Harvesting Infrared Photons with Tricarbocyanine Dye Clusters

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*Received: June 12, 2006; In Final Form: July 21, 2006*

The absorption of 4,5-benzoindotricarbocyanine dye (IR125) in the infrared can be tuned by controlling the type of aggregation in different media. Molecular clusters of this dye formed in a mixed solvent show broad absorption in the 550−950 nm region as compared to the absorption bands of J- and H-type aggregates. The molecular clusters of the carbocyanine dye are electrophoretically deposited as thin film on optically transparent electrodes using a dc electric field. These tricarbocyanine dye cluster films are photoactive in the infrared region and produce cathodic current when employed as photocathode in a photoelectrochemical cell. Transient absorption spectroscopy of the molecular clusters show short-lived singlet state in the picosecond time scale (lifetime 6 ps) and a charge separated state in the nanosecond time scale. Implication of such dye cluster films for harvesting infrared photons in a photoelectrochemical cell is discussed.

Introduction

Many research groups are currently involved in improving the efficiency of dye sensitized solar cells and organic photovoltaic cells.[1−5] Although such cells produce power conversion efficiency in the range of ∼11%, efforts are underway to further improve their performance. Most of these cells respond mostly in the visible, a limitation imposed by the sensitizing dye or the polymer. This scenario leaves a major fraction of incident infrared light untapped. Relatively few attempts have been made to employ light harvesting sensitizers that absorb in the infrared.[6−9] In a recent study we have shown that charge-transfer interaction between an excited sensitizer and redox molecule can be used to broaden the spectral response of the photoelectrochemical cell.[10] For example, the charge-transfer interaction between free base porphyrin and fullerene is effective in harvesting photons both in the visible and infrared region.[11]

Carbocyanine dyes have the potential of harvesting photons in the red-infrared region. A commonly employed laser dye (IR125) in its monomeric form exhibits a sharp absorption and emission in the infrared region. These properties have found applications in lasing,[12] photography,[13] and photodynamic therapy.[14] Some attempts have been made to understand photochemical properties and photoinduced electron-transfer process of tricarbocyanine dyes.[15,16] An interesting aspect of this dye is its ability to undergo intermolecular interaction and produce H-type and J-type aggregates.[13] Such a property is convenient to tune the absorptive range of a photoelectrochemical cell.

SCHEME 1: Using an Electron Mediator to Shuttle Electrons for Sensitizer Regeneration
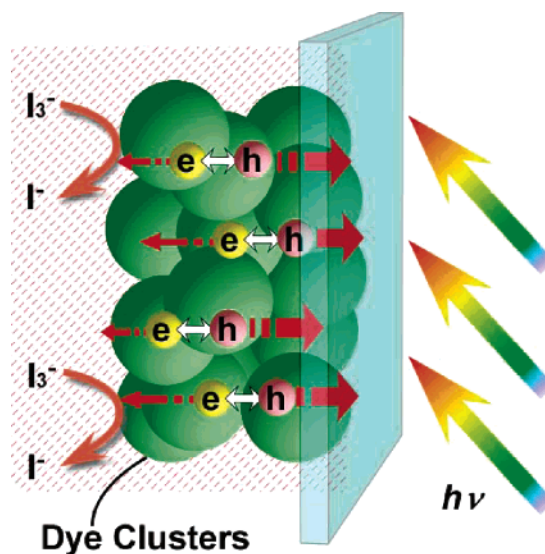
We have now made use of the self-assembling property of 4,5-benzoindotricarbocyanine dye to obtain molecular clusters and assemble them on a conducting glass electrode. The principle of photoinduced charge separation in such organic cluster film is illustrated in Scheme 1. Preliminary results that describe the photoelectrochemical and transient absorption behavior of carbocyanine dye cluster films are presented.

Experimental Section

Materials and Methods. 4,5-Benzoindotricarbocyanine, TCC dye, (commercial name IR125, Exciton Corp.), and the materials used were of the purest quality available and used as received. Absorption spectra were recorded using a Varian model CARY

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50 biospectrophotometer. A glass sheet with deposited indium−tin-oxide (obtained from Pilkington) cleaned ultrasonically in 2-propanol was used as an optically transparent electrode (OTE). All solutions used in absorption measurement contained 10 μM of monomeric TCC dye. AFM measurements were carried out with a Nanoscope IIIa (Digital Instruments, Veeco) at room temperature and in air with tapping mode.

IR125
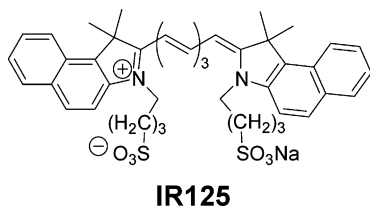
Deposition of Dye Clusters. The procedure was similar to the one described earlier for C_{60} and porphyrin clusters.[17,18] Dye clusters were prepared by injecting 20 μl of TCC dye solution in methylene chloride (1.5 mM) into 1 mL of mixed solvent of toluene and acetonitrile (25:2, v/v). These clusters were then electrophoretically deposited on the electrodes by applying a dc electric field.

Photoelectrochemical Measurements. Photoelectrochemical measurements were performed using a standard three-electrode cell consisting of a dye deposited OTE working electrode, SCE reference electrode, and Pt wire gauze counter electrode. Unless otherwise specified, all photoelectrochemical measurements were carried out in acetonitrile containing 0.3 M LiI and 0.05 M I_2 at 298 K.

Photocurrents at different applied potentials were measured using a Princeton Applied Research model PARSTAT 2263 potentiostat. A collimated light beam from an Oriel 100 W halogen lamp with a 500 nm (in the 700−1000 nm region) or a 370 nm (in the 400−700 nm region) cutoff filter was used for excitation of the electrodes. A Bausch and Lomb high-intensity grating monochromator was introduced into the path of the excitation beam for selecting appropriate wavelength. The incident photon-to-photocurrent efficiency (IPCE) at various excitation wavelengths was determined from the following expression:

$$\text{IPCE}(\%) = \frac{i_{sc}}{I_{inc}} \frac{1240}{\lambda} \times 100 \tag{1}$$

where i_{sc} is the short-circuit photocurrent (A/cm^2), I_{inc} is the incident light intensity (W/cm^2), and λ is the excitation wavelength. $I-V$ characteristics were recorded by same measurement system under irradiation of white light (100 mW/cm^2) without the monochromator and SCE reference electrode. A 400 nm cutoff filter was introduced in the path of the light beam.

Femtosecond Transient Absorption Spectroscopy. Ultrafast transient absorption experiments were conducted using a Clark-MXR 2010 laser system and an optical detection system provided by Ultrafast Systems (Helios). The source for the pump and probe pulses is the fundamental of the Clark laser system (775 nm, 1 mJ/pulse, fwhm 130 fs, 1 kHz repetition rate). 5% of the output is used to generate white light continuum probe pulses. Prior to creating the white light probe, the fundamental is fed through a delay line providing an experimental time window of 1.6 ns with a maximum step resolution of 7 fs. The pump beam is attenuated to 5 μJ/pulse with a spot size of 2 mm (diameter) at the sample where it is merged with the white light incident on the sample cell with an angle <10°. After
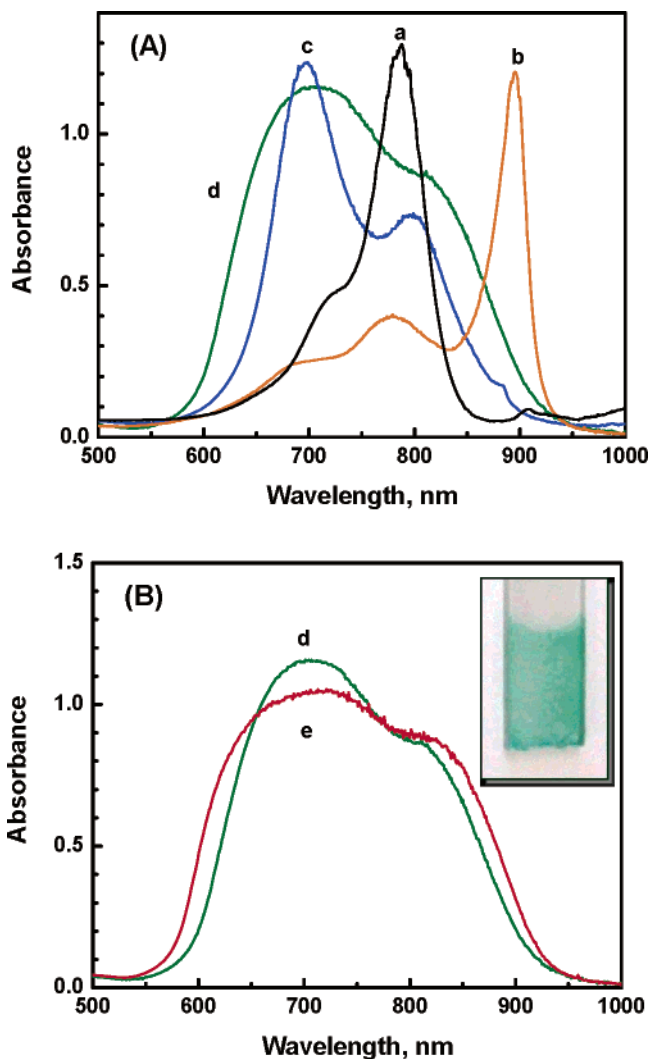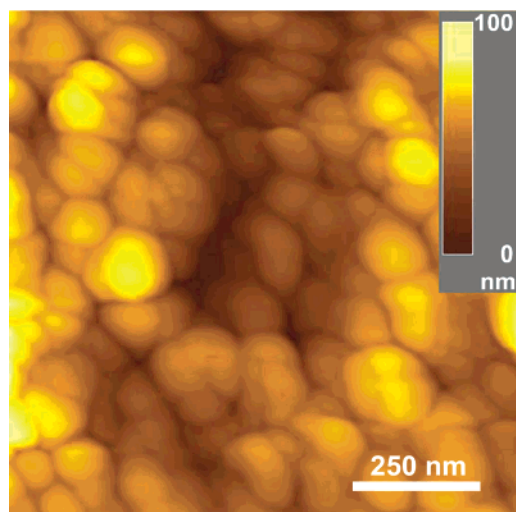

Figure 1. Absorption spectra of (A) dye monomer and aggregates formed in (a) methanol, (b) water, (c) methylene chloride, and (d) toluene/acetonitrile solution and (B) (e) TCC dye cluster film cast on conducting glass using electrophoretic deposition of clusters (spectrum d) from solution. The inset shows the dye cluster film on a conducting glass electrode.

passing through the samples, the probe is focused onto a 200 μm core fiber connected to a CCD spectrograph (Ocean Optics, S2000 UV−vis (425−800 nm), or Sensors Unlimited, SU-LDV-512LDB (750−1200 nm)), enabling time-resolved spectra to be recorded. Typically, 5000 excitation pulses are averaged to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths are assembled from the time-resolved data. All measurements were conducted at room temperature.

Results and Discussion

Absorption Properties of TCC Dye Aggregates. The tricarbocyanine dye (TCC) in its monomeric form exhibits sharp absorption band at 800 nm. The aggregation of the dye can be induced in an orderly fashion by carefully tuning the medium conditions. The absorption spectra of monomer and aggregate forms of the dye in different solvents are shown in Figure 1A. When kept stirred in water at 65 °C for 32 h, one can obtain J-aggregates with an absorption maximum at 900 nm (spectrum b in Figure 1A).[19] On the other hand H-aggregates are produced in methylene chloride medium. The observed shift in the absorption maximum is in agreement with the allowed transition for J- and H- type aggregates.[13]

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Figure 2. AFM image of TCC dye clusters deposited on a conducting glass electrode.

Figure 3. Incident photon to charge carrier generation efficiency (IPCE) of TCC cluster film electrode (OTE/(TCC)$_n$) in contact with I$^-$ and I$_3^-$ electrolyte in acetonitrile. The absorption spectrum of the electrode is also displayed.

The absorption features presented in Figure 1 show the possibility of manipulating photon harvest over a wide region in the infrared. Specifically, molecular clusters of TCC dye prepared in mixed solvents provide a wide IR-window for light absorption. The clusters were prepared by adding a known amount of H-aggregated TCC dye solution of methylene chloride to a mixed solvent of toluene and acetonitrile. The absorption spectrum of the TCC dye clusters exhibit strong absorption in the 550−950 nm region (spectrum d in Figure 1A). This broad absorption band covers the absorption range beyond the typical H-type aggregate form. This is indicative of the fact that higher aggregates other than dimers contribute to the absorption spectra. A detailed account of dimer and trimer forms of thionine was discussed in our earlier studies.[20]

For TCC clusters the electrophoretic deposition was an effective method to cast a robust film on optically transparent electrode (OTE). The absorption spectrum of the film (Figure 1B) cast on glass electrode reflects the solution spectra of the dye. Electrophoretically deposited cluster films show broad absorption in the infrared region. This is indicative of the fact that we are able to retain the respective cluster or aggregate forms in the film. The cluster films were further characterized using atomic force microscopy (Figure 2). The AFM image shows that the film consists of close packed spherical clusters of diameter ~100 nm. The porous morphology of the dye cluster films provides a large surface area for undergoing charge transfer across the interface. For comparison, aggregate forms of the TCC dye were drop cast on a glass slide to obtain thin films (see Supporting Information).

Photocurrent Generation at a TCC Dye Modified Electrode. The cluster films cast on conducting glass electrode (OTE/(TCC)$_n$) were photoactive and generated photocurrent in a photoelectrochemical cell when irradiated with infrared light. Figure 3 shows the incident photon to charge carrier generation efficiency (IPCE) of OTE electrodes modified with TCC clusters. The experiments were carried out in a two-arm flat cell and the illumination area was limited to 0.32 cm^2. The TCC cluster-modified OTE electrode shows photocurrent response in the infrared with a maximum IPCE around 2%. The absorption spectrum of the cluster film shows a close match of the spectral response in the 550−950 nm region. However, it is interesting to note that the IPCE at longer wavelengths (> 700 nm) is relatively lower compared to the response at shorter
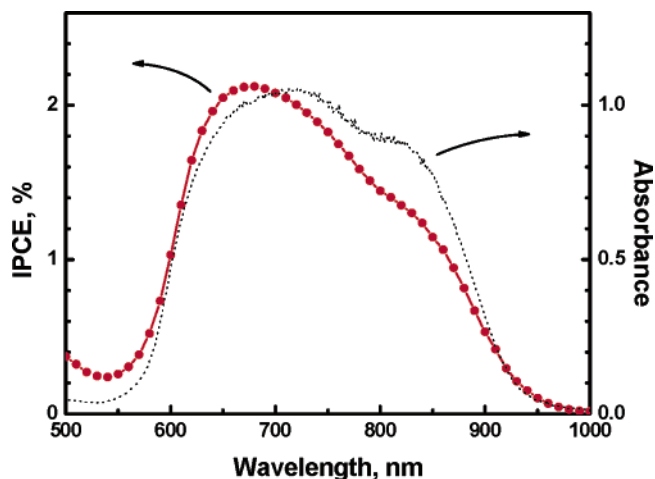
wavelength. The mismatch between the absorption and IPCE spectra is indicative of the fact that different forms of aggregates contribute to photocurrent generation with different photoconversion efficiency. As shown in the Supporting Information, the J-aggregates have relatively lower efficiency. Thus, H-aggregates are the predominant species in the cluster film that are responsible for the photocurrent generation. Variation in the photosensitizing properties of merocyanine aggregates has also been observed earlier.[21]

The photocurrent generation in these films is dependent on the exciton diffusion and charge separation following the infrared excitation. The mechanism is similar to the one observed for organic semiconductors.[5,22] In the present case, the photocurrent generation is facilitated by the hole transport to the collecting electrode surface and scavenging of electrons by the redox couple (I$_3^-$/I$^-$) at the electrolyte interface. The domination of the hole transport in the TCC cluster film is evident from the cathodic photocurrent seen during the operation of the photoelectrochemical cell. To confirm the organic semiconductor behavior of TCC cluster film, we probed the photovoltage generation in the absence of a redox couple. A photovoltage of the order of 100 mV was observed even when a redox couple was excluded from the electrolyte (namely in neat acetonitrile containing 0.1 M tetrabutylammonium perchlorate). Based on this observation we can rule out the electron-transfer process between excited dye and iodide redox couple as the contributing factor to the observed photoelectrochemical effect. This is in contrast to the photogalvanic mechanism of photocurrent generation at a C$_{60}$ cluster film.[17] Thus, we can conclude that the semiconducting property of the TCC cluster film is responsible for the photocurrent generation in TCC cluster films.

The low IPCE of TCC cluster film shows that the charge separation is relatively poor. The zero current potential or flat band potential condition is observed at +0.085 V. The charge separation at this potential becomes negligible. Upon application of an external bias it is possible to improve the charge separation. The *I*−*V* characteristics shown in Figure 4 shows increased cathodic photocurrent at negative applied potentials. Even application of −0.1 V versus SCE is sufficient to boost the photocurrent generation. The cathodic photocurrent generation at TCC film electrode suggests the domination of hole transport to the working electrode, a behavior commonly observed with p-type semiconductors.
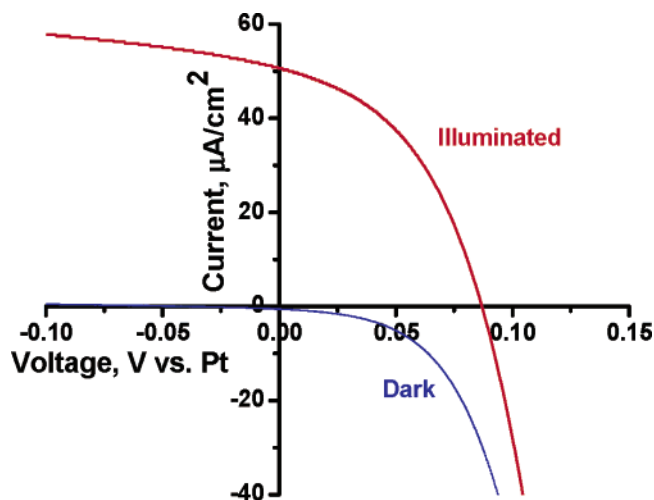
Figure 4. *I−V* characteristics of the OTE/(TCC)$_n$ electrode in dark and under IR illumination (λ > 550 nm) (electrolyte: I$^-$/I$_3^-$ redox couple in acetonitrile).

Femtosecond Spectroscopy of Ultrafast Events during the Photoexcitation of TCC Clusters. The time-resolved absorption spectra of the transients formed following 775 nm laser pulse excitation of TCC clusters in solution and films were recorded using femtosecond pump−probe spectroscopy (Figure 5A).

Because of its absorption in the infrared, TCC clusters are excited to their singlet state during 775 nm laser pulse excitation. The formation of the singlet excited state is evident from the transient absorption spectrum recorded immediately after 130 fs laser pulse excitation. The decay of this absorption band in the visible parallels the bleaching recovery in the infrared region for clusters in solution and film. For TCC clusters in solution, the decay of the singlet excited state and the recovery of the bleached absorption are completed within 600 ps. The lifetime of the singlet excited state as determined from the first-order kinetic fit is 6 ps. An excited singlet of H-aggregate usually decays into excited triplet state via an allowed intersystem crossing process.[23,24] For TCC clusters in solution, we do not observe any long-lived transients, thus ruling out accumulation of triplet or charge separated states. It is likely that the excitation of TCC clusters in solution is dominated by the formation of an excitonic state which quickly recombines to generate the ground-state molecules.

The TCC cluster films on the other hand show the formation of a long-lived transient. A residual absorption is seen in the transient spectrum recorded 600 ps after laser pulse excitation. The broad absorption of this long-lived spectrum is different from the one recorded at early times. The dye cation and anion generated via pulse radiolysis show absorption in the 450−625 nm. These observations indicate that charge separated products accumulate following the initial singlet/exciton decay. Comparison of the kinetic traces at 560 nm in Figure 5B and C confirms the presence of a long-lived product only in the cluster film. Such a long-lived product supports the argument for the photoinduced charge separation leading to the generation of photocurrent at TCC films. Future studies will focus on elucidation of the events that follow the initial excitation of the dye clusters and to improve the performance of infrared sensitive photoelectrochemical cells.

Conclusions

Molecular clusters of a carbocyanine dye, IR125, exhibit broad absorption in the infrared. Deposition of these clusters
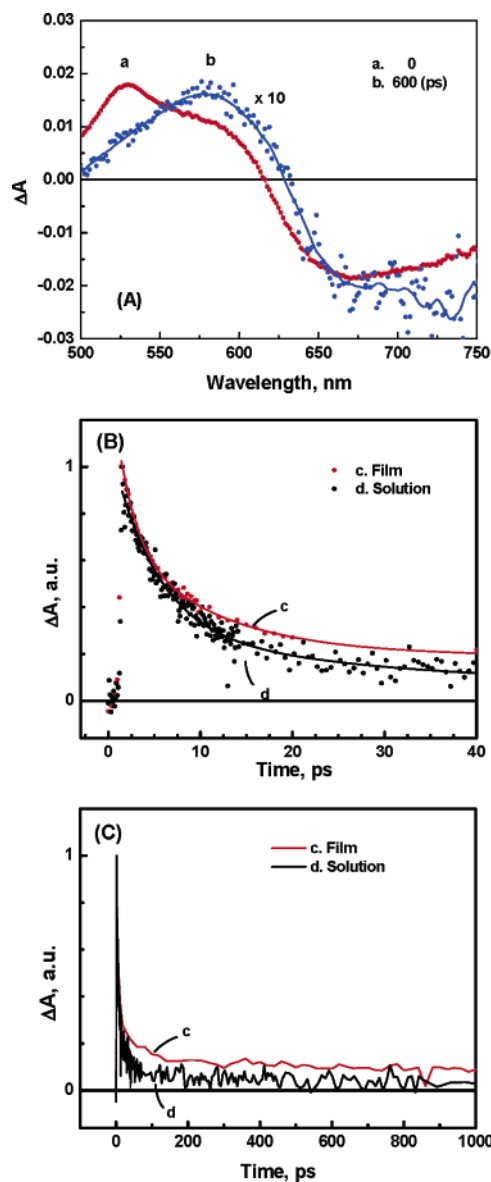
Figure 5. (A) Difference absorption spectra of TCC cluster film cast on conducting glass electrode (OTE/(TCC)$_n$) recorded after 775 nm laser pulse excitation at probe wavelengths at (a) 0 and (b) 600 picoseconds. Absorption−time profiles recorded at 560 nm for the (B) short time and (C) long time scales for (c) OTE/(TCC)$_n$ and (d) (TCC)$_n$ cluster suspension in toluene.

on a conducting glass electrode facilitates harvesting of infrared photons in a photoelectrochemical cell. Presence of long-lived transient species confirms the charge separation in these films following IR excitation. Further improvement in the charge separation efficiency is necessary to optimize the performance of these infrared sensitive dye films.

Supporting Information Available: Absorption spectrum and IPCE response of J-aggregates of TCC dye, Figure S1. This

material is available free of charge via the Internet at http://pubs.acs.org.

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