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Organizing supramolecular functional dye-zeolite crystals

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Artificial photonic antenna systems have been realised by incorporating organic dyes in a microporous material.[1] We have been using zeolite L in most of our experiments as it has proven to be a very versatile host material. Zeolite L crystals are cylindrically shaped, porous aluminosilicates featuring a hexagonal symmetry. The size and aspect ratio of the crystallites can be tuned over a wide range. A nanometre sized crystal consists of many thousand one dimensional channels oriented parallel to the cylinder axis. These can be filled with suitable organic guests. Geometrical constrains of the hosts framework lead to supramolecular organisation of the guests in the channels. Thus very high concentrations of monomeric dye molecules can be realized. A special twist is added to these systems by plugging the channel openings with a second type of fluorescent dye, which we call stopcock molecule. The two types of molecules are precisely tuned to each other; the stopcocks are able to accept excitation energy from the dyes inside the channel, but cannot pass it back.

The supramolecular organization of dyes inside the zeolite channels is what we call the *first stage of organization*. It allows light harvesting within the volume of a dye-loaded zeolite L crystal and also radiationless energy transport to either the cylinder ends or centre. The *second stage of organization* represents the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite L channels, which can then trap or inject electronic excitation energy. The *third stage of organization* is realised by interfacing the material to an external device via a stopcock intermediate. We recently have observed that electronic excitation energy transfer in dye-zeolite L materials occurs along a well specified axis.[2] This important finding means that organized, unidirectional materials can be prepared. In order to achieve this, we have developed methods to synthesize zeolite L monolayers, fill them with dyes, and to finally add a stopcock.[3] These procedures and their repercussions on the design of novel materials will be discussed.

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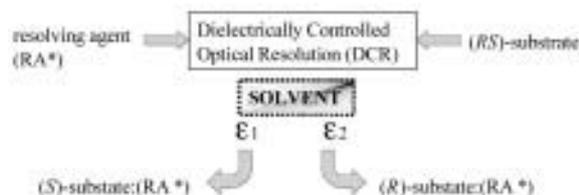
Molecular Mechanism of Dielectrically Controlled Optical Resolution (DCR)

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Optical resolution via diastereomeric salt formation method is regarded to be the most convenient for industrial-scale production of pure optical isomers. It has been generally accepted that a specific chiral resolving agent only acts on one of the stereoisomers and produces the less-soluble salt containing one stereoisomer. Therefore the opposite stereoisomer must be resolved by the enantiomorph of the chiral resolving agent based on the conventional wisdom. We recently have found that the dielectric constant (ϵ) of the solvent system significantly affects the optical resolution in several resolution systems such as (RS)- α -amino- ϵ -caprolactam with N-tosyl-(S)-phenyl alanine [1] and (RS)-1-phenyl-2-(4-methylphenyl) ethylamine with (S)-mandelic acid [2]. In these systems, by use of the dielectrically controlled resolution (DCR) method we can obtain both enantiomorphs of the target molecules to be optically selected as less-soluble salts by use of only one enantiomer of a resolution agent as shown below.



DCR is not only industrially attractive, but it is also very interesting phenomenon from scientific point of view. We are investigating molecular mechanism underlying this phenomenon. In the present study, a common molecular mechanism observed in four resolution systems including the above two examples will be discussed. Less-soluble diastereomeric salts separated from these resolution systems were crystallized and the crystal structures were compared. In the crystals of less-soluble salts obtained from solvent with larger dielectric constant, distances between hydrophilic layers or columns are significantly longer than the corresponding distances in the counterparts. Since molecular recognition between substrate and resolving agent takes place around hydrophilic regions, change of the intermolecular contacts between hydrophilic groups considerably affect molecular recognition. These examples indicate that DCR should be observed in many molecular recognition systems in general.

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