



# The effect of the negative charge density on switchable properties of pseudoisocyanine dye



Marián Matejdes<sup>a,c,\*</sup>, Daisuke Himeno<sup>b</sup>, Yasutaka Suzuki<sup>a</sup>, Jun Kawamata<sup>a</sup>

<sup>a</sup> Graduate School of Medicine, Yamaguchi University, Yamaguchi 753-8512, Japan

<sup>b</sup> Graduate School of Science and Engineering, Yamaguchi University, Yamaguchi 753-8512, Japan

<sup>c</sup> Slovak Academy of Sciences, Institute of Inorganic Chemistry, Dúbravská cesta 9, SK-84536 Bratislava, Slovakia

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## ABSTRACT

The effect of Na-montmorillonite (Mt) and synthetic stevensite (Ste) on the switchable properties of intercalated cationic cyanine dye, 1,1'-diethyl-2,2'-cyanine (pseudoisocyanine, PIC) was investigated. The switching between non-aggregated and J-type aggregated states of PIC was performed by adding and removing of dimethyl sulfoxide (DMSO) from the interlayer space. It was found that the photophysical properties of PIC after addition of DMSO are significantly influenced by the negative charge density of layered silicate. Due to this effect the J-type aggregates were after swelling with DMSO formed only in the PIC/Mt hybrid films. Photophysical response and the stability of PIC species in PIC/Mt hybrid film was tested within 20 cycles of adding and removing of DMSO from the interlayer space. During these cycles the stability of PIC species was proved to be sufficient, indicating that presented experimental approach is able to enhance the use and scope of materials consisting of J-type dye molecular assemblies.

## 1. Introduction

Molecular switches are of great interest over the past decades (Liljeroth et al., 2007; Leyssner et al., 2010). Activation of functional states of molecular switches can be achieved by different external stimuli approaches, for example by electrons (Gopakumar et al., 2012), light (Comstock et al., 2010), or electric field (Alemani et al., 2006). Advantage which arises from the utilization of organic molecules in molecular switches is that they often possess properties, such as monodispersity, self-assembly ability, etc. New devices with properties that are superior to conventional devices can be build up from molecules with specific functionality, and nowadays one of the promising low cost bottom up approach capable to integrate molecules into well-ordered structures is the self-assembly method (Gunnlaugsson, 2016).

Dye molecules with extended planar  $\pi$ -electron systems can under certain conditions undergo a phenomenon called self-aggregation (Steiger et al., 2009). Mutual interaction between transition dipole moments of neighboring molecules can result in excitonic coupling (Aragó and Troisi, 2015) which can affect the optical properties dramatically. In general, excitonic coupling gives rise to formation of H-type and J-type assemblies. J-type assembly exhibit red-shifted sharp absorption band of relatively high molar absorption coefficient, and is

recognized for its exciton transport and also for electron and hole transport properties (Gao et al., 2015). Due to these properties it can be utilized in several applications, like organic field effect transistors (Ribierre et al., 2012) or artificial light-harvesting systems (Walker et al., 2010).

Controlling the presence of various species, for example monomers and J-aggregates, with different optical properties is 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). Highly organized J-aggregate and monomer assemblies 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; Shinozaki and Nakato, 2004), and silicates (Bujdák, 2014; Matejdes et al., 2015; Sasai et al., 2009). In order to preserve the transparency of functional materials in optical frequency region, smectite type clay minerals as inorganic hosts are often employed (Epelde-Elezcano et al., 2016). Due to the isomorphic substitutions occurring in their octahedral or tetrahedral sheet, they possess a negative layer charge which is compensated by exchangeable inorganic cations located in the interlayer space (Brigatti et al., 2013). The extent of isomorphic substitutions determines the ability of the smectite type clay mineral to absorb

\* Corresponding author at: Graduate School of Medicine, Yamaguchi University, Yamaguchi 753-8512, Japan.  
E-mail address: [marian@yamaguchi-u.ac.jp](mailto:marian@yamaguchi-u.ac.jp) (M. Matejdes).

cationic or polar species, and is expressed by cation exchange capacity (CEC) parameter. It is generally known, that the CEC value significantly influences the way how the organic species are distributed in the interlayer space (Bujdák, 2006). Relationship between the value of CEC and the distribution of methylene blue at the surface of montmorillonites with reduced layer charge was shown by Bujdák and Komadel (1997). This study confirmed that high CEC value promotes the formation of methylene blue aggregates, while low CEC value rather maintain the dye in monomeric form. This behavior can be explained in terms of different intermolecular distances, which are shorter for high CEC values, and longer for lower CEC values. It was shown that the ratio between monomeric and aggregated form of methylene blue can be controlled by the CEC, and thus the methylene blue was later used as a probe with the ability to determine the CEC values of clay minerals (Czimerova et al., 2006).

The orientational behavior of dicationic porphyrins at the surface of Sumecton SA (Sap) in various solvents has been studied by Eguchi et al. (2013). Within this study, it was found that the porphyrin molecule is oriented in parallel fashion with respect to surface of clay mineral, if the used solvent is protic, and in tilted fashion, if the solvent is aprotic. The main parameter responsible for different orientational behavior is the ability of the solvents to form H-bonds. This statement was proved by the thermodynamic study which showed that the hydrophobic interaction between porphyrin hydrophobic moiety and the clay mineral surface is more effective in protic and not effective in aprotic solvent. We believe that in terms of orientational change the PIC molecule behaves in similar fashion like previously described porphyrin molecule. The switching between PIC monomers and PIC J-aggregates intercalated in the interlayer space of Sap has been already realized in our previous study (Matejdes et al., 2017). Switching strategy is based on simple adding and removing the DMSO molecules from the interlayer space. Presence of DMSO molecules in the interlayer space increases the height of the interlayer space and also induces orientational change of PIC molecules which may result in effective excitonic coupling, or in other words, in the formation of J-aggregates. In this work, two different smectite type clay minerals were used, Ste and Mt. They differ not only in their particle size and CEC, but also in their structure. Ste has trioctahedral structure and the isomorphous substitutions are located in the tetrahedral sheet, whereas Mt has dioctahedral structure with the isomorphous substitutions located in the octahedral sheet (Brigatti et al., 2013). The objective of this work is to demonstrate the effect of negative charge density on the formation of PIC J-aggregates after swelling with DMSO, and to compare these results with results obtained for Sap in our previous study. We assume that the presented results will be a good basis for the future development of practical 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 deionized water was purified with a Milli-Q system (Millipore). For the construction of the thin films were used Ste and Mt. These layered silicates (LS) were obtained from Kunimine Industries, Tokyo, Japan, and were used as received without any further purification. According to the product characterization data sheet the average particle diameter of Ste is about 40 nm. The diameter of the Mt particles is larger and fall in the range 300–1000 nm. The cation exchange CEC of Ste and Mt are 0.40 and 1.15 meq/g, respectively (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 used LS. In the first step, an appropriate volume of DMSO solution of PIC ( $5 \times 10^{-5}$  M) was gradually added to LS dispersion prepared by 20 min ultra-sonication. The amounts of used LS and PIC in the final dispersion volume (100 mL) are listed in Table 1. In the second step, the resulting PIC/LS dispersion was subsequently filtered through a PTFE

**Table 1**  
Composition of the final suspensions.

	Ste		Mt	
	10, 30	50, 70	10, 30	50, 70
CEC loading level (%)	10, 30	50, 70	10, 30	50, 70
weight of LS (mg)	0.690	0.345	0.240	0.120
amount of PIC ( $10^{-5}$ mmol)	2.76 <sup>a/</sup> 8.28 <sup>b</sup>	6.90 <sup>c/</sup> 9.66 <sup>d</sup>	2.76 <sup>a/</sup> 8.28 <sup>b</sup>	6.90 <sup>c/</sup> 9.66 <sup>d</sup>

<sup>a</sup> 10% CEC loading level.

<sup>b</sup> 30% CEC loading level.

<sup>c</sup> 50% CEC loading level.

<sup>d</sup> 70% CEC loading level.

membrane filter with 0.1  $\mu$ m pore size. In every loading level the filtrate was colorless, and thus we assume that due to the high affinity of PIC toward LS 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  $\text{SO}_4^{2-}$ . Prepared thin films samples were afterwards dried at 70 °C for 20 min. The swelling step was carried out by dropping 10  $\mu$ l of DMSO onto the surface of prepared hybrid film. DMSO was removed from the interlayer space of prepared hybrid film by washing the sample with 500  $\mu$ l of EtOH. Remaining EtOH was subsequently removed by drying at 70 °C for 2 min.

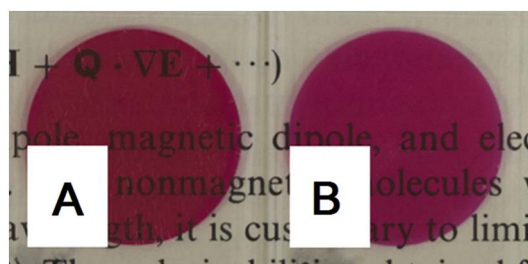
Absorption spectra were recorded using a V-670 UV-Vis-NIR double beam absorption spectrophotometer (Jasco Co., Ltd.). UV-Vis spectrum of the prepared sample was measured in three steps: (i) right after the sample was prepared, (ii) after swelling with DMSO while the sample was immersed in hexane and (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  $2\theta$  range from 2° to 10°, using a step of 0.05°  $2\theta$  operating at 40 kV and 40 mA with  $\text{CuK}\alpha$  radiation was used. The UV-Vis absorption and XRD measurements were performed at room temperature.

In order to compare the effect of layered silicate on the J-aggregates formation, the negative layer charge has been calculated. Details of the calculation method are reported elsewhere (Bujdák and Iyi, 2008). The ratio between monomeric and J-aggregated PIC molecules in Mt films has been evaluated with SVD-ALS algorithm by analyzing data obtained from UV-Vis measurements (Maeder, 2007).

## 3. Results and discussion

### 3.1. PIC J-aggregates

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



**Fig. 1.** Photograph of (A) PIC/Ste and (B) PIC/Mt thin films prepared at 70% CEC loading level.

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