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Research paper

Controlled formation of pseudoisocyanine J-aggregates in the interlayer space of synthetic saponite

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ABSTRACT

In presented work dye assemblies with J-type intermolecular coupling, which are well recognized not only for their exciton transport but also for hole and electron transport properties were investigated. The use of materials consisting of J-type dye assemblies can be significantly enhanced if their photonic properties can be controlled by some external stimuli. For these reasons the switching abilities between J-type aggregated and non-aggregated states of a cationic cyanine dye, 1,1′-diethyl-2,2′-cyanine (pseudoisocyanine, PIC) intercalated in the interlayer space of synthetic saponite (Sap) were compared. The switching was performed by adding and removing of dimethyl sulfoxide (DMSO) from the interlayer space. The PIC/Sap hybrid film prepared at 70% CEC loading level has shown excellent stability within 20 cycles of photophysical response after adding and removing of DMSO from the interlayer space, indicating that presented experimental approach can be useful in the future development of artificial light harvesting or semiconductor systems with controllable properties.

1. Introduction

Molecular switches attract intensive investigation of scientific community over the past decades (Repp et al., 2004; Liljeroth et al., 2007; Leyssner et al., 2010). To activate the functional states of molecular switches between bistable (Leoni et al., 2011) or even multiple (Auwarter et al., 2012) achievable states, different external stimuli approaches were investigated. Activation of different photonic states was achieved by application of electrons (Gopakumar et al., 2012), light (Comstock et al., 2010), electric field (Alemani et al., 2006) or even chemical modifications (Liu et al., 2013). The photonic properties of molecules can be switched by dipole orientations (Zhang et al., 2014), charge states (Swart et al., 2011), conformational change (Morgenstern, 2009), spin states (Miyamachi et al., 2012) or by chemical bond formation (Mohn et al., 2010). One of the main advantage to utilize organic molecules is that they often possess unique properties, such as monodispersity, self-assembly ability, flexible and low cost solution synthesis, etc. Therefore, the rational design of organic molecules with specific functionality and with suitable arrangements promises new devices with functions and properties that are superior to conventional devices. One of the promising low cost bottom up approach to achieve appropriate molecular arrangements is the self-assembly method, which is capable to integrate the molecules into well-ordered structures (Gunnlaugsson, 2016). A major advantage of this method is that the molecules can be immobilized and isolated in a repetitive and spatially ordered manner.

For dye molecules possessing extended planar π-electron systems it is common that, under certain conditions, the molecules can undergo a phenomenon called self-aggregation (Steiger et al., 2009). Due to excitonic coupling (Aragó and Troisi, 2015) between transition dipole moments of neighboring molecules a dramatic change of the optical properties can be observed. With respect to spatial orientation of dipoles relative to aggregate axis, the excitonic coupling between organic molecules results in H-aggregate with blue-shifted absorption band with respect to monomer or in J-aggregate exhibiting red-shifted absorption band. Presence of sharp spectral band of relatively high molar absorption coefficients located at long wavelength region is one of the most interesting property of J-aggregates. J-aggregates have attracted interest also due to their non-linear optical properties which are enhanced in comparison to their monomeric counterparts (Nakata et al., 2011). The useful properties of J-aggregates which arise from J-type brickwork arrangements (Würthner et al., 2011) in organic solid-state materials have been well recognized for exciton transport and also for electron or hole transport properties, and thus they can be employed in applications like organic field effect transistors (Ribierre et al., 2012) or artificial light-harvesting systems (Walker et al., 2010). Other applications arising from the properties of J-aggregates are spectral-hole burning phenomena (Tani et al., 1995), colorimetric and

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fluorescent sensing methods (Kaiser et al., 2007), photoinduced reductions of noble metal ions (Kirstein et al., 2006), and generation of molecular hydrogen (Königstein and Bauer, 1993).

The possibility to control the presence of various species, for example monomers and J-aggregates, with different optical properties is a very important feature and offers the opportunity to utilize the optical properties of different stable states in photonic and optoelectronic devices such as optical memories and switches (Zhao et al., 2011). J-aggregate and monomer assemblies with high degree of organization were already prepared on planar surfaces and stabilized as intercalated species on various substrates of layered, two-dimensional structures (Mashtalir et al., 2014) including phosphates (Bureš et al., 2016), niobates (Hattori et al., 2006), and silicates (Bujdák, 2014; Matejdes et al., 2015; Epelde-Elezcano et al., 2016). The switching between monomers and J-aggregates could be realized in a similar strategy as the one which was used for switching between monomers and excimer of dicationic pyridinium salts (Tominaga et al., 2016). It was believed that similar strategy would be able to change the distribution of monomer and J-aggregate species located in the interlayer space of layered silicate, by simply adding and removing of DMSO molecules from the interlayer space. The mechanism of switching is based on the swelling ability of Sap, which can incorporate water or polar organic solvents (like DMSO) into its interlayer space. Due to the solvent incorporation the interlayer space of Sap expands and the pyridinium molecules are reorganized in a different manner compared to dried state. Such mechanism enabled switching between monomer and excimer, and thus similar mechanism could be expected in hybrid layered materials containing organic molecules which are able to form J-aggregates. To date the most attention was attracted by PIC (Fig. S1) dye due to its ability to form J-aggregates (Würthner et al., 2011). Formation of the PIC J-aggregates has been reported for various types of reaction systems, e.g., solutions (Takazawa et al., 2004), interfaces (Yao et al., 2008), and for these reasons we decided to use the PIC and Sap for preparation of hybrid material with switchable optical properties.

The PIC J-aggregates formation in the interlayer space of layered silicates was published in several studies (Miyamoto et al., 2000; Bujdák and Iyi, 2008), despite this fact the hybrid material with switching properties based on monomeric and J-aggregate state has never been reported. The objective of this work is to demonstrate that the presence of different types of the PIC species, specifically PIC J-aggregates and PIC monomers, in the interlayer space of Sap can be controlled reversibly by external stimuli represented by the presence of specific solvent. We assume that the presented technique and results will be a good basis for the future development of practical systems such as artificial light harvesting or memory systems with controllable properties.

2. Experimental details

PIC, DMSO, hexane and ethyl alcohol (EtOH) were purchased from Tokyo Chemical Industry Company and used as received. The de-ionized water was purified with a Milli-Q system (Millipore). For the construction of the thin films Sumecton SA was used. This layered silicate is a commercially available synthetic saponite obtained from Kunimine Industries, Tokyo, Japan, and was used as received without any further purification. According to the product characterization data sheet the average particle diameter of Sap particles is about 50 nm. The cation exchange capacity (CEC) of Sap is 0.70 meq/g (Kunimine Industries Co. Ltd.; Kakegawa et al., 2003). The hybrid films were prepared with PIC loading levels 10, 30, 50 and 70% of PIC amount vs. the CEC of Sap. A precipitation from dispersion was observed at 80% and higher CEC loading levels, and thus loading levels above 70% were not included in the investigated sample set. In the first step, an appropriate volume of DMSO solution of PIC (5×10^{-2} mM) was gradually added to the Sap dispersion prepared by 20 min ultra-sonication. The amounts of Sap and PIC in the final dispersion volume (100 mL) are listed in Table S1. In the second step, the resulting PIC/Sap dispersion was subsequently filtered through a PTFE membrane filter with 0.1 μm pore size. In every CEC loading level the filtrate was colorless, and thus we assume that due to the high affinity of PIC towards Sap surface, the ion exchange reaction was 100% completed. In the third step after filtration, the prepared thin film was transferred from membrane onto the surface of UV–Vis transparent quartz glass slide. The quartz glass was cleaned prior to use by sonication in water for 1 h, then cleaned with 1 M sulphuric acid solution and finally washed with large amount of deionized water to remove the excess of SO_4^{2-}. Prepared thin films samples were afterwards dried at 70 °C for 20 min. The swelling step was carried out by dropping 10 μl of DMSO onto the surface of prepared hybrid film. DMSO was removed from the interlayer space of prepared hybrid films by washing the sample with 500 μl of EtOH. Remaining EtOH was subsequently removed by drying at 70 °C for 2 min.

Absorption spectra were recorded using a V-670 UV–Vis-NIR double beam absorption spectrophotometer (Jasco Co., Ltd.). UV–Vis spectrum of the prepared sample was measured in three steps: (i) right after the sample was prepared, (ii) after swelling with DMSO while the sample was immersed in hexane and (iii) after the sample was washed with EtOH and dried. The basal reflection of the sample (before and after swelling with DMSO) was measured using a multipurpose X-ray diffractometer Ultima IV (Rigaku Co., Ltd.) in the in-plane mode. For this purpose a 2θ range from 2° to 10°, using a step of 0.05° 2θ operating at 40 kV and 40 mA with CuK$_\alpha$ radiation was used. The UV–Vis absorption and XRD measurements were performed at room temperature.

3. Results and discussion

3.1. PIC J-aggregates

The photograph of prepared PIC/Sap hybrid film is shown in Fig. 1 and indicates the relatively high transparency of the film suitable for absorption measurements in the UV–Vis region.

The molar absorption coefficients of PIC/Sap hybrid film in air (before and after swelling with DMSO) at the PIC loading level 70% of CEC compared with solution of PIC in DMSO are shown in Fig. 2. The spectral integral values reached comparable levels (PIC/Sap film before swelling = 0.56 L mol^{-1}, PIC/Sap after swelling = 0.57 L mol^{-1} and PIC solution = 0.53 L mol^{-1}). The highest molar absorption coefficient of PIC in DMSO solution was located at 530 nm (ε = 83.800 L mol^{-1} cm^{-1}) and 498 nm (ε = 55.000 L mol^{-1} cm^{-1}), accompanied by vibronic shoulder in shorter wavelength region. These transitions are assigned to PIC monomeric molecules (Würthner et al., 2011), and in the case of PIC/Sap hybrid film these monomer bands are slightly shifted to shorter wavelengths, specifically to 528 nm and 492 nm. Observed spectral shifts are related to the adsorption of PIC onto the Sap particles. It is known, that the surface of layered silicates is less polar than DMSO (Schoonheydt and Johnston, 2013), and thus the observed shift can be explained by a change in the polarity of the surroundings. The absorption spectra of PIC/Sap hybrid film before swelling with DMSO revealed

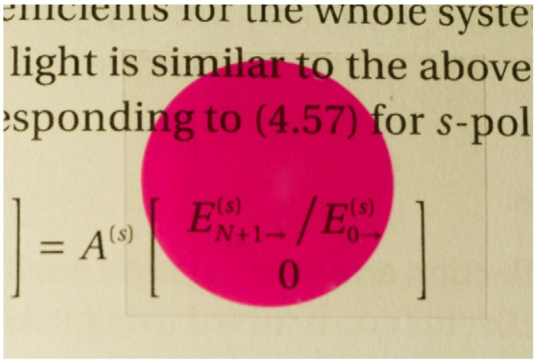

Fig. 1. Photograph of PIC/Sap thin film prepared at 70% CEC loading level.