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

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Abstract

In presented work were investigated 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. 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 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.

Keywords: swelling; organic-inorganic hybrid material; cyanine dye; absorption spectroscopy; optical switches

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 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 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 from 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 base 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 commercially available synthetic saponite obtained from Kunimine Industries, Tokyo, Japan, and was used as received without any further purification. According to the producers 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 dispersion prepared by 20 minutes ultra-sonication. The amounts of Sap and PIC in the final dispersion volume (100 ml) are listed in Tab. 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 toward Sap surface, the ion exchange reaction was 100% completed. In the third step after filtration, 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 hour, afterwards cleaned with 1 M sulphuric acid solution and finally washed with large amount of deionized water to remove the excess of SO_4^{2-} anions. Prepared thin films samples were afterwards dried at 70°C for 20 minutes. The swelling step was carried out by dropping a 10 μl of DMSO onto the surface of prepared hybrid film. The step in which the DMSO was removed from the interlayer space of prepared hybrid film was done by washing the sample with 500 μl of EtOH. Remaining EtOH was subsequently removed by drying at 70°C for 2 minutes.

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 kept during the measurement 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_α radiation was used. The UV-Vis absorption and XRD measurements were done 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.

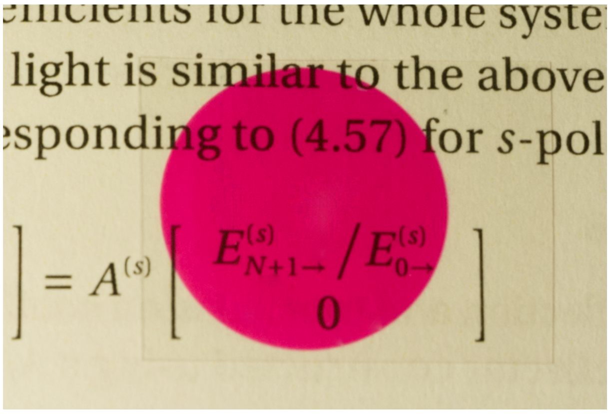

Fig. 1. Photograph of PIC/Sap thin film prepared at 70% CEC loading level.

The molar absorption coefficients of PIC/Sap hybrid film on 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 magnitude levels (PIC/Sap film before swelling = 0.56 $\mathrm{L \cdot mol^{-1}}$, PIC/Sap after swelling = 0.57 $\mathrm{L \cdot mol^{-1}}$ and PIC solution = 0.53 $\mathrm{L \cdot mol^{-1}}$). The highest molar absorption coefficient values of PIC in DMSO solution were located at 530 nm ($\varepsilon = 83800$ $\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}$) and 498 nm ($\varepsilon = 55000$ $\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}$), 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 an emerging shoulder at 569 nm, which according to Bujdák (Bujdák and Iyi, 2008) corresponds to PIC J-aggregate. The PIC J-aggregate band located at 569 nm ($\varepsilon = 86000$ L·mol^{-1}·cm^{-1}) became sharper and more intense after the PIC/Sap hybrid film was swollen with DMSO.

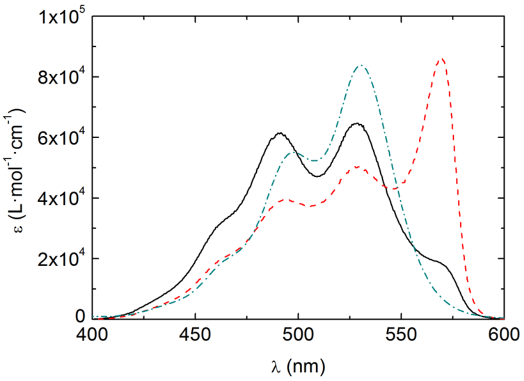

Fig. 2. Molar absorption coefficients of the PIC/Sap hybrid film at 70% loading vs CEC before swelling (black solid line), after swelling with DMSO (red dashed line) and PIC solution in DMSO (blue dash-dotted line).

The phenomenon of PIC J-aggregates formation was already observed in aqueous solution with high PIC concentration independently by Jelley (Jelley, 1936) and Scheibe (Scheibe et al., 1937) 80 years ago. They came to the conclusion that this considerable spectral change is a result of the vicinity effect of the adjacent PIC molecules and as such can be effectively mimicked in the interlayer space of Sap.

3.2. Effect of the CEC loading level on the formation of PIC J-aggregates

The absorption spectra of PIC/Sap hybrid films at various CEC loading levels were measured in time, and the resulting molar absorption coefficients are shown in Fig. 3. The inclusion of time parameter in these measurements is important because this parameter is able to reveal any ongoing changes occurring in studied samples. The matrices were divided into three sections (Fig. 3b) and each matrix corresponds to one sample.

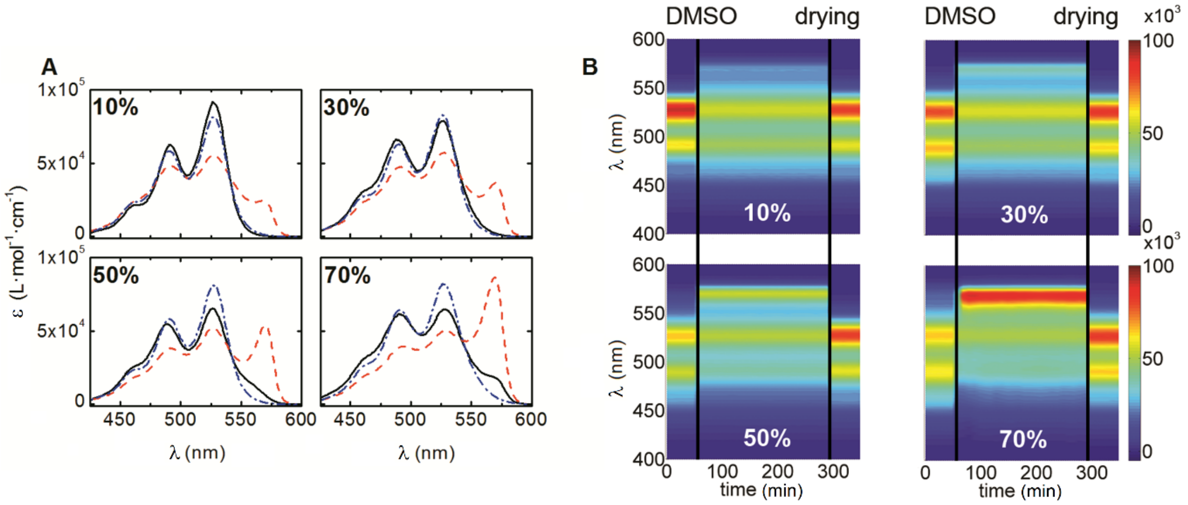

Fig. 3. Molar absorption coefficients of PIC/Sap hybrid films obtained from UV Vis absorption measurements (CEC loading levels are indicated in figures). (a) Spectra taken before swelling (black solid line, t = 0 min), after swelling (red dashed line, t = 180 min) and after DMSO removal by washing and drying process (blue dash-dotted line, t = 290 min). (b) Molar absorption coefficients obtained from time UV Vis absorption measurements (Δt = 10 min). The color coded z-axis represents molar absorption coefficient (L·mol^{-1}·cm^{-1}). Times when DMSO was applied and removed by washing and drying process are indicated by vertical black lines, which divide the data matrices into 3 sections. First section contains measurements which were obtained prior to swelling with DMSO, measurements in the second section were obtained after swelling with DMSO, while the sample was immersed in hexane. The third section contains measurements which were taken after the sample was washed with EtOH and dried at 70°C for 5 minutes.

It was found that the immersion of the sample into hexane was essential because the formation of PIC J-aggregates without hexane was only temporary in the order of few tens of minutes (Fig. S2). We assume that this behavior was caused by the hygroscopicity of DMSO. Presence of water molecules in the interlayer space of the sample does not allow an effective orientational reorganization of the organic molecules (Takagi et al., 2010), and thus, the equilibrium between PIC species was shifted towards PIC monomers. To suppress absorption of water from air, hexane which is immiscible with water and also with DMSO was used. The application of hexane keeps at same time DMSO molecules trapped in the interlayer space, and thus, the PIC J-aggregates can be stabilized over a long period of time (Fig. S3). The molar absorption coefficients of PIC/Sap samples before swelling with DMSO shows differences in spectral response. At higher CEC loading levels an emerging shoulder at 569 nm was observed indicating a minor formation of PIC J-aggregate (Fig. 3a). To estimate the organization of PIC molecules in the interlayer space, an X-ray diffraction (XRD) measurement was performed to obtain information about changes in the first basal reflection. The height of the interlayer space occupied with PIC cations was calculated as the difference between the measured d001-value and the known thickness of the Sap layer (0.96 nm). The formation of PIC J-aggregates in PIC/Sap samples at higher CEC loading levels prior to application of DMSO is caused by a closer arrangement of PIC molecules at the surface of Sap. This assumption was confirmed also by the XRD measurements in which the height of the interlayer space with respect to CEC loading level systematically increased from 0.52 to 0.76 nm, indicating a partial overlap between adjacent PIC molecules (Fig. 4). After swelling with DMSO the height of the interlayer space increased to approx. 1.32 nm and a significant PIC J-aggregate formation was observed at 569 nm (Fig. 3).

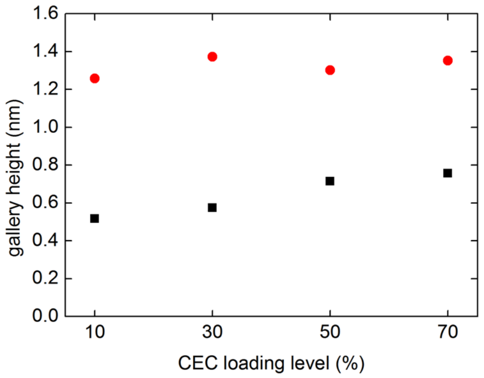

Fig. 4. Interlayer space height of PIC/Sap hybrid films prepared at different CEC loading levels before (black squares) and after swelling with DMSO (red circles).

The proximity of adjacent PIC molecules can be controlled, as can be seen from Figs. 3a and 3b, by the used CEC loading level. The CEC loading level directly influenced the observed spectral response between PIC monomers and PIC J-aggregates in PIC/Sap samples. After swelling with DMSO, the composition between PIC species is with increasing CEC loading level shifted towards PIC J-aggregates. To emphasize the effect of the CEC loading level the ratio between molar absorption coefficients of J-aggregate band at 569 nm and of monomer at 492 nm with respect to CEC loading level has been evaluated (Fig. 5). Obtained results indicate that the CEC loading level is an important parameter which can be used to control required relative distribution of PIC monomers and PIC J-aggregates. Another interesting feature of PIC/Sap films prepared at 10, 30 and 50% CEC loading levels was that their absorption spectra after washing out the DMSO with EtOH and drying was similar to the shape of the absorption spectra prior to application of DMSO (Figs. 3a and 3b). This behavior indicates the swelling reversibility, because removal of DMSO molecules from the interlayer space results in the return of PIC species to their initial state.

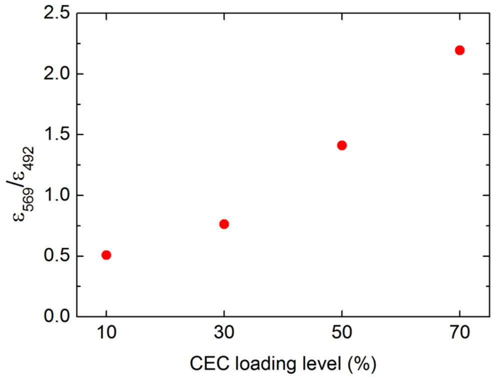

Fig. 5. Ratio between the values of molar absorption coefficients at 569 and 492 nm observed for PIC/Sap hybrid films prepared at different CEC loading levels.

3.3. Switching properties of PIC/Sap film

In the previous subsection was shown that the presence of the PIC species, specifically PIC J-aggregates and PIC monomers, in the interlayer space of Sap can be controlled by adding and removing of DMSO. The most suitable sample for the demonstration purposes of switching properties is the PIC/Sap sample prepared at 70% CEC loading level. Fig. 6 shows the variation in the absorbance recorded at 569 nm. The observed variation is a consequence of repeating steps during which the sample was swollen with DMSO, washed with EtOH and dried. After swelling with DMSO the absorbance at 569 nm reached values around 1.7. indicating the presence of PIC J-aggregates. The absorbance decreased to values about 0.1. after the PIC molecules rearranged to monomers as a consequence of the removal of the DMSO molecules from the interlayer space of Sap by application of EtOH washing with consequent drying. These results proved that the prepared hybrid films can be switched between two stable states by an external stimuli, and can be further utilized as a molecular switch.

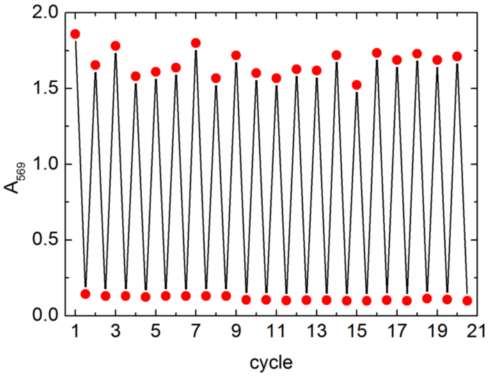

Fig. 6. Variation of the absorbance recorded at 569 nm after repeated DMSO application and DMSO removal steps. As sample was used PIC/Sap hybrid film prepared at 70% CEC loading level.

4. Conclusion

In this study was examined the effect of the CEC loading level onto the PIC J-aggregate vs. PIC monomer species formation in the interlayer space of synthetic saponite. It was found that this parameter has significant influence onto the PIC species arrangements and interactions. After swelling with DMSO the amount of PIC J-aggregates significantly increased. When the DMSO molecules have been removed from the interlayer space of the PIC/Sap samples the PIC species arrangements returned to state which was observed prior to application of DMSO. The reversible switching between PIC monomer and PIC J-aggregate have been demonstrated at the PIC/Sap hybrid film prepared at 70% CEC loading level. Within 20 repetition cycles the sample after swelling step has not shown systematic decrease in absorbance. As the switching between PIC monomers and PIC J-aggregates is not accompanied by a change in the chemical structure, the achieved repeatability can be higher than in molecular switches based on chemical structure change, what makes these systems more attractive for practical applications. Despite the fact that the PIC J-aggregates formation in the interlayer space of layered silicates was published in several studies, the reversible formation of PIC J-aggregates and PIC monomers in hybrid films is demonstrated in this study for the first time. It can be assumed that the presented technique will be useful in the future development of practical systems such as artificial light harvesting systems with controllable properties.

Acknowledgements

Our gratitude belongs to Dr. M. Janek who has helped to improve the language and style of this manuscript. This work was supported by JSPS KAKENHI Grant Numbers JP15F15742, JP15K13676. This publication is the result of the project for overseas researchers under postdoctoral fellowship of Japan Society for the Promotion of Science.

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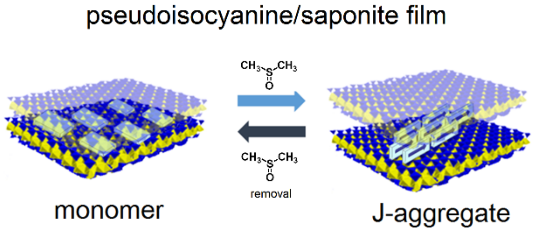
Graphical abstract



Supporting information

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

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Tab. S1. Composition of the final dispersion.

CEC loading level (%)			10, 30	50, 70		
weight of Sap (mg)			0.394	0.197		
amount of PIC (10^{-5} mmol)			2.76[a]/8.27[b]	6.90[c]/9.65[d]		

[a] at 10% CEC loading level
[b] at 30% CEC loading level
[c] at 50% CEC loading level
[d] at 70% CEC loading level

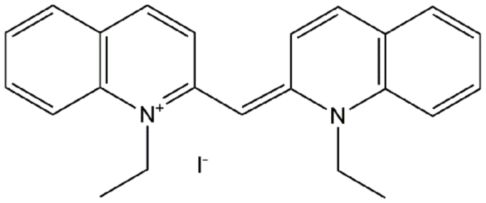

Fig. S1. Structural formula of pseudoisocyanine.

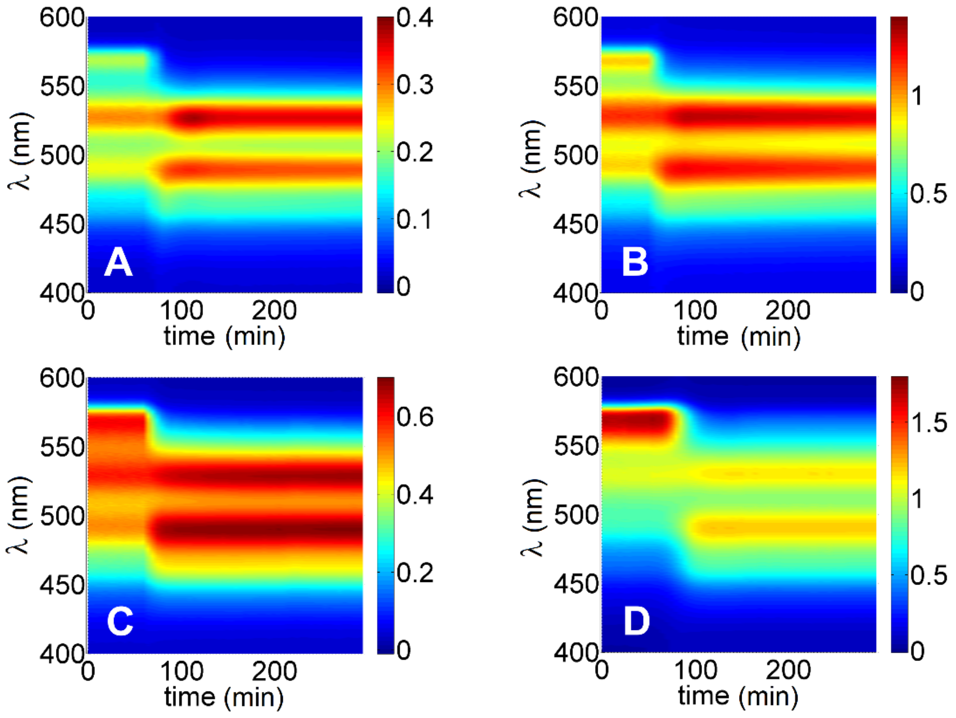

Fig. S2. Temporary formation of PIC J-aggregates in PIC/Sap hybrid films prepared at (a) 10%, (b) 30%, (c) 50% and (d) 70% CEC loading level. The measurements were taken right after application of DMSO (Δt = 5 min). The color coded z-axis represents the absorbance.

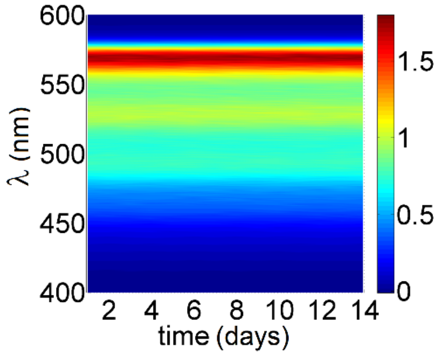

Fig. S3. Stabilization of PIC J-aggregates in PIC/Sap hybrid film prepared at 70% CEC loading level. The sample was after application of DMSO kept in hexane for 14 days. Measurements were taken after every 24 hours. The color coded z-axis represents the absorbance.