst for O_2 evolution, the oxidation of H_2O by Ce^{4+} has a half-reaction time of 30 min.[57] By contrast, the reduction of Ce^{4+} in 1 mol dm^{-3} H_2SO_4 with dye IV present was complete within seconds. We interpret this as indicating that H_2O is oxidized by Ce^{4+} *via* the transient species $IV^{\cdot+}$ to O_2, although no O_2 has been detected so far due to the low/high solubility of dye IV/O_2 in 1 mol dm^{-3} H_2SO_4.

Provided that the photoreduction of MV^{2+} proceeds according to fig. 2(*a*) and that the back reaction between $MV^{\cdot+}$ and $IV^{\cdot+}$ can be inhibited, a complete photolytic water splitting cycle using dye IV, MV^{2+} and a noble-metal catalyst such as colloidal Pt[4] (for water reduction *via* $MV^{\cdot+}$) can be envisaged. To our knowledge this would be the first example of such a cycle based solely upon a purely organic dye.

As shown in scheme 3 below, dye IV could function as a reducing agent in its excited state IV* and as an oxidant in its oxidized state $IV^{\cdot+}$. The expensive RuO_2 catalyst for the oxidation of H_2O[4] could, therefore, be omitted:

scheme 3

$$IV \xrightarrow{h\nu} IV^*$$

$$IV^* + MV^{2+} \rightarrow IV^{\cdot+} + MV^{\cdot+}$$

$$IV^{\cdot+} + \tfrac{1}{2}H_2O \rightarrow IV + \tfrac{1}{4}O_2 + H^+$$

$$MV^{\cdot+} + H_2O \xrightarrow{Pt} MV^{2+} + \tfrac{1}{2}H_2 + OH^-$$

However, the occurrence of $IV^{\cdot+}$ in the reactions of scheme 3 has first to be proved. Further experiments are under way.

Financial support by the S.R.C. and the Swiss National Foundation (M.F.) are gratefully acknowledged. We also would like to thank Mr R. B. Girling for technical assistance.

APPENDIX

DETERMINATION OF QUANTUM YIELDS OF $MV^{\cdot+}$ FORMATION

When solutions of dye IV and MV^{2+} are irradiated with $\lambda_{\text{exc}} = 406.7$ or 457.9 nm, two processes lead to $MV^{\cdot+}$ formation: (i) *via* direct excitation of MV^{2+} and (ii) *via* excitation of dye IV. In order to determine the quantum yield for process (ii), the numbers of photons absorbed by dye IV and MV^{2+} have to be known, as well as the amount of $MV^{\cdot+}$ produced by each of the two processes. For the situation here

$$A_M \ll A_S, \quad A = \varepsilon c l \tag{A 1}$$

where A is the absorbance, ε is the molar decadic absorption coefficient, c is the concentration, l is the cell path length and subscripts M and S denote methyl viologen dichloride and sensitizer IV, respectively. One then obtains

$$\Delta I_M(M) = +I_0(1-10^{-A_M}) \tag{A 2}$$

and

$$\Delta I_S(M+S) \approx -I_0(10^{-A_{M+S}} - 10^{-A_M}) \tag{A 3}$$

where I_0 is the radiation (einstein cm^{-2} s^{-1}) incident on the sample cell and $\Delta I_{\mathrm{M,S}}(\mathrm{M, M+S})$ are the radiations absorbed by M or S in solutions containing only M or both M and S, respectively.

Since the average rate $F(\mathrm{M})$ of $\mathrm{MV}^{\cdot +}$ formation for solutions containing only MV^{2+} is known (table 4), we obtain the amount of $\mathrm{MV}^{\cdot +}$ in solutions containing both MV^{2+} and dye IV but produced solely by direct MV^{2+} excitation

$$\mathrm{MV}_{\mathrm{M}}^{\cdot +}(\mathrm{M+S}) = Pt\frac{\Delta I_{\mathrm{M}}(\mathrm{M+S})}{\Delta I_{\mathrm{M}}(\mathrm{M})}F(\mathrm{M}) \qquad (\mathrm{A}\ 4)$$

where P is the laser power in W and t is the irradiation time in s. This value $\mathrm{MV}_{\mathrm{M}}^{+\cdot}(\mathrm{M+S})$ is then subtracted from the observed amount of $\mathrm{MV}^{+\cdot}$ in solutions containing M+S. Example for the solutions used, with $\lambda_{\mathrm{exc}} = 406.7$ nm: $A_{\mathrm{M}} = 0.019$, $A_{\mathrm{S}} = 2.666$

$$\frac{\Delta I_{\mathrm{M}}(\mathrm{M+S})}{\Delta I_{\mathrm{M}}(\mathrm{M})} = 2.2\times 10^{-3}.$$

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