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ARTICLE

Shining the Light on Clay-Chromophore Hybrids: Layered Templates for Accelerated Ring Closure Photo-Oxidation

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A Templates with specific microenvironments have been long employed to facilitate specialized reactions. From enzymes to metal organic frameworks (MOFs), various systems have exerted their prowess to effect specific chemical reactions. We here report, for the first time, acceleration of a ring closure photo-oxidation due to the specific structural constraints provided by layered materials. A stilbene derivative has been used as a prototype reactant and the di-hydrophenanthrene intermediate has been isolated and characterized en route to complete photo-oxidation. Combining the gathered evidence, possible mechanism for the chemical transformation has been proposed. Kinetic analysis showed that layered materials help to manipulate the rate of electrocyclic ring closure and in turn accelerate the complete reaction sequence. The structural microenvironment induced by layered materials could be a unique platform to probe and stabilize plethora of photo-oxidative reactions and intermediates.

Introduction

Molecular templates have been long known to provide local environments for specific chemical reactions by virtue of its structural and functional prowess. Enzymes, DNA are some naturally occurring examples.¹ Interior environment of polymers, artificial cage like systems such as MOFs and their discrete versions have been well explored for probing interesting reactions and intermediates.^{2,3} Unique chemical reactions have also been demonstrated by exploiting inorganic layered compounds with functional interlayer galleries⁴ which can be considered as analogues of aforementioned inorganic templates and thus can be explored for reactions susceptible to confinement effects.⁵ Layered compounds such as clay have been a subject of interest in a wide variety of fields especially for studying the photo-physical properties of dye conjugates.⁶ Chemical reactions that are governed by light are most susceptible to pre-organization. However only handful of light mediated chemical transformations have been carried out on clay surfaces and ring closure photo-oxidation of stilbene systems have been one of the rarely investigated themes in clay microenvironments.⁵ Furthermore the sensitizers employed for these photo-oxidation reactions (external

sensitizers or inherent ions in the clay) photo- resulted in either [2+2] dimers or fission products of the ethylene bond.⁷ Ring closure photo oxidation reactions in stilbene systems to phenanthrene derivatives are synthetically important as they are one of the important steps in synthesis of various poly-aromatic hydro-carbons.⁸ This reaction has also been studied in detail with special impetus on trapping the di-hydrophenanthrene intermediate. The di-hydrophenanthrene derivative has been isolated only in anaerobic conditions and has been a key step in control-ling the rate of the overall reaction.^{9,10} In the reaction sequence ring closure turns out to be the slower step and hence the rate determining step. As soon as di-hydrophenanthrene is formed it is oxidized to its phenanthrene analogue.^{9,10} Hence, increasing the rate of ring closure will enhance the rate of phenanthrene formation. Generally, these reactions are carried out in presence of an oxidizing agent such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or I₂, owing to the slow photo-chemical reaction rate.¹¹ It has therefore been a challenge to look for a strategy to enhance the rate of such reactions photo-chemically.

In this manuscript we, for the first time, observe that kinetic pathways of organic photo reactions can be modulated on layered inorganic templates. Photoreactions on stilbene derivatives have been a research venue for decades; however it has been shown for the first time in this manuscript that its ring closure photo-oxidation kinetics can be biased while it is conjugated on an inorganic clay surface. To add to the novelty of the manuscript, during the photo-reaction process we have isolated a di-hydro phenanthrene derivative as an intermediate which has proved to be a challenging task in the past. These derivatives are generally very unstable and their

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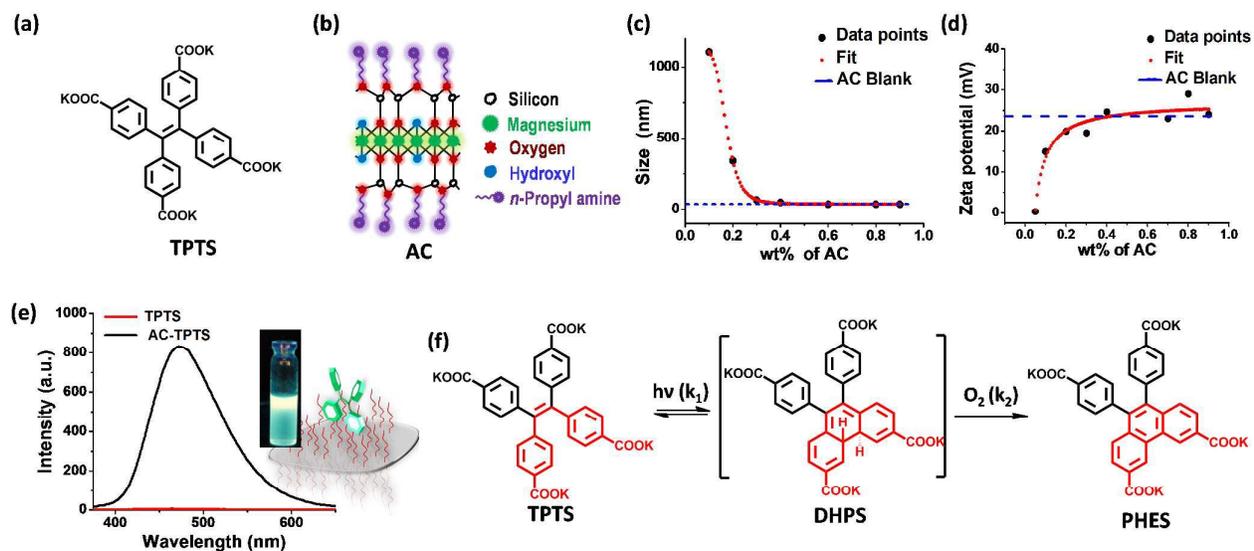


Figure 1. (a) Molecular structure of TPTS, (b) Schematic showing the structure of Amino clay (AC), (c) and (d) DLS and Zeta potential trends of TPTS (10^{-4} M) with various weight percentages of AC. (e) Emission spectra showing the enhanced emission from TPTS (10^{-4} M) on binding to AC (0.9 wt%), this dye conjugated state has been designated as AC-TPTS, ($l = 1$ cm, $\lambda_{exc} = 350$ nm, water) (inset shows the photograph of 365 nm illuminated solution of the clay-dye conjugate alongside the respective schematic). (f) Reaction sequence showing the expected photo-oxidation reaction undergone by TPTS (stilbene moieties marked in red). k_1 , and k_2 mentioned above the arrowheads are the forward rate constants.

complete characterization as done in this manuscript is very rare.

Results and Discussion

Design Strategy.

The inorganic template we have used to construct the microenvironment for chemical modification is amino clay (AC).^{12a} It has a structure analogous to 2:1 trioctahedral smectite with an approximate composition of $R_3Si_8Mg_6O_{16}(OH)_4$, where R stands for covalently linked aminopropyl chains (Figure 1b). These clays do not have sensitizing action because of the absence of metal ions such as Al^{3+} and Fe^{3+} .¹²

Moreover, the optically transparent nature of the AC facilitates photochemical reactions and its high dispersity helps in maintaining the reaction mixture homogeneous. AC when mixed in water undergoes exfoliation, resulting in a clear solution, owing to the spontaneous protonation of the amine groups on the surface. Recently many possibilities that can arise from the use of amino clay (AC) as a soft hybrid for various photo-physical prospects have been explored.¹²

Tetraphenylethylene (TPE) and its derivatives are stilbene analogues having a rich history of photo-physical and photo-chemical phenomena.¹⁴ With regards to photo-physical properties they are known to show higher quantum yield of emission once their rotating phenyl propellers are arrested in motion.¹⁵ Enhanced emission due to restricted rotation has been used extensively for applications in opto-electronics and as fluorescent probes.¹⁵ On the other hand TPEs, being derivatives of stilbenes, also undergo the unique photo-chemical modifications such as the photo-oxidation which yields the phenanthrene derivative after a [4+2] electrocyclic

ring closure.⁹ We envisage that conjugating TPE moieties on clay can result in restricted rotation of the phenyl rings which can enhance the probability of ring closure. Considering the nature of our inorganic template (positively charged amino clay) a negatively charged TPE derivative was selected i.e. tetraphenylethylene tetra potassium salt (TPTS) (Figure 1a). TPTS was synthesized according to the known procedure¹⁶ and the molecule was characterized by NMR spectroscopy and mass spectrometry (MS) (Figure S1-S3). TPTS has been studied in the past for its restricted rotation in MOFs by Dincă *et al.*¹⁷ Photochemistry on this molecule however has not been explored. Considering the classic model of electrocyclic ring closure, photo-oxidation of TPTS is expected to proceed to phenanthrene derivative (PHES) via a 4,4'-di-hydro phenanthrene intermediate (DHPS) (Figure 1f).⁹

Clay-Dye conjugation.

Preliminary experiments suggested that TPTS when conjugated with AC results in restriction of rotation of phenyl rings. The flattening of ¹H-NMR peaks and the emission enhancement in the clay-dye conjugate (AC-TPTS) (Figure 1e) strongly support the restricted rotation of phenyl rings on clay surfaces (Figure S4). To further understand the characteristics of the clay-dye conjugate, to a fixed concentration of aq. TPTS (10^{-4} M) various wt% of AC were added and their dynamic light scattering (DLS) and Zeta potential data were recorded (Figure 1c-d). It can be evidently seen that beyond neutralization point in zeta potential (0 mV at 0.03 wt%), size and charge density of the conjugate approaches that of single AC sheets. Therefore to study the photochemistry of TPTS on clay surface, concentration of AC is fixed at 0.9 wt% as it ensures complete binding and a highly homogenous dispersion.

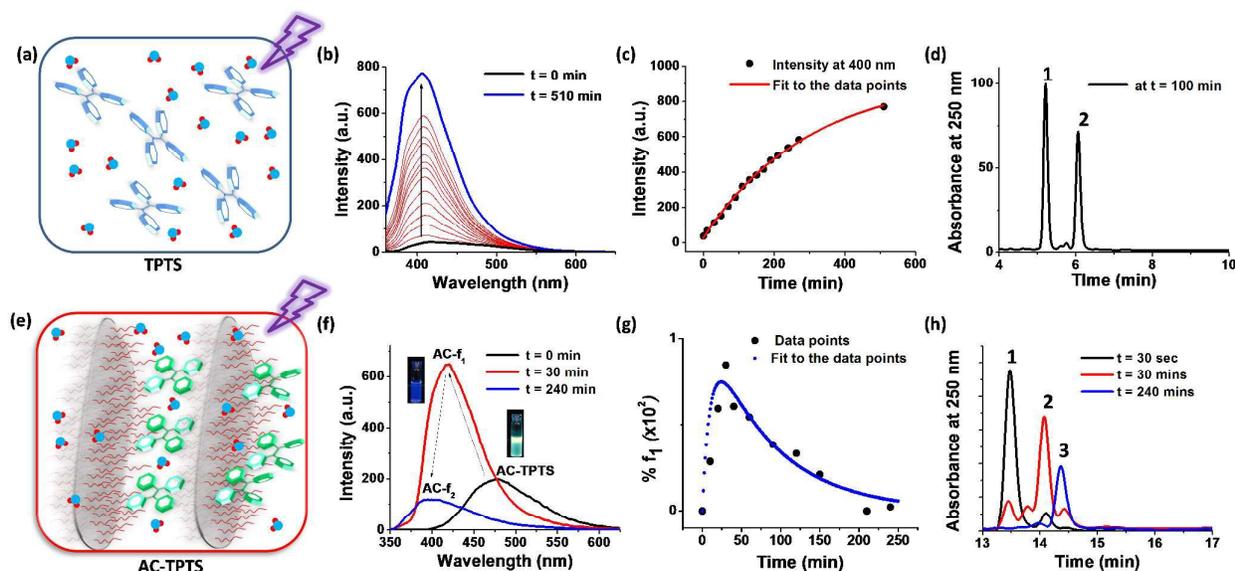


Figure 2. (a)-(d) (top panels) Represent the photo-oxidation of nascent **TPTS** while (e)-(h) (bottom panels) represent photo-oxidation of the **TPTS** and **AC** conjugate in aqueous solution ($[TPTS] = 10^{-4} M$, $l = 1$ cm, $\lambda_{exc} = 350$ nm, water). (a) Schematic representation of irradiation of nascent **TPTS** molecules in water, (b) Time dependent emission spectra of photo-oxidation of aqueous **TPTS** solution under 254 nm irradiation, (c) Fluorescence intensity trace at 400 nm of the photo-oxidation profile of **TPTS**, (d) HPLC chromatograph after 100 mins of irradiation probed at 250 nm absorption¹³, (e) Schematic representation of irradiation of **TPTS** and **AC** conjugate, (f) Time dependent emission spectra of photo-oxidation of **TPTS** ($10^{-4} M$) and **AC** (0.9 wt%) conjugate under 254 nm irradiation (inset shows the photographs of 365 nm illuminated solutions of **AC-TPTS** and **AC-f₁**), (g) Fluorescence intensity trace at 400 nm of the photo-oxidation profile of **TPTS** and **AC** conjugate and (h) HPLC chromatograph at various times of irradiation probed at 250 nm absorption.¹³

Photochemical studies.

Before analysing the photo-chemical characteristics of **AC-TPTS** we sought to understand the chemistry of aqueous **TPTS** solution under light (Top panel, Figure 2). A $10^{-4} M$ solution of **TPTS** was irradiated under a 254 nm lamp (Figure 2a,b). Initially at $t = 0$ the emission is quenched due to non-radiative decay processes.⁸ With time the evolution of an emission with λ_{max} at 404 nm could be observed (Figure 2b) signifying the formation of phenanthrene derivative. The intensity of the band at 400 nm was plotted against time which showed a monotonic increase in intensity (Figure 2c). The reaction took around 750 mins to complete. Liquid chromatography-mass spectrometry (LC-MS) analysis of a 100 min aliquot showed two peaks (marked as 1 and 2 in Figure 2d). The UV/vis absorption spectra and MS of fraction 1 corroborated with the starting material (**TPTS**) while fraction 2 pertained to **PHES**, as evident from the $[M-2]$ ion in MS signifying loss of two protons due to oxidative ring closure (Figure S5,6). Time dependent 1H -NMR measurements were made of the irradiated sample and visual interpretation of the 1H -NMR showed signs of C_2 -symmetric species being formed which also confirms the existence of the phenanthrene derivative (Figure S7). Having known that the chemistry involving in the photo-conversion of stilbene derivatives to phenanthrene is a two-step process (Figure 1f), observation of a monotonic conversion into the final product points to the case of series reactions with $k_2 > k_1$. Considering the fact that di-hydrophenanthrene intermediate is highly susceptible to oxidation, the hypothesis seems reasonable.⁹ Therefore the evolution of phenanthrene can be

fit into this specific limiting case of reaction in series and rate constant can be extracted (Figure S8). However from the steady state data only the slower reaction step (k_1) i.e. the rate constant involved in electrocyclic ring closure, can be extracted (Figure S9). After fitting to an appropriate function k_1 was found to be $3.7 \times 10^{-3} s^{-1}$.

Interestingly, on the other hand clay-dye conjugate (**AC-TPTS**) (Figure 2e) when irradiated with 254 nm light showed the progression to the final photoproduct via a two-step process as evident from the corresponding fluorescence changes (Figure 2f-g, S10). Initial state **AC-TPTS** ($\lambda_{max} = 475$ nm) after 30 mins went to a state **AC-f₁** ($\lambda_{max} = 420$ nm) and then finally after 240 mins to **AC-f₂** ($\lambda_{max} = 400$ nm). **AC-TPTS** to **AC-f₁** transition was rapid and reached a maximum at around 30 mins. Transformation of **AC-f₁** to **AC-f₂** was rather slow and took another 210 mins to complete (Figure 2f). Remarkably the photo oxidation was complete in 240 mins which was one third of the time taken without **AC**. The compositions **f₁** and **f₂** were extracted from the clay conjugates (**AC-f₁** and **AC-f₂** respectively) and were analysed by LC-MS (Figure 2h, S11-14). LC-MS of **f₂** showed the formation of phenanthrene (**PHES**, marked with 3 in Figure 2h). UV/vis absorption and Electrospray ionization-Mass spectrometry (ESI-MS) performed on this fraction also corroborated with the conclusion that the **f₂** is predominantly a phenanthrene derivative (**PHES**) (Figure S14). LC-MS of **AC-TPTS** extract after 30 seconds of irradiation was majorly comprised of the starting material (**TPTS**, marked as 1 in Fig Figures 2h, S14). It did however show traces of an intermediate peak (retention time (r.t.) = 14 mins) which

eventually became the major peak in fraction f_1 after 30 mins (marked with 2 in Figure 2h). Chromatogram after 30 mins was also accompanied by a minor peak (r.t. = 13.8 mins) which due to the very less yield could not be further analysed. Interestingly, UV/vis absorption of this fraction showed a red shifted band (366, 377 nm) as compared to the starting material (330 nm)(Figure S13). ESI-MS analysis however showed that the mass of this intermediate was same as the starting material (Figure 3a, S14). This evidence hints towards f_1 to be comprised of a di-hydrophenanthrene derivative. Attenuated total reflectance-infra red (ATR-IR) analysis done on the intermediate showed the shifting of C-H stretch to a lower wavenumber (2962 to 2924 cm^{-1}) as compared to the TPTS acid which also signifies the introduction of a sp^3 hybridized C-H bond (Figure S15).

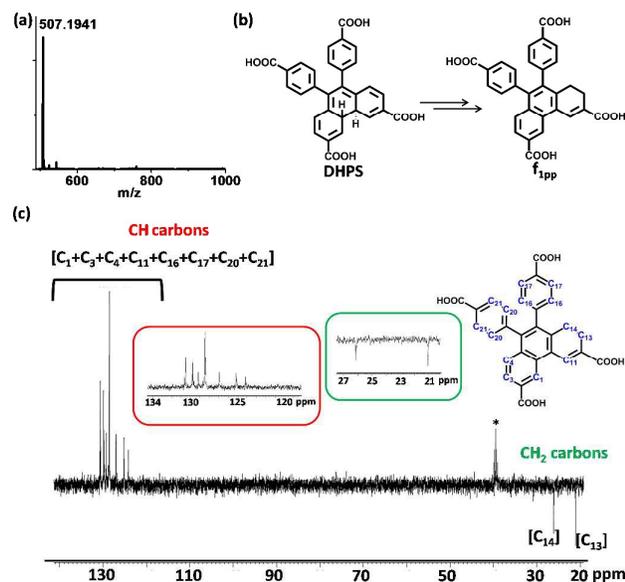


Figure 3. (a) Shows the ESI-HRMS of f_{1pp} in negative ion mode, (b) Chemical transformation of DHPS to f_{1pp} and (c) shows DEPT spectra of f_{1pp} in CD_3OD (inset showing the zoomed ppm regions (120-134 and 21-27) and f_{1pp} structure with designated -CH and -CH₂ carbons, * signifies DMSO-d₆ peak).

Since di-hydro phenanthrene derivatives have been rarely isolated and characterized we decided to do extensive characterization of these species.¹⁰ To our surprise the isolated derivative from fraction f_1 was majorly 1,2-di-hydro derivative (f_{1pp}) instead of the 4,4'-di-hydro derivative (DHPS, Figure 3b) (vide infra). Owing to the intermediates good oxygen tolerance it was possible for us to do extensive NMR characterization and elucidate its structure. Distortionless enhancement by polarization transfer (DEPT) analysis showed that f_{1pp} comprises of -CH₂ carbons as shown by negative peaks in Figure 3c (peaks in the region 20-30 ppm). Counting the number of -CH and -CH₂ peaks it became evident that the di-hydro derivative is indeed an isomerized counterpart of DHPS. Visual interpretation of ^1H and ^{13}C -NMR showed that the spectra deviates from C_2 -symmetric spectra obtained for phenanthrene (Figure 4, S16-22). Moreover in ^1H -NMR two

triplets could be clearly seen in the low field region of 2.6-2.8 ppm. From heteronuclear correlation spectra (HETCOR) these ^1H -peaks at around 2.6-2.8 ppm could be correlated with the -CH₂ peaks as determined by DEPT (Figure S23). The remainder of the -CH correlations were also made once the 2D spectra was analysed (Figure S24). Having understood the carbon skeleton of the molecule we went ahead to decipher the proton correlation existing in f_{1pp} .

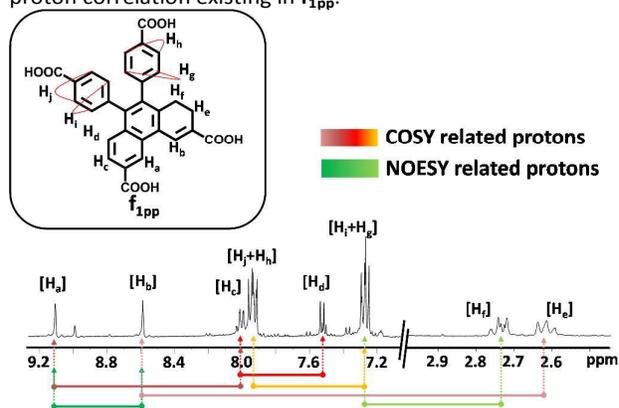


Figure 4. ^1H -NMR spectra of f_{1pp} in CD_3OD (inset shows the molecular structure of f_{1pp} with designated protons). Lines and arrows below the ^1H -spectra show the summary of ^1H correlations observed in f_{1pp} .

^1H -correlation spectroscopy (COSY) helped in understanding the through bond proton connections of the molecule (f_{1pp} , Figure 4, S25-27). Protons H_i and H_g correlated with H_j and H_h respectively confirming the nascent aromatic structure of part of the molecule which did not take part in the photo-reaction (Figure 4, S25). Proton H_c correlated with H_d confirming the presence of an aromatic system in the modified part of the molecule (Figure 4, S25). Proton designated as H_a correlated with another aromatic proton H_e which signified a four proton meta coupling (Figure 4, S26). Moreover, proton H_b correlated with the low field -CH₂ proton signifying a four bond allylic coupling (Figure 4, S27). These two observations stated above strongly confirm that one part of the ring is aromatic and the other is not, thus explaining the loss of C_2 -symmetry of the ^1H -NMR spectra. Furthermore these H_a and H_b proton were found to correlate in the nuclear overhauser effect (NOE) spectra, thus confirming the relation between the aromatic and the non-aromatic parts (Figure 4, S28). Also H_f correlated to H_g via NOE, proving the connection between the photo-modified and nascent parts of the molecule (Figure 4, S28). Thus, the results derived from NMR spectra con-firmed that the di-hydrophenanthrene (Peak 2 in Figure 2h) that we obtained is the 1,2-di-hydro derivative (f_{1pp}). In addition to above discussed photoproducts the fraction f_1 and f_2 also contained decarboxylated products of di-hydrophenanthrene intermediate (f_{1dc}) and phenanthrene respectively, as a minor product, as elucidated from the chromatogram peaks at higher retention times, which has also been characterized with various techniques (Figure S12, 29-33). We hypothesize that the parent structure of f_{1pp} and f_{1dc} is indeed DHPS and f_{1pp} is perhaps formed by a sequence of [1,3]-sigmatropic shifts from

DHPS (Figure S34). We also hypothesize that the origin of the decarboxylated derivative is an offshoot of the main reaction step. Thus the net composition of **DHPS** formed could be approximately translated to the summation of f_{1pp} and f_{1dc} (Figure S34).

Coming back to the reaction in series scheme the time evolution shown in Figure 2g resembles the one in which $k_1 > k_2$ (Figure S35). Hence fitting the kinetics to the appropriate function we derived the rate constants as $k_1 = 0.1 \text{ s}^{-1}$ and $k_2 = 1.2 \times 10^{-2} \text{ s}^{-1}$ (Figure S36). This particular photo-activity also suggests that in clay conjugates, k_1 was enhanced 100 fold compared to the nascent **TPTS** solution. The enhancement was to the extent that k_1 eventually became larger than k_2 hence suggesting that rate of formation of **DHPS** became higher than the rate of its subsequent oxidation. **DHPS** however is not photo-stable and owing to its photo-reactivity, is converted to f_{1pp} which is eventually oxidized to form **PHES** (Figure S34). To the best of our knowledge observations made above make this the only system in which the di-hydro phenanthrene derivative has been observed in aerobic conditions with a complete elucidation of the structure.

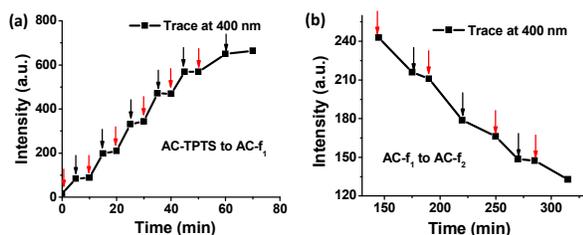
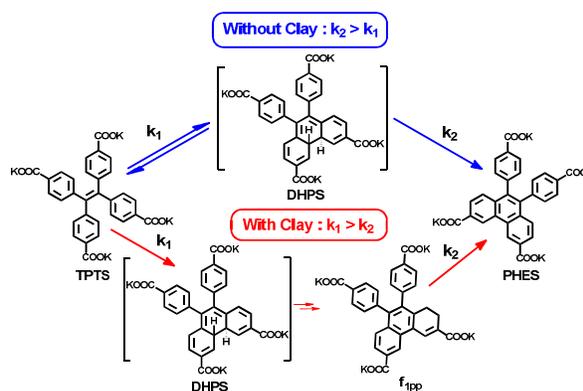


Figure 5. (a) and (b) showing the emission intensity of AC (0.9 wt%) conjugated **TPTS** (10^{-4} M) ($l = 1 \text{ cm}$, $\lambda_{exc} = 350 \text{ nm}$, water) followed at 400 nm under light (red arrows, 254 nm irradiation) and dark conditions (Black arrows) for various times (a: **AC-TPTS** to **AC-f₁**, b: **AC-f₁** to **AC-f₂**)

Di-hydro phenanthrene derivatives are known to be highly susceptible to oxidation and most times atmospheric oxygen is capable to converting them to their oxidized counterpart.⁹ Therefore to a methanol solution of f_{1pp} we purged oxygen gas for over 30 mins. To our surprise absolutely no change was observed in UV/vis absorption and fluorescence measurements (Figure S37). This was quite anomalous as it hinted towards the fact that oxidation of f_{1pp} to phenanthrene is not driven by oxygen alone which is contrary to conventional wisdom. Figure 5a-b show that as the 254 nm irradiation over the clay-dye conjugates (**AC-TPTS**) is switched off, rates of both processes (**AC-TPTS** to **AC-f₁** and **AC-f₁** to **AC-f₂**) are significantly retarded. This points to the fact that not only **TPTS** to f_{1pp} is governed by light; f_{1pp} to **PHES** is also critically photo-controlled. Since the final oxidation cannot be done by light alone this hints that in this case f_{1pp} to **PHES** is a rare situation of “true” photo-oxidation which refers to interaction of the excited state of the molecule with oxygen to give the oxidation product.¹⁸ Furthermore, we investigated the possibility of propyl amine chains (which are a component of **AC**) acting as a base in the photo reaction.¹⁹ Hence, we carried out the irradiation of **TPTS** in presence of varying amounts of *n*-propyl

amine (Figure S38-40). Kinetics of these transformations was far too slow, to be compared with **AC**, to have any significant impact on the reaction outcome (Figure S41-42). These results clearly rule out the contribution of amino propyl groups as a base in clay for influencing the reaction rates and thus further reiterate that the conformation restriction perhaps plays a major role in the transformation.^{20,21}



Scheme 1. Reaction sequence for nascent **TPTS** (Blue arrows) and **TPTS** inside **AC** (Red arrows).

Conclusions

In conclusion we have successfully shown that interlayer galleries can be used as a template to explore the increased rate of photo-oxidations in stilbene like systems. We show that there is a marked change in rate constants of photo-oxidation once **TPTS** is conjugated in galleries of amino clay (Scheme 1). This change points towards the use of restricted rotation of phenyl rings of **TPTS** on the **AC** sheet being an important factor in tipping the scales of rate constants. On clay the ring closure, which was initially a slow step, becomes 100 times faster hence overtaking the oxidation step. Even though one of the demanding features of this conjugate is that it perhaps requires a strong association of the substrates to the template, hence the use of negatively charged molecules for a positively charged template, this presents a unique case in which electrocyclic ring closure was modulated on clay surfaces. This system also presents a unique study where, the usually unstable, di-hydrophenanthrene derivative was isolated in the form of 1,2-di-hydro phenanthrene and structurally analysed giving a major insight into the reaction process. The study thus opens the door to investigations of reactions involving variety of chromophores on layered materials as well as other variety of organic-inorganic hybrids and not just for their rate of reactions but also for stabilization of unusual intermediate states which can be achieved by this strategy.²²

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- An interesting result was published as this manuscript was being prepared; He, Z.; Shan, L.; Mei, J.; Wang, H.; Lam, J. W. Y.; Sung, H. H.-Y.; Williams, I. D.; Gu, X.; Miao, Q.; Tang, B. Z. *Chem. Sci.* 2015, **6**, 3538). This paper describes the formation of di-hydrophenanthrene derivative upon aggregation and the stabilization has been pointed towards the molecular design with more π rings. Thus the stabilization of intermediate and subsequent oxidation perhaps has some bearing on the electronic effects as a result of functional groups present in the molecule as well.
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