The Structure of Benzimidazole Cyanine Dyes, Their Spectroscopy and Their Performance in Photographic Emulsions

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The multi-step synthesis of two benzimidazole trimethine cyanines as possible green sensitizing dyes (Gs3-1, Gs3-2) is reported. Compounds were characterized from UV-Vis, mass spectroscopic and NMR data. The charge density distributions of the two compounds, calculated using the semi-empirical MOPAC 93 package, are in agreement with assignments in NMR spectroscopy. Sensitizing properties of the cyanine dyes were evaluated in actual photographic T-grain emulsions.

Introduction

Silver halide crystals, which constitute the sensitive elements in most photographic processes, have only significant sensitivity in the ultraviolet, violet and blue region, while the human eye is sensitive to the part of the electromagnetic spectrum between $\lambda = 400$ and 700 nm. Since silver halide emulsions are unaffected by green, yellow, orange and red light, these "colour-blind" materials give photographs in which the tone values are distorted and therefore can not be used as the basis for colour photography. The sensitivity of silver halide must be extended from $\lambda = 480$ nm (blue light), into the $\lambda = 500-600$ nm (green light) and 600-700 nm (red light) regions of the visible spectrum in order to produce colour photographic products.

Benzimidazole cyanine dyes are of industrial importance as green-sensitizing dyes in the spectral sensitization of emulsion microcrystals in negative filmmaking^[1-3]. In continuation of our research program into functional dyes^[4-6], we report the multi-step synthesis of two benzimidazole carbocyanine dyes, the general formula of which is given in Figure 1. FAB-MS proved to be an efficient technique to determine the structure of the final dye as well as intermediate compounds. Compounds were further characterized by UV-Vis spectroscopy and NMR measurements. The structures of the benzimidazole trimethine cyanine dyes were also studied by semi-empirical MOPAC 93 calculations, and the charge distributions correlated with the NMR spectra. Finally, the dyes were tested for solubility, sensitizing efficiency and dyeing extent (residual dye density).





Synthesis

The benzimidazole trimethine cyanine dyes (Gs3-1, Gs3-2) were prepared by a multi-stage reaction in which all steps proceeded under nitrogen atmosphere. First, the appropriate heterocyclic compound carrying an active methyl group in the 2-position was quaternized at the nitrogen atom. The resulting (QM) salt then reacted with diphenylformamidine to produce the corresponding intermediate, an anilido-vinyl compound (often called ICI intermediate). Subsequently, the ICI intermediate was further coupled with *p*-toluenesulfonyl chloride to become more reactive. Finally, the activated ICI intermediate was reacted with the appropriate QM salt in the presence of triethylamine to obtain the final dye. Details regarding the synthesis of Gs3-1 are depicted in Figure 2, and in the Experimental Section.

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Figure 2a. Synthetic route towards Gs3-1: preparation of QM salts



Figure 2b. Synthetic route towards Gs3-1: preparation of the ICI intermediates



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Figure 2c. Synthetic route towards Gs3-1: final coupling to the dye



Mass Spectra

Like many organic salts, cyanine dye salts resist ionization by traditional gas-phase methods due to poor volatility and thermal instability. In such cases FAB spectra have proven particularly useful^[4-6]. For example, when examining an iodide compound, an intense signal of the intact ion $[M - I]^+$ was always observed. Also, the loss of a methyl and/or an ethyl group from the intact ion could be seen although the signal intensity was often low. Moreover, for Gs3-2, the intensity of the isotopic molecular ions at m/z = M, M+2, M+4, M+6 and M+8 proved the presence of four chlorine atoms. Similarly for the intermediates QM3, ICI4, ICI5 and ICI6 as well as Gs3-1, the intensities at m/z = M, M+2 and M+4 proved the presence of two chlorine atoms as the proposed structures require.

More information may be obtained from FAB-MSMS spectra compared to ordinary FAB spectra. The exact identification of daughter-parent relationship allows extra structural information and details of the fragmentation process to be obtained. Table 1 summarizes the data of the daughter spectra obtained from the original intact molecular ions. It may be noted that ICI6 exhibits γ -fission with respect to the imidazole moiety (this is equal to β -fission with respect to the phenyl ring) as well as a fragmentation reaction that cleaves the imidazole ring. These processes are shown in Figure 3. The γ -fission may be seen as the formation of a stable positive ion containing an aromatic sevenmembered ring with two nitrogen atoms (see Figure 3 for a possible structure). The cleavage of the imidazole ring may be induced by the expulsion of a stable molecule (see Figure

3). As follows from the data in Table 1 and as explained in Figure 4, similar fragmentation patterns of the benzimidazole ring seem to occur in the dyes Gs3-1 and Gs3-2.

Table 1. Characteristic m/z values in FAB-MSMS mass spectra

QM2:	1,3-diethyl-5-(diethylamino)-2-methyl-
<i>m</i> /z-values	260 M ⁺ ; 216 M ₁ = M - (CH ₂ - 2 CH ₃); 188 M ₂ = M ₁ - (CH ₂ =CH ₂); 160 M ₃ = M ₂ -
QM3:	(CH ₂ =CH ₂) 5,6-dichloro-1,3-diethyl-2-methyl- benzimidazolium <i>p</i> -toluenesulfonate
<i>m/z</i> -values	257 M^+ ; $229 \text{ M}_1 = \text{M} - (\text{CH}_2 = \text{CH}_2)$; $201 \text{ M}_2 = \text{M}_2 = (\text{CH}_2 = \text{CH}_2)$; $166 \text{ M}_2 = \text{M}_2 = C$
ICI4:	2-(2'-anilinoethenyl)-5,6-dichloro-1,3-
<i>m</i> / <i>z</i> -values	detuyloenzimidazonum p-toruenesuitonate 360 M^+ ; $267 \text{ M}_1 = \text{M} - \text{H} - (\text{C}_6\text{H}_5 - \text{NH})$; $239 \text{ M}_2 = \text{M}_1 - (\text{CH}=\text{CH}_2)$; $130 \text{ M}_3 = \text{C}_6\text{H}_5 - \text{NH} - \text{CH} - \text{CH} - \text{C}$; $229 \text{ M}_4 = \text{M} - \text{M}_2$; 201
	$M_5 = M_4 - (CH_2 = CH_2)$ $M_5 = M_4 - (CH_2 = CH_2)$
1016:	anilino)ethenyl]benzimidazolium chloride
<i>m</i> / <i>z</i> -values ^[a]	514 M^4 ; 359 $M_1 = M - (CH_3 - C_6H_5 - SO_2)$; 267 $(M_2 = M_1 - H - (C_6H_5 - NH);$ 239 $M_3 = M_2 - (CH_2 = CH_2);$ 131 $M_4 = C_6H_5 - NH - CH - CH - CH;$ 228 $M_5 = M - M_4;$ 200 $M_6 = M_6;$ 200 $M_6 = M_6;$ 200 $M_6 = M_6;$ 200 $M_6 = M_6;$ 200 $M_6;$ 200 $M_6 = M_6;$ 200 $M_6;$
Gs3-1:	5,6-dichloro-2-{1-[3-(5-diethylamino-1,3-diethyl- 1,3-diethyl-2- benzimidazolylidene)propenyl]}benzimidazolium
<i>m</i> / <i>z</i> -values	526 M ⁺ ; 497 M ₁ = M - Et; 468 M ₂ = M ₁ - Et; 298 M ₃ = M - 228 (i.e. M - M ₄ + 2); 230 M ₄ = 230 (b-fission ^[b]); 202 M ₅ = M ₄ - (CH ₂ =CH ₂) 770 β_{e} fission ^[b]
GS3-2:	5,6-dichloro-2-{1-[3-(5,6-dichloro-1,3-diethyl-2- benzimidazolylidene)propenyl]}-1,3- diethylbenzimidazolium iodide
<i>m</i> / <i>z</i> -values	523 M ⁺ (³⁷ Cl ₁) ³⁵ Cl ₃); 494 M ₁ = M - Et; 465 M ₂ = M ₁ - Et; 295 M ₃ = M - 228; 228 M ₄ = 230 (b-fission ^[b]) - 2; 200 M ₅ = M ₄ - (CH ₂ =CH ₂); 267 β-fission ^[b] ; 239 M ₆ = β-fission - (CH ₂ CH ₂)

^[a] See Figure 3 for details. - ^[b] See Figure 4 for details.

NMR Measurements

The atomic numbering scheme used in the NMR interpretations is shown in Figure 1. The results of QM2, Gs3-1 and Gs3-2 are shown in Tables 2, 3 and 4, respectively.

Upon inspection, the data (Figure 5) show that the order of ¹H and ¹³C shifts along the trimethine chain are the same as observed earlier in similar green sensitizing dyes^[4-6]. The shifts reflect differences in the electron distribution, which can be rationalized with the electron-in-a-box description^[7-9]. In the trimethine chain, the number of π -electrons equals 8, and thus in the HOMO there is a minimum in the π -density at the position of the central C atom. In accordance with this view one observes in all trimethine series significantly higher shift values (downfield shifts) in the central than in the adjoining C, H nuclei.

Finally, it was noted that the vicinal coupling constant ${}^{3}J$ [H(8), H(9)] = 13.5 Hz, which shows the *E* configuration of the -C(8)-C(9)- moiety of Gs3-2. Similar coupling constants were observed for H(8), H(9) and H(10) in Gs3-1. Figure 3. Fragmentation details of the intermediate ICI6



MOPAC Calculation

Since no experimental geometries are available for the dyes, we used the semi-empirical MOPAC 93 package in the AM1 approach to calculate the fully relaxed geometry of Gs3-1 and Gs3-2. Based on these optimized geometries, charge distributions were calculated (see Figure 6). A comparison with NMR data (Figure 5, Tables 3 and 4) shows the following. First, the charges on the central atoms C(9)of the trimethine cyanine systems (N=C-C=C-C=C-N) are positive, and compared to C(8) and C(10) indicate minimum π -density. Furthermore, in Gs3-1 the charge on C(10) is more negative than that on C(8), which indicates that the chemical shifts values of H(10), C(10) should be lower than of H(8), C(8) (upfield shifts). This result is in line with our interpretation of the NMR measurements. Second, the electron density on the N atoms follows the order: N(1), N(3)< N(1'), N(3') < Phenyl-N, a result also reflected in the NMR data. In fact, in the ¹H and ¹³C spectra of Gs3-1, the ethyl groups attached to the N positions show as expected, the chemical shift order: N(1), N(3) > N(1'), N(3') > Phenyl-N.



Figure 4. Fragmentation details of Gs3-1 (top) and Gs3-2 (bottom)

Gs3-2

Figure 5. ¹H and ¹³C-chemical shifts (ppm) in Gs-1 and Gs3-2



UV-Vis Spectra and Performance in Photographic Emulsions

It seems appropriate to comment here on the preparation of photographic emulsions. For full details, however, we refer to the technical literature^[10-14]. The process consists of three basic stages.

The first contains the precipitation and physical ripening of the silver halide crystals. In the double-jet method employed here, an aqueous solution of silver nitrate and gelatin and an aqueous solution of an alkali halide and gelatin are added to the precipitation vessel through separate feed lines at the same time, but the feed rate is not necessarily the same over the whole period. To make a monodisperse emulsion (i.e. silver halide crystallites of a narrow size distribution), the halide concentration is kept low (10^{-3} mol L^{-1}). This requires a careful balancing of the silver nitrate addition, which is achieved by on-line electronic measurement and feed-back of the silver ion concentration (controlled pAg). The process allows to a large extent the control of the number of nuclei formed in the nucleation phase, the morphology of the crystallites and even the stacking

Figure 6. Charge distributions in Gs3-1 and Gs3-2; upper, Gs3-1; lower, Gs3-2



faults. With a high pAg and a high inlet rate at the beginning of the precipitation, the grains (microcrystallites) will be almost exclusively tabular grains (T-grains). This grain shape is most desired in modern photographic emulsions because of the resulting improved sensitivity and granularity. Most important for the present purpose is that the high surface-to-volume ratio makes T-grains especially suitable for adsorption of sensitizing dyes. In the present case we used an aqueous solution of gelatin (2%) and AgNO₃ Table 2. ¹H and ¹³C-chemical shifts (in ppm relative to TMS) and coupling constants (in Hz) of QM2 in deuteriated DMSO at $30 \,^{\circ}$ C. The atomic numbering is given in Figure 1; atom H(i) is attached to C(i); d signifies doublet, dd double doublet; q quartet and t triplet

atom	chem. shift	area	coupling constant	atom	chem. shift
		het	erocyclic ring		
				C(2)	146.6
				C(3a)	132.2
H(4)	6.96	1H,d	⁴ J=1.5	C(4)	92.3
.,				C(5)	147.5
H(6)	7.00	1H,dd	³ J=9; ⁴ J=1.5	C(6)	112.1
H(7)	7.72	1H,d	³ <i>J</i> =9	C(7)	113.1
				C(7a)	121.0
CH ₃ (C2)	2.82			$CH_3(C2)$	10.1
		N	1 substituents		
CH.	4 42 ^[b]	2H a	³ I=5	CH,	44 0 ^[d]
CH ₂ CH ₃	1.35 ^[c]	3H,t	³ <i>J</i> =5	CH ₃	14.1 ^[c]
		N	3 substituents		
Сн.	4 40 ^[b]	2H a	3 /=5	CH	44 2 ^[d]
CH ₂ CH ₃	1.34 ^[c]	3H,t	³ <i>J</i> =5	CH ₃	13.8 ^[e]
		phen	yl-N substituents		
CH	3.45	2H.a	³ <i>J</i> =6.9	CH ₂	39.5 ^[a]
CH ₃	1.12	3H,t	³ <i>J</i> =6.9	CH ₃	12.0

 $^{[a]}$ The chemical shift of CH₂ group coindices with those of the solvent DMSO. - $^{[b]}$ May be interchanged. - $^{[c]}$ May be interchanged. - $^{[e]}$ May be interchanged.

Table 3. ¹H and ¹³C-chemical shifts (in ppm relative to TMS) and coupling constants (in Hz) of Gs3-1 in deuteriated DMSO at 30° C; the atomic numbering is given in Figure 1; atom H(i) is attached to C(i)

atom	chem. shift	area	coupling const	atom	chem. shift
		het	terocyclic ring		
			···	C(2)	146.2
				C(3a)	133.0
H(4)	6.79	1H,d	$^{4}J=1$	C(4)	92.0
				C(5)	147.5
H(6)	6.81	1H,dd	$^{3}J=9;^{4}J=1$	C(6)	110.2
H(7)	7.49	1H,d	$^{3}J=9$	C(7)	111.2
				C(7a)	122.3
H(8)	$6.01^{[a]}$	1H,d	$^{3}J=13.5$	C(8)	88.3 ^[a]
H(9)	7.71	1H,dd	<i>J</i> =13.5	C(9)	139.9
H(10)	5.61 ^[a]	1H,d	³ J=13.5	C(10)	80.1 ^[a]
				C(2')	146.0
				C(3a'),	132.2
				C(7a')	
H(4'),H(7')	7.78	2H,s		C(4'), C(7')	109.7
				C(5'), C(6')	124.6
	-	N(1),	N(3) substituents		
CH	4.33	4H,q	³ J=6	CH ₂	44.12
CH_{3}	1.40	6H,t	³ J=6	CH ₃	13.73
.,		<i>,</i>		.,	13.54
		N(1'),	N(3') substituents	_	
CH.	4 72	4H a	³ . <i>I</i> =7	CH	39.50 ^[b]
CH ₂	1.34	6H,t	³ <i>J</i> =7	CH ₃	12.88
,		pheny	ył-N substituents		
<u></u> СН.	3.43	2H a	³ <i>I</i> =7	CH.	39 30 ^[b]
CH.	1 1 2	211,q 3H t	${}^{3}I=7$	CH ₂	12.15
	1.12	511,1	J=/	0113	12.15

^[a] May be interchanged. - ^[b] The chemical shift of CH₂ group coincides with those of the solvent DMSO.

Table 4. ¹H chemical shifts (im ppm relative to TMS) of Gs3- $2^{[a]}$ in deuterated DMSO at 30 °C; the atomic numbering is given in Figure 1

H4, H7	7.98(2H)
H8, H10	5.96(2H)
H9	7.82(1H)
N-CH ₂	4.31(8H)
CH ₃	1.36(12H)

^[a] The solubility of Gs3-2 was too low to measure the ¹³C-NMR spectrum.

Table 5. Sensitometric properties of the green-sensitizing dyes Gs3-1 and Gs3-2; (A): number of ml added of a 0.2% solution of dye in methanol to 50 g photographic emulsion; D_0 , D_{max} : minimum and maximum optical density of exposed photographic plate; S: sensitivity of photographic plate in DIN; γ : contrast

Dye no.	A (ml)	D _o	S (DIN)	γ	D _{max}	residual color
Control	0	0.09	21	3.0	5.67	
Gs3-1	2	0.65	10	2.5	5.42	no
	3	0.65	8	3.0	5.77	
	4	0.90	5	2.4	5.38	
Control	0	0.07	21.5	2.4	5.05	
Gs3-2	0.5	0.09	20.0	1.9	4.35	no
	1	0.09	21.5	2.1	4.53	
	2	0.10	23.5	2.2	4.35	

with a ratio of gelatin-to-silver at 2.5. The other aqueous solution contained gelatine and potassium bromide with potassium iodide such that the total iodide content in the silver halide grain is 1.5 mol%. These solutions were added simultaneously under agitation over a period of 110 min. keeping the temperature of the mixture at 70 °C and the pAg at 9.0. Under these conditions, the nucleation time is 1 minute and the times needed for growth and shelling 50 and 54 minutes, respectively.

In the second phase, the soluble salts generated during precipitation are removed. To do so, the gelatin emulsion is coagulated with a 10% polystyrene sulfonate solution, washed 3 to 4 times with distilled water to the desired degree of residual salt content and then redispersed at pH > 6.

In the third stage, the photographic sensitivity of the grains is significantly enhanced by adding certain sulfur and gold containing compounds. Such compounds give rise to so-called sensitivity centers, which in turn increase the number of surface sites where latent-image specks are formed upon exposure to light. It should be noted that latent-image specks at the surface are developable, and those in the interior of the crystals are not. To increase the number of sensitivity centers at the surface of the redispersed T-grains, some sodium thiosulfate and some gold chloride is added to the redispersed emulsion at pAg = 8, pH = 7 and $50 \degree C$. We used 0.3 ml of an 0.1% sodium thiosulfate solution and 0.75 ml of an 0.167% HAuCl₄ solution per 100 g emulsion. The S + Au chemical sensitization is stopped by cooling after about 1 h, when the sensitivity is at a maximum and fog is still low. The latter parameters are monitored by sampling the emulsion at intervals, coating it on a support

and performing the photographic tests. This type of chemical sensitisation is thought to produce Ag_2S and mixed $(Ag,Au)_2S$ species, which adsorb on the grain surfaces. On exposure, latent-image specks consisting of only a few silver atoms (developable interstitial Ag_n clusters with $n \leq 4$) are formed preferentially at these Ag_2S and $(Ag,Au)_2S$ sensitivity specks. Just before the S + Au sensitization is started, the spectral sensitizing dye (here Gs3-1 or Gs3-2) is added to the emulsion. Such dye covers a part of the grain surface during the digestion and so acts as a site director for the topology of the sensitivity specks. The later resulting topology of latent-image centers may in favourable cases lead to further gain in sensitivity. However, this does not happen with all sensitizing dyes.

As stated above, the chemically and spectrally sensitized emulsion is coated on a support and the film is finally dried. Film strips were exposed using a tungsten lamp (5500 K) and exposure times stepped up with 1/20 sec. employing a Xang Fong (Shanghai, P. R. China) exposure meter. The strips were developed in D-19 b developer for 5 min. at 20 °C, followed by fixation in F-5 fixer for 40 min. Density, fog and maximum density of the dried films were measured. Transmission densities were used to construct the characteristic curve from which sensitivity (speed) and contrast followed^[14]. The average grain size of the microcrystals of the emulsion was 0.78 µm as determined by electron microscopy and an image analyser.

The results are given in Table 5. It follows that, despite their large structural similarity, Gs3-2 shows sensitizing properties in T-grain emulsions, while Gs3-1 is a strong desensitizer. Although the complexity of the sensitizing process^[15–17] precludes a full explanation, some comments may be given. The role of a sensitizing dye in a photographic emulsion is to extend the light sensitivity of silver halides beyond the blue region of the spectrum (AgCl limit 420 nm: AgBr limit 470 nm; AgI limit 520 nm). To do so, the dye is promoted from the ground state S_0 to the singlet excited state S_1 by absorption of a photon. In photographic negative materials the excited electrons are transferred from the S_1 state to the conduction band of the silver halide. These electrons are used to reduce interstitial silver ions to silver atoms, which after several subsequent absorption events aggregate until a silver cluster of sufficient size (≥4 atoms) is formed. This cluster is the latent-image speck. An efficient electron transfer requires the S₁ state to be energetically slightly above the bottom of the silver halide conduction band. Apparently this is the case for Gs3-2, not unexpected, because substitution of one N-C₂H₅ group in Gs3-2 by N(CH₂)₃SO₃, or by N(CH₂)₄SO₃ produces sensitizers employed in commercial color films. Unfotunately, Gs3-2 is too poorly soluble to be of practical value. It was hoped, and indeed observed, that Gs3-1 has a higher solubility. The difference in sensitizing properties may be understood from electrochemical principles, although other reasons may not be excluded such as the presence of impurities or the failure to form suitable aggregates. Introduction of electron acceptors raises the reduction potential, and introduction of electron donors lowers the reduction potential compared to the unsubstituted parent compound. Since reduction potentials can be expected to qualitatively follow the same order as electron affinities and energies of lowest unoccupied molecular orbitals (LUMO), the S1 state of Gs3-1 can be expected to be below the S_1 state of Gs3-2. Extrapolation of a correlation between Hammett constants and reduction potentials^[18-21] suggests a substantial decrease of the LUMO-HOMO energies of Gs3-1 compared to those of Gs3-2. The more the LUMO energy of the dye falls below the energy of the conduction band of the silver halide, the less efficient is the electron transfer from S_1 to the grain. This obviously impairs the ability of the dye to sensitize the photographic emulsion for green light. The concomitant decrease in the dye's HOMO energy rationalizes why a suitable UV absorption maximum is not a sufficient criterion for a sensitizer. In addition to the above, the dye becomes increasingly important in reoxidizing previously formed latent-image specks, as well as in accepting photoelectrons while they are generated in the grains, and even in accepting electrons from the grain's valence band. These processes turn a dye into a desensitizer and cause fogging of the film. The latter is in line with an observation that substituents lowering the basicity of the benzimidazole moiety are essential in order to control fog.

Experimental Section

Mass Spectra: FAB spectra were obtained using a Finnigan TSQ 70 mass spectrometer equipped with an ION TECH FAB gun which operated at 8 kV on Xenon. Positive ion FAB spectra were recorded under control of the Finnigan data system by repetitive scanning over the range m/z = 50 to m/z = 1000 with a scan rate of 1 sec. Prior to analysis, the products were mixed with trifluoroacetic acid/glycerol. - NMR Measurements: ¹H and ¹³C-NMR spectra of the intermediate compound QM2 and the final dyes Gs3-1, Gs3-2 were recorded in deuteriated dimethyl sulfoxide solution at 30 °C. A Varian Unity spectrometer, operating at 400 MHz for proton and at 100 MHz for carbon, respectively, was used in conjugation with a Sun Spark (Palo Alto, CA) data system. Tetramethylsilane was used as the internal standard. Chemical shift assignments are based on carbon-hydrogen 2D correlation spectra obtained during previous work on cyanine dyes^[6], combined with the known spectrum of benzimidazole and standard substituent increments^[22,23]. - UV/Vis: Spectra were recorded at room temperature on an UV-8415A spectrophotometer. The absorption spectra of the dyes were determined from methanol solutions (dye concentration about 5×10^{-6} mol/L). The absorption maxima of Gs3-1 and Gs3-2 were found at $\lambda_{max} = 514$ nm.

Synthetic Experiments

5,6-Dichloro-1-ethyl-2-methylbenzimidazole was kindly supplied by the Laboratory of Photographic Chemistry, Academia Sinica, Beijing, P. R. China. Other starting products were obtained commercially (Aldrich).

QMI: 5-Amino-2-methylbenzimidazole^[24]: 5 g Raney nickel (activated catalyst, 50% slurry in water, purchased from JANSSEN CHIMICA) was placed in a 1000 ml pressure vessel; a filtered solution of 18 g (0.1 mol) 2-methyl-5-nitrobenzimidazole was added, and the vessel was connected to a hydrogen cylinder (Series 3910 shaker type hydrogenation apparatus). The system was evacuated three times to 40-50 Torr and pressurized with hydrogen to 30-40 p.s.i. After a final evacuation, hydrogen was introduced into the

vessel until the pressure reached 40 p.s.i. (ca. 2.8 atm). The reaction was allowed to proceed for 48 hours with shaking until no further decrease of the pressure occurred. The catalyst was removed by filtration and washed with 50 ml of ethanol. The filtrates were combined, and the solvent removed by distillation under reduced pressure. After drying in vacuum, 13 g of product was obtained. Yield: 87%; m.p. 70-72 °C. – The nitro group is very easily reduced with Raney nickel catalyst and the reaction can also be executed under normal atmospheric pressure. Yield: 50%; m.p. 70°C. Liquid chromatography of the compound showed only one peak, for which by mass spectrometry a molecular ion M^+ was observed at m/z = 147.

1,3-Diethyl-5-(diethylamino)-2-methylbenzimidazolium OM2: Iodide^[25]: 5-Amino-2-methylbenzimidazole (2.5 g, 0.02 mol) and NaHCO₃ (8.4 g, 0.1 mol) were suspended in 32 ml H₂O. Next, 12 ml (0.09 mol) $(C_2H_5)_2SO_4$ was dropped into the solution under vigorous stirring. The reaction mixture was heated to 50 °C for 100 hours. After cooling to 0°C, 9 g KI was added and the stirring was continued for one hour, during which the product precipitated. It was washed with 20 ml 30% KI solution in water, and 30 ml ether, crystallized from ethanol and dried in vacuum. A brown-colored product (6 g) was obtained. Yield: 50%; m.p. 180-182°C.

QM3: 5,6-Dichloro-1,3-diethyl-2-methylbenzimidazolium p-Toluenesulfonate: A mixture of 5,6-dichloro-1-ethyl-2-methylbenzimidazole (10 g, 0.044 mol), and ethyl p-toluenesulfonate (8.6 g, 0.044 mol) was heated at 160 °C for two hours. After slight cooling, 50 ml acetone was cautiously added to prevent the formation of lumps. After further cooling a precipitate formed, which was filtered and dried in vacuum; 19 g of white product was obtained. Yield: 100%; m.p. 275-277°C.

ICI4: 2-(2'-Anilinoethenyl)-5,6-dichloro-1,3-diethylbenzimidazolium p-Toluenesulfonate^[26]: A mixture of QM3 (19 g, 0.044 mol) and diphenylformamide (12 g, 0.06 mol) was heated on a metal bath at 170°C under vacuum (0~1 Torr) for 80 minutes. The by-product, aniline, was distilled off during the reaction. The reaction product was cooled and washed with an ice-cold mixture of ether/acetone (10:1; v:v); 20 g of product was obtained. Yield: 85%; m.p. 224-226°C.

2-(2'-Anilinoethenyl)-5,6-dichloro-1,3-diethylbenzimida-ICI5: zole^[6]: ICI4 (5.6 g, 0.01 mol) was dissolved in acetone and 10 ml of a NaOH solution (0.8 g in 10 ml water) was added. The mixture of the two solutions was stirred at room temperature for two hours and then poured onto 700 g ice to precipitate the product. After filtration, the precipitate was washed with acetone and ether, and dried in vacuum; 3.1 g of light red powder was obtained. Yield: 82%; m.p. 89°C.

ICI6: 5,6-Dichloro-1,3-diethyl-2[2'-(N-p-tolylsulfphonylanilino)ethenyl]benzimidazolium Chloride^[26]: ICI5 (3 g, 0.008 mol) and (1.6 g, 0.008 mol) p-toluenesulfonyl chloride were dissolved separately in 20 ml acetone each. The solutions were mixed and the mixture was stirred for four hours at room temperature. The formed precipitate was filtered, washed with ether and acetone, and dried in vacuum. Yield: 3.3 g, 72%; m.p. 190°C.

5,6-Dichloro-2-{1-[3-(5-diethylamino-1,3-2-{1-[3-(2-Gs3-1: benzimidazolylidene)propenyl]}-3-diethylbenzimidazolium Iodide^[26]: A solution of 2.21 g (0.005 mol) ICI6, 1.56 g (0.005 mol) QM2 and

4 ml triethylamine (NEt₃) in 20 ml pyridine was refluxed under nitrogen atmosphere for 45 minutes. The solution was cooled, and 80 ml ether was added. The resulting precipitate was dissolved in 30 ml methanol. To this solution 20 ml of a 25% aqueous KI solution (preheated to 80°C) was added and the mixture refluxed for 20 minutes. After cooling, the crude precipitated dye was filtered, washed with water and acetone; 1 g (38% yield) of crude product was obtained, which was crystallized three times from ethanol; m.p. 280-282 °C. - Elemental analyses: found C 51.56%, H 5.83%, N 10.09%; calculated for C₂₉H₃₈Cl₂N₅I C 53.22%, H 6.01%, N 10.70%. - Compound Gs3-2 was synthesized similarly. Equal molar amounts of ICI6 and QM3 were reacted using the same conditions as above. Yield: 50%; m.p.: 290-292°C.

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