

Spectroscopic and Photocatalytic Properties of Organic Tetracene Nanoparticles in Aqueous Solution

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A colloidal suspension of nanoparticles of the conjugated organic molecule tetracene is made by injecting a small amount of concentrated tetracene/tetrahydrofuran solution into water. The resulting nanoparticles are characterized by atomic force microscopy, their optical absorption and emission spectra, and their fluorescence decay times and quantum yields. Their optical properties in room-temperature aqueous solution are similar to what is observed for bulk polycrystalline films of tetracene, indicating a substantial amount of crystallinity. Due to their high surface area, these organic semiconductor nanoparticles demonstrate photocatalytic activity toward several different organic dye molecules in aqueous solution. The kinetics and oxygen dependence of the reactions are consistent with a heterogeneous type I reaction, similar to what is observed for other semiconductor photocatalysts, and the quantum yields at high surface coverage and low light intensity are comparable to those of inorganic photocatalysts.

Introduction

Colloidal semiconductor particles have found many applications in areas ranging from solar cells to photocatalysis to fluorescent labeling. In most cases, the semiconductor is composed of inorganic materials¹ or metals.² Recently there has been a surge of interest in the properties of organic semiconductors, both oligomeric and polymeric, mainly for applications in electronic devices such as light-emitting diodes and plastic transistors. It is an open question as to what extent such organic materials can mimic the properties of inorganic semiconductors. Two possible obstacles are the lower chemical stability of organic materials relative to inorganics and their lower charge mobility due to stronger electron–phonon coupling and greater structural disorder. Such concerns apply to both bulk samples and nanoparticles. As part of our research into the role of nanometer-scale domains in conjugated polymer thin films, we became interested in the properties of nanometer-size aggregates of organic molecules. We have found that colloidal suspensions of tetracene particles in aqueous solution are spectroscopically similar to solid films of polycrystalline tetracene and that they possess photocatalytic properties qualitatively similar to those observed for inorganic semiconductor particles.

In this paper, we describe the preparation and characterization of tetracene nanocrystals in aqueous solution. Using a simple reprecipitation method, we prepare a dilute solution of tetracene nanoparticles in water. Examination of the particles using atomic force microscopy demonstrates their large polydispersity when prepared this way. Nevertheless, these samples have well-defined spectral properties similar to those of polycrystalline thin films of tetracene. In particular, they have a smaller fluorescence quantum yield and shorter lifetime relative to monomeric tetracene in dilute solution. Their stability, on the other hand, is at least 5 times greater than that of monomeric tetracene. Most interestingly, these organic nanoparticles demonstrate photocatalytic activity toward other organic

molecules, in this case organic dye molecules. Photosensitization reactions are commonly classified as type I reactions, where the absorber reacts directly with the substrate via a charge-transfer mechanism, or type II reactions, where the absorber transfers energy to singlet oxygen, which then reacts with the substrate. Although tetracene is a known photosensitizer of singlet oxygen, the mechanism of the photocatalytic destruction of the dye molecules does not depend on the presence of oxygen, implying a type I mechanism. The reaction kinetics is consistent with a heterogeneous process, most likely involving adsorption of the substrate onto the organic particle, where it then undergoes photo-oxidation. The fact that an organic semiconductor like tetracene has reasonable stability in aqueous solution and also non-negligible photocatalytic activity under visible illumination suggests that such materials may be worth investigating as alternatives to inorganic semiconductors in applications such as photoremediation of wastewater³ and solar energy conversion.⁴

Experimental Section

Tetracene Nanoparticle Synthesis. Tetracene (TCI) is used as received. Tetrahydrofuran (THF; Aldrich, Optima grade) is vacuum-distilled before use, while the water was obtained from a MilliQ filtration system (Millipore). An 8×10^{-4} M solution of tetracene in tetrahydrofuran is made just before use, and 100 μ L of this solution is injected into 10 mL of vigorously stirring distilled water. This solution is covered with foil to minimize light exposure and stirred for at least another 10 min to ensure complete mixing. The resulting solution is a clear, pale yellow.

Tetracene Nanoparticle Characterization. To examine the physical dimensions of the suspended particles, a drop of the solution is deposited on a freshly cleaved mica surface (SPI, V1 mica) and dried under a stream of filtered nitrogen. Atomic force microscopy of the dispersed particles was done using tapping mode to avoid perturbing the particles with a Veeco Instruments Dimension 3000 atomic force microscope (AFM).

The tetracene/water samples are also characterized by their steady-state UV–vis absorption (using an Ocean Optics SD2000

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absorption spectrometer) and fluorescence emission (using a Jobin-Yvon/Spex Fluoromax2 fluorimeter). For the fluorescence measurements, the solutions are diluted to a peak optical density of less than 0.1 in order to prevent self-absorption effects. The emission and excitation slit widths are 0.25 mm, and the background due to the neat solvent is subtracted from the data. Relative fluorescence quantum yields are computed using standard methods. Fluorescence lifetimes are measured by exciting the samples with femtosecond pulses centered at 400 nm and collecting the emission using a picosecond streak camera (Hamamatsu Streakscope).

Photocatalysis Measurements. To measure the photocatalytic activity of the tetracene particles, two substrate molecules are used. Solutions (4×10^{-6} M) of the laser dye 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide (HITCI) (Lambda Physik) in distilled water were filtered and mixed with specified volumes of the tetracene/water solution. Solutions (3×10^{-5} M) of dihydrorhodamine (Molecular Probes) in a 1:5 ethanol/water solution were also made and again combined with different volumes of the tetracene/water solution. Typically, 1 mL of the tetracene/water solution is added to 10 mL of the dye solution. Both types of solutions are made the day of the experiment and stored in a refrigerator, wrapped in foil, until use. To control the oxygen content of the solutions, argon gas is bubbled through the solutions for 5–20 min depending on the volume. The amount of oxygen is measured using an oxygen detector (Biological Oxygen Monitor model 5300, YSI Inc.) and varies between approximately 5×10^{-5} M under air to 5×10^{-6} M after degassing. Solutions in deuterium oxide are made in exactly the same way as described above, except that D₂O is substituted for H₂O.

The photoreactions of the tetracene particles with the organic substrates are initiated using a mercury arc lamp with a 520 nm band-pass filter whose full width at half-maximum is 10 nm. The transmitted light ranges from 515 to 525 nm, with an intensity of 0.5–1.0 mW/cm². This leads to a maximum flux of 2.5×10^{15} photons/cm²/s incident on the sample. The solutions are sealed in a 1 cm path length cuvette and stirred during illumination. Absorption spectra are taken every 1–3 min to monitor the course of the reaction. The change in oxygen concentration during a run is not detectable.

Results and Discussion

The reprecipitation^{5,6} of tetracene into water is expected to result in a broad distribution of particle sizes, as observed previously for perylene.⁷ In Figure 1, we show a tapping mode AFM image of the nanoparticles on a mica surface. The particles have many different sizes and shapes, although all are less than one micron in diameter. A rough cataloging of the particle size and shape distribution reveals that the average particle is ~ 60 nm in diameter and 10 nm thick. Such pancake-shaped nanoparticles are expected for tetracene, which crystallizes more readily along the *ab* plane than along the direction of the long molecular axis, resulting in macroscopic crystalline flakes. The origin of the polydispersity lies in the fact that we cannot take advantage of the strategies used by other workers to control the sizes of inorganic nanocrystals, since no covalently bonded capping groups are used. Previous workers have shown that increasing the temperature and/or the volume of injected tetracene solution can increase the average size of the organic colloidal particles,⁷ but there is no evidence that the size distribution can be narrowed in this manner. The weak van der Waals interactions that drive aggregation of tetracene molecules also permit the particles to aggregate themselves, as can be seen for several particles in Figure

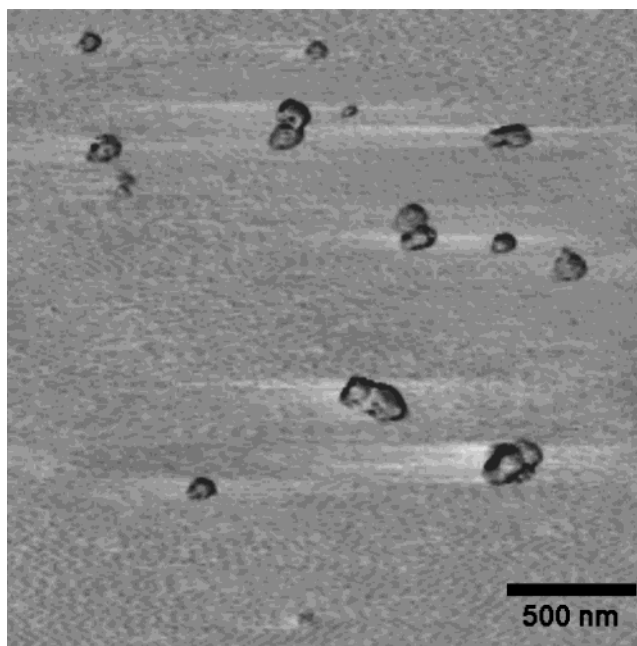


Figure 1. Atomic force microscopy phase image of reprecipitated tetracene nanoparticles deposited on a cleaved mica surface.

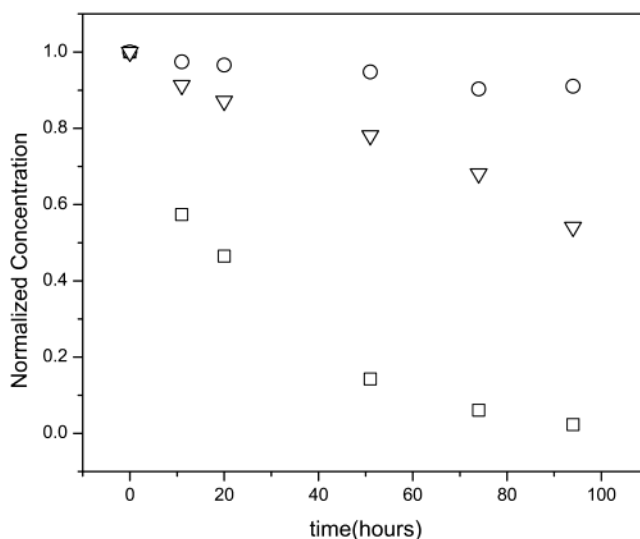


Figure 2. Time-dependent decay of 10^{-6} M tetracene in THF exposed to light (squares), tetracene nanoparticles in water exposed to light (triangles), and tetracene nanoparticles in water in the absence of light (circles). All concentrations are measured by visible absorption.

1. This tendency to aggregate prevented us from using dynamic light scattering to characterize the particle size distribution. At concentrations where a reasonable signal level could be obtained (~ 1 mg/mL), the solution was cloudy and larger particles were clearly visible by eye. A value for the mean size on the order of 100 nm could still be obtained from the data analysis, but the accompanying variance was so large that we did not think this value was meaningful.

Despite their tendency to aggregate, these nanoparticles are remarkably stable in dilute aqueous solution. This can be seen in Figure 2, which compares the stability of 10^{-6} M monomeric tetracene in THF with that of the tetracene nanoparticles in water. The disappearance of the tetracene is monitored using absorption spectroscopy. The solutions are stored under ambient atmosphere at room temperature and either covered in foil or exposed to

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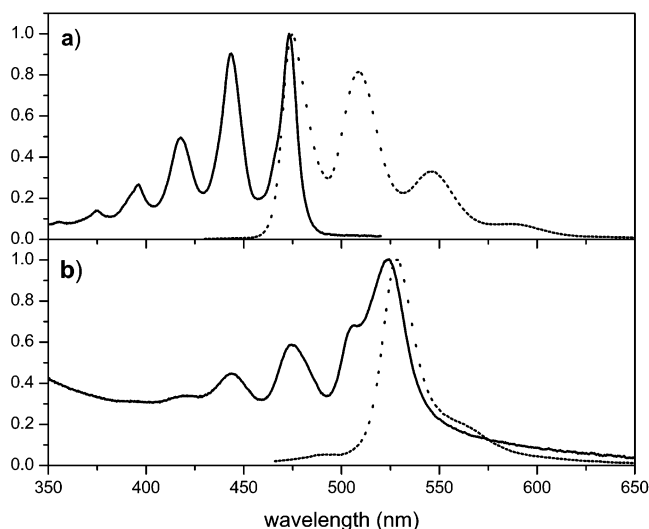


Figure 3. (a) Normalized absorption (solid) and fluorescence (dashed) spectra of tetracene in THF. (b) Normalized absorption (solid) and fluorescence (dashed) spectra of tetracene nanoparticles in water. The small shoulder at 490 nm in the fluorescence spectrum is due to scattered excitation light.

room light. The $1/e$ decay time for tetracene in THF is 25 h, regardless of light exposure, while the nanocrystals have a $1/e$ decay time of ~ 135 h. This factor of 5 in the relative stability increases considerably when the samples are not exposed to light. For samples kept in the dark, tetracene in THF disappeared at the same rate, while the tetracene nanoparticles in water decayed by less than 5% over the course of 100 h. The fact that the degradation of the nanoparticles is accelerated by exposure to light suggests that particle aggregation and precipitation are negligible over the course of a week, and we have observed that solutions of tetracene particles are stable for at least several weeks when care is taken to avoid light exposure. Tetracene in oxygenated organic solvents can react due to a variety of processes, including photodimerization⁸ and peroxidation.^{9,10} The edge-to-face packing of tetracene molecules in the crystalline state should also prevent the adoption of a cofacial arrangement necessary for creation of the bridged photodimer. The increased photostability of the nanoparticles may also be due to the dense packing of the tetracene molecules in the solid particles, which prevents easy access of reactive molecules such as oxygen to tetracene molecules in the interior of the particle. Overall, even in oxygenated aqueous solutions under ambient light, the stability of nanocrystalline tetracene is enhanced by at least a factor of 5 relative to that of monomeric tetracene in organic solvents.

To obtain information about the geometric arrangement of tetracene molecules in these nanoparticles, we have examined how the spectral properties change in going from monomeric tetracene to the nanoparticles. Figure 3a shows the absorption and emission spectra of a dilute solution of tetracene in THF. The absorption consists of a progression of evenly spaced vibronic peaks and is mirrored by the emission line shape. The fluorescence decay in a nondegassed solution is purely single-exponential with a lifetime of 5 ns, similar to what has been observed previously for tetracene in organic solvents. Figure 3b shows the absorption and emission spectra of

the tetracene nanoparticles formed by reprecipitation into water. The lowest energy absorption peak has undergone a 50 nm redshift, from 473 to 523 nm, and has developed a pronounced shoulder at 510 nm. Both the redshift and the new shoulder have been observed in both single-crystal and polycrystalline samples of tetracene.^{11–13} The shift is due to the polarizable environment of the surrounding tetracene, which lowers the energy of the transition just as a polarizable solvent would. The shoulder is due to intermolecular excitonic coupling between the two non-equivalent tetracene molecules in the crystalline unit cell, which leads to the well-known Davydov splitting observed in the absorption spectrum of a variety of molecular crystals. The presence of this splitting indicates at least some degree of crystalline order in the particles. The fluorescence spectrum is no longer a mirror image of the absorption but instead reflects the lowest exciton state in the aggregate. No emission from monomeric tetracene could be observed in these aqueous solutions. The fluorescence decay is nonexponential with a much shorter lifetime (120 ps) and lower quantum yield (by a factor of 9) than that of monomeric tetracene. The enhanced nonradiative decay rate, which is also observed in solid films,¹⁴ can result from several different mechanisms, including intersystem crossing to the triplet state, energy transfer to low-energy quenching defects or surface states, or exciton dissociation into charge-separated states. All of these processes have been observed in bulk crystals of tetracene,^{15,16} although their relative magnitudes have not been quantitatively established. The fact that tetracene reprecipitated into water forms nanoparticles whose spectral properties are similar to those of polycrystalline tetracene films is not surprising in light of earlier work on perylene and other organic molecules. Matsui¹⁷ and Oelkrug^{18,19} have both shown that such nanoparticles can be useful models to help understand the properties of related solid-state systems.

The fact that most of the absorbed photons do not result in fluorescence and that the nanocrystals slowly degrade under visible illumination suggests that these particles can initiate photochemical reactions. A clue to the identity of these reactions may be obtained by observing what happens when a second molecule is added to a solution containing the nanocrystals. We have examined the influence of the tetracene nanoparticles on the photochemistry of two organic molecules, HITCI and dihydro-rhodamine (DHR), whose structures are shown in Figure 4. Figure 5a shows how the absorption spectrum of a solution containing both the nanocrystals, whose peak absorption is 0.02 at 525 nm, and HITCI, whose peak absorption in water occurs at 735 nm, changes under visible illumination. The actual concentrations of both the tetracene molecules and HITCI molecules are actually similar, 8×10^{-6} M for tetracene and 5×10^{-6} M for HITCI,

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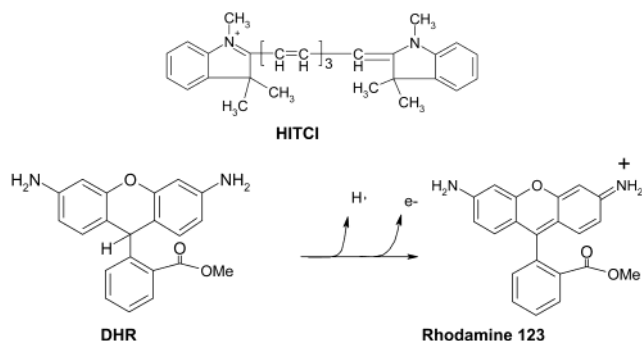


Figure 4. (a) Structure of the cyanine dye 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide (HITCI). (b) Oxidation mechanism of dihydrorhodamine (DHR) resulting in Rhodamine 123.

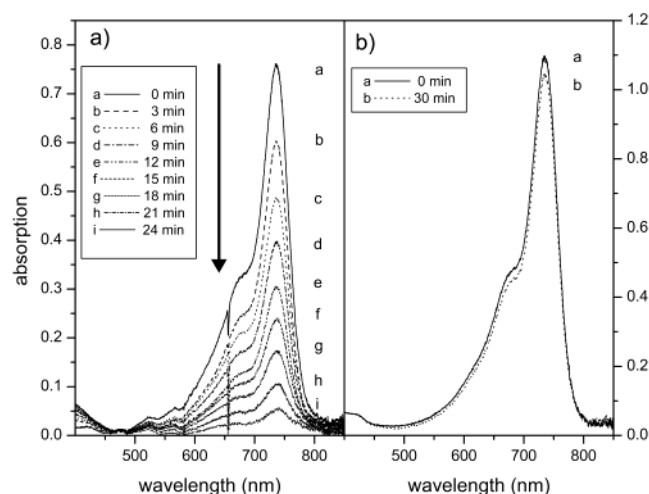


Figure 5. (a) Time-dependent change of the absorption spectrum for an air-saturated aqueous solution containing tetracene nanoparticles and the cyanine dye HITCI during illumination at 520 nm at room temperature. The tetracene nanoparticle absorption at 523 nm is barely visible under the short-wavelength wing of the HITCI. The spike at 665 nm is an artifact due to the detector. (b) Time-dependent absorption spectrum of an air-saturated solution containing only HITCI during illumination at 520 nm.

but the tetracene is aggregated and the concentration of these aggregates, which contain on average 10^5 – 10^6 molecules, is orders of magnitude lower than the concentration of the HITCI. The solution is exposed to narrowband illumination centered at 520 nm, near the peak of the tetracene absorption, with an intensity of 2 mW/cm² or less. Over the course of 30 min, the HITCI absorption disappears while the small tetracene absorption does not change. The reaction rate depends linearly on both the amount of tetracene and the light intensity up to 2 mW/cm². Illumination of the tetracene solution for several hours does not diminish its ability to degrade the HITCI. In the absence of tetracene, the HITCI is virtually unaffected by visible illumination, as shown in Figure 5b. In the absence of light, the HITCI/tetracene solution is also stable. When a solution of monomeric tetracene and HITCI in tetrahydrofuran is illuminated at 450 nm, no decrease in the HITCI absorption is observed over the course of 1 h. These control experiments prove that the photodestruction of HITCI only occurs in aqueous solution with tetracene nanoparticles.

The reaction kinetics of both the HITCI destruction and DHR oxidation is nonexponential. Figure 6 plots the disappearance of the HITCI under illumination, with a logarithmic plot in the figure inset. The time dependence

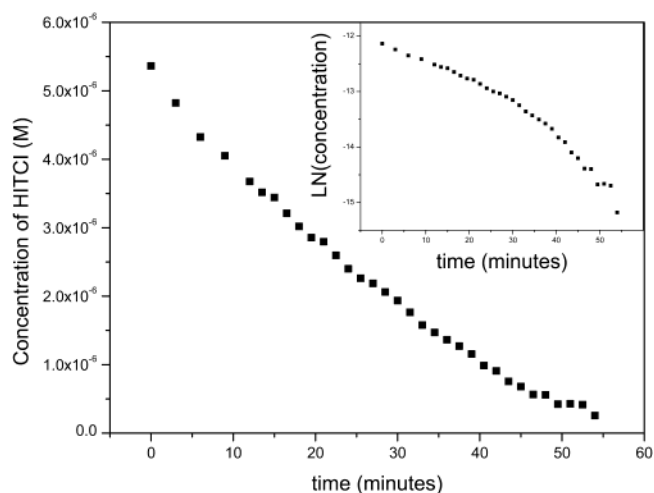


Figure 6. Linear decay of HITCI absorption at 735 nm in the presence of tetracene nanoparticles during illumination at 520 nm. The intensity of light used in this experiment was half that used for the experiment shown in Figure 5. Inset: logarithmic decay of HITCI absorption.

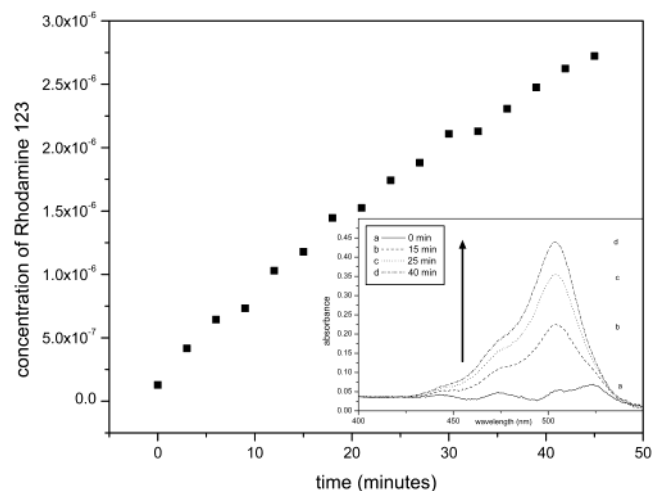


Figure 7. Linear growth of Rhodamine 123 concentration in an air-saturated aqueous solution containing tetracene nanoparticles and DHR which is exposed to 520 nm light. Inset: Experimental absorption spectrum at four different times showing the growth of the Rhodamine 123 absorption peak, centered at 503 nm, over the tetracene nanoparticle absorption peak at 523 nm.

of this reaction is close to linear as opposed to exponential, suggesting a constant reaction rate independent of concentration in the range studied. Such behavior, which results from a zeroth-order rate, is often observed in heterogeneous reactions.^{20,21} Further support for the zeroth-order rate behavior is obtained from the kinetics of the DHR reaction, where the concentration of the product increases linearly with time over almost 2 orders of magnitude, as shown in Figure 7. In this reaction, the DHR is oxidized from the leuco form, which absorbs in the ultraviolet, to the visible-absorbing cation by hydrogen atom extraction and the loss of an electron, as outlined in Figure 4. In both cases, the data are consistent with a reaction controlled by adsorption/desorption onto a different phase, most likely the surface of the nanoparticle. A model commonly used to interpret kinetic behavior in

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photocatalysis is the Langmuir–Hinshelwood mechanism,²² which takes the surface coverage into account and yields a rate law of the form

$$\frac{\partial[\text{HITCI}]}{\partial t} = \frac{k\kappa[\text{HITCI}]}{1 + \kappa[\text{HITCI}]} \rightarrow k \quad \text{when } \kappa[\text{HITCI}] \text{ is } \gg 1 \quad (1)$$

where k is the reaction rate and κ is the ratio of adsorption/desorption rates.²⁰ At high HITCI concentrations, where the surface coverage is close to unity, this equation predicts a constant rate k , which depends on factors such as light intensity and the concentration of tetracene. Rather than trying to make detailed fits to the data in Figures 6 and 7, we extract a more physically meaningful quantity, namely, the photochemical quantum yield. We can estimate this by assuming that the nanocrystal sites are completely occupied by HITCI molecules at the concentrations used in this work, consistent with the zeroth-order kinetics observed. In this case, we do not have to worry about modeling the adsorption/desorption kinetics, since once a photon is absorbed there is a molecule nearby for immediate reaction. The yield in this case is just the number of molecules destroyed divided by the number of photons absorbed per unit volume and time. Given a tetracene absorbance of 0.011, an intensity of 0.8 mW/cm², and from the data in Figure 5 a change in concentration over 3 min of 3×10^{-7} M, we calculate an effective quantum yield of 0.02 for this reaction when the tetracene sites are saturated. A similar calculation for the DHR data in Figure 7 results in a similar yield of 0.01. We estimate that these numbers are correct to within a factor of 2, mainly due to uncertainty in the photon flux resulting from variations in the beam profile and lamp power. These values for the photocatalytic quantum yield are similar to what has been measured for inorganic systems such as TiO₂.^{21–23}

Tetracene in organic solvents has a triplet quantum yield of about 65%²⁴ and is known to be an efficient photosensitizer of singlet oxygen.²⁵ To test whether the observed photochemistry is due to a “type II” reaction where singlet oxygen acts as an intermediate between the excited tetracene and the organic substrate, we performed several control experiments. First, we degassed the tetracene/HITCI samples prior to illumination by bubbling argon gas through them. In this way, we were able to lower the measured oxygen concentration by a factor of 10. The rate of HITCI photodegradation remained constant to within the experimental error, as did the rate of DHR oxidation. Next, we substituted D₂O for H₂O in the solutions. Deuteration has been shown to increase the lifetime of singlet oxygen by an order of magnitude, greatly increasing its diffusion length and reaction probability.²⁶ Again, we observed no change in the experimental reaction rate. In the case of tetracene particles, photocatalytic activity does not appear to require the presence of oxygen, unlike many organic photosensitizers such as Rose Bengal which act primarily through a type II mechanism that involves singlet oxygen. Such a mech-

anism gives rise to simple first-order reaction kinetics, and the rate should depend sensitively on both oxygen concentration and the lifetime of singlet oxygen in the solution. This dependence is not observed in the photocatalysis by tetracene nanocrystals.

Rather than a type II mechanism, where the rate is controlled by the encounter rate between the particle and freely diffusing HITCI or oxygen, the observed zeroth-order kinetics for the HITCI degradation and DHR oxidation is instead consistent with a heterogeneous catalytic process, for example, a Langmuir–Hinshelwood mechanism, where the rate is controlled by the availability of active sites on the particle surface. Even though they are salts, dyes such as HITCI have large hydrophobic regions and are known to associate with other hydrophobic molecules in aqueous solution, including themselves. Once adsorbed, the exact photochemistry that occurs is an open question, as is often the case in photocatalysis. Photocatalytic activity under visible illumination has been observed previously for conjugated organic molecules, although usually in conjunction with other redox-active species or in organic solvents. The most relevant example is probably the charge-transfer reactions that triplet C₆₀ undergoes in benzonitrile with a variety of organic substrates.²⁷ Previous workers have shown that charge transfer is enhanced when C₆₀ molecules form larger clusters on the 100 nm to 1 micron scale.^{28,29} It is possible that similar photoprocesses may occur in the tetracene particles and that surface charges result in a reaction between photoexcited tetracene and the adsorbed dyes. The detailed catalytic mechanism is unknown, but may be analogous to the “anoxic” mechanism of TiO₂, where the substrate is directly oxidized without the need for oxygen.³⁰ Since the mechanism of HITCI destruction has not been determined and the oxidation of DHR to Rhodamine 123 is a multistep process without a single oxidation potential to compare to that of tetracene, we have not attempted to propose a detailed mechanism for the photocatalytic process. Although tetracene has a small oxidation potential (0.77 V versus a saturated calomel electrode³¹), its excited state oxidation potential (in either the singlet or, more likely, the triplet state) may be significantly larger. It is also possible that a defect site or surface state might act as a more potent oxidizing agent. Further studies are needed to determine if such a process is feasible for these materials.

Conclusions

From this work, we have seen that organic semiconductor nanoparticles made using a simple reprecipitation method possess interesting and perhaps useful properties. We have characterized their size and spectroscopic properties in room-temperature aqueous solution, which provide evidence that their internal structure is similar to that of polycrystalline solid films of tetracene. Furthermore, these nanoparticles have significant photocatalytic activity toward other organic molecules, specifically organic dyes. As is often the case in photocatalysis, the exact mechanism of reaction is not well-understood, but it likely involves adsorption onto the particle surface, followed by electron-transfer chemistry. This conclusion

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is consistent with the observed kinetics and the lack of any effect of oxygen on the reaction rate. If this is the case, then the reaction is similar to what has been observed previously for inorganic semiconductor photocatalysis. The use of organic semiconductors in aqueous solution brings two potential advantages relative to a large band gap semiconductor such as TiO_2 : the ability to drive the reaction using visible wavelengths as opposed to near-ultraviolet and the possibility of very low costs. When these particles are compared to inorganic semiconductor nanoparticles, the two main disadvantages of tetracene nanoparticles are their limited stability and their polydispersity. The first problem may be addressed by chemical modification or encapsulation. The lack of size control is harder to overcome, since these aggregates are held together by weak van der Waals interactions rather than covalent bonds, and these weaker forces are harder to

control chemically. Since the photocatalytic activity should depend on the surface area, the controlled synthesis of small particles with high surface-to-volume ratios would be desirable. Despite these issues, such organic materials clearly merit closer examination of their photophysics and reactivity.

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