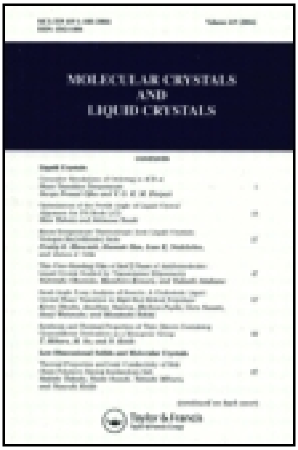

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Lars Dähne [a]

[a] Humboldt University, Berlin, FRG

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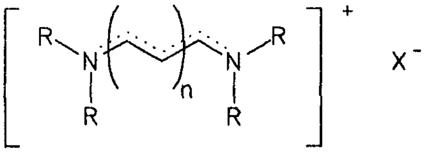
DESIGN AND SYNTHESIS OF HIGHLY POLARIZABLE ORGANIC MATERIALS

LARS DÄHNE
Humboldt University, Berlin, FRG

Abstract The intermolecular interactions in the crystalline state of bisdimethylaminoheptamethinium chloride a highly polarizable cyanine dye have been investigated. The highly dense arrangement of cations in layers results in strong interactions between them. Therefore the optical properties fluorescence and absorption differ drastically between solution and crystalline state. Furthermore the crystals show an extraordinary reflection over the whole visible region.
The four moles crystal water can be removed reversibly. This changes the transmission of the crystal. The synthesis of similar dye crystals shows, that small variations of the anions or substituents yields crystals without such strong interactions and resulting in a loss of the discussed properties.

Introduction

In concentrated solutions many dyes form one dimensional stacks of molecules[1] in consequence of their tendency of aggregation. The strenght of the aggregation depends on both the steric design and the largeness of the π-electron system.



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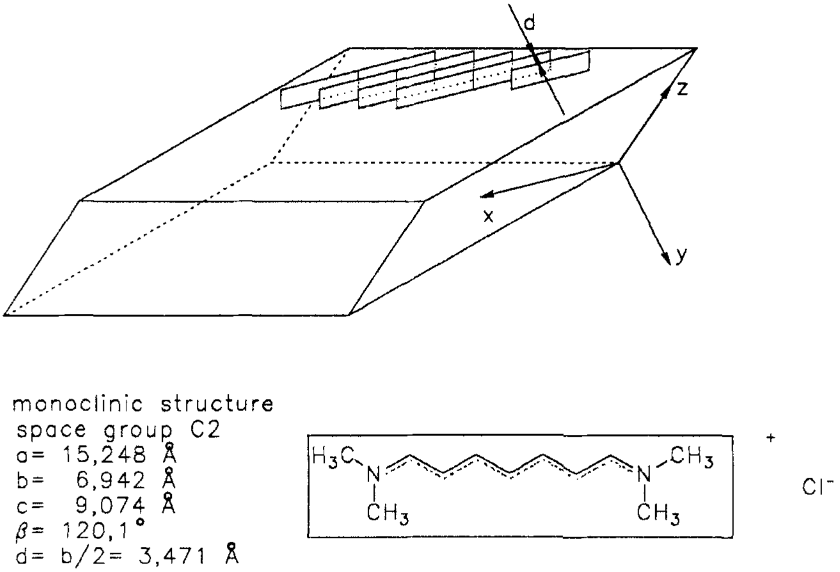
Flat polymethines **1** have an especially high tendency of aggregation[2]. The energy conduction in these aggregates was proofed by photon echo experiments[3]. As sensitizer of silver halides the polymethine aggregates conduct the excitation energy through several molecules.

In the crystalline state of polymethines KULPE[4] has proofed aggregates of dyes too. During the crystallisation the growth tendency of ionic crystals competes with the tendency of aggregates formation. FUHS et.al.[5] has published a report about polymethine crystal with strong reflectance and photoconductivity. TANAKA[6] has investigated several modifications of bisdimethylaminopentamethinium perchlorate crystals 1 (n=2) and has found an excitonic interaction energy of 0,97 eV in one form with metallic appearence.

From these examples we draw the conclusion, that dye crystals with very dense aggregation of polymethine cations may have extraordinary properties, like energy- and electron conductivity or nonlinear optical properties.

Experimental

We have found, that there are extraordinary strong interactions between the dye cations in crystals of bisdimethylaminoheptamethinium chloride 1 (n=3) (abbreviated BDHCl).



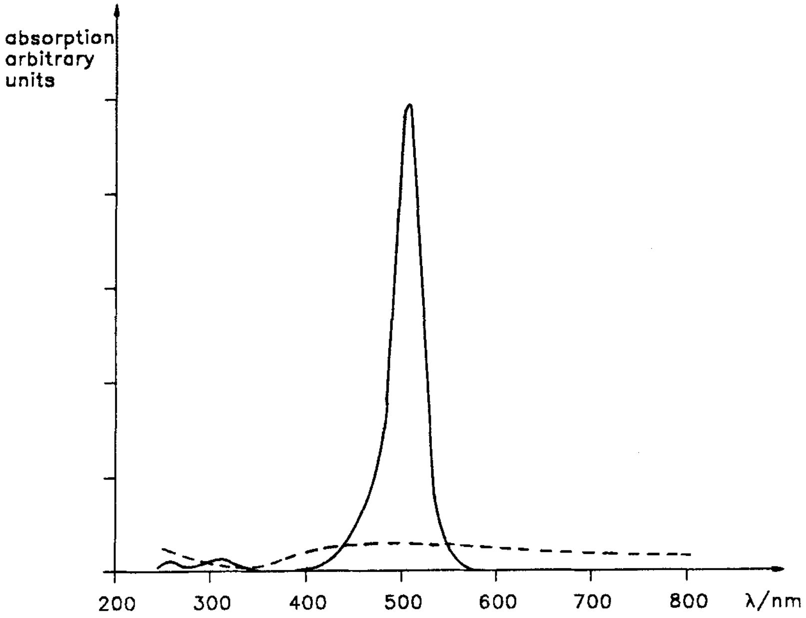
monoclinic structure
space group C2
a= 15,248 Å
b= 6,942 Å
c= 9,074 Å
β= 120,1°
d= b/2= 3,471 Å

FIGURE 1 Structure of BDHCl crystal

This compound was synthesized[7] and single crystals were cultured from the liquid phase until a length of 35 mm was reached. Compared with other organic materials the 001-face shows extraordinary high reflection about the whole visible spectral region. The X-ray analysis[8] suggestes a layer structure in a monoclinic C2-lattice (FIG.1). The distance between the moleculs in b-direction is only 3.47 A (graphit 3.35 A). The chloride anions are placed between the cation layers. Their charge is shielded from 4 water molecules each. In this case the crystal structure is dominated by the tendency of aggregation. In consequence of their unusual layer structure the crystals show additionally uncommon properties like for example reversible water exchange.

Results

1) absorption properties of the crystals



(- - -): absorption of thin crystal layer x 10
(——): absorption of methanolic solution of this crystal layer

FIGURE 2 Absorption properties of BDHCl

BDHCl shows different absorption spectra in solution and in the crystalline state (FIG.2). The sharp absorption band of the monomer in solution at 510 nm disappeares at changing the crystalline state. It is replaced by a broad band between 400 and 800 nm the absorbance of which is 100 times smaller. Considering the exciton model of KASHA[9] the very strong interactions between the cations cause a broadening of the excited singlet state. Further results concerning the absorption and the excitonic energy delocalisation by measuring the polarized reflection spectra of single crystals in depending on the direction of the crystal planes are expected for the near future.

2) fluorescence properties

The fluorescence spectra of BDHCl are different from the spectra obtained from crystal powder (FIG.3), which are depending on the excitation energy. This results to another relaxation behaviour and to other energy levels in the solid state.

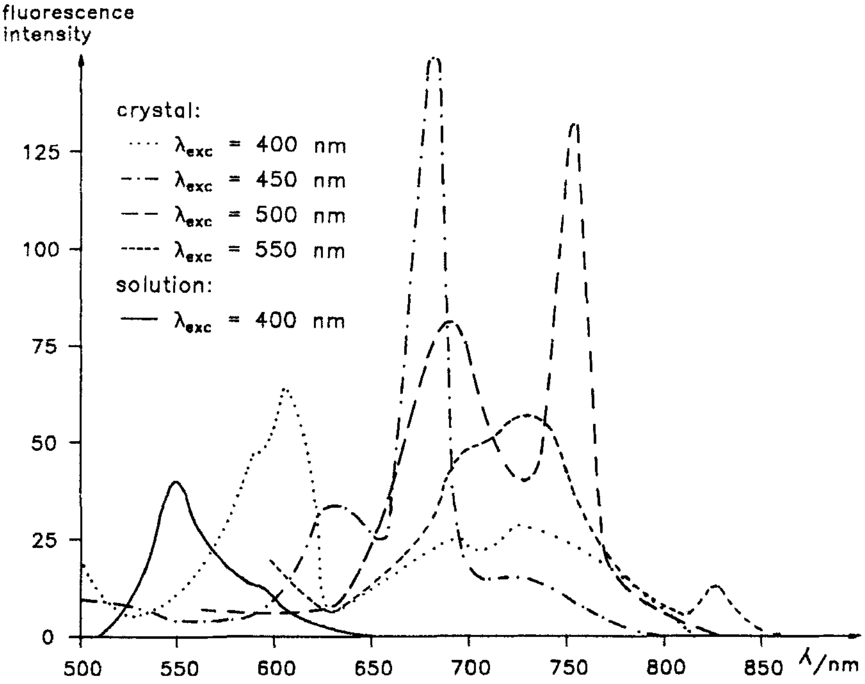


FIGURE 3 Fluorescence properties of BDHCl

3) reversible exchange of crystal water

It is possible, to remove the crystal water from BDHCl crystals by vacuum or by heat. The external structure is stable during the water extrusion (topotactic reaction). Within three days at atmospheric pressure, room temperature and 60-80 % humidity the crystals retake the four moles water in an exothermic reaction. Instead of water the crystals may also introduce D_2O. By water extrusion the absorption of crystals is enhanced and shifted to longer wavelengths.

4) influence of anions on the crystal structur

More crystals of BDH^+ were designed by means of the exchange of anions (TAB.1). Screening crystallographic investigations on powder samples show, that crystals which look a like may have several structures.

TABLE 1 salts of BDH^+

anion	morphology of crystal	some properties
Cl^-	prismatic	silvery reflection
Br^-	prismatic	silvery reflection
N_3^-	prismatic	silvery reflection
J^-	irregular polyeder	grey metallic
ClO_4^-	Needles	green gold reflection

5) synthesis of further simple heptamethines

The methylgroups were substituted by phenylgroups or hydrogen atoms. The following dyes (TAB.2) were synthesized.

TABLE 2 Synthesized dyes **1**

R_1	R_2	R_3	R_4	X^-	λ/nm	ε/l/molcm	crystal
CH_3	CH_3	CH_3	CH_3	Cl^-	510	95 000	metallic
CH_3	phenyl	CH_3	phenyl	Cl^-	553	105 000	violet
CH_3	phenyl	H	phenyl	ClO_4^-	525	115 000	blue green
H	phenyl	H	phenyl	Cl^-	592	104 000	dark blue
CH_3	H	CH_3	H	Cl^-	493	123 000	red brown
H	H	H	H	Cl^-	at -20°C decomposition		red

All these dyes despite of the first do not show metallic reflectance in the crystalline state. So we can assume, that small substituents on the open chain cyanine are necessary for strong interactions, but they don't lead to them automatically.

Conclusions:

There exist strong interactions between the π-electron systems of the BDH cations in the crystal state. That leads to a drastic alteration of the fluorescence and absorbance compared with properties in solution as well as to an extraordinary reflection. The order of cations in crystals is similar to that aggregates in solution. For these reasons it is possible , that the crystals are capable for energy or electron conduction. Results concerning conductivity are expected for the future.

Hitherto only the BHC cation with chloride, bromide and azide as anions produce such metallic crystals. All other attempts to vary the cations lead to common dye crystals without reflection. As fare as we know there are optimal interactions between polymethine cations in BDHC crystals.

References:

1)D.L.Smith, Phot.Sci.Eng. 18 (1974) 309;
S.Kulpe et al., Phot.Sci.Eng. 20 (1976) 205
2)G.Scheibe et al., Naturwissenschaften 27 (1939) 499;
Tetrahedron Lett. (1970) 3067
3)D.A.Wiersma et al., Chem.Phys.Lett. 165 (1990) 45
4)A.P.Marchetti et al., Phot.Sci.Eng. 20 (1976) 107;
J.Chem.Phys. 64 (1980) 3109
5)H.J.Hesse, W.Fuhs, Chem.Phys.Lett. 41 (1976) 104
D.Hauschild et al., Phys.stat.sol.(b) 91 (1979) 447
6)J.Tanaka et al., Bull.Chem.Soc.Japan, 53 (1980) 3109
7)B.Grimm, Dissertation A, Berlin East (1974)
8)P.Groth, Acta Chem.Scand., Ser B41 (1987) 547
9)E.G.McRae, M.Kasha, Australian J.Chem. 14 (1961) 329