Influence of the N-Alkyl Chain Length on the J-Aggregation Behavior of a Cyanine Dye

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A new series of benzimidocarbocyanine dyes having different N-alkyl chain lengths (C_2–C_{12}) but the same chromophoric system was synthesized to investigate the effect of the dye structure on the photophysical properties of J-aggregate-forming dyes. For these dyes, the number of J-absorption bands depends on the chain length of the alkyl substituents, whereas the fluorescence emission spectra exhibit only a single J-band. Furthermore, an increase in the N-alkyl-chain length leads to a strong decrease in the bandwidth of the J-absorption and emission bands.

INTRODUCTION

Under appropriate conditions, cyanine dyes exhibit a narrow, intense, and, with respect to the monomer band, red-shifted absorption band which is attributed to J-aggregates. In these J-aggregates, the optical transitions of the dye molecules are coupled due to electromagnetic intermolecular interactions. Such aggregates are of great fundamental interest, especially for energy or charge transfer processes in photosynthetic and biological systems. Concerning the photographic process, J-aggregates are essential for the effective spectral sensitization of silver halide emulsions because of their narrow absorption band [1]. Although a large number of dyes have been examined, there is still little knowledge of a relationship between aggregation behavior and dye structure. For the well-studied J-aggregates of *p*seudo-*iso*cyanine (PIC), the energy migration mechanism postulated by Scheibe *et al.* [2] was confirmed by hole-

burning [3,4], photon-echo [3,5], and time-resolved fluorescence experiments [5].
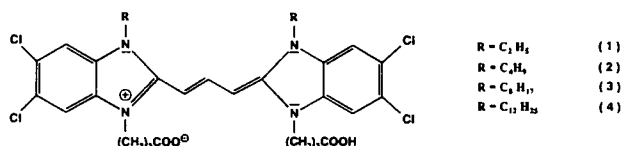
Previously, the temperature-dependent dynamics of the photophysical processes were investigated for a dye having the same chromophore as the dyes studied in this paper but with sulfonate groups replacing the carboxylate substituents [6–8]. Since it has recently been found that the aggregation behavior of polymethine-like dyes can be influenced by the chain length of the substituents [9], this parameter was varied, aiming at an enlargement of the aggregate size. In the following paper, the steady-state absorption and fluorescence spectra of 1–4 were determined to investigate the influence of the dye structure on J-aggregation and energy migration in the aggregates. Special attention was paid to an increasing bathochromic shift of the aggregate absorption bands relative to the monomer and a decrease in the bandwidth of the absorption and emission bands. Both effects sug-

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gest an increasing number of coupling molecules in these aggregates [10,11].

EXPERIMENTAL

The dyes were prepared as described in Ref. 12. Because of their low solubility in water, the dye samples were dissolved in NaOH which was diluted with doubly distilled water. The monomer spectra were obtained for solutions of the dye in methanol, where no aggregation takes place. Dye concentrations were in the range of 10^{-4} M. The absorption spectra were acquired with a UV–vis spectrophotometer (Carl-Zeiss Specord M 400) using cuvettes with layer thicknesses between 5 and 498 μm. Fluorescence spectra were performed by the front face excitation method using a Perkin–Elmer LS-50 spectrofluorometer.

RESULTS

The absorption spectra of the monomeric dyes 1–4 in methanolic solution are nearly identical, showing a maximum at 520 ± 1 nm. However, in 10^{-3} N NaOH, dyes 1–4 form J-aggregates which exhibit absorption bands with strongly different spectral positions and different bandwidths (Fig. 1). These properties are concentration independent. A dramatic change in the spectral behavior of these dyes is observed when increasing the chain length from the n-butyl (2) to the n-octyl (3) chain. Whereas for 1 and 2 only *one* J-band is found, at 595 and 587 nm, respectively, 3 and 4 exhibit an additional J-band
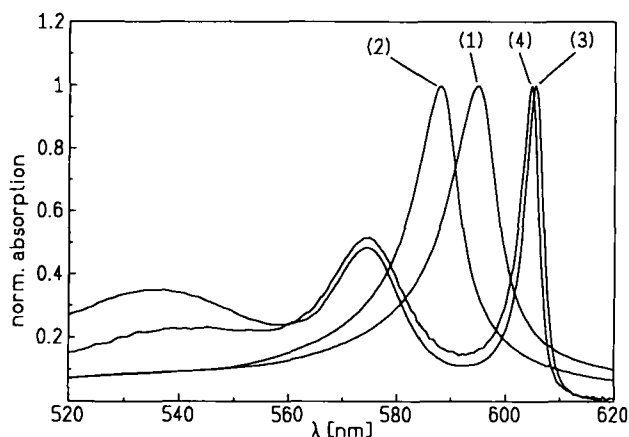
at longer wavelengths (605 and 604 nm). By increasing the chain length of the alkyl group from four to eight methylene groups, a strong decrease in bandwidth, from 349 to 118 cm^{-1}, is also achieved (Fig. 3B). Similar to the absorption spectra, the fluorescence spectra of the dye monomers show no difference between 1 and 4. For solutions of dye in 10^{-3} N NaOH, the normalized fluorescence emission spectra of 1–4 are depicted in Fig. 2. For all the dyes, only one emission band is observed. The fact that both spectral position and bandwidth are independent of the excitation wavelength in the range between 540 and 600 nm and the "red" J-band position of 3 and 4 in the absorption and emission spectra show similar spectral dependences on the chain length (Figs 3A and C) suggests that the observed fluorescence originates from the low-energy exciton transition.

Regarding a general dependence of the spectroscopic properties on the N-alkyl substituents, a continuous blue shift of the J-band with increasing chain length can be recognized taking into account the short-wavelength J-band of 3 and 4. The high-energy limit for this shift seems to be at *ca.* 573 nm. Since 3 shows both the biggest bathochromic shift of the absorption and emission bands compared to those of the monomer and the smallest bandwidth (FWHM) (Fig. 3), we assume that the N-n-octyl chain gives the best condition for J-aggregates with large coupling domains. Further examinations are in progress and will be published elsewhere.

SUMMARY

For the first time, the aim to increase the size of J-aggregates is realized simply by varying the chain length
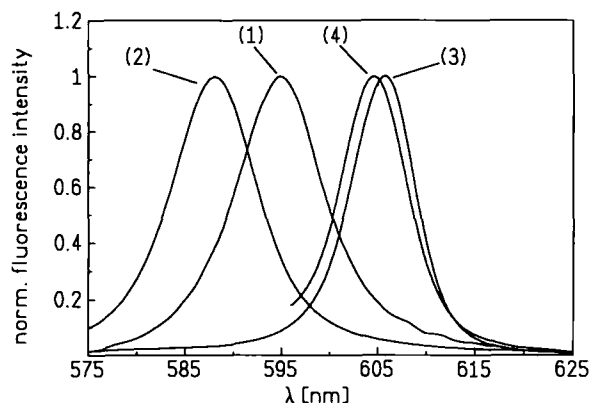

Fig. 1. Normalized absorption spectra of 1–4 in 10^{-3} N NaOH at room temperature.

Fig. 2. Normalized emission spectra of dyes 1–4 in 10^{-3} N NaOH at room temperature. Excitation wavelength: 550 nm for dyes 1–3 and 585 nm for dye 4.
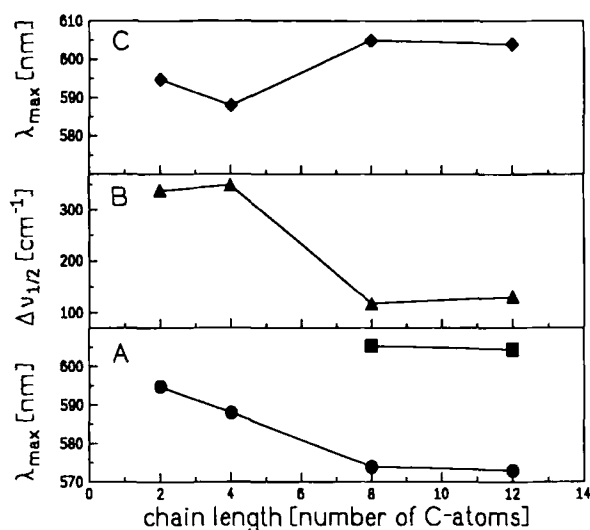
Fig. 3. Dependence of the spectroscopic characteristics on the chain length of the N-alkyl substituents. (A) Spectral position of the J-band maxima (absorption). Circles, "red" J-band; squares, "blue" J-band. (B) Bandwidth (FWHM) of the J-absorption band (for dyes 3 and 4, only the values for the "red" J-band are shown). (C) Spectral position of the J-band maxima (emission).

of the N-alkyl substituents of a benzimidocarbocyanine chromophore. Strong differences were observed regarding the number of J-bands, their bandwidth, and their spectral position. For the investigation of energy migration phenomena, dye 3 with N-*n*-octyl substituents seems

to be the most suitable one because of the large red shift and the small bandwidth of its J-band.

ACKNOWLEDGMENTS

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