# Synthesis and UV/Vis Spectra of J-Aggregating 5,5′,6,6′-Tetrachlorobenzimidacarbocyanine Dyes for Artificial Light-Harvesting Systems and for Asymmetrical Generation of Supramolecular Helices

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*In commemoration of Walter König and of Günter Scheibe*[†]

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A new class of dyes, in which the self-assembling property of surfactants is combined with the capability for light energy propagation over long distances in dye J-aggregates, is described. This has been achieved by the syntheses of achiral 5,5′,6,6′-tetrachlorobenzimidacarbocyanine dyes **1**, possessing systematically varied hydrophobic and hydrophilic substituents at their nitrogen atoms. These substituents are introduced into the 5,6-dichlorobenzimidazole precursor **3** by substitution, either firstly by nucleophilic reaction with ω-bromoalkylnitriles and secondly by quaternization with alkyl bromides (route II) or firstly by nucleophilic reaction with alkyl bromides and secondly by quaternization with ω-bromoalkylnitriles or ω-bromoalkyl esters (route III) and subsequent saponification. The UV/Vis spectra of 20 differently substituted dyes containing the same chromophore **1** have been investigated. The spectra of the dye monomers in dimethyl sulfoxide are nearly identical, with no signs of optically activity, whereas in aqueous alkaline solutions quite different spectra are obtained for the dyes, indicating the formation of different aggregates depending on the nitrogen substituents. One of these types of J-aggregate is optically inactive and displays a single red-shifted (with respect to the dye monomers) absorption band, resembling the behaviour of J-aggregates of common cyanine dyes. In the cases of strongly amphiphilic 5,5′,6,6′-benzimidacarbocyanines **1** with 1,1′-dialkyl substituents longer than hexyl and 3,3′-bis(2-carboxyethyl), 3,3′-bis(3-carboxypropyl) or 3,3′-bis(3-sulfopropyl) substituents, a new type of J-aggregate is formed, and is distinguished by a doubly or even triply split J-absorption band that displays optical activity. A third type of aggregate showing different spectral behaviour occurs when the dyes contain very short 3,3′-bis(carboxymethyl) substituents or strongly hydrophobic fluorinated octyl groups, or when all four nitrogen atoms are identically substituted by hydrophilic 3-carboxypropyl groups. The various types of dye aggregates have been characterized through UV/Vis spectroscopic parameters such as the positions and widths of the absorption and fluorescence bands, the Stokes′ shifts, the coupling constants, and the strength of the J-band splitting. The results provide new prospects for the development of new artificial light-harvesting systems as well as for the understanding of the evolution of asymmetry in the biosphere.

## Introduction

Cyanines are common dyes in spectral sensitization of photoinduced electron transfer (PET) reactions, used in silver halide photography since 1873.[1] In the last three decades they have been widely applied in laser physics as active laser media and passive Q-switches,[2] as well as in nonlinear optics.[3] In a polar environment such as water, many cyanine dyes form so-called J-aggregates, which possess red-shifted and remarkably narrow J-bands of very high absorbance and fluorescence intensity relative to the absorption spectra of the corresponding monomeric molecules.[4] Such aggregates are increasingly becoming important in high technology fields such as imaging sciences, photonics, optoelectronics and nonlinear optics, because they are capable of very fast electron transfer and excitonic energy propagation processes across long distances. In this way they are able to store light energy and to release it at any time and at any spot where it is needed.[5,6] Furthermore, these properties also make them candidates for artificial light-harvesting systems in PET reactions.[7]

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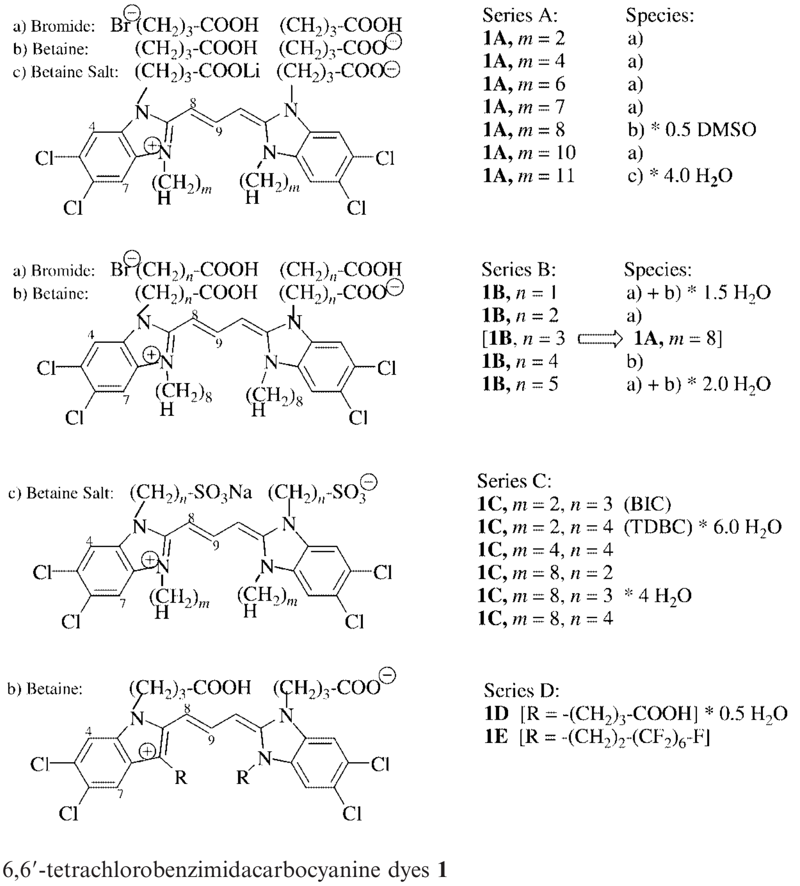
Hitherto, the main obstacle for broader applications of J-aggregates in the fields described above had been that the morphologies of the J-aggregates could not be controlled. It was only by chance that one-dimensional threads or two-dimensional layers were formed when cyanine dyes were dissolved in aqueous solutions,[4] adsorbed on silver halides,[8] or embedded in Langmuir−Blodgett layers.[7] In order to overcome this problem, the J-aggregation capability of cyanine dyes was combined by one of us[6,9] with the well explored self-organization property of amphiphilic molecules in supramolecular chemistry,[10] by making the cyanine molecules themselves strongly amphiphilic through the introduction on one hand of hydrophobic substituents such as long alkyl groups and, on the other hand, of polar, hydrophilic substituents such as acidoalkyl groups.[9,11]

The 5,5′,6,6′-tetrachloro-1,1′-dialkyl-3,3′-bis(ω-acidoalkyl)benzimidacarbocyanine chromophore **1** (c.f. Scheme 1) was used first, as a model compound. The J-aggregates of the 1,1′-diethyl-3,3′-bis(4-sulfobutyl)-substituted chromophore (dye, **1C**, *m* = 2, *n* = 4) are applied technically in spectral sensitization of photographic silver halide emulsions.[4] The free energy for aggregate formation of these compounds is much higher than any other intermolecular interaction energy in organic chemistry, amounting to 96 kJ·mol$^{-1}$ per dye dimer.[12] The exciton propagation ability of these J-aggregates has been intensely investigated by time-resolved laser spectroscopic techniques such as time-resolved fluorescence spectroscopy, ultrafast pump-probe spectroscopy and accumulated photon echo experiments.[13,14] Their exciton delocalization length spans over about 40 molecules at 1.5 K.[13] Even at room temperature it amounts to about 15 molecules.[14]

Self-organization of dye **1** derivatives in aqueous alkaline solution yields supramolecular entities with distinct spectral behaviour[11,15] and different morphologies[16] depending on the various substituents on the 1,1′,3,3′-nitrogen atoms. Even minor structural variations in the substituents may effect drastic changes in the supramolecules' architectures, apart from certain spectral modifications. For instance, dye **1C**, *m* = 2, *n* = 4, forms achiral monomolecular layers in a "brickwork" arrangement,[4,16] dye **1C**, *m* = 8, *n* = 3, generates optically active nanotubes,[17] dye **1B**, *n* = 3, with 3,3′-bis(3-carboxypropyl) substituents instead of 3,3′-bis(3-sulfopropyl) moieties, is likewise optically active[18] and gives chiral superhelices of unequal parity,[16,19] while dye **1B**, *n* = 4, with 3-carboxypropyl groups each prolonged only by one methylene group, yields stacks of achiral bilayer ribbons.[16] The spectral behaviour and morphologies of such nanoparticles are further strongly modified in the presence of surfactants[15,20,21] and of alcohols.[15,22,23] For instance, the superhelices of dye **1B**, *n* = 3, can be uncoiled to form single helices,[23] converted into nanotubes of varying diameters,[20,21] or even transformed into single- and double-walled vesicles.[20]

The excitonic energy propagation abilities indicated by the spectral behaviour in the visible region are maintained in most of the self-organized supramolecular particles of dyes **1**. Owing to the spectral behaviour in the visible region, the



Scheme 1. Investigated 5,5′6,6′-tetrachlorobenzimidacarbocyanine dyes **1**

excitonic energy propagation ability is maintained in most of the self-organized supramolecular particles of dyes **1**. This has been definitely verified in the case of the cylindrical helices of dye **1A**, $m = 8$, by use of time-resolved fluorescence spectroscopy, ultrafast pump-probe spectroscopy and accumulated photon echo experiments.[24,25] It turned out[25] that the excitons are not only cyclically delocalized through the ring planes of the cylinders but also along certain segments of them. The delocalization lengths of the excitons in cylindrical helices amount to about 95 molecules at 1.5 K and are reduced to about 70 molecules at 80 K.

Previously in supramolecular chemistry it has been assumed that the driving forces of self-organization are usually hydrogen bonding, hydrophobicity, van der Waals, Coulomb and charge transfer interactions and, occasionally, weak π-π interactions of aromatic building units.[10,26] Such forces have free energies of association approaching 60 kJ·mol$^{-1}$ at maximum.[10,15] By way of contrast, the prevailing driving force of self-organization of J-aggregates is the already mentioned, much stronger π-π coupling between the chromophores, reaching values of 100 kJ·mol$^{-1}$ and more.[12,15] The strong coupling is obviously caused by the extremely high π-electronic polarizabilities of polymethine dyes,[27] which closely approach the ideal polymethine state.[5]

This new class of supramolecular ***amphi***philes with ***p***igment ***i***nteraction ***p***erforming ***e***xciton migration has been designated **amphipipes**.[22] The new linear and nonlinear spectral features of cylindrically shaped amphipipes prompted Knoester et al. to extend the molecular exciton model developed by McRae and Kasha for one- and two-dimensional J-aggregates[28] to three-dimensional molecular cylinders.[22,29,30]

An especially interesting topic in this new field of research is the spontaneous generation of optically active J-aggregates from the achiral dye monomers, first discovered by De Rossi et al.,[18] using dye **1A**, $m = 8$, with 1,1′-dioctyl and 3,3′-carboxypropyl substituents. The J-absorption band is split into two or even three peaks, depending on the preparation conditions.[15,22] These peaks exhibit strong circular dichroism in the form of couplets, which had first been interpreted in terms of Davydov splitting caused by the presence of translationally nonequivalent molecules in the unit cell.[18] Later, H. Kuhn et al.[31] and Kirstein et al.[11] suggested helical models to explain the J-aggregates' optical activity. This was indeed confirmed by von Berlepsch et al.,[16] by cryotransmission electron microscopy (cryo-TEM). The J-aggregates of dye **1A**, $m = 8$ (identical with **1B**, $n = 3$, cf. Table 1) spontaneously and enantioselectively generate the previously mentioned superhelices consisting of three to ten rope-like twisted single strands, the spectral behaviour of which correlates well with Knoester's new exciton model for three-dimensional molecular cylinders, as described above.

Table 1. UV/Vis absorption and fluorescence data of monomeric dyes **1** in dimethyl sulfoxide solution: Maximum molar extinction coefficient: $\varepsilon_{max}$; wavelength of the absorption (abs) and fluorescence (em) maximum: $\lambda_{max}$; halfwidth (FWHM) of the absorption (abs) and fluorescence (em) band: $\Delta\tilde{\nu}_{1/2}$; Stokes′ shift: $\Delta_{Stokes}$

| Dye | $\varepsilon_{max}$[a] [10$^3$ cm$^2$ mmol$^{-1}$] | $\lambda_{max}^{abs}$ [nm] | $\Delta\tilde{\nu}_{1/2}^{abs}$ [cm$^{-1}$] | $\lambda_{max}^{em}$ [nm] | $\Delta\tilde{\nu}_{1/2}^{em}$ [cm$^{-1}$] | $\Delta_{Stokes}$ [cm$^{-1}$] | Aggregate Type |
|---|---|---|---|---|---|---|---|
| | | | **Series A** | | | | |
| **1A**, $m = 2$ | 71% | 524.5 | 1142 | 540 | 1052 | 547 | I |
| **1A**, $m = 4$ | 51% | 528.5 | 1215 | 547 | 1072 | 640 | I |
| **1A,** $m = 6$ | 184.0 | 528 | 1114 | 545 | 1051 | 591 | I |
| **1A,** $m = 7$ | 89% | 528 | 1357 | 546 | 1044 | 624 | II |
| **1A,** $m = 8$ | 185.5 ±2.4 | 528 | 1436 | 547 | 1038 | 693 | II |
| **1A**, $m = 10$ | 56% | 527 | 1421 | 546 | 1045 | 660 | II |
| **1A**, $m = 11$ | 51% | 527 | 1395 | 546 | 1050 | 660 | II, I |
| **1A**, $m = 12$ | 22% | 529 | 1249 | 546 | 1099 | 589 | II |
| | | | **Series B** | | | | |
| **1B**, $n = 1$ | 85% | 526 | 1068 | 540 | 912 | 493 | III |
| **1B**, $n = 2$ | 65% | 527 | 1208 | 545 | 980 | 627 | III |
| **1B**, $n = 3$[b] | 185.5 ±2.4 | 528 | 1436 | 547 | 1038 | 693 | II |
| **1B**, $n = 4$ | 183.1 ±2.7 | 529 | 1262 | 544 | 1052 | 521 | I |
| **1B**, $n = 5$ | 81% | 528 | 1345 | 546 | 1037 | 624 | I |
| | | | **Series C** | | | | |
| **1C,** (BIC) $m = 2$, $n = 3$ | 77% | 525.7 | 1195 | 542 | 1004 | 572 | I |
| **1C,** (TDBC) $m = 2$, $n = 4$ | 185.6 ±1.1 | 525 | 1157 | 543 | 1024 | 631 | I |
| **1C**, $m = 4$, $n = 4$ | 21% | 528 | 1297 | 546 | 1036 | 624 | I |
| **1C**, $m = 8$, $n = 2$[c] | 182.1 ±2.2 | 529 | 1922 | 549 | 1058 | 689 | III |
| **1C**, $m = 8$, $n = 3$ | 183.3 ±3.1 | 528.5 | 1373 | 547 | 1015 | 658 | I + II |
| **1C**, $m = 8$, $n = 4$ | 27% | 528 | 1326 | 546 | 983 | 624 | I |
| | | | **Series D/E** | | | | |
| **1D** | 83% | 527 | 1357 | 545.5 | 1091 | 644 | III |
| **1E** | 56% | 525.1 | 1755 | 548 | 1074 | 796 | III |

[a] Percentage of $\varepsilon_{max}$ calculated on the assumption that the average molar extinction coefficient $\varepsilon_{max}$ of dyes **1** amounts to 185.0 [10$^3$ cm$^2$ mmol$^{-1}$]. [b] Identical with **1A**, $m = 8$. [c] In methanol.

In order to obtain deeper insight into the relationships between the structures of the dye monomers and the morphologies of their supramolecular aggregates, the substituents on the 1,1′- and 3,3′-nitrogen atoms of the 5,5′,6,6′-tetrachlorobenzimidacarbocyanine chromophore **1** were systematically varied, and the spectral behaviour in the visible region both of the monomers and of the aggregates of these new dyes in solution is described.

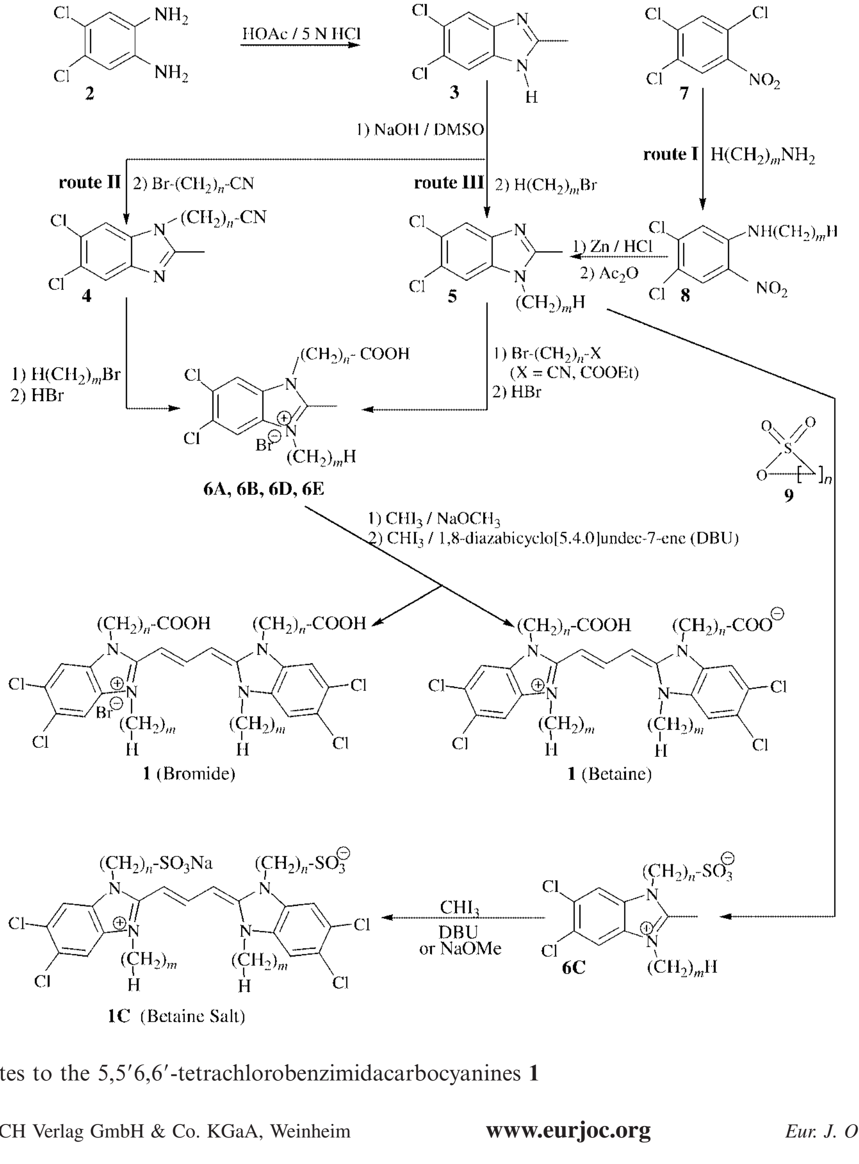
## Results and Discussion

### Synthetic Routes

According to the literature, 5,5′,6,6′-tetrachloro-1,1′-di-*n*-alkyl-3,3′-bis(ω-carboxyalkyl)benzimidacarbocyanine dyes **1** are synthesized in a four-step procedure (c.f. Scheme 2, route I) starting from 2,4,5-trichloronitrobenzene **7**, which is converted by treatment with *n*-alkylamines into 4,5-dichloro-*ortho*-nitroanilines **8**. Reduction and simultaneous cyclization with acetic acid then gives 4,5-dichloro-2-methylbenzimidazoles **5**. These are quaternized, either with the respective sultones in the case of the 3,3′-di-(ω-sulfoalkyl) substituted dyes, or with ω-bromoalkylnitriles or alkanoic acid ethyl esters in the case of the 3,3′-bis(ω-carboxyalkyl) substituted dyes, and subsequently saponified. Two equivalents of the 1-alkyl-3-(ω-carboxyalkyl)-5,6-dichloro-2-methylbenzimidazolium bromides **6** thus obtained are transformed into the respective benzimidacarbocyanine dyes **1** by treatment with iodoform in the presence of sodium methoxide.[9]

For economic reasons we developed new synthetic routes, also shown in Scheme 2. 4,5-Dichloro-*ortho*-phenylenediamine (**2**) was condensed with acetic acid according to Dandegaonker and Kanabur,[32] yielding the 5,6-dichlorobenzimidazole **3**, which serves as the starting compound for variation both of the substituents on the 1,1′- and the 3,3′-nitrogen atoms.

In reaction route II, the 3-(3-cyanopropyl) group is first introduced through nucleophilic reaction between **3** and ω-bromoalkylnitriles to give compounds **4**, which are concomitantly quaternized with *n*-alkyl bromides and hydrolysed to give 1-alkyl-3-(3-carboxypropyl)-5,6-dichlorobenzimidazoles **6**. Finally, as in ref.[9] condensation of two equivalents of **6** with iodoform in alkaline medium gives dyes **1**.



Scheme 2. Synthetic routes to the 5,5′6,6′-tetrachlorobenzimidacarbocyanines **1**

If 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is used instead of the common sodium methoxide, the reaction can be performed at room temperature.

In reaction route III, the 1-alkyl substituents are first introduced in **3** by nucleophilic reaction with the corresponding alkyl bromides, giving compounds **5**. These are transformed into precursors **6** through quaternization either with ω-bromoalkanoic acid ethyl esters or with ω-bromoalkylnitriles, with subsequent hydrolysis. In the case of the 3,3′-bis(ω-sulfoalkyl)-substituted dyes, quaternization is achieved through the usual reaction with the corresponding sultones.[33] Dyes **1** were purified in the usual way[9] by precipitation from methanol or dimethyl sulfoxide solutions by addition of small amounts of water.

The dyes **1** thus synthesized are compiled in Scheme 1 and are classified into Series **1A**, which possess constant 3,3′-bis(3-carboxypropyl) groups and varied 1,1′-dialkyl groups of different chain length, Series **1B**, with constant 1,1′-dioctyl substituents and varied 3,3′-bis(ω-carboxyalkyl) groups of different lengths, and Series **1C**, containing 1,1′-dialkyl and 3,3′-bis(ω-sulfoalkyl) substituents with diverse variation in their lengths. Finally, dyes **1D** and **1E** possess 1,1′- and 3,3′-substituents of different kinds.

Dyes **1** exist as three differently ionized species (c.f. Schemes 1 and 2). When two protonated carboxylic groups are present the positive charge of the chromophore is compensated by a bromide counter-ion, as in **1A**, *m* = 8 [species a) in Scheme 1]. Such species are designated ”bromides”. In the case of the ”betaines”, one carboxylate anion compensates for the positively charged chromophore [species b) in Scheme 1]. Some dyes, such as **1B**, *n* = 1 and **1B**, *n* = 5, were obtained as mixtures of the bromide and betaine moieties. Exchange of the remaining carboxylic proton for a metal ion yields ”betaine salts” such as **1A**, *m* = 11, and the dyes of Series **1C**, which usually form hydrates [species c) in Scheme 1].

The varying compositions of some dyes, containing different portions of bromide, betaine, betaine salt, and crystal water or other solvent molecules, which may even change from sample to sample, hampers the definite analytical characterization of the synthesized dyes. Furthermore, elemental analysis is highly inaccurate because the molecular formulas, and thus the elemental compositions, of the dye betaines **1** are very similar to those of two betainic precursor molecules **6** [e.g. **1A**, *m* = 8: $C_{41}H_{54}Cl_4N_4O_4$, 808.70; 2 × (**6**, *m* = 8): $C_{40}H_{56}Cl_4N_4O_4$, 798.71]. Only combined HPLC and MS measurements were able to show that dyes **1** would often contain some greater or lesser portion of the corresponding precursor **6**, indicating an incomplete reaction between **6** and iodoform to give dyes **1**. This is the reason why we had originally reported about variable molar extinction coefficients ($\varepsilon_{max}$) of dyes **1** between 20.0 and 180.0 $10^3$ $cm^2$/mmol.[9] Although quantitative separation of the amphiphilic dyes **1** from their amphiphilic precursors **6** can be achieved by recrystallization from dimethyl sulfoxide with a temperature gradient between 5 and 100 °C,[15] this was carried out only with dyes **1A**, *m* = 6; **1A**, *m* = 8 (equal to **1B**, *n* = 3); **1B**, *n* = 4; **1C**, *m* = 2, *n* = 4; **1C**, *m* = 8, *n* = 2; and **1C**, *m* = 8, *n* = 3, because of the very poor yields of this procedure. This limitation was considered justifiable since the main objective of the syntheses was to investigate relationships between the structures of monomeric chromophores and their ability to generate supramolecular aggregates in solution. Since the precursors **6** do not absorb in the visible region and as all dyes give the same anion of the ”betaine salt” in aqueous sodium hydroxide solution independently of the composition of the solid dye samples, it is assumed that the molar extinction coefficients of all dyes **1** should be about $185.0{\cdot}10^3$ $cm^2$/mmol.

## UV/Vis-Spectra

### Monomeric Dyes

The positions and widths (FWHM) of the visible region absorption and fluorescence bands of the monomeric dyes **1** in dimethyl sulfoxide solution at room temperature are independent of concentration and are nearly identical, as shown in Table 1. As mentioned above, their maximum molar extinction coefficient ($\varepsilon_{max}$) was assumed to be $185.0{\cdot}10^3$ $cm^2$/mmol. The purities of the dyes indicated in Table 1 were calculated from this value, and the measured $\varepsilon_{max}$ values of the dyes' aggregates used in Figure 1−5 were corrected accordingly.

In Series A, with constant 3,3′-bis(3-carboxypropyl) substituents and 1,1′-dialkyl groups of varied lengths, the positions of the absorption wavelengths are slightly red-shifted from 524.5 nm to 529.0 nm with lengthening of the alkyl chains. Broadening of the bandwidth from about 1140 $cm^{-1}$ to 1400 $cm^{-1}$ takes place concomitantly. The same effect happens with the fluorescence maxima, which are shifted from about 540 nm to 547 nm, causing increase in the Stokes' shifts from about 550 $cm^{-1}$ to 650 $cm^{-1}$. Unlike those of the absorption bands, the widths of the fluorescence bands remain nearly constant, being narrower than the absorption bands at about (900 ± 150) $cm^{-1}$ .

Similar behaviour can be observed in Series B, with constant 1,1′-dioctyl groups and varying 3,3′-bis(ω-carboxyalkyl) substituents. The positions of the absorption and fluorescence maxima are the more red-shifted the greater the ω-carboxyalkyl chain length, again causing increases in the Stokes' shifts. In this case the widths of the absorption and fluorescence bands increase with growing chain length in the 3,3′- substituents. This may presumably indicate stronger steric impact.

The spectroscopic data for dye **D**, with four equal *N*-carboxypropyl substituents, are similar to those of dyes **1A** with alkyl groups of medium length, such as **1A**, *m* = 7. The same is true for the absorption maximum of dye **E**, the structure of which is nearly identical to that of dye **1A**, *m* = 8, except for the substitution of the 1,1′-dioctyl groups by fluorinated ones, possessing much higher hydrophobicity. The half-width of this dye, at 1755 $cm^{-1}$, is the broadest of all the dyes investigated.

### Aggregated Dyes

Much more interesting is the spectral behaviour of dyes **1** in $10^{-2}$ M aqueous sodium hydroxide solution. Alkaline conditions are necessary in order to ensure that the second carboxy groups of the dyes' bromide and betaine species are ionized to form the betaine salt anions (Schemes 1−2). Furthermore, because of the poor solubilities of most of the dyes in sodium hydroxide solution, methanolic stock solutions were prepared in some instances and diluted with $10^{-2}$ M sodium hydroxide solution by at least 1:10 or more, to produce methanol contents of less than 10% (v/v) in the final samples. The absorption bands of the aggregated dyes are usually strongly red-shifted with respect to their monomers, indicating the existence of J-aggregates. Their spectroscopic data in the visible region are listed in Table 2. Only a few examples also show hypsochromically shifted H-bands. Because of the typical exchange-narrowing of the J-absorp-

Table 2. UV/Vis absorption and fluorescence data of J-aggregates in aqueous solution: wavelength of the absorption (abs) and fluorescence (em) maximum: $\lambda_{max}$; halfwidth (FWHM) of the long-wave absorption (abs) and fluorescence (em) band: $\Delta\tilde{\nu}_{1/2}$; coupling strength: $\Delta\tilde{\nu}$; exciton splitting: Δ. (* : Using the long wavelength absorption band)

| Dye | Aggregate Type | $\lambda_{max}^{abs}$ [nm] | $\Delta\tilde{\nu}_{1/2}^{abs}$ [cm$^{-1}$] | $\Delta\tilde{\nu}_{1/2}^{abs}$ [nm] | $\Delta\tilde{\nu}_{1/2}^{em}$ [cm$^{-1}$] | $\Delta\tilde{\nu}$ [cm$^{-1}$] | Δ | Remarks | Circular Dichroism |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **Series A** | | | | | |
| **1A**, $m = 2$[a] | I | 595 | 340 | 595 | 304 | 2259 | – | monomer-aggregate equilibrium | none |
| **1A**, $m = 4$[a] | I | 587 | 350 | 588 | 280 | 1886 | – | monomer-aggregate equilibrium | none |
| **1A**, $m = 6$[b] | I | 578 | 291 | 580 | 339 | 1638 | – | monomer-aggregate equilibrium | none |
| **1A**, $m = 7$[b] | II | 578/602 | 312* | 601 | 199 | 2314* | 691 | no monomer detectable | yes |
| **1A**, $m = 8$[a] | II | 562/583, 600 | 120* | 602 | 216 | 2273* | 486 | | yes |
| **1A**, $m = 10$[a] | II | 575/606 | 153* | 606 | 210 | 2460* | 876 | no monomer detectable | yes |
| **1A**, $m = 11$[a] | II | 578/605 | 219* | 605 | 175 | 2446* | 772 | no monomer detectable | yes |
| **1A**, $m = 12$[a] | II | 573/604 | 130* | 604.5 | 232 | 2347* | 896 | temperature-dependent changes of the spectrum | yes |
| | | | | **Series B** | | | | | |
| **1B**, $n = 1$[b] | III | 483/574 | 405* | fluorescence not detectable | | 1589* | – | H-aggregates | none |
| **1B**, $n = 2$[a] | III | 590/601 | 244* | fluorescence not detectable | | 2336* | 813 | time dependent equilibrium | yes |
| **1B**, $n = 2$[a] | I | 593 | 633 | fluorescence not detectable | | 2112 | – | time dependent equilibrium after 6 days | none |
| **1B**, $n = 3$[a] | II | 562/583, 600 | 120* | 602 | 216 | 2273* | 486 | | yes |
| **1B**, $n = 4$[c] | I | 586 | 307 | 585 | 333 | 1875 | – | no monomer detectable | none |
| **1B**, $n = 5$[a] | I | 582 | 365 | 582 | 315 | 1757 | – | monomer aggregate equilibrium | none |
| | | | | **Series C** | | | | | |
| **1C,** (BIC), $m = 2$, $n = 3$[a] | I | 588.5 | 331 | 588.5 | 292 | 2030 | – | monomer detectable | none |
| **1C,** (TDBC), $\boldsymbol{m = 2}$, $\boldsymbol{n = 4}$[c] | I | 587 | 212 | 588 | 260 | 2011 | – | monomer detectable | none |
| **1C**, $m = 4$, $n = 4$[a] | I | 585.5 | 237 | 585.5 | 282 | 1860 | – | monomer aggregate equilibrium | none |
| **1C**, $m = 8$, $n = 2$[b] | III | 502/585 | 184* | 586 | 358 | 1809* | – | H-aggregates | [d] |
| **1C**, $m = 8$, $n = 3$[a] | II | 584/601 | 234* | 601 | 397 | 2283 | 484 | time dependent equilibrium | yes |
| **1C**, $m = 8$, $n = 3$[a] | I | 591.5 | 410 | fluorescence not detectable | | 2015 | – | time dependent equilibrium | none |
| **1C**, $m = 8$, $n = 4$[b] | I | 595 | 322 | 599 | 296 | 2132 | – | no monomer detectable | none |
| | | | | **Series D/E** | | | | | |
| **1D**[b] | III | 519 | 1134 | 538 | 1428 | | – | only monomer detectable | none |
| **1E**[b] | III | 546 | 1298 | fluorescence not detectable | | 829 | – | J-aggregates | none |

[a] $10^{-2}$ M aqueous sodium hydroxide solution. [b] $10^{-2}$ M aqueous sodium hydroxide solution containing up to 10% (v/v) methanol. [c] $10^{-3}$ M aqueous sodium hydroxide solution.

tion bands,[30,34] their half-widths (FWHM) are smaller than those of the longest-wavelength absorption bands of their monomers by factors of 2 to 9 (Table 1).

### Type I J-Aggregates

The observed spectra in the visible region can be grouped into three characteristic types (Table 2). In principle, J-aggregates of type I show the same behaviour as the well-known TDBC (**1C**, $m = 2$, $n = 4$) J-aggregates. Only one J-absorption band is formed, displaying strong resonance fluorescence in the immediate neighbourhood of the absorption band. All J-aggregates are optically inactive, and the maximum molar extinction coefficient (ε) strongly increases with increasing concentration. The aggregates exist in equilibria with monomer molecules, as shown by the existence of isosbestic points. Figure 1 shows the absorption spectrum of dye **1A**, $m = 6$ at different concentrations as an example, while two further examples of the ε concentration dependence of type I J-aggregates are shown in Figure 2. No monomer absorption could be detected with dyes **1B**, $n = 4$ and **1C**, $m = 8$, $n = 4$, due to their very strong aggregation tendency.

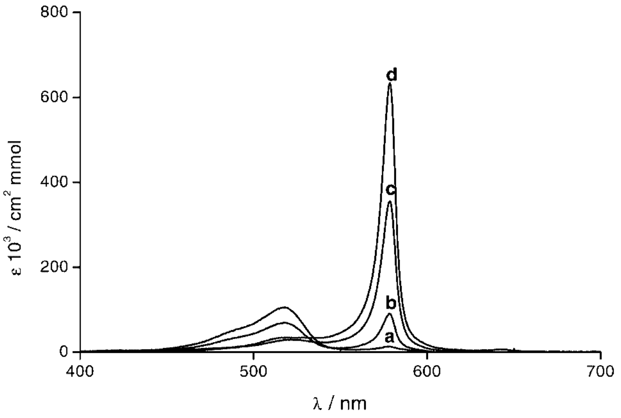


Figure 1. Absorption spectra of dye **1A**, $m = 6$ in $10^{-2}$ M aqueous sodium hydroxide solution at different concentrations and room temperature, representing type I J-aggregates a: $6.7 \times 10^{-7}$ M; b: $2.0 \times 10^{-6}$ M; c: $1.9 \times 10^{-5}$ M; d: $4.0 \times 10^{-4}$ M

Unlike those in the spectra of the monomer dyes, the positions, and halfwidths, of the type I J-aggregate bands vary with the length of the 1,1′-alkyl substituents. In series A, dyes **1A,** $m = 2$; **1A**, $m = 4$ and **1A**, $m = 6$, the absorption maxima are the more blue-shifted the longer the chain lengths of the 1,1′-dialkyl groups. On the other hand, FWHM of the absorption and fluorescence band vary arbitrarily. The half-width of the absorption band of the dye J-aggregate **1A**, $m = 6$, at 291 $\text{cm}^{-1}$, is clearly smaller than those of others, whereas it is dye **1A**, $m = 4$, that has the smallest fluorescence band, with FWHM equal to 280 $\text{cm}^{-1}$.

In series B, only the J-aggregates of dyes **1B**, $n = 4$, and **1B**, $n = 5$, belong to type I, showing features nearly the same as in dye **1A**, $m = 6$.

In series C, all dye J-aggregates belong to type I, with the exception of dye **1C**, $m = 8$, $n = 3$. Astonishingly, in the dye series **1C**, $m = 2$, $n = 4$; **1C**, $m = 4$, $n = 4$; and **1C**, $m = 8$, $n = 4$, with elongated 1,1′-alkyl substituents, the J-aggregates of the 1,1′-dibutyl derivative **1C**, $m = 4$, $n = 4$, have the shortest absorption and fluorescence band wavelengths, whereas the widths of both bands increase continuously with elongation of the alkyl groups. On the other hand, the widths of both bands are less in the J-aggregates of dye **1C**, $m = 2$, $n = 4$, containing longer 3,3′-sulfoalkyl chains than the related dye **1C**, $m = 2$, $n = 3$.

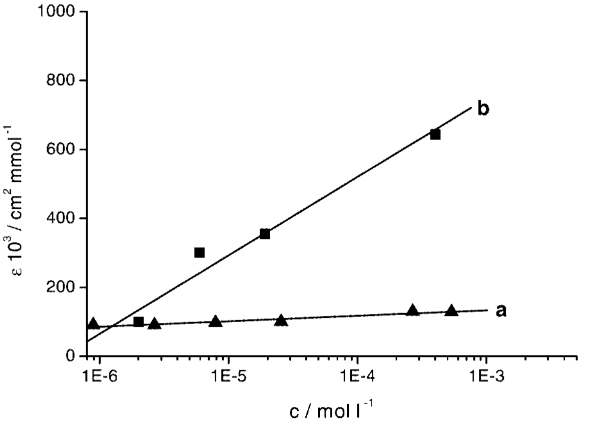


Figure 2. Maximum molar extinction coefficients (ε) of type I J-aggregates in $10^{-2}$ M aqueous sodium hydroxide solution containing up to 10% (v/v) methanol at room temperature and dependence on concentration $c$ ($r$ = correlation coefficient); a: **1C**, $m = 8$, $n = 2$; $r = 0.96$ b: **1A**, $m = 6$; $r = 0.99$

The coupling strength $\Delta\tilde{\nu}$ between the molecules within the J-aggregates can be estimated from the red shifts between the positions of the absorption maxima of the monomers and those of the J-aggregates.[35] In series A these decrease with increasing 1,1′-alkyl chain length, probably due to enhanced steric hindrance. The same is true with series B when the 3,3′-bis(ω-carboxyalkyl) chains are lengthened.

In series C, the J-aggregates of the two dyes with the 3,3′-bis(3-sulfopropyl) substituents − **1C**, $m = 2$, $n = 3$ and **1C**, $m = 8$, $n = 3$ − have nearly the same coupling strength. In J-aggregates of dyes with 3,3′-bis(4-sulfobutyl) substituents the coupling strength of the 1,1′-dibutyl-substituted J-aggregates **1C**, $m = 4$, $n = 4$ is the smallest, in relation to those of the related dyes **1C**, $m = 2$, $n = 4$ (TDBC) and **1C**, $m = 8$, $n = 4$, having shorter or longer 1,1′-dialkyl substituents, respectively, the same as with series A.

### Type II J-Aggregates

Type II J-aggregates are characterized by an exciton-split J-band, the components of which display optical activity.[11,18] It turns out that the basic precondition for the formation of this type is the amphiphilic nature of the dye monomers, with 1,1′-dialkyl substituents longer than hexyl and 3,3′-bis(ω-carboxyalkyl) substituents with ethyl or propyl chains. As can be seen in Table 2, the dyes **1A**, $m = 7$; **1A**, $m = 8$; **1A**, $m = 10$; **1A**, $m = 11$; **1A**, $m = 12$; **1B**, $n = 2$; **1B**, $n = 3$; and **1C**, $m = 8$, $n = 3$ belong to this type. As

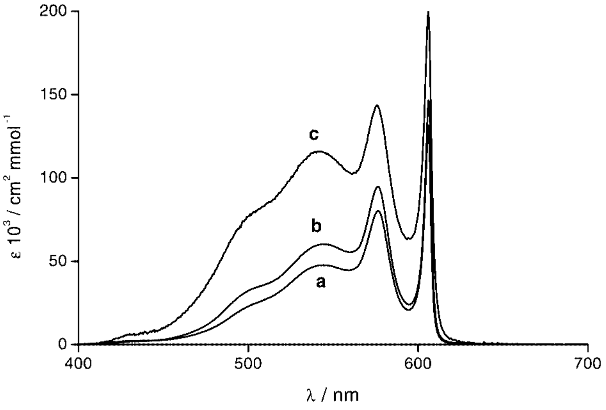


Figure 3. Absorption spectra of dye **1A**, $m = 10$ in $10^{-2}$ M aqueous sodium hydroxide solution at different concentrations and room temperature, representing type II J-aggregates; a: $1.7 \times 10^{-5}$ M; b: $2.2 \times 10^{-5}$ M; c: $4.4 \times 10^{-4}$ M

an example, Figure 3 shows the concentration-dependent spectra of the J-aggregates of dye **1A**, $m = 10$. Unlike the case of type I J-aggregates, there is no equilibrium between dye monomers and J-aggregates, although the shoulder near to 510 nm seems to indicate the presence of a certain amount of monomers absorbing at 527 nm. Figure 4 gives the concentration dependence of the molar extinction coefficients (ε) of the J-aggregates of dyes **1A**, $m = 7$ and **1A**, $m = 8$. The slope of this dependence is evidently lower than that of type I J-aggregates. Depending on concentration, temperature and alcohol content, the J-aggregates of dyes **1A**, $m = 11$; **1B**, $n = 2$; and **1C**, $m = 8$, $n = 3$, are in equilibrium with type I J-aggregates.

Usually, the ratio between the maximum intensities of the two exciton split components of the J-absorption band indicated in Table 2 remains constant at different concentrations. It may change in some instances, however, due to overlap with a third absorption band at higher energies, which appears in Figure 3 at around 540 nm. The origin of this band is disputed. Its appearance strongly depends on the preparation conditions of the J-aggregates and on the alcohol content of the alkaline aqueous solution.[15,22,23]

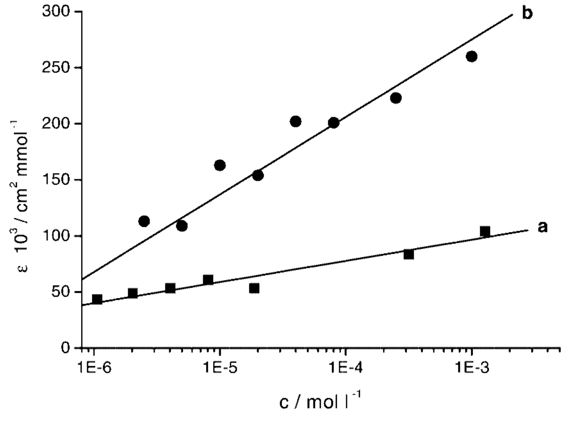


Figure 4. Maximum molar extinction coefficients (ε) of the long-wave exciton split J-absorption band of type II J-aggregates in $10^{-2}$ M aqueous sodium hydroxide solution containing up to 10% (v/v) methanol at room temperature and dependence on concentration $c$ ($r$ = correlation coefficient); a: **1A**, $m = 7$; $r = 0.97$ b: **1A**, $m = 8$; $r = 0.98$

As with type I J-aggregates, the positions and the half-widths of the components of the exciton-split J-bands vary with the nitrogen substituents. The most impressive results are the very small bandwidths of the longest-wavelength components of dyes **1A**, $m = 8$, and **1A**, $m = 12$, which amount to 120 to 130 $cm^{-1}$, respectively. These are the smallest values ever observed in conjugated organic compounds at room temperature. Furthermore, the degree of exciton splitting (Δ) varies from dye to dye. As it depends on the intermolecular arrangement of the molecules in the crystal lattice it is understandable that it may depend on the substitution pattern of dyes **1**.

It must be emphasized that no exciton splitting takes place in the fluorescence spectra. The emission is nearly in resonance with the longest-wavelength component of the J-absorption band, the same as with the J-aggregates of type I. However, as discussed elsewhere,[24] the fluorescence kinetics of type I and type II J-aggregates are quite different. Type I J-aggregates exhibit single-exponential fluorescence decay at low temperature,[13] whereas the fluorescence decay of type II J-aggregates is multi-exponential.[36] The pressure dependence of the absorption and fluorescence spectra, measured up to 50 kbar, is also completely different in the two aggregate types, intimating for the first time that type II J-aggregates might be hollow cylinders.[37]

For estimation of the coupling strengths $\Delta\tilde{\nu}$ between the dye molecules in type II J-aggregates, the differences between the maximum absorption wavelengths of the dye monomers and the positions of the longest-wavelength components of the exciton-split J-bands are given in Table 2. As with type I J-aggregates, the coupling strongly depends on the nitrogen substituents. In all instances it is greater than 2000 $cm^{-1}$ meaning that on average the coupling is stronger than in type I J-aggregates.

## Type III Dye Aggregates

The type III aggregates in Table 2 include some exceptional cases. Aqueous sodium hydroxide solutions of dye **1D**, with four 1,1′,3,3′-(3-carboxypropyl) substituents, consist only of monomers, with an absorption maximum at 519 nm and a fluorescence maximum at 538 nm. Its absorption spectrum in $10^{-2}$ M aqueous sodium hydroxide solution is concentration-independent between $10^{-6}$ and $10^{-3}$ mol/L.

The absorption spectrum of dye **1E**, which contains two fluorinated 1,1′-dioctyl groups of very high hydrophobicity, in aqueous sodium hydroxide solution is shown in the upper part of Figure 5. The compound has a very broad spectrum that, apart from the monomer absorption at 528 nm, seems to consist of a blue-shifted H-band indicated as a shoulder at 480 nm and a red-shifted broad J-band close to 560 nm, which does not fluoresce. Its absorption spectrum is like-

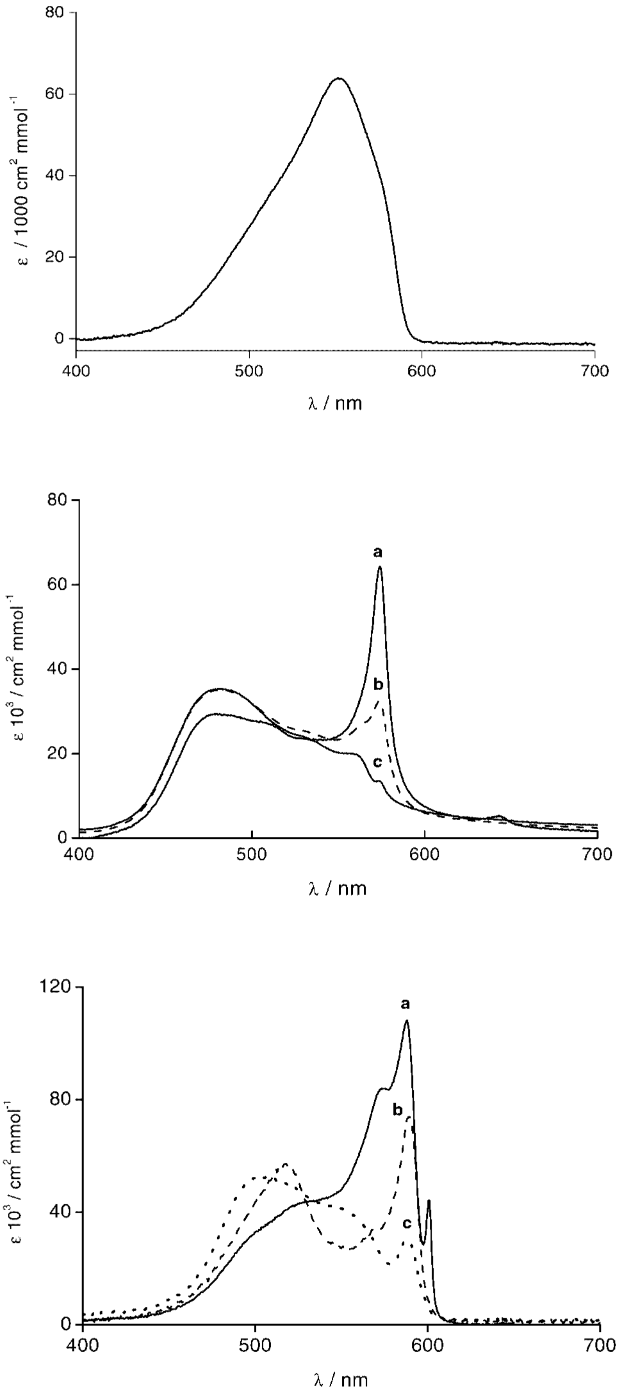


Figure 5. Absorption spectra of dyes belonging to the type III J-aggregates in $10^{-2}$ M aqueous sodium hydroxide solution (**1 B**, *n* = 2) or in aqueous sodium hydroxide solution containing up to 10% (v/v) methanol (**1E**, **1 B**, *n* = 1) at room temperature above: dye **1E;** middle: dye **1B**, *n* = 1; a: $1.0 \times 10^{-5}$ M ;b: $2.8 \times 10^{-5}$ M, *c*: $4.5 \times 10^{-5}$ M below: dye **1B**, *n* = 2; a: $2.3 \times 10^{-7}$ M ; b: $9.5 \times 10^{-7}$ M; c: $2.8 \times 10^{-6}$ M

wise concentration-independent between $10^{-6}$ and $10^{-3}$ mol/L.

The J-aggregates of dyes **1B**, *n* = 1; **1B**, *n* = 2 and **1C**, *m* = 8, *n* = 2, may be added to type III because their concentration- and time-dependent spectra in aqueous sodium hydroxide solution are rather complicated. The absorption spectrum of dye **1B**, *n* = 1, is shown in the middle part of Figure 5. Besides the J-band at 574 nm, it also shows a pronounced H-band at 483 nm. The absorption spectrum of dye **1B**, *n* = 2, shown in the lower part of Figure 5, displays several absorption bands at longer and shorter wavelengths than the monomers, varying strongly with concentration and preparation conditions. The absorption spectrum of dye **1C**, *m* = 8, *n* = 2, with a J-band at 585 nm, a shoulder at 541 nm and an H-band at 502 nm, is similar to that of dye **1B**, *n* = 1.

## Conclusions

The synthesis of 5,5′,6,6′-tetrachlorobenzimidacarbocyanine dyes **1** via the benzimidazoles **3** opens alternative routes for the introduction of different substituents at the 1,1′- or 3,3′-positions of the dyes through the use of the common precursor **3**. This offers new potential for wide variation of the substitution patterns of dyes **1** at their nitrogen atoms.

Whereas the UV/Vis spectra of the monomeric dyes **1** with their different substituents at the nitrogen atoms are nearly identical, the spectra of their aggregates in alkaline aqueous solution can be controlled by the nature of their 1,1′- and 3,3′-substituents. Three different types of aggregates can be distinguished. The first type are dyes with *n*-alkyl substituents shorter than heptyl, which usually exhibit only one red-shifted J-aggregate absorption band, as is also well-known with many other cyanine dyes. Such dyes either form monomolecular layers or bilayer ribbons, as has been demonstrated by cryo-TEM investigations.[16] The second type are dyes containing 1,1′-diheptyl and longer alkyl groups in combination with 3,3′-bis(2-acidoethyl) or 3,3′-bis(3-acidopropyl) substituents. These dyes possess exciton split J-bands, which exhibit circular dichroism in the form of couplets. It is feasible to assume that the common cause of this behaviour is spontaneous and asymmetrical generation of supramolecular helices, as had been shown by cryo-TEM in the case of dye **1A**, *m* = 8.[16,19] The third type are exceptional dyes of very high hydrophilicity or hydrophobicity, such as **1D**, **1E**, and **1B**, *n* = 1. Such dyes give H-aggregates that also display blue-shifted absorption bands. The self-organization of dyes **1** is therefore obviously governed by their molecular configurations and conformations, which have their origins in rather sensitive equilibria between the dyes' coupling strengths, steric factors, as well as in the hydrophobic and hydrogen-bridging forces of their substituents.[38]

## Outlook

As the research team for amphipipes no longer exists, owing to the retirement of its team leader (S.D.), it is hoped that the following outlook will stimulate further research in this challenging new field. It will be easy to start with work as some of the dyes described have recently become commercially available.[39]

(i) Apart from dyes **1** investigated in this paper, nothing is known about the influence of further structural alterations on the amphipipe features, such as lengthening and/or substitutions of the polymethine chain, symmetrical and asymmetrical variation of the heterocyclic residues, or modifications of the substituents' acidic/basic natures. The search for other chromophores that form J-aggregates would also be important. For instance, the strange physicochemical properties of the J-aggregates of amphiphilic merocyanine dyes synthesized by Balli et al.[40] already point to the existence of amphipipes with entirely different molecular structures.

(ii) As the spectral behaviour and the morphology of each amphipipe usually depends strongly on its microenvironment (e.g., on the presence of hydroxylic compounds, surfactants, and presumably of proteins), the number of possible amphipipe architectures still to be brought to light will be raised exponentially when such compounds are intercalated in amphipipes.

(iii) As exciton delocalization is the most important feature of the new self-organized nanoscopic particles, the dynamics of this process need to be investigated in detail in terms of their dependence on the amphipipes' morphologies and on their molecular structures.

(iv) Almost nothing is known about the ability of amphipipes to spectrally sensitize photoinduced electron transfer (PET) reactions. However, there is little doubt that they will do so, because J-aggregates act as spectral sensitizers in photographic processes and it has recently been shown that the supramolecular J-aggregates of pseudoisocyanine (PIC) spectrally sensitize hydrogen production in the presence of electron acceptors and donors.[41] Thus the development of artificial light-harvesting systems seems possible. It might be even conceivable to mimic natural photosynthetic reaction centres through intercalation of amphiphilic molecules with strong electron acceptor and/or electron donor functions into amphipipes.

(v) Finally, the spontaneous and asymmetrical generation of helical amphipipes in alkaline aqueous solution provides new model systems with which to acquire deeper insight in the evolution of the asymmetry of life.[42] In the case of dye **1A**, $m = 8$, the asymmetrical generation of superhelices seems to be promoted by intramolecular interaction between the two hydrophobic octyl groups, as well as by the formation of an intramolecular hydrogen bond, both of which are able to induce an intramolecular twist of a single molecule.[19,38] As a twisted molecule can only dimerize with another one with the same twist sign, the handedness will be preserved. Such a dimer then acts as a template for the generation of a helix, which transfers its chirality to most of the subsequently formed helices. Since there is equal probability that the first formed dimer will have either left-handed or right-handed twist, one has to expect that on repetition of the experiment, samples with preferred left-handed and with preferred right-handed helices should be obtained with equal parity. This, indeed, happened in our first experiments.[18] However, this could be not confirmed when the purified dye **1A**, $m = 8$, described in this paper was used. In this case, helices with a positive CD couplet were preferentially generated.[15,43] These contradictory results urgently need further investigation.

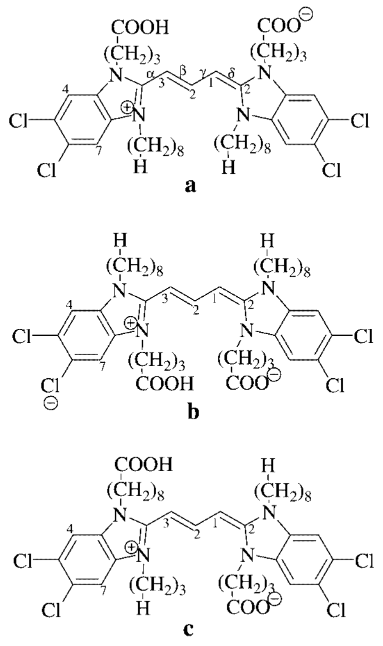
Furthermore, dye **1A**, $m = 8$ also seems to be a promising model compound with which to test results of vortex-induced chirality recently published by Ribo et al.[44] The authors claim that the handedness of helical aggregates formed by self-organization of mutually shifted disk-like porphyrin molecules is governed by the direction of the vortex flow. In the case of dye **1A**, $m = 8$, it would be not the mutual shift of aggregated molecules but the twist direction of the molecules that would determine the handedness of the first formed helical dye dimer. If the twist of the molecules can be controlled by the direction of a vortex flow, this could offer the potential to induce chirality by macroscopic mechanical forces.

## Experimental Section

**General:** As the IUPAC nomenclature of polymethine dyes is rather complicated we applied the designations used in scientific photography, which emphasizes the true symmetrical $C_{2v}$ structure of the dyes with equivalent terminal heterocycles. Examples of the correct IUPAC designation of some configurations of dye **1A**, $m = 8$ that have been determined by X-ray structure analyses in the crystalline state and by NMR COSY and NOESY experiments in the liquid state[38] are given in Scheme 3. The all-*trans* configuration **a** is the prevailing one.
Measurements in solutions were performed under argon. For preparation of monomeric dye solutions the samples were dissolved in dimethyl sulfoxide by sonication for two minutes. In order to prepare J-aggregate solutions the samples were either directly dissolved in $10^{-2}$ M aqueous sodium hydroxide solution by stirring under argon for 2 d, or else a methanolic stock solution was prepared and then diluted with $10^{-2}$ M aqueous sodium hydroxide solution, it being ensured that the final methanol content did not exceed 10% (v/v).

UV/Vis spectra were run at room temperature either with a Zeiss Specord M 400 spectrometer or with a Bruins Omega 10 spectrometer. The maximum molar extinction coefficients ($\varepsilon_{max}$) [$10^3$ $cm^2 \cdot mmol^{-1}$] of dye **1** monomers given in Table 1 are mean values, each of three independent determinations. In instances of contaminated dye samples the purity of the dye is given as a percentage determined on the assumption that the $\varepsilon_{max}$ values of all dyes in dimethyl sulfoxide solution are equal and amount to 185.0 $10^3$ $cm^2 \cdot mmol^{-1}$. The J-aggregates' maximum extinction coefficients ($\varepsilon$) used in the Figures have been corrected for the varying purities of the different dyes indicated in Table 1. The values apply to the weight of monomeric molecules, which means that, in principle, they should be multiplied by the (unknown) number of coupled molecules. For solutions at concentrations higher than $10^{-4}$ mol/L, microcuvettes (20−500 μm) were used. The data measured at those concentrations therefore have an error of ± 15%.

Fluorescence spectra were recorded with a 8100 spectrofluorimeter from Spectronics Instruments. The fluorescence spectra of monomeric molecules were excited at 475 nm. Fluorescence spectra of J-aggregates were excited at 500 nm and a front face equipment was



Scheme 3. *cis-trans* Configurations of 5,5′,6,6′-tetrachloro-1,1′-dioctyl-3,3′-bis(3-carboxypropyl)benzimidacarbocyanine dye **1A**, $m = 8$. The IUPAC designations are (letter s means formal single bond): a: 4-{2(*E*)-[2(*E*),3(s*E*)-(3-carboxypropyl-5,6-dichloro-1-octyl-3*H*-benzimidazol-1-ium-2-yl)prop-2-en-1-ylidene]-5,6-dichloro-3-octyl-2,3-dihydro-1*H*-benzimidazol-1-yl}butanoate; b: 4-{2(*Z*)-[2(*E*),3(s*Z*)-(3-carboxypropyl-5,6-dichloro-1-octyl-3*H*-benzimidazol-1-ium-2-yl)prop-2-en-1-ylidene]-5,6-dichloro-3-octyl-2,3-dihydro-1*H*-benzimidazol-1-yl}butanoate; c. 4-{2(*Z*)-[2(*E*),3(s*E*)-(3-carboxypropyl-5,6-dichloro-1-octyl-3*H*-benzimidazol-1-ium-2-yl)prop-2-en-1-ylidene]-5,6-dichloro-3-octyl-2,3-dihydro-1*H*-benzimidazol-1-yl}butanoate

used to prevent reabsorption. All fluorescence spectra were corrected for the wavelength sensitivity of the spectrometer and the intensity fluctuations of the excitation lamp.

$^1$H NMR spectra were recorded either with a Varian Unity$_{\text{plus}}$ 500 (500 MHz) or with a Varian Unity$_{\text{plus}}$ 300 (300 MHz) spectrometer. Tetramethylsilane (TMS) was used as reference compound.

LSIMS mass spectra were determined with an Autospec spectrometer (Micromass) with Magic Bullet as matrix. HPLC/MS was used to test purification procedures of dyes **1A**, $m = 8$, and **1B**, $n = 4$. For the same purpose, thermoanalytical investigations DTA/MS (ESI positive) were performed in a SETARAM TAG 24/16 thermobalance. Samples (1−5 mg) were heated at 5 K/min to 200 °C in loosely covered ceramic crucibles under an argon flow. A Finnigan MAT 95 high-resolution mass spectrometer was additionally applied for the purified dye **1A**, $m = 8$.

**Sources of Compounds:** 1-Aminohexane (99%), 1-bromoheptane (99%), 1-bromooctane (99%), 1-bromodecane (98%), 1-bromoundecane (98%), 4-bromobutyronitrile (97%), Ethyl bromoacetate (98%), ethyl 3-bromopropionate (99%), ethyl 5-bromopentanoate (98%), ethyl 6-bromohexanoate (99%), 1,8-diazabicyclo[5.4.0]-undec-7-ene (98%), 1,3-propanesultone (99%), sodium bromide (99%), hydrobromic acid (48% w/w aq. soln.), absolute *N*,*N*-dimethylformamide (99.8%, water < 0.005%), and absolute methanol (99.8%, water < 0.005%) were purchased from Aldrich. Other solvents used were of HPLC grade. The water used was deionized. (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl) iodide (97%) was obtained from ABCR GmbH (Gelest, Inc, USA). Iodoform (99%), sodium hydroxide (99%), and acetic acid (96%) were purchased from Merck. 4,5-Dichloro-1,2-phenylenediamine (**2**) (97%), lithium hydroxide monohydrate (99%) and 1,2,4-trichloro-5-nitrobenzene (**7**) (97%) were obtained from Fluka.

The dyes 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-bis(3-sulfopropyl)-benzimidacarbocyanine (BIC) **1C**, $m = 2$, $n = 3$; 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-bis(4-sulfobutyl)benzimidacarbocyanine (TDBC) **1C**, $m = 2$, $n = 4$; 5,5′,6,6′-tetrachloro-1,1′-dioctyl-3,3′-bis(3-sulfoethyl)benzimidacarbocyanine **1C**, $m = 8$, $n = 2$; 5,5′,6,6′-tetrachloro-1,1′-dioctyl-3,3′-bis(3-sulfopropyl)benzimidacarbocyanine **1C**, $m = 8$, $n = 3$; and 3,3′-bis(3-carboxypropyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine **1A**, $m = 8$ were purchased from FEW Chemicals GmbH.[39] Dye **1C**, $m = 2$, $n = 4$ (TDBC) contained 6 mol crystal water. Dye **1A**, $m = 8$, was a 1:1 mixture of the bromide and the betaine. Recrystallization from dimethyl sulfoxide (DMSO) yielded the pure betaine, containing 0.5 mol DMSO. The dyes **1A**, $m = 2$; **1A**, $m = 4$; **1A**, $m = 6$; **1A**, $m = 12$; **1C**, $m = 4$, $n = 4$; and **1C** $m = 8$, $n = 4$, were provided by the authors of ref.[9] Recrystallization of **1A**, $m = 6$, from DMSO gave the pure betaine, containing 1 mol crystal water and 2 mol DMSO. If the synthesis of the dyes was repeated, the analytical data and those of their precursors are indicated in the following descriptions.

### Preparation of the Intermediate Compounds

**4,5-Dichloro-*N*-hexyl-2-nitroaniline (8, *m* = 6):** This compound was prepared according to ref.[9] by treatment of 2,4,5-trichloronitrobenzene (**7**) with 1-aminohexane. Melting point, yield, and CHN analysis are compiled in Table 3.

**5,6,-Dichloro-1-hexyl-2-methylbenzimidazole 5, *m* = 6:** This compound was prepared according to ref.[9] by reduction of **8**, $m = 6$, and cyclization with acetic acid.

Table 3. Melting points, yields, empirical formulae, molecular mass and CHN elemental analysis for compounds **4**, **5** and **8**

| Compound | M.p. (°C) | Yield (%) | Empirical formula | Mol. mass (g/mol) | C content calcd. | C content found | H content calcd. | H content found | N content calcd. | N content Found |
|---|---|---|---|---|---|---|---|---|---|---|
| **4**, $n = 3$ | 150−152 | 43 | $C_{12}H_{11}Cl_2N_3$ | 268.15 | 53.75 | 53.50 | 4.14 | 4.07 | 15.67 | 15.56 |
| **5**, $m = 6$ | 111−113 | 47 | $C_{14}H_{18}Cl_2N_2$ | 285.22 | 58.95 | 58.27 | 6.36 | 6.41 | 9.82 | 9.49 |
| **5**, $m = 7$ | 89−90 | 44 | $C_{15}H_{20}Cl_2N_2$ | 299.24 | 60.21 | 60.35 | 6.74 | 6.94 | 9.36 | 9.24 |
| **5**, $m = 8$[a] | 107−109 | 69 | $C_{16}H_{22}Cl_2N_2$ | 313.29 | 61.34 | 60.14 | 7.08 | 6.85 | 8.94 | 8.70 |
| **5**, $m = 11$ | 89−90 | 51 | $C_{19}H_{28}Cl_2N_2$ | 355.35 | 64.22 | 64.25 | 7.94 | 8.20 | 7.88 | 7.65 |
| **8**, $m = 6$ | 34−35 | 25 | $C_{12}H_{16}Cl_2N_2O_2$ | 291.19 | 49.50 | 49.40 | 5.54 | 5.64 | 9.62 | 9.52 |

[a] Synthesized as in ref.[9].

**3-(3-Carboxypropyl)-5,6-dichloro-1-hexyl-2-methylbenzimidazolium Bromide 6A, *m* = 6 and 3-(3-Carboxypropyl)-5,6-dichloro-1-heptyl-2-methylbenzimidazolium Bromide 6A, *m* = 7:** These compounds were prepared according to ref.[9] from **5**, *m* = 6, and **5**, *m* = 7, respectively, by treatment with 4-bromobutyronitrile and subsequent hydrolysis. Melting points, yields and CHN analyses of the compounds are compiled in Table 3.

$^1$H NMR: **4, *n* = 3** ($\mathrm{CDCl_3}$): δ = 2.13−2.22 (m, 2 H, $\mathrm{NCH_2C}H_2$), 2.40 (t, $\mathrm{NCC}H_2$, *J* = 6.6 Hz, 2 H), 2.64 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.25 (t, *J* = 7.1 Hz, 2 H, $\mathrm{NC}H_2$), 7.41 (s, 1 H, 7-H), 7.76 (s, 1 H, 4-H) ppm; **5, *m* = 6** ($\mathrm{CDCl_3}$): δ = 0.89 (t, *J* = 7.0 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.27−1.36 (m, 6 H, 3 × $\mathrm{C}H_2$), 1.75−1.78 (m, 2 H, $\mathrm{NCH_2C}H_2$), 2.58 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.03 (t, *J* = 7.5 Hz, 2 H, $\mathrm{NC}H_2$), 7.37 (s, 1 H, 7-H), 7.74 (s, 1 H, 4-H) ppm; **5, *m* = 7** ($\mathrm{CDCl_3}$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.28−1.35 (m, 8 H, 4 × $\mathrm{C}H_2$), 1.75−1.81 (m, 2 H, $\mathrm{NCH_2C}H_2$), 2.58 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.03 (t, *J* = 7.5 Hz, 2 H, $\mathrm{NC}H_2$), 7.37 (s, 1 H, 7-H), 7.74 (s, 1 H, 4-H) ppm; **5, *m* = 8** ($\mathrm{CDCl_3}$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.26−1.33 (m, 10 H, 5 × $\mathrm{C}H_2$), 1.74−1.79 (m, 2 H, $\mathrm{NCH_2C}H_2$), 2.58 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.03 (t, *J* = 7.4 Hz, 2 H, $\mathrm{NC}H_2$), 7.36 (s, 1 H, 7-H), 7.74 (s, 1 H, 4-H) ppm; **5, *m* = 11** ([D$_6$]DMSO): δ = 0.85 (t, *J* = 6.7 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.22−1.27 (m, 16 H, 8 × $\mathrm{C}H_2$), 1.65−1.70 (m, 2 H, $\mathrm{NCH_2C}H_2$), 2.53 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.17 (t, *J* = 7.3 Hz, 2 H, $\mathrm{NC}H_2$), 7.74 (s, 1 H, 7-H), 7.87 (s, 1 H, 4-H) ppm; **8, *m* = 6** ($\mathrm{CDCl_3}$): δ = 0.91 (t, *J* = 7.0 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.31−1.47 (m, 6 H, 3 × $\mathrm{C}H_2$), 1.68−1.77 (m, 2 H, $\mathrm{NCH_2C}H_2$), 3.22−3.28 (m, 2 H, $\mathrm{NC}H_2$), 6.95 (s, 1 H, 3-H), 7.95 (br. s, 1 H, $\mathrm{N}H$), 8.26 (s, 1 H, 6-H) ppm.

**General Procedure for the Preparation of 5,6-Dichloro-1-(3-cyanopropyl)-2-methylbenzimidazole 4, *n* = 3; 5,6-Dichloro-1-heptyl-2-methylbenzimidazole 5, *m* = 7; 5,6-Dichloro-2-methyl-1-octylbenzimidazole 5, *m* = 8; and 5,6-Dichloro-2-methyl-1-undecylbenzimidazole 5, *m* = 11:** 5,6-Dichloro-2-methylbenzimidazole (**3**) was dissolved in dimethyl sulfoxide under the reaction conditions given in Table 4. After addition of the appropriate amount of pulverized sodium hydroxide, the solution was stirred at room temperature for 4 h. The reactant was then added. Further stirring at room temperature for the time given, subsequent filtration, and washing of the residue with water and *n*-hexane yielded **5**, *m* = 7; **5**, *m* = 8; and **5**, *m* = 11, respectively. Purification by hot extraction with hexane likewise gave the products listed in Table 3. Product **5**, *m* = 11, was additionally recrystallized from toluene/cyclohexane, 1:4 (v/v). In order to precipitate **4**, *n* = 3, from the stirred solution it was necessary to add water (100 mL). After filtration, the residue was washed with water (300 mL), dried, extracted hot with toluene and recrystallized from ethanol. Melting points, yields, and CHN analyses of the compounds are also listed in Table 3.

Table 4. Reaction conditions for synthesis of the benzimidazoles **4** and **5**

| | | **4**, *n* = 3 | **5**, *m* = 7 | **5**, *m* = 8 | **5**, *m* = 11 |
|---|---|---|---|---|---|
| Starting material **3** | (g) | 25.0 | 7.0 | 15.0 | 12.0 |
| | (mmol) | 124.0 | 34.8 | 74.6 | 59.7 |
| DMSO | (ml) | 50 | 75 | 150 | 100 |
| NaOH | (g) | 5.60 | 1.68 | 4.00 | 2.64 |
| | (mmol) | 140 | 42 | 100 | 65.9 |
| Reactant[a] | | 1 | 2 | 3 | 4 |
| | (g) | 20.7 | 7.52 | 29.0 | 15.5 |
| | (mmol) | 140 | 42.0 | 150 | 66 |
| Reaction time | (days) | 4 | 1 | 3 | 3 |
| Product | (g) | 14.3[b] | 4.62 | 16.1 | 10.7[b] |
| | (mmol) | 53.3. | 15.4 | 51.4 | 30.1 |

[a] 1: 4-bromobutyronitrile; 2: 1-bromoheptane; 3: 1-bromooctane; 4: 1-bromoundecane. [b] after additional purification, see text.

**General Procedures for the Preparation of 3-(3-Carboxypropyl)-5,6-dichloro-2-methyl-1-octylbenzimidazolium Bromide 6A, *m* = 8; 3-(3-Carboxypropyl)-5,6-dichloro-1-decyl-2-methylbenzimidazolium Bromide 6A, *m* = 10; 3-(3-Carboxypropyl)-5,6-dichloro-2-methyl-1-undecylbenzimidazolium Bromide 6A, m = 11; 3-(Carboxymethyl)-5,6-dichloro-2-methyl-1-octylbenzimidazolium Bromide 6B, *n* = 1; 3-(2-Carboxyethyl)-5,6-dichloro-2-methyl-1-octylbenzimidazolium Bromide 6B, *n* = 2; 3-(4-Carboxybutyl)-5,6-dichloro-2-methyl-1-octylbenzimidazolium Bromide 6B, *n* = 4); 3-(5-Carboxypentyl)-5,6-dichloro-2-methyl-1-octylbenzimidazolium Bromide 6B, *n* = 5; 5,6-Dichloro-2-methyl-1-octyl-3-(3-sulfopropyl)benzimidazolium Bromide 6C, *m* = 8, *n* = 3**; and **3-(3-Carboxypropyl)-5,6-dichloro-1-(1-*H*,1-*H*,2-*H*,2-*H*-perfluorooctyl)-2-methylbenzimidazolium Bromide 6E:**

The reaction conditions are listed in Table 5. As with dyes **1**, **6A** in all formulas is (*n* = 3) and **6B** in all formulas is (*m* = 8). The formula of **6E** given in Scheme 2 means (*n* = 3) and $-(\mathrm{CH_2})_2-(\mathrm{CF_2})_6-\mathrm{F}$ instead of $-(\mathrm{CH_2})_8\mathrm{H}$.

The appropriate 3-alkyl-5,6-dichlorobenzimidazoles **4** or **5** were heated with an excess of the corresponding reactant with the reaction times $t_1$ and temperatures $T_1$ given in Table 5. Each reaction product was suspended in acetone (20−30 mL) and heated for 30 minutes. After cooling to room temperature, the residue was filtered off and washed with acetone (20−30 mL). The sulfobetaine **6C**, *m* = 8, *n* = 3, was purified by heating in acetone (70 mL), filtration after cooling to room temperature, and washing of the residue with acetone (50 mL). This procedure was repeated twice. The ester or nitrile groups of the intermediate products were subsequently hydrolysed by heating at reflux in half-diluted hydrobromic acid (48% in weight, aq. soln, 40−60 mL) for the time $t_2$ indicated in Table 5. After the mixture had cooled to room temperature, the precipitate was filtered off and washed with aqueous hydrobromic acid (5% w/w, 10 mL). The obtained salt was dissolved in boiling water (50−100 mL) and filtered hot. In order to avoid the formation of betaine salts, the hot filtrate was mixed with aqueous hydrobromic acid (48% in weight, 2−5 mL). The crystallized benzimidazoles **6** were isolated by removal of the mother liquor by suction, washed with aqueous hydrobromic acid (5% in weight, 10 mL) and dried in air. Melting points, yields and CHN analyses are compiled in Table 6.

$^1$H NMR: **6A, *m* = 6**, ($\mathrm{CD_3OD}$): δ = 0.92 (t, *J* = 7.1 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.35−1.47 (m, 6 H, 3 × $\mathrm{C}H_2$), 1.86−1.91 (m, 2 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_2}$), 2.12−2.17 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_2COOH}$), 2.54 (t, *J* = 6.6 Hz, 2 H, $\mathrm{C}H_2\mathrm{COOH}$), 2.97 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.44−4.55 (m, 4 H, $\mathrm{NC}H_2$), 8.28 (s, 1 H, 4/7-H), 8.34 (s, 1 H, 4/7-H) ppm; **6A, *m* = 7**, ([D$_6$]DMSO): δ = 0.86 (t, *J* = 6.8 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.27−1.34 (m, 8 H, 4 × $\mathrm{C}H_2$), 1.73−1.76 (m, 2 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_2}$), 1.97−2.02 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_2COOH}$), 2.43 (t, *J* = 7.3 Hz, 2 H, $\mathrm{C}H_2\mathrm{COOH}$), 2.92 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.42−4.49 (m, 4 H, $\mathrm{NC}H_2$), 8.55 (s, 1 H, 4/7-H), 8.56 (s, 1 H, 4/7-H), 12.27 (br. s, 1 H, $\mathrm{COO}H$) ppm; **6A, *m* = 8**, ([D$_6$]DMSO): δ = 0.84 (t, *J* = 6.5 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.24−1.31 (m, 10 H, 5 × $\mathrm{C}H_2$), 1.72−1.74 (m, 2 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_2}$), 1.95−2.00 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_2COOH}$), 2.42 (t, *J* = 7.2 Hz, 2 H, $\mathrm{C}H_2\mathrm{COOH}$), 2.92 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.41−4.49 (m, 4 H, $\mathrm{NC}H_2$), 8.56 (s, 2 H, 4-H and 7-H) ppm; **6A, *m* = 10**, ([D$_6$]DMSO): δ = 0.85 (t, *J* = 6.7 Hz, 3 H, $\mathrm{CH_2C}H_3$), 1.24−1.33 (m, 14 H, 7 × $\mathrm{C}H_2$), 1.71−1.76 (m, 2 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_2}$), 1.95−2.05 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_2COOH}$), 2.43 (t, *J* = 7.2 Hz, 2 H, $\mathrm{C}H_2\mathrm{COOH}$), 2.93 (s, 3 H, $\mathrm{2\text{-}C}H_3$), 4.43−4.51 (m,

Table 5. Reaction conditions for synthesis of the benzimidazole bromides **6**

| | **6A**, $m = 6$[a] | **6A**, $m = 7$[a] | **6A**, $m = 8$ | **6A**, $m = 10$ | **6A**, $m = 11$ | **6B**, $n = 1$ | **6B**, $n = 2$ | **6B**, $n = 4$ | **6B**, $n = 5$ | **6C**, $n = 3$, $m = 8$ | **6E** see text |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Starting material | **5**, $m = 6$ | **5**, $m = 7$ | **5**, $m = 8$ | **4**, n = 3 | **5**, $m = 11$ | **5**, $m = 8$ | **5**, $m = 8$ | **5**, $m = 8$ | **5**, $m = 8$ | **5**, $m = 8$ | **4**, $n = 3$ |
| (mmol) | | | 9.58 | 18.6 | 11.3 | 19.2 | 16.0 | 16.0 | 9.99 | 24.9 | 14.9 |
| (g) | | | 3.00 | 5.00 | 4.00 | 6.00 | 5.00 | 5.00 | 3.13 | 7.80 | 4.00 |
| Reactant[b] | 1 | 1 | 1 | 2 | 1 | 3 | 4 | 5 | 6 | 7 | 8 |
| (mmol) | | | 15.0 | 20.0 | 13.0 | 30.1 | 24.0 | 24.0 | 20.0 | 28.7 | 16.5 |
| (g) | | | 2.22 | 4.42 | 1.92 | 5.02 | 4.34 | 5.02 | 4.46 | 3.50 | 7.80 |
| $T_1$ (°C) | 100 | 100 | 150 | 180 | 150 | 150 | 150 | 150 | 150 | 150 | 180 |
| $t_1$ (h) | 5 | 5 | 2 | 2 | 3 | 2 | 2 | 2 | 2 | 3 | 2 |
| $t_2$ (h) | 12 | 12 | 4 | 6 | 6 | 4 | 4 | 4 | 4 | – | 7 |
| Product (g) | | | 3.60 | 5.81 | 3.80 | 6.21 | 1.95 | 5.42 | 3.18 | 5.73 | 3.47 |
| Product (mmol) | | | 7.50 | 11.4 | 7.27 | 13.7 | 4.18 | 11.0 | 6.26 | 13.2 | 4.66 |

[a] Kindly provided by the authors of ref.[9] [b] 1: 4-Bromobutyronitrile; 2: 1-decyl bromide; 3: ethyl bromoacetate; 4: ethyl 3-bromopropionate; 5: ethyl 5-bromopentanoate; 6: ethyl 6-bromohexanoate; 7: 1,3-propanesultone; 8: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl iodide.

Table 6. Melting points, yields, empirical formulas, molecular weights and CHN elemental analyses for compounds **6**

| Compound | M.p. (°C) | Yield (%) | Empirical formula | Mol. mass (g/mol) | C content calcd. | C content found | H content calcd. | H content found | N content calcd. | N content found |
|---|---|---|---|---|---|---|---|---|---|---|
| **6A**, $m = 6$ | 252–253 | 29 | $C_{18}H_{25}BrCl_2N_2O_2$ | 452.25 | 47.81 | 47.82 | 5.57 | 5.59 | 6.19 | 6.32 |
| **6A**, $m = 7$ | 246–247 | 54 | $C_{19}H_{27}BrCl_2N_2O_2$ | 466.27 | 48.94 | 48.94 | 5.84 | 5.86 | 6.01 | 6.05 |
| **6A**, $m = 8$[a] | 206–207 | 78 | $C_{20}H_{29}BrCl_2N_2O_2$ | 480.23 | 50.01 | 48.07 | 6.09 | 5.85 | 5.83 | 5.82 |
| **6A**, $m = 10$ | 156–157 | 61 | $C_{22}H_{33}BrCl_2N_2O_2$ | 508.32 | 51.98 | 51.77 | 6.54 | 6.56 | 5.51 | 5.51 |
| **6A**, $m = 11$ | 156–157 | 64 | $C_{23}H_{35}BrCl_2N_2O_2$ | 522.35 | 52.89 | 52.89 | 6.75 | 6.70 | 5.36 | 5.44 |
| **6B**, $n = 1$ | 214–216 | 71 | $C_{18}H_{25}BrCl_2N_2O_2$ | 452.22 | 47.81 | 47.44 | 5.57 | 5.67 | 6.20 | 6.03 |
| **6B**, $n = 2$ | 200–201 | 26 | $C_{19}H_{27}BrCl_2N_2O_2$ | 466.24 | 48.95 | 48.69 | 5.84 | 5.85 | 6.01 | 5.95 |
| **6B**, $n = 4$ | 214–215 | 69 | $C_{21}H_{31}BrCl_2N_2O_2$ | 494.30 | 51.03 | 51.01 | 6.32 | 6.44 | 5.67 | 5.45 |
| **6B**, $n = 5$ | 254–255 | 63 | $C_{22}H_{33}BrCl_2N_2O_2$ | 508.32 | 51.98 | 52.08 | 6.54 | 6.68 | 5.51 | 5.41 |
| **6C**, $m = 8$, $n = 3$ | 281–282 | 53 | $C_{19}H_{28}Cl_2N_2O_3S$ | 435.41 | 52.41 | 51.91 | 6.48 | 6.44 | 6.43 | 6.26 |
| **6D**, see text | 236–238 | 29 | $C_{16}H_{19}BrCl_2N_2O_4\cdot H_2O$ | 472.16 | 40.70 | 40.76 | 4.48 | 4.50 | 5.93 | 6.03 |
| **6E**, see text | 197–200 | 31 | $C_{20}H_{16}Br_{0.35}Cl_2F_{13}I_{0.65}N_2O_2$ | 744.69 | F-content: calcd.: 33.17 found: 33.19 | | | | | |

[a] Ref.[9]: 207–209 °C.

4 H, NC$H_2$), 8.56 (s, 2 H, 4-H and 7-H), 12.23 (br. s, 1 H, COO$H$) ppm; **6A, *m* = 11**, ([D$_6$]DMSO): δ = 0.85 (t, $J$ = 6.7 Hz, 3 H, CH$_2$C$H_3$), 1.24–1.32 (m, 16 H, 8 × C$H_2$), 1.73–1.75 (m, 2 H, NCH$_2$C$H_2$CH$_2$CH$_2$), 1.97–2.02 (m, 2 H, C$H_2$CH$_2$COOH), 2.43 (t, $J$ = 7.3 Hz, 2 H, C$H_2$COOH), 2.92 (s, 3 H, 2-C$H_3$), 4.42–4.49 (m, 4 H, NC$H_2$), 8.555 (s, 1 H, 4/7-H), 8.560 (s, 1 H, 4/7-H), 12.26 (s, 1 H, COO$H$) ppm; **6B, *n* = 1**, ([D$_6$]DMSO): δ = 0.85 (t, $J$ = 6.9 Hz, 3 H, CH$_2$C$H_3$), 1.23–1.33 (m, 10 H, 5 × C$H_2$), 1.74–1.77 (m, 2 H, NCH$_2$C$H_2$), 2.89 (s, 3 H, 2-C$H_3$), 4.54 (t, $J$ = 7.5 Hz, 2 H, NC$H_2$), 5.36 (s, 2 H, NC$H_2$CO$_2$H), 8.54 (s, 1 H, 4/7-H), 8.60 (s, 1 H, 4/7-H) ppm; **6B, *n* = 2**, ([D$_6$]DMSO): δ = 0.86 (t, $J$ = 7.0 Hz, 3 H, CH$_2$C$H_3$), 1.25–1.37 (m, 10 H, 5 × C$H_2$), 1.71–1.77 (m, 2 H, NCH$_2$C$H_2$CH$_2$), 2.90 (t, $J$ = 6.8 Hz, 2 H, NCH$_2$C$H_2$COOH), 2.96 (s, 3 H, 2-C$H_3$), 4.47 (t, $J$ = 7.5 Hz, 2 H, NC$H_2$CH$_2$CH$_2$), 4.65 (t, 2 H, NC$H_2$CH$_2$CO$_2$H), 8.55 (s, 1 H, 4/7-H), 8.56 (s, 1 H, 4/7-H), 12.59 (br. s, 1 H, COO$H$) ppm; **6B, *n* = 4**, ([D$_6$]DMSO): δ = 0.86 (t, $J$ = 6.9 Hz, 3 H, CH$_2$C$H_3$), 1.24–1.39 (m, 10 H, 5 × C$H_2$), 1.57–1.63 (m, 2 H, C$H_2$CH$_2$CO$_2$H), 1.72–1.82 (m, 4 H, NCH$_2$C$H_2$), 2.29 (t, $J$ = 7.4 Hz, 2 H, C$H_2$COOH), 2.93 (s, 3 H, 2-C$H_3$), 4.44–4.50 (m, 4 H, NC$H_2$), 8.565 (s, 1 H, 4/7-H), 8.569 (s, 1 H, 4/7-H), 12.08 (br. s, 1 H, COO$H$) ppm; **6B, *n* = 5**, (CD$_3$OD): δ = 0.89 (t, $J$ = 7.0 Hz, 3 H, CH$_2$C$H_3$), 1.30–1.52 (m, 12 H, 6 × C$H_2$), 1.64–1.70 (m, 2 H, C$H_2$CH$_2$CO$_2$H), 1.86–1.94 (m, 4 H, NCH$_2$C$H_2$), 2.32 (t, $J$ = 7.3 Hz, 2 H, C$H_2$COOH), 2.95 (s, 3 H, 2-C$H_3$), 4.46–4.50 (m, 4 H, NC$H_2$), 8.28 (s, 1 H, 4/7-H), 8.30 (s, 1 H, 4/7-H) ppm; **6C, *m* = 8, *n* = 3** ([D$_6$]DMSO): δ = 0.86 (t, $J$ = 6.6 Hz, 3 H, CH$_2$C$H_3$), 1.25–1.32 (m, 10 H, 5 × C$H_2$), 1.73–1.75 (m, 2 H, NCH$_2$C$H_2$CH$_2$CH$_2$), 2.07–2.14 (m, 2 H, C$H_2$CH$_2$S), 2.55 (t, $J$ = 6.9 Hz, 2 H, C$H_2$S), 2.91 (s, 3 H, 2-C$H_3$), 4.41 (t, $J$ = 7.4 Hz, 2 H, NC$H_2$CH$_2$CH$_2$CH$_2$), 4.61 (t, $J$ = 7.4 Hz, 2 H, SCH$_2$CH$_2$C$H_2$), 8.52 (s, 1 H, 4/7-H), 8.58 (s, 1 H, 4/7-H) ppm; **6D** (CD$_3$OD): δ = 2.13–2.18 (m, 4 H, NCH$_2$C$H_2$), 2.55 (t, $J$ = 6.5 Hz, 4 H, C$H_2$COOH), 3.00 (s, 3 H, 2-C$H_3$), 4.53 (t, $J$ = 7.7 Hz, 4 H, NC$H_2$), 8.34 (s, 2 H, 4-H and 7-H) ppm; **6E** ([D$_6$]DMSO): δ = 1.96–2.01 (m, 2 H, C$H_2$CH$_2$COOH), 2.43 (t, $J$ = 7.4 Hz, 2 H, C$H_2$COOH),

2.97 (s, 3 H, 2-C$H_3$), 2.94−3.08 (m, 2 H, C$H_2$C$F_2$), 4.51 (t, $J$ = 7.5 Hz, 2 H, NC$H_2$C$H_2$C$H_2$), 4.86 (t, $J$ = 7.1 Hz, 2 H, NC$H_2$C$H_2$C$F_2$),), 8.56 (s, 1 H, 4/7-H), 8.59 (s, 1 H, 4/7-H) ppm.

**1,3-Bis(3-carboxypropyl)-5,6-dichloro-2-methylbenzimidazolium Bromide 6D:** Compound **6D** [the formula given in Scheme 2 means ($n$ = 3) and $-(CH_2)_3-COOH$ instead of $-(CH_2)_mH$] was prepared from **3** by addition of sodium hydroxide (0.80 g, 20.0 mmol) to a solution of **3** (4.02 g, 20.0 mmol) in dimethyl sulfoxide (30 mL). This solution was stirred at room temperature for 3 h. 4-Bromobutyronitrile (3.70 g, 25.0 mmol) was then added and stirring was continued for 1 d. Water (20 mL) was then added, and the precipitate was filtered off, washed with water (100 mL) and dried. The product was again heated at 150 °C with 4-bromobutyronitrile (7.40 g, 50.0 mmol) for 4 h. After cooling to room temperature, the mixture was suspended in acetone (20 mL), stirred for 1 h and filtered. The residue was washed with acetone (30 mL), dried, mixed with water (20 mL) and hydrobromic acid (48% in weight, aq. soln., 20 mL) and heated under reflux for 4 h. After filtration the product was washed with water (100 mL) and recrystallized from hydrobromic acid (5% w/w). The yield of **6D**·$H_2O$ was 2.70 g (5.72 mmol). Melting points, yields, and CHN analyses are also given in Table 6.

**General Procedure for the Preparation of 3,3′-Bis(3-carboxypropyl)-5,5′,6,6′-tetrachloro-1,1′-diheptylbenzimidacarbocyanine 1A, *m* = 7; 3,3′-Bis(3-carboxypropyl)-5,5′,6,6′-tetrachloro-1,1′-didecylbenzimidacarbocyanine 1A, *m* = 10; 3,3′-Bis(3-carboxypropyl)-5,5′,6,6′-tetrachloro-1,1′-diundecylbenzimidacarbocyanine Lithium Salt Betaine 1A, *m* = 11; 3,3′-Bis(carboxymethyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine 1B, *n* = 1; and 3,3′-Bis(3-carboxypropyl)-5,5′,6,6′-tetrachloro-1,1′-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzimidacarbocyanine 1E:** A 1.5-fold molar excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added dropwise with stirring at room temperature to the appropriate benzimidazolium bromide **6** and iodoform in dimethylformamide according to the reaction conditions given in Table 7. The solution warmed up slightly. After 3 h, a further 1.5-fold molar excess of DBU was added and stirring was continued for 12 h.

For workup of **1A**, $m$ = 10; **1B**, $n$ = 1; and **1E** the reaction mixture was dropped into water (50 mL) containing acetic acid (1 mL) and an excess of sodium bromide (4.0 g, 38.9 mmol), and the residue was isolated by removal of the mother liquor by suction and washed with water. The residue was then dissolved in dimethyl sulfoxide (100 mL), filtered and again dropped into a solution of acetic acid (1 mL) and sodium bromide (4.0 g, 38.9 mmol) in water (200 mL). The obtained dye was isolated by removal of the mother liquor by suction, washed with water (50 mL), once more dissolved in dimethyl sulfoxide (100 mL; 200 mL for **1E**) and filtered. A solution of acetic acid (1 mL) and sodium bromide (2.0 g, 19.4 mmol) in water (50 mL; for **1E**: 100 mL water, 2 mL acetic acid, 4.0 g (38.9 mmol) sodium bromide) was gently dropped into the dye solution, which was stored at 6 °C for 12 h, isolated by removal of the mother liquor by suction, washed with water (100 mL) and dried to yield dyes **1A**, $m$ = 10 and **1B**, $n$ = 1 as green powders and **1E** (1.01 g) as a red powder.

In order to workup **1A**, $m$ = 7, the reaction mixture was dropped into water (200 mL) containing acetic acid (4 mL) and sodium bromide (12 g, 117 mmol). The dye was isolated by removal of the mother liquor by suction and dissolved in 200 mL methanol. Precipitation by addition of water (50 mL), storing for 24 h at 6 °C, filtration and washing with water (100 mL) yielded **1A**, $m$ = 7.

For workup of **1A**, $m$ = 11 the reaction mixture was dropped into water (50 mL) containing acetic acid (1 mL) and sodium bromide (4 g, 38.9 mmol). The precipitate was isolated by removal of the mother liquor by suction and washed with water (50 mL). The dye was the tetrahydrate of the betaine lithium salt.

**3,3′-Bis(2-carboxyethyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine 1B, *n* = 2, 3,3′-Bis(4-carboxybutyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine 1B, *n* = 4, 3,3′-Bis(5-carboxypentyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine 1B, *n* = 5; 1,1′3,3′-Tetrakis(3-carboxypropyl)-5,5′,6,6′-tetrachlorobenzimidacarbocyanine 1D:**

The appropriate benzimidazolium bromide **6** and iodoform were similarly mixed with half the total amount of methanol according to the reaction conditions given in Table 7. The second half of the methanol, containing metallic sodium [**1B**, $n$ = 2: (0.40 g, 17.4 mmol); **1B**, $n$ = 4: (0.38 g, 16.5 mmol); **1B**, $n$ = 5: 19 g (8.26 mmol); **1D**: (0.37 g, 16.1 mmol)] was then added dropwise and the mixture were heated at reflux for 30 minutes (**1D**: 5 minutes). The reddish-violet reaction mixture was poured into a solution consisting of aqueous sodium hydroxide (1 N, 200 mL), methanol (200 mL) and sodium bromide (8.0 g, 77.7 mmol). After acidification with glacial acetic acid the precipitates of **1B**, $n$ = 2; **1B,** $n$ = 4 and **1B**, $n$ = 5 were isolated by removal of the mother liquor by suction and washed with water.

In order to purify **1B**, $n$ = 2 and **1B**, $n$ = 5, the residue was extracted hot with methanol, the extraction volume was concentrated to 150 mL under reduced pressure, and the solution was added dropwise to a solution of sodium bromide (5.0 g, 48.6 mmol) in water (150 mL). The precipitated dye was isolated by removal of the mother liquor by suction, washed with water and dried, yielding **1B**, $n$ = 2 and **1B**, $n$ = 5.

In order to isolate **1B**, $n$ = 4, the residue was dissolved in dimethyl sulfoxide (200 mL) and filtered. The filtrate was added dropwise to a solution of acetic acid (2 mL) and sodium bromide (5.0 g) in water (100 mL). After the mixture had been kept at 6 °C for 24 h, water (100 mL) was added and the precipitate was filtered off, washed with water and dried, yielding the bromide of **1B**, $n$ = 4, m.p. 98−104 °C. Recrystallization from DMSO gave the pure betaine, m.p. 203−206 °C.

Table 7. Reaction conditions for synthesis of the 5,5′,6,6′-tetrachlorobenzimidacarbocyanines

| Product | **1A**, $m$ = 7 | **1A**, $m$ = 10 | **1A**, $m$ = 11 | **1B**, $n$ = 1 | **1B**, $n$ = 2 | **1B**, $n$ = 4 | **1B**, $n$ = 5 | **1D**, see text | **1E**, see text |
|---|---|---|---|---|---|---|---|---|---|
| Starting material | **6A**, $m$ = 7 | **6A**, $m$ = 10 | **6A**, $m$ = 11 | **6B**, $n$ = 1 | **6B**, $n$ = 2 | **6B**, $n$ = 4 | **6B**, $n$ = 5 | **6D**, see text | **6E**, see text |
| (g) (mmol) | 6.60 14.2 | 2.00 3.93 | 3.50 6.70 | 2.49 5.51 | 1.94 4.16 | 3.00 6.07 | 1.53 3.01 | 2.00 4.24 | 3.00 4.03 |
| $CHI_3$ (g) (mmol) | 2.83 7.19 | 0.79 2.01 | 1.34 3.40 | 1.10 2.79 | 1.29 3.28 | 1.22 3.10 | 0.69 1.75 | 0.98 2.49 | 0.85 2.16 |
| Solvent (ml) | DMF (30) | DMF (8) | DMF (14) | DMF (10) | MeOH (16) | MeOH (16) | MeOH (8) | MeOH (8) | DMF (10) |
| Product (g) | 2.24 | 0.18 | 0.29 | 0.54 | 0.27 | 0.78 | 0.41, | 0.35, | 0.56, |
| (mmol) | 2.60 | 0.20 | 0.30 | 0.70 | 0.32 | 0.85 | 0.45 | 0.46 | 0.44 |
| Colour | red | green | green | green | red | green | green | red | red |

Table 8. Melting points, yields, empirical formulas, molecular weights, mass spectra and $^1$H NMR chemical shifts of the polymethinic 8,8′,9-H and aromatic 4,4′,7,7′ protons of the 5,5′,6,6′-tetrachlorobenzimidacarbocyanine dyes **1**

| Dye | M.p. (°C) | Yield (%) | Empirical formula | Mol. mass (g/mol) | MS[a] (*m*/*z*) | | $^1$H NMR[b] 8,8′-H | 9-H | 4,7-H | 4′,7′-H |
|---|---|---|---|---|---|---|---|---|---|---|
| **1A**, *m* = 6 | 145−146 | 9 | $C_{37}H_{47}BrCl_4N_4O_4$ | 833.56 | 754[c] | $[M + H]^+$ | 5.97 | 7.86 | 8.00 | 8.01 |
| **1A**, *m* = 7 | 126−129 | 37 | $C_{39}H_{51}BrCl_4N_4O_4$ | 861.62 | 782[c] | $[M + H]^+$ | 5.91 | 7.87 | 7.99 | 8.01 |
| **1A**, *m* = 8 | > 150[d] | 14 | $C_{41}H_{54}Cl_4N_4O_4$ * 0.5DMSO | 847.78 | 809.2961[e][f] | $[M + H]^+$ | 5.95 | 7.86 | 7.99 | 8.01 |
| **1A**, *m* = 10 | 105−109 | 10 | $C_{45}H_{63}BrCl_4N_4O_4$ | 945.73 | 866[c] | $[M + H]^+$ | 5.93 | 7.83 | 7.27 | 7.51 |
| **1A**, *m* = 11 | 128−134 | 9 | $C_{47}H_{65}Cl_4LiN_4O_4$ * $4H_2O$ | 970.87 | 905[e][g] | $[Li_2M]^+$ | 5.97 | 7.87 | 8.01 | 8.02 |
| **1B**[h], *n* = 1 | 220−224 | 26 | $C_{37}H_{46}Cl_4N_4O_4$ * $1.5H_2O$ | 779.63 | 754[e] | $[M + H]^+$ | 5.76 | 7.80 | 7.93 | 7.96 |
| **1B**, *n* = 2 | 111−117 | 17 | $C_{39}H_{51}BrCl_4N_4O_4$ | 861.57 | 782[c] | $[M + H]^+$ | 5.84 | 7.86 | 8.00 | 8.02 |
| **1B**, *n* = 4 | > 188[d] | 28 | $C_{43}H_{58}Cl_4N_4O_4$ | 836.77 | 838 | $[M + H]^+$ | 5.86 | 7.85 | 8.02 | 8.03 |
| **1B**[h], *n* = 5 | 105−111 | 30 | $C_{45}H_{62}Cl_4N_4O_4$ * $2H_2O$ | 900.85 | 866[e] | $[M + H]^+$ | 5.80 | 7.84 | 7.99 | |
| **1C**, *m* = 8, *n* = 3 | 251−255 | 25 | $C_{39}H_{53}Cl_4N_4NaO_6S_2$ * $4H_2O$ | 974.85<br>765.47 | 925[e,g] | $[Na_2M]^+$ | 5.91 | 7.88 | 8.00 | 8.08 |
| **1D** | 262−264 | 22 | $C_{33}H_{34}Cl_4N_4O_8$ * $0.5H_2O$ | | 758[e] | $[M + H]^+$ | 5.85 | 7.83 | 7.90 | |
| **1E** | 138−145 | 22 | $C_{41}H_{28}Cl_4F_{26}N_4O_4$ | 1276.47 | 1276 | $[\text{betaine}]^+$ | 5.83 | 8.04 | 7.34 | 7.44 |

[a] According to Cl/Br elemental analyses, dye **1B**, *n* = 1 contained 5% dye bromide and **1B**, *n* = 5 10% bromide. [b] Beginning of thermal decomposition according to DTA. [c] Usually the basis peak is given. With dyes **1B**, *n* = 1 and **1D** only, the masses of the molecular ions possessed relative intensities of 14% and 34%, respectively, indicating partial decomposition of the dyes during the ionization procedure. The given mass numbers of the molecular ions corresponded to the natural composition of the chlorine isotopes $^{35}Cl_3{}^{37}Cl$. [d] Split off HBr. [e] Split off solvent molecules. [f] High resolution MS, $^{35}Cl$ = 34.968853; $^{37}Cl$ = 36.965903. [g] Substitution of $H^+$ by $Li^+$ or $Na^+$, respectively. [h] Solvent: [D6]dimethyl sulfoxide, with the exception of **1A**, *m* = 10; **1A**, *m* = 11 and **1E**, the NMR spectra of which were measured in chloroform-$D_1$. The protons in the 8,8′-position give a doublet, that in 9-position a triplet with coupling constants $^3J_{8/9}$ = 13−14 Hz. Whereas the chemical shifts of the 8-H and 9-H protons were nearly independent of the nitrogen substituents in the 1- and the 3-positions, as well as of the solvent used, the singlets of the aromatic protons in the 4- and the 7-positions were significantly shifted to higher fields in chloroform than in DMSO.

For workup of **1D**, the reddish-violet reaction mixture was poured into an aqueous solution (400 mL) of sodium hydroxide (8.0 g, 200 mmol) and sodium bromide (8.0 g, 77.7 mmol) and stirred for 1 h. After filtration, acetic acid (20 mL) was added and the solution was stored for 2 d. The precipitate was isolated by removal of the mother liquor by suction, washed three times with cold ethanol (40 mL each), and heated in ethanol (80 mL) for 10 minutes. After cooling to room temperature, dye **1D** was isolated by removal of the mother liquor by suction and dried in vacuo over $P_4O_{10}$.

Melting points, yields, mass spectra and the $^1$H NMR chemical shifts of the aromatic and polymethinic protons of the dyes are compiled in Table 8.

$^1$H NMR: **1A, *m* = 6**, ([D$_6$]DMSO): δ = 0.79−0.85 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.20−1.35 (m, 12 H, 6 × $\mathrm{C}\mathit{H}_2$), 1.72−1.82 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2}$), 1.82−1.95 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2COOH}$), 2.12−2.19 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.11−4.41 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1A, *m* = 7**, ([D$_6$]DMSO): δ = 0.79−0.83 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.18−1.35 (m, 16 H, 8 × $\mathrm{C}\mathit{H}_2$), 1.71−1.80 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2}$), 1.85−1.97 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2COOH}$), 2.26−2.30 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.23−4.33 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1A, *m* = 8**, ([D$_6$]DMSO): δ = 0.78−0.82 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.16−1.35 (m, 20 H, 10 × $\mathrm{C}\mathit{H}_2$), 1.72−1.80 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2}$), 1.86−1.95 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2COOH}$), 2.20−2.28 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.20−4.35 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1A, *m* = 10**, ($CDCl_3$): δ = 0.85 (t, *J* = 6.9 Hz, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.23−1.35 (m, 28 H, 14 × $\mathrm{C}\mathit{H}_2$), 1.82−1.87 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2}$), 2.02−2.09 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2COOH}$), 2.48−2.52 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.20−4.25 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1A, *m* = 11**, ([D$_6$]DMSO): δ = 0.79−0.84 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.17−1.27 (m, 32 H, 16 × $\mathrm{C}\mathit{H}_2$), 1.72−1.80 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2}$), 1.85−1.92 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2COOH}$), 2.12−2.15 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.20−4.36 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1B, *n* = 1**, ([D$_6$]DMSO): δ = 0.80−0.83 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.20−1.35 (m, 20 H, 10 × $\mathrm{C}\mathit{H}_2$), 1.61−1.72 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2$), 4.12−4.20 (m, 4 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2}$), 5.03 (s, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CO_2H}$) ppm; **1B, *n* = 2**, ([D$_6$]DMSO): δ = 0.79−0.83 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.15−1.28 (m, 20 H, $10\mathrm{C}\mathit{H}_2$), 1.65−1.75 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.73−2.78 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{COOH}$), 4.24−4.30 (m, 4 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2}$), 4.45−4.48 (m, 4 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2COOH}$) ppm; **1B, *n* = 4** ([D$_6$]DMSO): δ = 0.78−0.83 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.19−1.27 (m, 20 H, 10 × $\mathrm{C}\mathit{H}_2$), 1.54−1.60 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2COOH}$), 1.70−1.75 (m, 8 H, $\mathrm{NCH_2C}\mathit{H}_2$), 2.22−2.27 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.29−4.47 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1B, *n* = 5** ([D$_6$]DMSO): δ = 0.78 (t, *J* = 6.8 Hz, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.13−1.30 (m, 24 H, 12 × $\mathrm{C}\mathit{H}_2$), 1.47−1.50 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2COOH}$), 1.68−1.72 (m, 8 H, $\mathrm{NCH_2C}\mathit{H}_2$), 2.02 (t, *J* = 7.1 Hz, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.24−4.29 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1C, *m* = 8, *n* = 3** ([D$_6$]DMSO): δ = 0.78−0.83 (m, 6 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.19−1.28 (m, 20 H, 10 × $\mathrm{C}\mathit{H}_2$), 1.72−1.78 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2}$), 2.04−2.08 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2S}$), 2.50−2.55 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{S}$), 4.29−4.34 (m, 4 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2CH_2}$), 4.40−4.44 (m, 4 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2S}$) ppm; **1D** ([D$_6$]DMSO): δ = 1.87−1.93 (m, 8 H, $\mathrm{NCH_2C}\mathit{H}_2$), 2.21−2.25 (m, 8 H, $\mathrm{C}\mathit{H}_2\mathrm{COOH}$), 4.21−4.26 (m, 8 H, $\mathrm{NC}\mathit{H}_2$) ppm; **1E** ($CDCl_3$): δ = 2.00−2.04 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.39−2.42 (m, 4 H, $\mathrm{NCH_2CH_2C}\mathit{H}_2$), 2.62−2.71 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CF_2}$), 4.18−4.22 (m, 4 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2}$), 4.60−4.65 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CF_2}$) ppm.

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