Electrostatic self assembly and characterization of ultra thin films of a secondary diazo dye

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Abstract In this communication characterization of Electrostatic Layer by Layer (ELBL) Self Assembled films of secondary diazo dye Congo Red (CR) by alternate adsorption of Poly (allyl amine hydrochloride) (PAH) and CR is reported. The UV-Vis absorption spectra and second derivative analysis of ELBL films revealed the formation of J aggregate of CR molecules in the films. The film growth without any material loss, during subsequent deposition was evident from the Layer effect study of the ELBL PAH-CR films. About 10 minutes of time was required to complete the interaction between CR and PAH molecule in a single bi-layer of ELBL film. Theoretical correlation of the experimental adsorption kinetics data for PAH-CR ELBL films was found to follow second order adsorption kinetic equation. The pH of solution was observed to influence the adsorption process of CR in the PAH-CR films inversely.

Keywords Congo Red, Electrostatic Layer by Layer, Adsorption, Electrostatic interaction

1. INTRODUCTION
Congo Red is a low molecular weight anionic secondary diazo dye used in variety of products such as consumable goods, textile and leather etc [1]. Formation of ultrathin films of organic dyes based on molecular self assembly is a very important novel technique to form structures for a huge number of technical applications as wetting, lubrication, adhesion, [2-4] molecular electronic devices, electroluminescent device and second harmonic generation [5-9].

Electrostatic Layer by Layer (ELBL) has been shown to be simple and versatile method for assembling thin films. In the recent times this method has been extended to a wide variety of interesting charged materials, metals and semiconductor nanoparticles [10]. The ELBL method has been also quite successful for the layering of biological components such as proteins, enzyme, cell membrane, Viruses, and DNA [11-12].

ELBL self assembled technique relies on the electrostatic interaction of anionic and cationic pair during successive deposition. There has been a significant progress in the field of fabrication of ELBL films of organic material which offers interesting electronic and optical properties. The fabrication and manipulation of molecular layers by this process is difficult due to presence of small numbers of charged groups in these molecules. Physi-absorption of such molecules is not straight forward and tremendous material loss is being reported of ELBL self assembled ultrathin films of organic molecules [13]. In this paper we report successful incorporation and detailed characterization of different photophysical properties of PAH-CR films formed by ELBL deposition technique. ELBL films of Congo Red (CR) are prepared without any material loss and further more, the adsorption kinetics were also studied along with the effect of pH of the electrolytic solution.

2. EXPERIMENTAL
Congo Red (CR) ($M_w=696.66$), purity > 99% and PAH ($M_w=70,000$), purity >99%, were purchased from Aldrich Chemical Co. and were used as received. The chemical structures of PAH and CR are shown in figure 1. The sequential adsorption of CR and PAH from dilute solution to form PAH-CR...
multilayer was carried out by the same procedure presented in previous work [12]. The electrolytic deposition bath was prepared with $10^3$ M aqueous solution using triple distilled deionised (18.2 MΩ) Millipore water. A thoroughly cleaned quartz substrate was first immersed into PAH aqueous solution for 15 minutes. After rinsing 3 times in Milli Q water (2 minutes each bath with agitation), the modified substrate was then transferred into the CR solution for 15 minutes, agitated and washed 3 times with water for 2 minutes. All the adsorption procedures were carried out at room temperature (approximately 25°C). The repetition of the whole sequence produced desired number of bi-layers of EBL films. The characterizations of PAH-CR EBL films have been done by UV-Vis absorption (Lambda -25 UV-Vis spectrometer, Perkin Elmer)

![Chemical structures of PAH and CR](image1.png)

**Fig.1** The chemical structures of PAH and CR

### 3. RESULTS AND DISCUSSION

Figure 2 shows the UV-Vis absorption spectra of aqueous solution of CR ($1 \times 10^{-5}$) and 1 bilayer EBL film of PAH-CR along with microcrystal (MC) of CR. The upper spectrum is the second derivative of the spectrum of 1 bilayer of PAH-CR film.
The UV-Vis absorption spectra of aqueous solution of CR (1 X 10^{-5}) and 1 bilayer ELBL film of PAH-CR along with microcrystal (MC) of CR. The upper spectrum is the second derivative of the spectrum of 1 bilayer of PAH-CR film.

From the calculation of Edwards and Woods\[14]\ it was found that the band at 339 nm is due to transition moment parallel to the short axis of CR and that for 500 nm band the transition moments are parallel to long axis of the molecule. Since there is a strong appearance of band at 520 nm in the ELBL film, it suggests that the CR molecules are aligned in such a way that the transition moments are along the longer axis. It is observed that the solution spectra has a shorter wavelength at 340 nm where as the band gets shifted to 350 nm in both ELBL films and MC. The maximum absorption of CR is at 495 nm and there is a red shift of about 15 nm compared with that of PAH-CR bilayer film. This spectroscopic red shift has been reported earlier and it is attributed to the formation of well ordered J aggregates in the film domain \[15\]. The band at 510 nm is a longer wavelength band, second derivative analysis revealed hidden component at 520 nm which is absent in the solution spectra. This may be due to the fact that in solution of CR molecules are in "monomer" form, minor band found at 520 nm in case of film can be related to CR molecules are in "associated" form. This appearance of new band is useful for finding the molecular association of CR species. According to the molecular excition theory \[18\] the energy difference between the excited monomer level and the exciton level is given by

\[ \Delta E = M^2 \left(1 - 3\cos \theta \right)/R^3 \]

Where M is the electric dipole transition moment and R is the distance between the molecules. Here is

http://www.chemistrymag.org/cji/2008/108038pe.htm
the angle between transition dipole moment and the molecular bonding axis. If $0^\circ < \theta < 54.7^\circ$, the excitation level is energetically located below the monomer level causing red shift in the electronic absorption spectrum creating J aggregates\(^{[19]}\). So by molecular excitation theory the red shift in the spectra can be identified as formation of J aggregates.

The location of the 520 nm band being close to that of the band exhibited by aggregated species can be said due to dominance of associated species over the monomeric species in the ELBL films. A schematic representation of the interaction scheme between PAH and CR molecules is shown in figure 3. The interaction scheme reveals that the anionic part of CR molecules interact with the cationic part of the PAH molecule forming complex species. In the complex species CR and PAH molecules get closer side by side and closer association of CR molecules take place which might cause the shift of absorption band in the PAH-RB ELBL films.

![Schematic Representation of the Interaction Scheme Between PAH and CR Molecules](image)

**Fig. 3** A schematic representation of the interaction scheme between PAH and CR molecules.

### 3.1 Layer Effect

Figure 4 shows the UV-Vis absorption spectra for the multilayer prepared by sequential deposition of PAH and CR from their dilute solution. It was observed that the absorption spectra of different layered (1- bilayers) PAH-CR ELBL Self assembled films show almost similar band pattern with characteristic peak at 350 nm and 510 nm irrespective of the layer number except an increase in absorption intensity. The characteristic peaks at 350 nm and 510 nm is due to $\pi - \pi^*$ transition\(^{[16]}\). Inset (a) of figure 4 is the plot of absorbance at 510 nm as a function of numbers of bilayer. A linear increase of intensity with a slope of 0.0051 O.D/ bilayer was observed which indicated that the sequential growth of PAH-CR assemblies was linear and reproducible.
Fig. 4 shows the UV-Vis absorption spectra for the multilayer prepared by sequential deposition of PAH and CR from their dilute solution. Inset (a) is the plot of absorbance at 510 nm as a function of numbers of bilayer. Inset (b) the ratio of intensities of aggregate and monomeric band as a function of number of layers deposited.

The electrostatic interaction between PAH and sulfonate anion of CR is crucial driving force in the formation of PAH-CR films. The formation of J aggregates among CR molecules leads to a considerable increase in the dye content in the composite films.

In order to know whether the nature of aggregation has changed as deposition progressed, we have plotted the ratio of intensities of aggregate and monomeric band as a function of number of layers deposited (Inset b of Figure 4). The ratio remained almost same for all the number of layers which indicated that there is no change of nature of aggregation during the deposition process.

### 3.2 Binding and material loss

The binding property and material loss of PAH–CR films prepared on the quartz surface was evaluated by UV-Vis absorption spectra of films after dipping in CR solution and PAH solution.
Fig. 5 shows the intensity of absorption maximum at 510 nm as a function of number of deposited layers. The (□) represent absorption maximum recorded after deposition of CR and (∆) represent the absorption maximum after each layer deposition of polycation (PAH).

Figure 5 shows the intensity of absorption maximum at 510 nm as a function of number of deposited layers. The (□) represent absorption maximum recorded after deposition of CR and (∆) represent the absorption maximum after each layer deposition of polycation (PAH). From the Figure it is evident that the absorption maxima increases after each CR layer and remained almost same after deposition of each PAH layer. This confirms that the CR molecules do not come out of the film during PAH deposition, which implies that the binding between PAH and CR molecules is very strong and thus PAH-CR EBL films are fabricated almost without any material loss.

3.3 Adsorption dynamics
Fig. 6 The adsorption of CR on the PAH films at different immersion times. Inset of figure 6 is a plot of the maximum absorbance as a function of time. The experimental result (solid line) and the dotted line in the inset of figure 6 show the curve generated by fitting to the second order kinetic rate equation.

Figure 6 shows the adsorption of CR on the PAH films at different immersion times. The adsorption takes place at a relatively fast rate in the first 10 minutes. The fast rate of adsorption initially is probably due to the availability of greater binding sites around the surface of PAH film on quartz substrate and in course of time all the interaction with CR molecules at all the binding sites gets over and no PAH remains free for further interaction. Inset of figure 6 is a plot of the maximum absorbance as a function of time. The experimental result (solid line) is found to fit well to the second order kinetic rate model given by the equation [17].

\[ A = k_1(1 - e^{-t/\tau_1}) + k_2(1 - e^{-t/\tau_2}) \]

Where \( A \) is the absorbance (taken as proportional to the amount of adsorbed material), \( k_1, k_2 \) and \( n \) are constants. \( \tau_1 \) and \( \tau_2 \) are the characteristic times. The dotted line in the inset of figure 6 shows the curve generated by fitting to the above equation. Table 1 shows the values of different parameters used for fitting the experimental data.

Table 1

<table>
<thead>
<tr>
<th>Parameters used in equation 1 for fitting Experimental data</th>
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<tr>
<td>( k_1 = 0.00996 \pm 0.001 )</td>
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3.4 Effect of pH and adsorption

A remarkable dependence on pH of the CR solution was found for PAH-CR films fabricated at different pH value of anionic solution. Figure 7 shows the absorption spectra of PAH-CR films fabricated at different pH of solution. It is observed that adsorption increased with the decrease of pH and decreased with the increase of pH. The increase in adsorption of CR molecules may be due to increased protonation of the amine group of NH₃⁺ of PAH. CR is an acidic dye and contains negatively charged SO₃⁻ group which facilitates a higher adsorption of dye at lower pH due to the increase in electrostatic attraction between negatively charged dye molecule and positively charged NH₃⁺ of PAH surface. At high pH the charged surface of PAH films interacts with the negative hydroxyl ions and thereby hinders the adsorption of CR molecules due to electrostatic repulsion at the binding sites as CR is a negatively charged anionic dye. Hydrogen bonding and Vanderwaals force may be responsible at higher pH of solution.

\[
\begin{align*}
  k_2 &= 0.00989 \pm 0.001 \\
  \tau_1(s) &= 6.884 \pm 0.61 \\
  \tau_2(s) &= 61.232 \pm 7.4
\end{align*}
\]

\[n = 1.0\]

Fig. 7 The absorption spectra of PAH-CR films fabricated at different pH of solution.
4. CONCLUSION
In summary, we have demonstrated successful fabrication of ELBL self-assembled films of PAH-CR without any material loss. The layer effect study showed an increase in absorption intensity with the increase of number of layers which confirmed the growth of film. The binding property study marked a successful incorporation of CR molecules in the PAH-CR ELBL films. Thorough analysis of UV-Vis absorption spectra and second derivative analysis revealed the formation of molecular aggregates of CR molecules in PAH-CR ELBL self-assembled films. The interaction process between PAH and CR molecules was found to complete in 10 minutes and the adsorption data were found to fit well to the second order adsorption model of describing interaction mechanism. There was an inverse variation of adsorption of CR molecules with the pH of the solution.

REFERENCES