

Lipophilic Optical Supramolecular Nano Devices in the Aqueous Phase

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Abstract

Nano micelles of sodium dodecyl sulphate in water were prepared as local lipophilic media for the organisation of interacting chromophores. Such arrangements were controlled by peripheric substituents to operate either as isolated chromophores or as skew oriented pairs where *H*-type transitions cause hypsochromic absorption and *J*-type transitions bathochromic fluorescence. As a consequence, large Stokes' shift could be obtained.

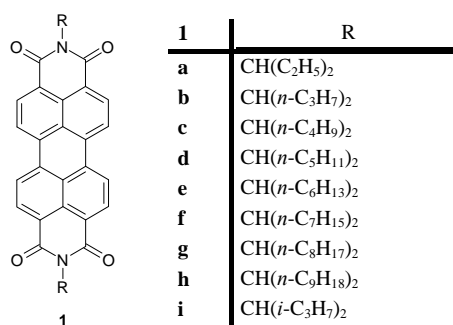
Keywords: Lipophilic Optical Supramolecular, Nano Device, Nano Micelle, Sodium Dodecyl Sulphate

1. Introduction

The investigation of light-driven processes is an attractive subject of research and will be applied in organic photovoltaic cells [1], photoelectrochemical cells (DSSC) [2], artificial photosynthesis [3] and organic conducting polymers [4]. The controlling of chromophores on the molecular scale is a prerequisite for the development of light-driven devices [4]. Commonly chromophoric systems are applied in media of similar polarity such as lipophilic systems in lipophilic media and hydrophilic system in hydrophilic ones. However, this means not only a restriction for the variety of combinations, but neglects also many possibilities given by the interaction of lipophilic and hydrophilic structures. We used such interactions for the preparation of nano micelles in order to incorporate lipophilic chromophores for their operation in the aqueous phase. Lipophilic organic chromophores in micelles of maleinated linseed oil were previously described [5], however, only isolated chromophores could be incorporated and the intrinsic light absorption of the detergent interferes with some applications of such systems. The development of more universal micellar dyes systems would bring about an appreciable progress.

2. Results and Discussion

We investigated various surfactants such as 1-dodecyl-sulphate or 2,3-dimethylnaphthalene-4-sulphonate [6] (Nekal®) and found the sodium salt of the former (SDS)



to be the most appropriate for the preparation of suitable nano micelles [7,8]. The lack of light absorption in the UVA and visible is of special advantage for optical applications. Perylene dyes [9] **1** (perylene-3,4:9,10-tetracarboxylic bisimides) were applied for incorporation into micelles because of their extraordinarily high stability and light fastness. The surfactant SDS was transformed to a gel [10], doped with dyes and then diluted with water where the application of ultra sonic is helpful, but not essential.

We applied the perylene derivatives **1a** ... **1h** where R are long-chain *sec*-alkyl groups [11] ("swallow-tail substituents") for solubilising and used the chain-lengths of R for controlling the arrangement in micelles. Unstructured nano particles could be obtained from all derivatives of **1** by means of sodium dodecyl sulphate; see **Figure 1** for the size distribution and **Figure 2** for the shape and structure. The behaviour of derivatives with short chains in R is complex: Particles with 70 nm (peak) were

obtained with the incorporation of the only slightly soluble **1a**, the size increases for **1b** to 100 nm and reaches nearly 200 nm for **1d**. **1c** is supposed to be an exception because of its labile crystal lattice [12] helping dispersion. A further increase of the chain lengths in R from **1d** to **1h** causes a successive decrease in the size of particles remarkably until below 40 nm for **1h**. The arrangement of nano particles in water remains stable for a long time: No degradation was observed over many months.

The arrangement of chromophores in the nano particles is indicated by their UV/Vis spectra reported in **Figure 3**. The spectrum of **1c** documents essentially isolated chromophores in the micelles and corresponds to the spectrum of the homogeneously dissolved **1e** in chloroform [13]. Some increase in intensity at 490 nm is found as well as a novel weaker absorption at 540 nm; compare

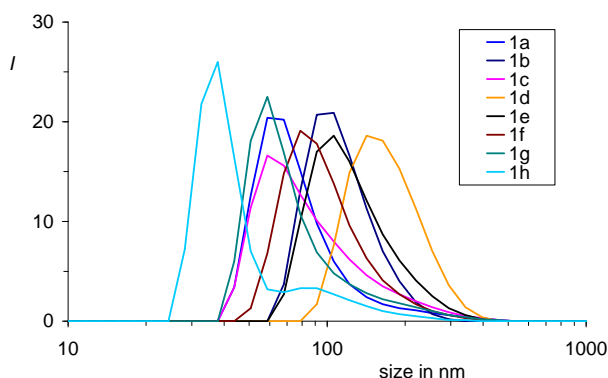


Figure 1. Size distribution of nano particles of **1** and SDS in water by DLS.

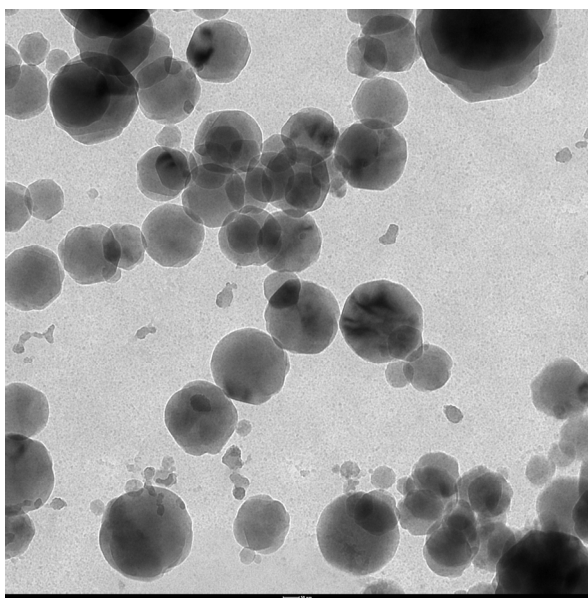


Figure 2. Cryo TEM micrograph of nano particles of **1e** and 1-dodecylsulphate in water. The diameter of the big particle left bottom left is 260 nm.

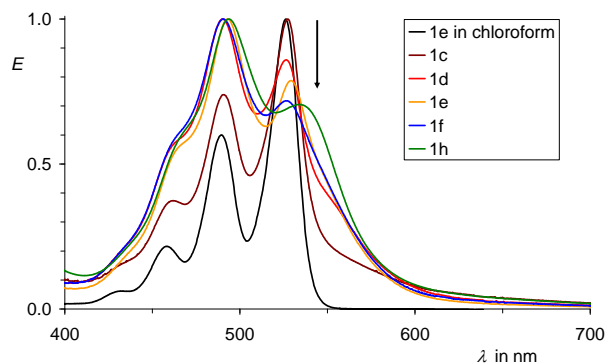


Figure 3. UV/Vis absorption spectra of derivatives of **1** in nano micelles compared with **1e** in chloroform.

Ref. [12,14]. These alterations are attributed to a minor amount of interacting chromophores. The extent of interaction can be controlled by the chain length of R in **1** where an increasing size of the aliphatic group causes a progressive damping of the absorption at 525 nm and an increase of intensity at about 490 and 540 nm. We interpret the occurrence of two novel bands as a consequence of a skew arrangement of the chromophores in the nano micellar particles where the hypsochromic *H*-type absorptions dominate over the bathochromic *J*-type according to their higher intensity [15]. The occurrence of two novel bands may be interpreted in terms of a Davydov splitting in the interacting chromophores [16] forming a more hypsochromic β - and a more bathochromic α -electronic transition compared with the isolated chromophore [5]. The intensities of these transitions depend on the orientation of the dipoles of electronic transition being parallel to the *N-N*-connection line in **1**. Collinearly oriented dipoles such as in **Figure 4**, left, favour the more hypsochromic β -transition [17] and suppress both the α -transition and fluorescence because of electrostatic interaction and symmetry of the electron movement [18]; see **Figure 4** left, and marked charges. On the other hand, a shifted arrangement of dipoles such as in **Figure 4**, right, suppresses the β -transition and allows both, the α -transition [19] and fluorescence [18]. Finally, a skew type arrangement allows both transitions where the intensities are controlled by the orientation of the transition dipoles.

The arrangements of two chromophores were further investigated by quantum chemical methods and an energetic minimum was found for the structure in **Figure 5**;



Figure 4. Arranged transition dipoles in aggregates.

the AM1 method was preferred because of many non-covalent interactions in the pair, whereas less reliable results are expected for DFT B3LYP calculations [20]. The structure of the dimer is presumably stabilised by electrostatic-interaction between electron rich and electron depleted atoms of the two dye molecules. As a consequence, a dihedral angle of some 60° between the skew arranged chromophores is formed allowing both the weak α and the strong β transition because of the dominating H -type interaction. This corresponds to the UV/vis spectra in **Figure 3** where a weaker bathochromic and a stronger hypsochromic absorption was found.

The light emission of the β -transition is symmetry forbidden and causes the fluorescence quenching of H -aggregates. This can be overcome by skew type arrangements such as in **Figure 5** where the α -transition becomes allowed. One may expect an internal energy conversion [21] from the excited electronic state of the β -transition to the excited state of the α -transition causing a bathochromically shifted fluorescence. This shift in fluorescence from isolated chromophores in the lipophilic chloroform to stacked chromophores in nano micelles reaches some 150 nm (5000 cm^{-1}) and is shown in **Figure 6**. A fine tuning can be achieved by the substituent R in **1**, both for the position of the bathochromic band of fluorescence and some residual fluorescence of isolated chromophores at 530 nm.

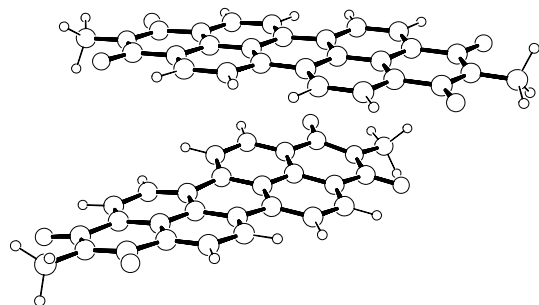


Figure 5. Calculated structure of a typical dimer of **1** with $R = \text{CH}_3$.

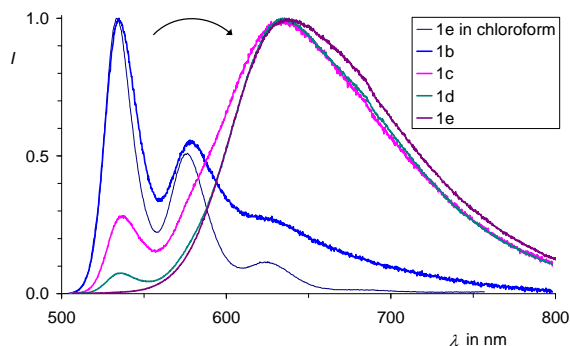


Figure 6. UV/Vis fluorescence spectra of derivatives of **1** in nano micelles compared with **1e** in chloroform.

The stacking of chromophores according to **Figure 5** is further confirmed by a comparison with the UV/Vis spectra of **2** [22]; see **Figure 7**, compare also Ref. [12,15] for comparable arrangements. The spectra of **1f** in micelles and **2** in homogeneous solution are very similar and both differ appreciably from **1e** and **1f**, respectively, in homogeneous solution; see **Figure 7**. Two chromophoric units of **1** are tied together in the cyclophane **2**. The twelve membered connecting aliphatic chains are small enough to keep the chromophores close together, but large enough to allow their optimal orientation. Thus a similar orientation as the aggregated **1f** in micelles is expected. This is indicated by the similarity of their UV/Vis spectra. Moreover, the fluorescence quantum yield of **2** is found to be 46% (integration until 900 nm) and is about the same as the fluorescence quantum yield of **1f** in the nano particles where 40% are observed. The appreciably smaller fluorescence quantum yield of the dimer of **1f** in micelles and **2**, respectively, compared with close to 100% of isolated dye molecules of **1f** in chloroform is interpreted as a consequence of similarly lower transition probability of the α -transition compared with the high transition probability for isolated chromophores.

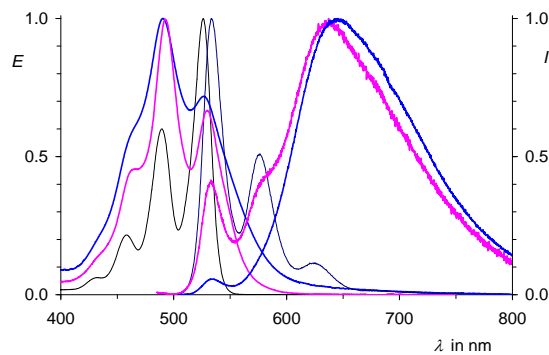
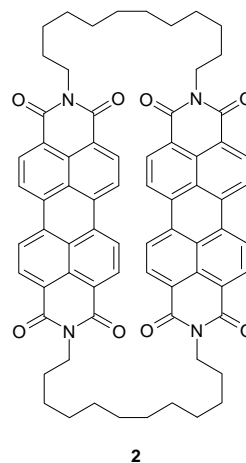


Figure 7. UV/Vis absorption (left) and fluorescence spectra (right). Blue: nano micelles of **1f**, magenta: **2** in chloroform, thin black: **1e** in chloroform.

3. Conclusion

Lipophilic chromophores can be introduced into the aqueous phase by means of micelle forming detergents such as 1-dodecyl sulphate (SDS) where local nano-dimensioned lipophilic cages were established for organising supramolecular interactions. Peripheral substituents control the interaction of chromophores by their size to form nano devices with special optical properties such as increased Stokes' shifts. This may be applied, for example, for solar energy collectors [23]. Even more complex functional structures may be constructed in such micellar nano devices.

4. Experimental

General UV/Vis spectra: Varian Cary 5000; fluorescence spectra: Varian Eclipse. The dyes **1** and **2** were prepared and purified according to the literature [11,22]. Preparation of nano particles in the aqueous phase: Sodium 1-dodecylsulphate (460 mg) and distilled water (1.7 g) were heated to 50°C to form a colourless gel. **1** (some 10 mg) and chloroform (60 mg, ca. 10 drops) were added at 50°C with subsequent ultra sonification for 10 min, treatment with distilled water (30 mL) and filtration (D5 glass filter). The nano particles in water remain unaltered for many months. Neither flocculation nor degradation of the strong fluorescence could be observed.

5. Acknowledgements

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