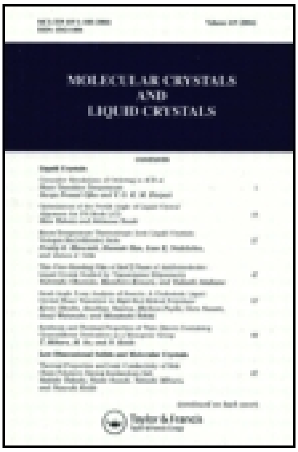

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SUPRAMOLECULAR AGGREGATES AND ION - BINDING IN PHOTOCHROMIC MOLECULES

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Abstract Photochromic dihydroindolizines linked to an anchor group allowing for supramolecular interaction are described. Four classes of molecules containing different anchor groups and their supramolecular interactions with ions and molecules are presented.

INTRODUCTION

Photochromic dihydroindolizines 1 (DHI's) were developped in our laboratory.[1] These molecules - constituting a new class of photochromes - have, as all photochromic materials, a high potential both in basic research as material science. Their light induced structure and property changes may be used in many processes such as opthalmic lenses, light shading devices, sensors, photoswitches, in displays and information recording or storage systems, as well as in photoresponsive enzymes.[1] In this paper molecules containing podand, crown or calixarene- anchor groups connected to the photochromic DHI- unit are presented. Four different classes (type A - D; see Fig. 1) are selected to demonstrate the effect of supramolecular interaction to the a) ground and b) excited state. (Table 1)

Ground state and excited state effects for these molecules will be presented and class A molecules will be described in these paper exemplarily.

Results

Supramolecular Effects: Supramolecular effects are based on molecular storage and supramolecular read out of molecular information .[2] Important is therefore molecular recognition. Recognition in supramolecular systems can depend on steric, interaction polarity, binding forces (electrostatic, hydrogen bonding, van der Waals forces), large areas, interaction sites, strong over all binding (high stability and high selectivity). Molecular photonics belong to this field thus opening a route to supramolecular devices for applications. Organization of molecular components in these aggregates in space, in energy and in time is essential.

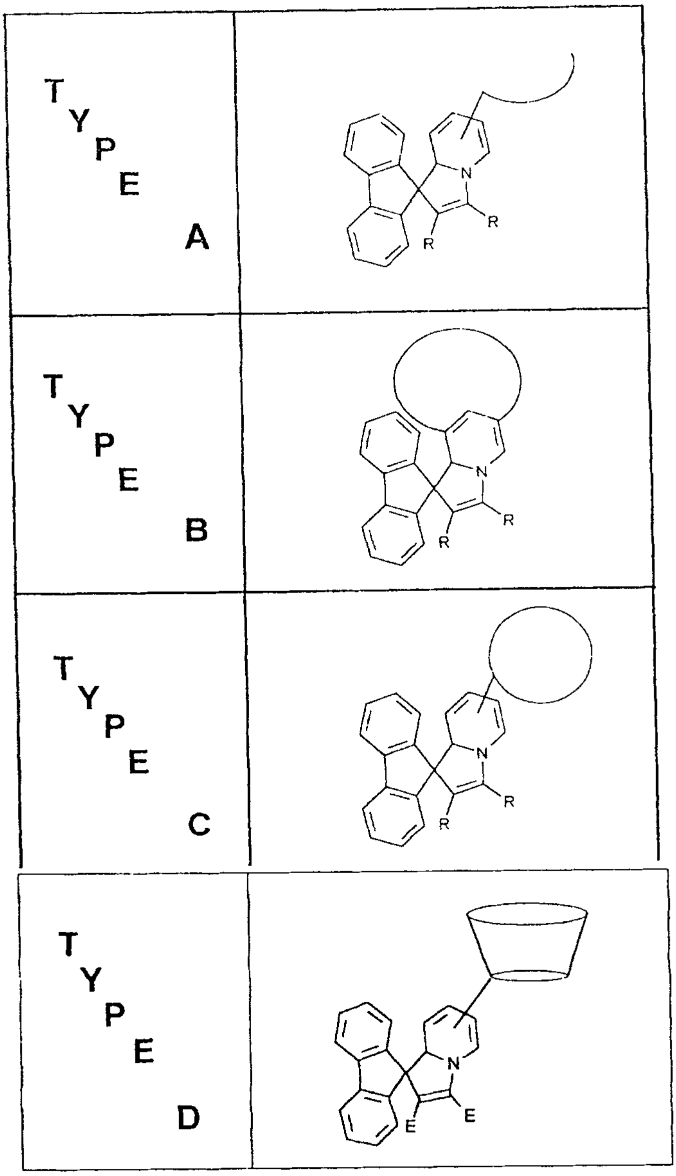
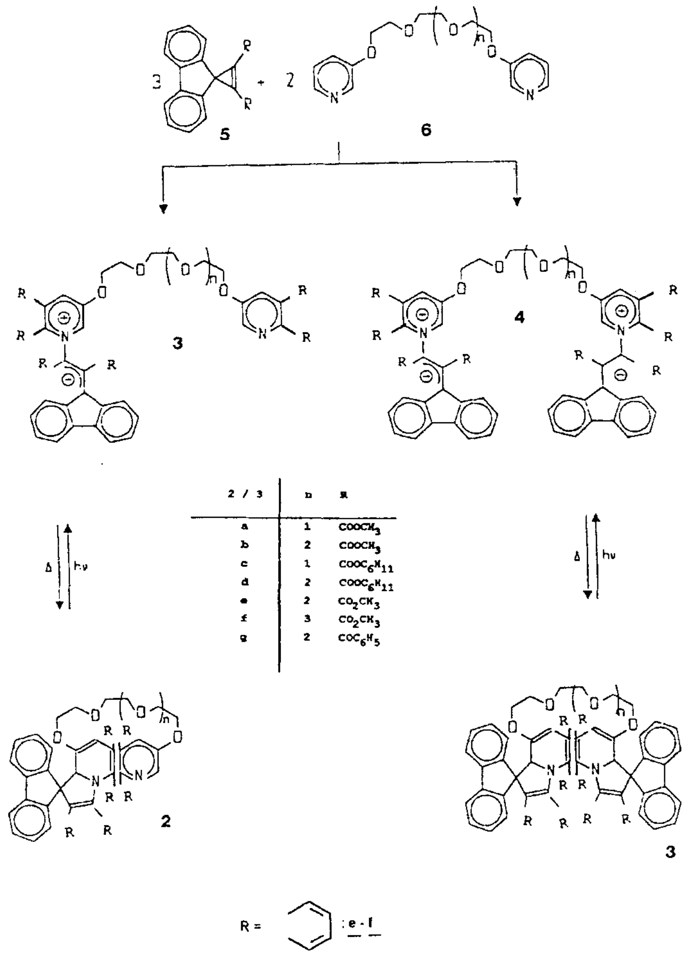


FIGURE 1 4 classes of DHI's for supramolecular interaction

Type - A molecules

The (mono-) 2 and (bi)photochromic 3 dihydroindolizines were made by the spirene route[3]. Thus the pyrrolo - derivatives 2a - d were obtained.



2 / 3	n	R
a	1	$COOCH_3$
b	2	$COOCH_3$
c	1	$COOC_6H_{11}$
d	2	$COOC_6H_{11}$
e	2	CO_2CH_3
f	3	CO_2CH_3
g	2	COC_6H_5

FIGURE 2 : Synthesis of new pyridylether - DHI 2 and 3

The quinolinyl - DHIs 2e - f were prepared analogously. Yields and melting points are given in table I. UV data are collected in table II.

Table I Yield and melting points of mono- and biphotochromic DHI's 2 and 3.

R	n	2	yield (%)	mp (°C)	3	yield (%)	mp (°C)	Mono : Bis
CO_2CH_3	1	a	28	75	a	60	83	1 : 2.1
CO_2CH_3	2	b	18	82	b	45	90	1 : 2.5
$CO_2C_6H_{11}$	1	c	22	70	c	40	80	1 : 1.8
$CO_2C_6H_{11}$	2	d	25	68	d	61	75	1 : 2.4
CO_2CH_3	2	e	36	75	a	16	89	2.3 : 1
CO_2CH_3	3	f	17	75	b	9	90	1.9 : 1
COC_6H_5	2	g	20	77	c	10	85	2.0 : 1

Ground state phenomena

Supramolecular effects should affect ground state phenomena such as reaction rates. The half life $\tau_{1/2} \sim 1/ k_r$ is a parameter reflecting this factor. It is given in table II. Adding Me^+- ions to 2 or 3 should bring about binding to give a supramolecular aggregate. If we add for instance alkaline ions, we see an effect. The number of binding sites is decisive[4]. 4 coordinating sites show a small effect, if we have five coordinating sites, a large effect is observed. Plotting $\tau_{1/2}$ in the presence of the metal ion over $\tau_{1/2}$ in the saltfree system gives the parameter shown in Fig. 2. This is characteristic for the supramolecular species with regard to the model without the guest. Clearly the half-life or its inverse the reaction rate is affected. $\tau_{1/2}$ is increased or in other words the rate k_r for the 1,5-electrocyclization is slowed down. Thus we have been able to tune a ground state property.

Table II UV - spectra and $\tau_{1/2}$ of DHI's 2 and betaines 3. ([a] Extremely small)

	λ_{max} (DHI) (nm)	log ε	λ_{max} (Betaine) (nm)	Color	$\tau_{1/2}$ (s)
2a	389	3.822	564	blue	265
2b	390	3.870	564	blue	272
2c	381	3.430	570	blue	162
2d	382	3.721	570	blue	175
3a	390	4.095	564	blue	275
3b	389	4.120	564	blue	280
3c	381	3.781	570	blue	168
3d	382	3.960	570	blue	156
2e	362	3.880	541	red	-[a]
2f	362	4.000	543	red	-[a]
2g	413	3.809	-	-	-[a]
3e	362	4.132	541	red	-[a]
3f	362	4.098	543	red	-[a]
3g	413	4.105	-	-	-[a]

Excited state phenomena

Can we also change the excited state properties, so that they are reflected in the photochemistry of supramolecular devices.[2] We have added alkaline and alkaline earth ions to quinolinyl - spirodihydroindolizines 2e - f. On addition of Sr^{2+} and Ba^{2+} that the wavelength of the longest absorption is shifted bathochromicly. Additionally the fluorescence quantum yield increases for Sr^{2+} and Ba^{2+} by a factor of 2. So the substrate selective optical signal generation or read out is possible. Such systems might be used as sensors or optrodes. If we go to six coordinating sites we see more dramatic effects. Again Sr^{2+} and Ba^{2+} - ions induce bathochromic shifts as well as a fluorescence increase. If we examine however a molecule with only four binding sites, we do not observe such an effect for Sr^{2+} and Ba^{2+}. However a selectivity for Ca^{2+} is detectable. In the molecules 2e - g as the model shows, we have a rather sterically encumbered system. The benzoyl groups play also an important role for binding. As one see from a CHARMm - calculation the interaction between the benzoyl groups and the cations in the colored form 5 should be quite pronounced. We assume that in addition to binding by the polyethyleneglycole groups we do have a π - complex with aromatic binding to the ion. As the nmr CIS - parameters show binding occurs mainly by the quinoline groups. We can deduce that very clearly from induced large shifts for all quinoline protons and the smaller shifts for the glycole system. We have determined the binding constants for these molecules to be of the order of 10 - 60 depending on the structure of 2 and 3.[7] Similar studies were carried out for type B, C[6] and D molecules. Results will be published else where in detail.

Conclusion

Ground state properties can be tuned such as:

- binding constants: moderate (type A, C) - good (type B, C), - reactivity tuning of electrocyclic process (k_r) : decrease of k_r is possible A, B (most efficient : type B); increase type C; no effect type D.

Excited state properties are affected: - increase of F - intensity (Φ_F) (type A and type B); bathochromic (type A, B) (smaller in C; no effect in D), hyperchromic effect (type A, B), hypochromic (F) and D.

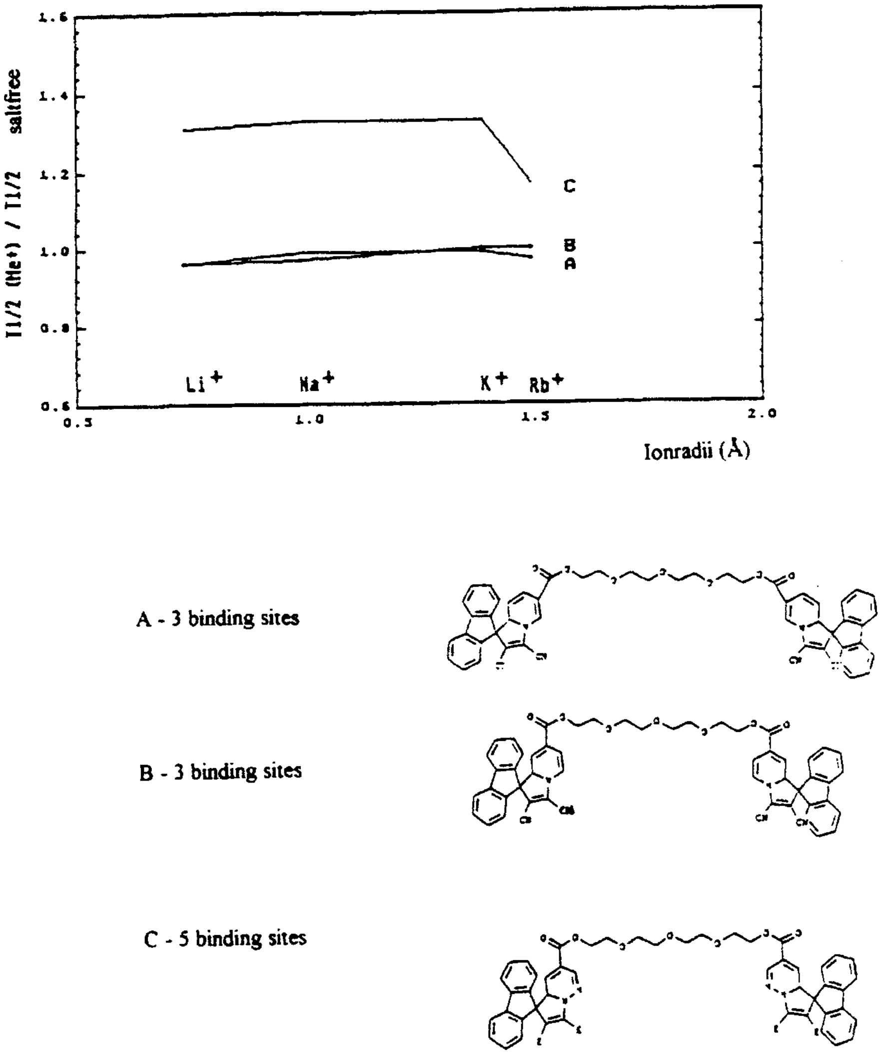


FIGURE 3 Relative changes of half lives of betaines on addition of alkaline ions (Methanol; c=5*10^{-5} mol/l)

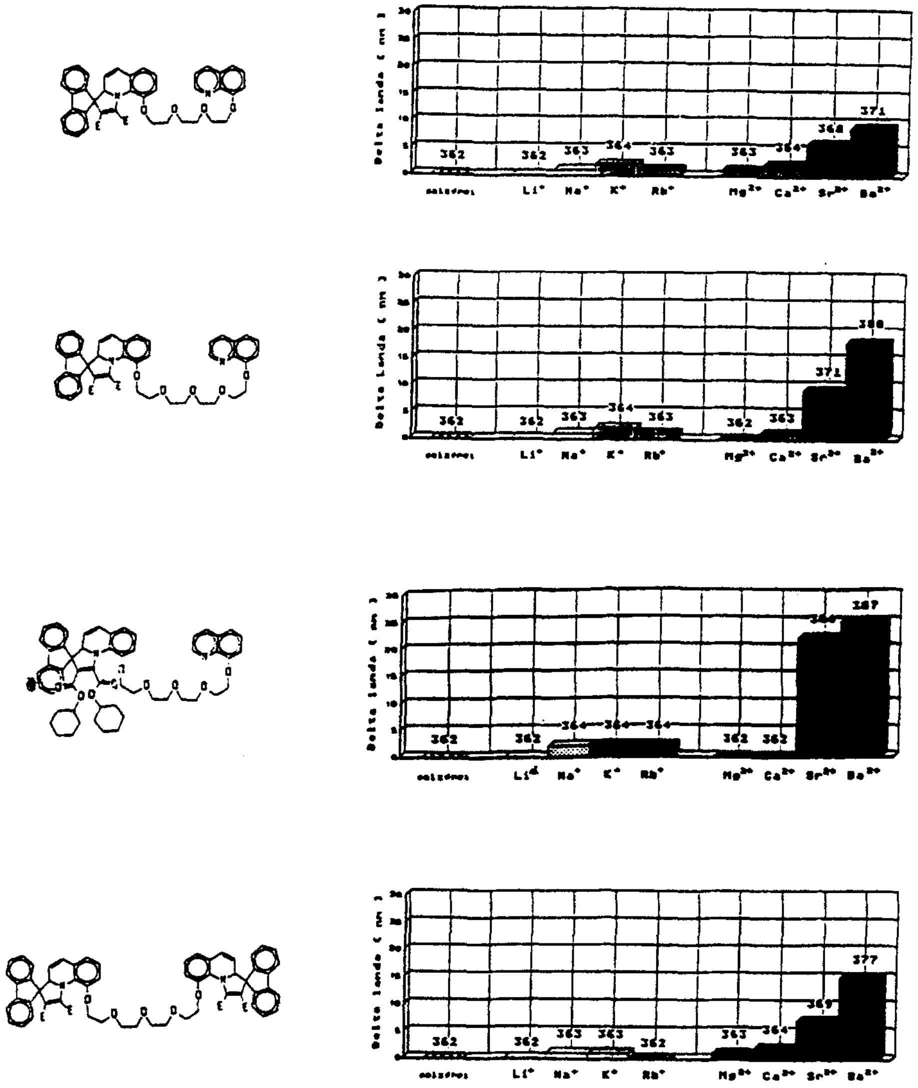


FIGURE 4 Relative changes of absorption on addition of alkaline and alkaline earth ions (Methanol; c=10^{-4} mol/l)

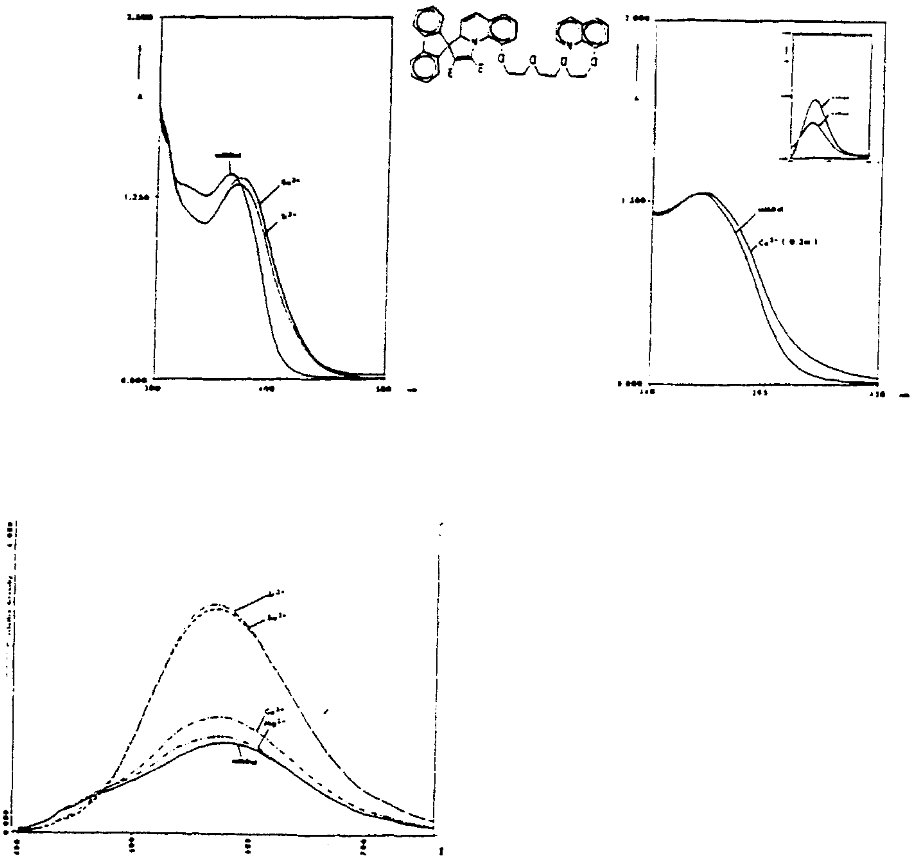


FIGURE 5 UV spectra and relative changes of absorption on addition of alkaline and alkaline earth ions (Methanol; $c=10^{-4}$ mol/l)

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