ZeoFRET® Nanochannel-Materials for Solar Energy Conversion Devices

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Assemblies, polymers, crystals, and biological structures bearing nanochannels have been studied for many decades. Examples of nano-channel materials are zeolites, zeotypes, cyclodextrins, urea based assem-blies, mesoporous silica materials, collagens, metal organic frameworks, as well as organic, carbon and metal oxide channels. All have been investigated to some extent as hosts for molecules, complexes, ions, or clusters. An infinite number of combinations and objects with different properties are, however, still waiting to be explored. One dimensional (1D) nanochannels have special properties which have recently attracted considerable attention. We distinguish between several types of 1D channels: single file, ordered assemblies, amorphous, “semicrystalline”, and crystalline. A common feature of 1D nanochannels is that they have only 2 entrances. Channels can therefore be open on both sides, plugged on one side, or plugged on both sides. This plugging can be isolating or it can be partial, allowing electrons, protons, or small molecules to pass, but blocking larger objects.[1]

The ZeoFRET® nanochannel-materials are highly organized dye-zeolite inclusion compounds with photonic antenna function. After absorption of the incident light by high local concentrations of dye molecules, the energy is transported by Förster resonance energy transfer (FRET) to an acceptor A. Large donor-to-acceptor (D:A) ratios and multi-donor systems are promising as active species in luminescent solar concentrators.[2] Large D:A ratios thereby open possibilities to reduce self-absorption while maintaining efficient light-harvesting.[3] An illustration of a zeolite L (ZL) channel with a D:A ratio of *n*:2 is shown in Fig. 1a while Fig. 2 shows the absorption and emission spectra of ZeoFRET® samples with D:A ratios of 33 and 52. In the latter case, one channel of ZL contains approximately 150 D and on average 1.5 A at each channel end.[3] These materials are

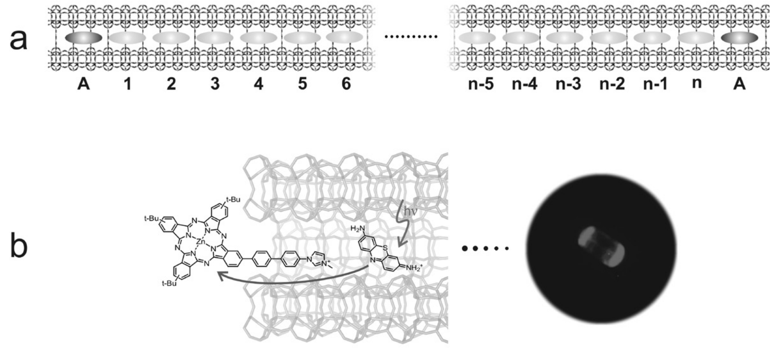

Figure 1. a) A channel of ZL containing *n* D and one A at each channel end. The D absorb the incoming light and transfer the energy to A, which subsequently emit light in a wavelength range where D do not absorb.[1] b) Energy transfer from a thionine to a ZnPc stopcock with a cationic tail and fluorescence microscopy image of a 5 μm long ZL crystal with ZnPc stopcocks located at the channel entrances.[5]

now tested for practical applications (see http://www.optical-additives.com).

Dye combinations with zinc phthalocyanine (ZnPc) molecules that are located at the entrances of the ZL channels are of interest for the sensitization of ZnPc-based solar cells.[4] However, selectively adsorbing ZnPc molecules at the channel entrances of ZL is challenging. We have therefore investigated van der Waals, electrostatic, and covalent binding, and developed methods that lead to a placement of the respective ZnPc at the ZL channel entrances in each of the three cases. Channel entrance adsorption of a ZnPc with

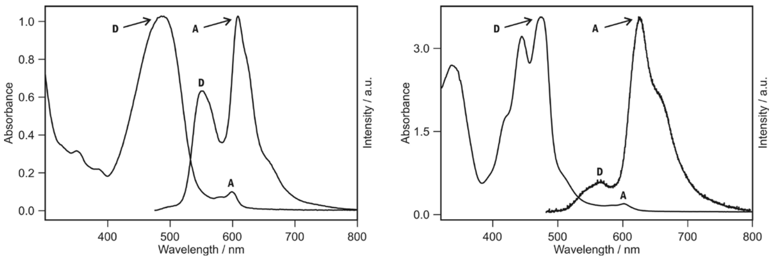

Figure 2. Left: Absorption and emission spectrum of a ZeoFRET® sample with a D:A ratio of 33. Right: The same for a sample with a D:A ratio of 52. The emission was measured upon excitation of D at 450 nm.

a cationic tail was found to be the most convenient route, making use of the exchange of charge-compensating cations in the ZL channels; Fig. 1b. Energy transfer from molecules in the ZL channels to the ZnPc molecules (acting as stopcocks) was observed.[5] The hexagonal ZL crystals can be assembled in several ways, subsequently inserting guests in the channels and adding stopcocks is possible if the free channel openings are not blocked or damaged during the preparation of the monolayer.[6]

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