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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.† 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.‡,3 Unique chemical reactions have also been demonstrated by exploiting inorganic layered compounds with functional interlayer galleries which can be considered as analogues of aforementioned inorganic templates and thus can be explored for reactions susceptible to confinement effects.‡ 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.§ 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...
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).\(^{1,2}\) It has a structure analogous to 2:1 trioctahedral smectite with an approximate composition of \(\text{R}_6\text{Si}_4\text{Mg}_8\text{O}_{20}(\text{OH})_8\), where \(\text{R}\) stands for covalently linked aminopropyl chains (Figure 1b). These clays do not have sensitizing action because of the absence of metal ions such as \(\text{Al}^{3+}\) and \(\text{Fe}^{3+}.\)\(^{1,2}\)

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.\(^{1,2}\)

Teraphenylethylene (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 optoelectronics 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 phanthenrene 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 procedure\(^{16}\) 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 \textit{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-hydrophenanthrene intermediate (DHP5) (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 \(^1\)H-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 ac. TPTS (10^-4M) 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.

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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^-4M) with various weight percentages of AC. (e) Emission spectra showing the enhanced emission from TPTS (10^-4M) on binding to AC (0.9 wt%), this dye conjugated state has been designated as AC-TPTS, \(\beta = 1\) cm, \(\lambda_{ex} = 350\) 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.

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spectrometry (LC-MS) analysis of a 100 min aliquot showed around 750 mins to complete. Liquid chromatography-mass starting material (absorption spectra and MS of fraction 1 corroborate d with the two peaks (marked as 1 and 2 in Figure 2d). The UV/ vis monotonic increase in intensity (Figure 2c). The reaction took band at 400 nm was plotted against time which showed a formation of phenanthrene derivative. The intensity of the This journal is © The Royal Society of Chemistry 20 xx decay processes.

Initially at t = 0 the emission is quenched due to non-radiative solution under light (Top panel, Figure 2). A 10

4 M, l = 1 cm, λexc = 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 absorption3. (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-f). (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.9

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 was quenched due to non-radiative decay processes.8 With time the evolution of an emission with λmax 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 C₂-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 k₂ > k₁. 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 (k₁) i.e. the rate constant involved in electrocyclic ring closure, can be extracted (Figure S9). After fitting to an appropriate function k₁ was found to be 3.7 x 10⁻¹ 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 (λmax = 475 nm) after 30 mins went to a state AC-f₁ (λmax = 420 nm) and then finally after 240 mins to AC-f₂ (λmax = 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 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 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 1 to be comprised of a di-hydrophenanthrene derivative. Attenuated total reflectance-Infrared (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).

Since di-hydro phenanthrene derivatives have been rarely isolated and characterized we decided to do extensive characterisation of these species. To our surprise the isolated derivative from fraction 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 $-\text{CH}_2$ carbons as shown by negative peaks in Figure 3c (peaks in the region 20-30 ppm). Counting the number of $-\text{CH}$ and $-\text{CH}_2$ peaks it became evident that the di-hydro derivative is indeed an isomerized counterpart of DHPS. Visual interpretation of $^1$H and $^{13}$C-NMR showed that the spectra deviates from C$_2$-symmetric spectra obtained for phenanthrene (Figure 4, S16-22). Moreover in $^1$H-NMR two triplets could be clearly seen in the low field region of 2.6-2.8 ppm. From heteronuclear correlation spectra (HETCOR) these $^1$H-peaks at around 2.6-2.8 ppm could be correlated with the $-\text{CH}_2$ peaks as determined by DEPT (Figure S23). The remainder of the $-\text{CH}$ 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 $f_{1pp}$.

$^1$H-correlation spectroscopy (COSY) helped in understanding the through bond proton connections of the molecule ($f_{1pp}$, Figure 4, S25-27). Protons $H_1$ and $H_6$ correlated with $H_i$ and $H_j$ respectively confirming the nascent aromatic structure of part of the molecule which did not take part in the photo-reaction (Figure 4, S25). Proton $H_6$ correlated with $H_4$ confirming the presence of an aromatic system in the modified part of the molecule (Figure 4, S25). Proton designated as $H_2$ correlated with another aromatic proton $H_4$ which signified a four proton meta coupling (Figure 4, S26). Moreover, proton $H_8$ correlated with the low field $-\text{CH}_2$ 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 $^1$H-NMR spectra. Furthermore these $H_2$ and $H_8$ 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 $H_7$ correlated with $H_8$ 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 1 and 2 also contained decarbonylated 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 \( f_{\text{pp}} \) and \( f_{\text{dc}} \) (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 \( f_{\text{pp}} \) 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.

![Diagram of chemical reactions](Figure 5. (a) and (b) showing the emission intensity of AC (0.9 wt%) conjugated TPTS \([10^{-7}\text{M}]\) (l = 1 cm, \( \lambda_{\text{ex}} = 350 \text{ nm} \), 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-f\( _1 \), (b) AC-f\( _1 \) to AC-f\( _2 \))]

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. Therefore to a methanol solution of \( f_{\text{pp}} \) 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 \( f_{\text{pp}} \) 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-f\( _1 \) and AC-f\( _1 \) to AC-f\( _2 \)) are significantly retarded. This points to the fact that not only TPTS to \( f_{\text{pp}} \) is governed by light; \( f_{\text{pp}} \) to PHES is also critically photo-controlled. Since the final oxidation cannot be done by light alone this hints that in this case \( f_{\text{pp}} \) 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. Furthermore, we investigated the possibility of propyl amine chains (which are a component of AC) acting as a base in the photo reaction. 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.

![Diagram of reaction sequence](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.

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Notes and references

17. Although irradiation of TPE derivatives have been attempted in the aggregated state (ref.9 b.f), it does not yield the intermediate but rather just the phenanthrene derivative. The molecule used is substituted with electron rich moieties and thus its oxidation rates would be significantly higher compared to ones with deactivate substituents such as in the present case.
18. 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. Y.-Y.; Williams, I. D.; Gu, X.; Miao, Q.; Tang, B. Z. Chem. Sci. 2015, 6, 3538. This paper describes the formation of dihydrophenanthrene 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.