Self-standing films of tetraindolyl derivative and saponite clay mineral with reversible colour switching properties

Surajit Sarkar\textsuperscript{a}, Barnali Deb\textsuperscript{b}, Bapi Dey\textsuperscript{a}, Sudip Suklabaidya\textsuperscript{a}, Santanu Chakraborty\textsuperscript{c}, Debajyoti Bhattacharjee\textsuperscript{a}, Swapan Majumdar\textsuperscript{a},\textsuperscript{**} Yasutaka Suzuki\textsuperscript{d}, Jun Kawamata\textsuperscript{d,***}, Syed Arshad Hussain\textsuperscript{a,***}

\textsuperscript{a} Thin Film and Nanoscience Laboratory, Department of Physics, Suryamaninagar, Agartala, 799022, West Tripura, Tripura, India
\textsuperscript{b} Department of Chemistry, Tripura University, Suryamaninagar, Agartala, 799022, West Tripura, Tripura, India
\textsuperscript{c} Department of Physics, NIT Agartala, Jiraniya, Agartala, 799046, West Tripura, Tripura, India
\textsuperscript{d} Department of Chemistry, Faculty of Science, Yamaguchi University, Yoshida, Yamaguchi, 753-8512, Japan

A B S T R A C T

Functional nanosized two-dimensional clay mineral particles are considered as ideal host materials to manipulate the properties of incorporated organic molecules due to their high cation exchange capacity, layer structure and intercalation properties. The interlayer height of clay layers can be manipulated by simultaneous wetting and drying steps. Here, we have studied the chromatic behaviour of an organic dye generated in-situ from 1,4-di-bis-indolymethylene-benzene in the interlayer space of synthetic saponite (SSA). Initially transparent, self-standing organo-clay hybrid films become red upon heating due to aerobic oxidation suggesting in-situ generation of organic dye and increases the planarity of the intercalated organic molecules. Upon swelling the same hybrid film becomes yellow, due to the partial disturbance in the planarity of generated dye via C-C bond rotation. Simultaneous heating and swelling resulted in a reversible colour transition (clearly visible through the naked eye) between red and yellow for at least 30 cycles. This kind of system may have potential applications as a colorimetric sensor and in the field of optics (optical switching and optical memory etc).

1. Introduction

The dependence of spectroscopic and physicochemical behaviour of molecular assemblies upon the molecular arrangement is a topic of current research. The properties of the molecules depend not only on their structure but also on their pattern of the organization when confined in various nano-sized spaces and in ultrathin films [1–5]. It has been observed that the photophysical and photochemical properties of dyes change markedly when incorporated into various host materials, such as micelles, mesoporous materials, zeolites, and swelling clay minerals with respect to the properties of these molecules in solution and in pure form [6–11]. In particular, the modulation of the optical properties is of increasing interest for the development of new generations of functional molecular materials, notably in the fields of optical communication and data processing, sensors and optical memory.

In this regard clay materials have attracted great interest as host materials over the past decade because of their unique interlayer space, flat large surface, negatively charged layer, ion-exchange properties, exfoliation/stacking ability of the layers and modifiability of their surface with cationic organic molecules [8–11]. The planarity of the \(\pi\)-conjugated system of the confined organic molecule is increased, which in turn extends the \(\pi\)-conjugation length. Also, the fluorescence quantum yield of the dyes is enhanced due to the suppression of vibrational motion of the confined molecules [8,12–15]. Accordingly, organic molecules confined in clay mineral-organic hybrid systems often exhibit unique spectroscopic properties that are not observed in the solution or crystalline states.

In general, organic molecules tend to aggregate due to hydrophobic-hydrophobic interaction, \(\pi\)-\(\pi\) stacking and Vander-Waals interaction [8, 16,17]. However, a large number of organic molecules can be incorporated in between the clay mineral layers without aggregation [18]. It has been shown that clay minerals can be used to control the molecular position, manipulate the molecular properties and provide a unique microenvironment for various photophysical reactions such as energy...
transfer [19], two-photon absorption [20].

Another interesting characteristic of clay minerals is swelling. As a result of swelling, the interlayer height is expanded compared to that in the dried state for both pure clay minerals as well as organic dye - clay mineral hybrid systems [21-25]. In the swollen state, the environment of intercalated molecule is different from that in the dried state. Due to this phenomenon, the spectroscopic features of the incorporated dyes change owing to the change of alignment and aggregation properties [8, 26,27]. In particular, the interlayer distance of the clay mineral layers change owing to the change of alignment and aggregation properties [8, 25]. Therefore, it might be possible that colour of the organic dye – clay mineral hybrid systems can be changed reversibly and the colours might be distinguishable with naked eye. Such dynamic materials will have potential applications in molecular devices like molecular wires, sensors, switches, logic gates, signal processors etc.

On the other hand, the indole scaffold has been identified as a prominent and privileged structural motif found in thousands of natural products that exhibit a wide range of important biological activities or bear technological interest [30-33]. In this context, bis(indol-3-yl) methane (BIMs) derivatives constitute an important sub-class with promising biological activities [34-38] and some of BIMs or their oxidized derivatives [39-44], are useful as dyes [45] and colorimetric chemosensors [46]. In this communication, we report remarkable reversible colour switching (red and yellow) behaviour of an inherently colourless compound 1,4-bis(di(1H-indol-3-yl)methyl)benzene(1, Fig. 1) [47,48] when incorporated into the interlayer space of saponite (SSA) upon drying and swelling. Tominaiga et al. (2016) reported the fluorescence colour switching of organic molecules confined into the interlayer space of clay minerals [8]. In the present case, the colour change is clearly visible to the naked eye [46]. Observed colour changes were found to be reversible for at least up to thirty cycles. We also demonstrate here the origin of such colour switching behaviour of this tetraindolyl derivative 1 in the hybrid system. There exist several reports showing reversible change in spectroscopic behaviour of organic molecules in organo-clay mineral hybrid systems [8,26]. Also organo-clay mineral mixed systems have been used as colorimetric humidity sensors [27,29]. To the best of our knowledge hardly there are any report showing organo-clay mineral hybrid system with direct (naked eye) colour switching accompanied by drying/swelling was found. Therefore, we believe that the present approach of controlling the supramolecular assembly of organic molecules into the interlayer space of clay minerals through drying and swelling provides a unique organo-clay mineral hybrid chromatic system with promising application potential.

2. Experimental section

2.1. Materials

Indole, N-methyl indole, terephthaldehyde, and 2,3-dichloro5,6-dicyano1,4-benzoquinone(DHQ) were purchased from Spectrum Pvt. Ltd and used as received. Spectroscopic grade methanol (SRL, India) was used as a solvent for preparation of the working solution. DMSO was purchased from Qualigens Fine Chemicals, India. Clay mineral SSA (Sumecton SA, Kunimine Industries) used in this study was collected from Clay Science Society of Japan. The stoichiometric formula of this SSA is \((\text{Si}_{1.30}\text{Al}_{0.30})\) \((\text{Mg}_{0.07}\text{Al}_{0.93})\) \(\text{O}_{20}(\text{OH})_{4}\) \(\text{Na}_{0.49}\text{Mg}_{0.14}\). The cation exchange capacity of it is 0.997 mequiv g\(^{-1}\) [8]. These materials were used as received.

2.2. Synthesis of 1,4-bis(di(1H-indol-3-yl)methyl)benzene(1)

A mixture of indole (4 mmol), terephthaldehyde (1 mmol) and an ion exchange resin (Amberlyst 15; 10 mg) in 10 mL of ethanol was stirred magnetically at 80 °C for 1 h. After the completion of reaction the solid product was dissolved by the addition of ethyl acetate (20 mL) and then filtered to remove Amberlyst 15. Evaporation of the solvent afforded a crude product which was purified by column chromatography over silica-gel (60-120) using ethyl acetate hexane as eluant (20-50%) [49]. Yield: 98%, m. p. > 250 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (bs, 4H, NH); 7.40 (d, \(J = 7.6\) Hz, 4H, NH); 7.08 (t, \(J = 7.2\) Hz, 2H, aromatic H); 7.04 (t, \(J = 8.0\) Hz, 4H, aromatic H); 7.28 (s, 2H, aromatic H); 7.25 (s, 4H, aromatic H); 7.17 (t, \(J = 8.8\) Hz, 4H, aromatic H); 7.04 (t, \(J = 8.0\) Hz, 4H, aromatic H); 6.33 (s, 4H, aromatic H); 5.80 (s, 2H, benzylic H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.6, 136.6, 128.5, 123.0, 121.8, 119.6, 118.7, 118.1, 111.1, 39.7, 38.0 ppm. HRMS calculated for \(\text{C}_{28}\text{H}_{22}\text{N}_2\) \(\text{O}_2\) \(\text{Al}_{0.93}\); \(m_\circ\) 482.1725; \(m_{cal}\) 482.1729.

2.3. Synthesis of oxidized form of 1 (2a)

To a stirred solution of 1 (0.5 mmol) in acetonitrile (5 mL), DDQ (0.75 mmol) was added at room temperature and stirring was continued for 4 h. The solid in the deep red coloured solution was collected by filtration. Analytically pure product was obtained by crystallisation from hot methanol. Yield: 20%, m. p. > 250 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.92 (s, 2H), 8.06 (bs, 2H), 7.52 (d, \(J = 7.2\) Hz, 4H); 7.37 (m, 6H, aromatic H); 7.18 (t, \(J = 7.2\) Hz, 2H, aromatic H); 7.08 (t, \(J = 7.2\) Hz, 2H, aromatic H); 6.90 (m, 6H, aromatic H); 6.64 (bs, 2H, aromatic H); 5.99 (s, 1H, benzylic H); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 147.9, 137.1, 129.2, 127.1, 124.2, 121.5, 121.2, 119.6, 118.7, 118.1, 112.0, 40.2 ppm (merged with DMSO peaks but confirmed by \(^1\)H-\(^1\)C correlation spectroscopy, Fig. S5 of supporting information). HRMS calculated for

![Fig. 1. Chemical structure of 1,4-bis(di(1H-indol-3-yl)methyl)benzene (1), Oxidized form of 1 (2a) and p-di[3,3’-bis(2-methylindolyl) methane]benzene(3).](image-url)
C₂₉H₂₈N⁺H⁻ 565.2392 found 565.4050. ¹H and ¹³C NMR spectrum of compound 2a have been shown in Figs. S4 and S5 of supporting information. Chemical structure of the oxidized form of 1 has been shown in 2a of Fig. 1. The compound was red coloured.

2.4. Synthesis of p-dil[(3,3′-bis(2-methylindolyl) methane]benzene (3)

A mixture of N-methyl indole (4 mmol), terephthaldehyde (1 mmol) and amberlyst 15 resin (10 mg) in 10 mL of ethanol was stirred magnetically at 80 °C for 1 h. After the completion of reaction, the solid product was dissolved by the addition of ethyl acetate (20 mL) and then filtered to remove Amberlyst 15. Evaporation of the solvent afforded a crude product that was purified by column chromatography over silica-gel (60-120) using ethyl acetate hexane as eluant (20-50%) [49]. Yield: 95%, m. p. 270 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 7.6 Hz, 4H, aromatic H), 7.33–7.30 (m, 9H, aromatic H), 7.24 (t, J = 7.6 Hz, 4H, aromatic H), 7.04 (t, J = 7.6 Hz, 4H, aromatic H), 6.58 (s, 4H, aromatic H), 5.89 (s, 2H, benzylic H), 3.71 (s, 12H, N-CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 137.4, 128.6, 128.3, 127.6, 121.3, 120.2, 118.5, 109.1, 110.5, 39.8, 32.7. ¹H and ¹³C NMR spectrum of compound 3 have been shown in Figs. S6 and S7 of supporting information. Chemical structure of tetraindolyl derivative 3 has been shown in 3 of Fig. 1. The compound was white coloured.

2.5. Fabrication of clay mineral-organic hybrid self-standing film

The organic dye-clay mineral composites were prepared by mixing an aqueous dispersion of clay mineral with the methanol solution of the organic compounds used in this study. Table S1 of supporting information shows the values (concentration and amount) used to prepare optimized clay mineral-organic hybrids. The composite was stirred for 30 min with a magnetic stirrer at room temperature. The hybrid films were prepared by filtration of the aqueous dispersion of organic-dye clay mineral composites under suction through a mixed cellulose ester membrane filter (Advantec, A010A025A; pore size: 100 nm; diameter: 25 mm). After filtration, the prepared hybrid film was transferred from the membrane onto the surface of a cleaned quartz glass slide for spectroscopic measurements.

2.6. Characterization

UV–Vis absorption spectra of solutions of compounds 1-3 and hybrid films, were recorded with a PerkinElmer, Lambda 25 spectrophotometer. A clean quartz slide was used as a reference. X-ray diffraction (XRD) measurement was recorded on a Bruker D8 advance. Data were recorded using monochromatic copper Kα radiation (wavelength 1.54 Å) and a 2θ step of 0.02°. Clay-dye hybrid film was dried by heating the film at 80 °C in an oven. Swelling of the dried film was done by touching the film with a cotton bud dipped into DMSO. Sony Cybershot DSC-W810/B 20.1 MP Digital camera was used for taking pictures of all self-standing films.

3. Result and discussion

The tetraindolyl derivative 1 was synthesized in 98% yield by the electrophilic substitution reaction of indole with terephthaldehyde using 4:1 M ratio with Amberlyst 15 as promoter [49]. It is noteworthy that 1 was obtained as the sole product of the reaction. Fig. 2 shows the absorption spectra of 1 in methanol (10⁻⁴ mol L⁻¹) and in 1-SSA hybrid film. Tetraindolyl derivative 1 solution spectrum exhibited a prominent absorption band with peak at 283 nm along with two weak humps at around 273 nm and 291 nm. We have also checked the absorption spectra by varying concentration within 0.5 × 10⁻³ to 10⁻⁴ mol L⁻¹ (Figure not shown). Identical spectral features were observed having linear dependence of intensity with concentration. This suggested that 1 remains as monomer in solution within this concentration range. On the other hand, 1 in the hybrid film also showed almost a similar spectral profile. This suggests that the molecular structure of 1 was not distorted upon incorporation in clay mineral-organic dye hybrid films [8].

Freshly prepared tetraindolyl derivative 1-SSA hybrid film was colourless and fully transparent (image a, Fig. 3). When this film was kept at 80 °C for 25 min the hybrid film was red (image b, Fig. 3) Two new bands with peak maxima at 404 nm and 510 nm (curve 2 of Fig. 4) appeared in addition to the original band of the freshly prepared film (curve 1, Fig. 4). When this red coloured film is swollen with DMSO, colour of the film changed from red to yellow (image c, Fig. 3). The corresponding absorption spectrum (curve 3, Fig. 4) revealed that the intensity of the bands at 404 nm and 510 nm decreases markedly. However the intensity of the 404 nm band was higher than that of the 510 nm band, suggesting that the 404 nm and 510 nm bands belong to 2 different species. Interestingly, when the same film is heated after washing out the DMSO, the red colour returned. The conclusion is that it is possible to have colour switching between red and yellow by changing from a dry film to swollen film and vice-versa. In order to check the solvent dependence of such colour switching upon swelling, we have checked using other solvents such as methanol, chloroform, water, ethanol, DMF etc. Interestingly, the colour switching behaviour remained almost the same independent of the solvent. However, we preferred to use DMSO due to its nonvolatile nature and high boiling point. In order to check the effect of dye loading on colour switching behaviour of tetraindolyl derivative 1 in dye-clay mineral hybrid film, we have prepared clay mineral-dye film with various percentage of dye loading viz. 5%–30%. The most intense colours were observed for the films with dye loading of 15% and above (Fig. 5). The corresponding
absorption spectra confirmed this behaviour. Under dried conditions the absorbance maximum occurred at 510 nm, whereas, in the swollen state the 404 nm band was dominant. However, the intensity of 510 nm band for dried film increased with dye loading. Corresponding absorption spectra are shown in Figs. S8a and S8b of supporting information.

It is relevant to mention that there exists several examples where planarity of the dye molecules with a planar π-conjugated system get enhanced when they are confined in the interlayer space of the clay mineral-dye hybrid films [8,9,27,28]. Pyridinium derivatives as well as Nile red showed enhanced planarity when confined into clay mineral layers [8,11]. Conjugation between indole rings is prevented due to the presence of benzylic CH in 1 and the dye-clay mineral hybrid film is colourless in ambient condition. We pre-assumed that the red colour developed upon heating in the tetraindolyl derivative 1-clay mineral film is due to the aerobic oxidation of molecule 1 to its fully oxidized form 2a (Fig. 1), which in turn enhances the conjugation via prototropic shift between two indole rings and makes the molecule planar. To prove our assumption of this colour changing phenomenon during heating on-off we have heated the tetraindolyl derivative 1-clay mineral hybrid film in vacuum at 80 °C in both dry (as prepared) and swollen state. No colour appeared in either case which indicated that oxygen in air played a crucial role in the formation of the dye 2a in the hybrid film. Corresponding images and spectra are shown in Fig. S9 of supporting information. In order to confirm our interpretation we have synthesized dye 2a using DDQ as oxidant [50,51] and acetonitrile as solvent and prepared the clay mineral – dye 2a hybrid films. This hybrid film is red-coloured. The absorption spectrum showed absorption maxima at 510 nm along with weak 404 nm band. Upon heating no further change in colour profile and hence spectral profile was observed. Upon swelling this film became yellow in colour. In the absorption spectrum the 404 nm band dominates over the 510 nm band [52]. Corresponding images and spectra are shown in Fig. S10 of supporting information. Upon swelling, the interlayer space of the clay mineral increases and the planarity of the 2a molecule disturbed slightly through C-C bond rotation of benzylic carbon and one of the indole ring (2a to 2b) as shown in Fig. 6. This inturn affects the conjugation and the colour switch from red to yellow occurred. Upon washing of this swollen film followed by heating the interlayer space of the clay mineral decreases and the molecule gets back to its original planarity with retention of red colour. To get a clear idea about the colour switching behaviour, we have synthesized tetraindolyl derivative 3 and prepared the tetraindolyl derivative 3-clay mineral hybrid film. The film is not fully transparent rather it shows a very minute shade of beige colour (image 1, Fig. S11a of supporting information). When the film is heated no marked change in the colour profile is observed (image 2, Fig. S11a of supporting information). The spectral profile (curve 2, Fig. S11b of supporting information) also did not show any significant change compared to that of freshly prepared films except slight change in intensity. When this dried film is swollen with DMSO, the film became fully transparent (image 3, Fig. S11a of supporting information) with the spectrum shown as curve 3 of Fig. S11b of supporting information. Due to the presence of methyl groups in the tetraindolyl derivative 3, oxidation of the molecule does not occur and hence no colour change is observed.

We have also performed the X-ray diffraction studies for the tetraindolyl derivative 1-clay mineral hybrid film to have idea about the interlayer space upon drying and swelling. Corresponding spectra are shown in Fig. S12 of supporting information. The interlayer space of the tetraindolyl derivative 1-clay mineral hybrid film in the dry prepared state was 0.636 nm. And in the dried state it was 0.538 nm. The latter value is very close to the thickness of the tetraindolyl derivative 1 viewed parallel to the π-conjugated system. The interlayer space of the tetraindolyl derivative 1-clay mineral film in swollen state was 0.859 nm. Due to this enhancement in interlayer space the microenvironment of the tetraindolyl derivative 1-clay mineral hybrid film is suitable for partial rotation of C-C bond and hence partial prevention of long conjugation through distortion of the molecules confined in the

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**Fig. 4.** UV–Vis absorption spectra of tetraindolyl derivative 1-SSA hybrid self-standing film with dye loading of 15% freshly prepared state (curve 1), dried state (curve 2) and swollen state (curve 3).

**Fig. 5.** Colours of tetraindolyl derivative 1-SSA hybrid self-standing films with various percentage of dye loading. Left, middle and right columns correspond to freshly prepared, dried state and swollen state respectively.
interlayer space. Accordingly colour switching can occur.

To check the role of the clay mineral on such colour switching we have studied the tetraindolyl derivative 1 in absence of clay mineral. Films of tetraindolyl derivative 1 were prepared, in the same way as the tetraindolyl derivative 1-clay mineral hybrid film was prepared. The film was transparent in the as prepared condition. Upon heating the film became red. But interestingly upon addition of DMSO no colour change occurred: the film remained red. The colour profile and the spectrum are shown in Fig. S13 of supporting information. The red colour is due to oxidation of molecule 1. The absence of a colour switch upon addition of DMSO indicates that the absence of a change in conjugation of the oxidized molecule, due to restricted C-C bond rotation. DMSO does not act as a solvent. In the interlayer space of clay minerals DMSO solvates the oxidized molecules and a colour switch occurs.

A schematic diagram showing the tetraindolyl derivative 1 molecule confined in between clay mineral layers under various conditions is shown in Fig. 7.

It has already been reported that interlayer spacing of swollen clay mineral–organic hybrid films readily decreased upon drying [8,26–29]. In the present case the interlayer spacing of the tetraindolyl derivative 1–SSA film increased upon swelling and decreased upon drying. This observation was found to be reversible. Due to this change in interlayer space, reorientation of molecules occurred in the clay–organic hybrid films resulting reversible colour switching behaviour.

We have also investigated the repeatability of the observed colour switching for the tetraindolyl derivative 1–SSA hybrid films. Fig. 8 shows the variation of 510 nm absorption band intensity of a tetraindolyl derivative 1–SSA hybrid film in the dried and swollen states. The absorbance values were taken from the unnormalized absorption spectra. It is shown that adding DMSO and removing the same followed by heating, reversible colour switching between red and yellow occurred at least up to 30 cycles.

4. Conclusions

We have prepared a hybrid film composed of tetraindolyl derivative and saponite which exhibits reversible colour switching behaviour (distinguishable with naked eye) upon heating and swelling with high repeatability. The chromism property appeared between the oxidized tetraindolyl derivative 1 in the absence (red colour) and presence of DMSO (yellow colour). Two types of chromophore exhibiting absorption maxima of 404 nm (for yellow colour) and 510 nm (for red colour) exist.
in the tetraindolyl derivative 1-SSA hybrid films. The relative population of these two can be switched by drying and swelling. This was possible by controlling the micro-environment of the interlayer space of saponite. Thus, the swelling property of organo-clay hybrid film can be tuned to obtain optical switching.

Author Contributions

J. K., S. M., and S. A. H. designed the work. B. D. and S. S. performed all experiments and data analysis. S. M. and B. D. synthesized the material. S. A. H., S. M. and S. S. wrote the manuscript with input from D. B., J. K., S. C. and Y-S.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpcs.2020.109487.

References
