

Evidence for exciton fission and fusion in a covalently linked tetracene dimer

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Abstract

A photophysical study of the covalently linked tetracene dimer 1,4-bis(tetracen-5-yl)benzene is presented. While the dimer's steady state spectroscopy is similar to that of monomeric tetracene, it also exhibits a long-lived fluorescence signal in solution and solid polyethylene films, which is absent in the monomer. The behavior of this long-lived component as a function of temperature and oxygenation provides evidence that a small (<1%) fraction of the singlet excited states undergoes fission into two triplet states, which recombine on the order of 100 ns. A kinetic model based on this mechanism fits the fluorescence decay data quantitatively.

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1. Introduction

Polyacenes like anthracene, tetracene and pentacene are prototypical conjugated organic semiconductors [1], and have been used extensively in organic electronic devices [2]. Many of the unique properties of these materials result from strong intermolecular interactions in the close-packed crystals. It is an interesting question whether soluble covalent assemblies of these molecules can also exhibit useful electronic or optical properties. The simplest example of such a covalent assembly is two anthracenes attached at the 9 and 10 positions by a single bond. The photophysical properties of this covalent dimer of anthracene, commonly known as bianthryl, and its larger analogs, have been extensively studied. While excitonic interactions between neighboring anthracenes lead to an enhancement of bianthryl's radiative rate and changes in the spectral lineshape [3], most studies have focused on the structure and formation time of the low-lying charge transfer state in polar solvents [4–7], since it provides a good model for testing theories of solvent-controlled electron transfer in a symmetric system.

We are interested in dimeric systems of larger polyacenes, like tetracene, since these molecules have unique properties not found in anthracene. In addition to its lower energy absorption, tetracene also exhibits exciton fission and fusion in its solid state [8,9]. The splitting of a singlet excited state in tetracene into a pair of triplets is energetically allowed due to the energy of the T_1 state being almost exactly 50% of the S_1 singlet energy [10]. This spin-allowed process is of particular interest since it can, in principle, lead to photochemical quantum yields greater than unity. In this Letter, we examine the photophysical properties of the molecule 1,4-bis(tetracen-5-yl)benzene, which we will refer to as bistetracene in contrast to tetracene. The structure of this molecule is shown in Fig. 1. We find that the steady-state spectral properties of bistetracene are quite similar to that of monomeric tetracene. There is evidence for weak excitonic coupling similar to what is observed in bianthryl, but no sign of a charge transfer state even in the most polar solvents. More importantly, we find evidence for a small singlet fission channel in this molecule, whose presence is deduced by the occurrence of a temperature-dependent delayed fluorescence due to recombination (fusion) of the triplet pair. Possible reasons for the low yield (<1%) of this process relative to exciton fission

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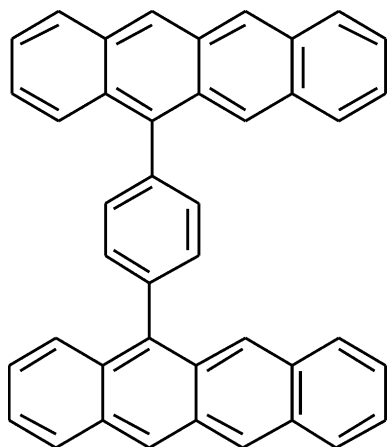


Fig. 1. Molecular structure of bistetracene (1,4-bis(tetracen-5-yl)benzene).

in solid tetracene ($\sim 50\%$) at room temperature are discussed. Despite the small contribution of this channel, it provides solid evidence that it is possible to design conjugated organic assemblies with properties analogous to those of solid-state samples.

2. Experimental

1,4-Bis(tetracen-5-yl)benzene was synthesized in two steps: bromination of tetracene to 5-bromotetracene, and Suzuki coupling of 5-bromotetracene with 1,4-phenylene diboronic acid. The modern popular approach for the monobromination of polycyclic arenes uses *N*-bromosuccinimide (NBS) in dimethylformamide (DMF) [11]. However, the low solubility of tetracene in DMF prevents direct application of this procedure. We used chloroform to obtain better solubility of the tetracene and a small amount of DMF for the NBS, which permitted the synthesis of 5-bromotetracene in high yield (90%). The Suzuki coupling of 5-bromotetracene with 1,4-phenylene diboronic acid using $\text{Pd}(\text{PPh}_3)_4$ as a catalyst formed the target compound only in a low yield ($\sim 10\%$). Varying the reaction conditions did not improve the yield. The combination $\text{Pd}_2(\text{dba})_3$ with DPEPhos (bis(2-(diphenylphosphino)phenyl)ether) as a ligand was described as an efficient catalyst for the Suzuki coupling of sterically hindered, ortho-disubstituted benzenes [12]. The application of this catalytic system to the coupling of 5-bromotetracene with 1,4-phenylene diboronic acid gave 1,4-bis-(tetracen-5-yl)benzene in 67% yield. Aqueous potassium carbonate was used instead of potassium phosphate in the original procedure. 1,4-Bis(tetracen-5-yl)benzene was purified using column chromatography and had $>98\%$ purity as confirmed by TLC, MS, and NMR data.

Tetracene was obtained from Tokyo Kasei Kogyo, Co., Ltd., benzene (spectroscopic grade) from EM Science, and low density polyethylene (LDPE) sheets from McMaster-Carr. The tetracene and bistetracene in LDPE samples were prepared by soaking the polymer sheet in saturated solutions of tetracene and bistetracene in benzene, respec-

tively, for 40 h at room temperature [13]. The concentration of bistetracene in LDPE was less than 10^{-5} M. Liquid samples were measured in 1 cm path length quartz cuvettes, while LDPE films were placed in an evacuated helium cryostat (Janis ST-100) in order to avoid photooxidation and oxygen quenching. Liquid samples were degassed by bubbling argon through them for 15 min. Samples were prepared with a peak optical density of less than 0.2 in order to prevent self-absorption effects.

Steady-state UV–Vis absorption and fluorescence data were taken using a Cary 50 Bio UV–Visible spectrometer and a Spex Fluorolog Tau-3 fluorescence spectrophotometer (excitation at 400 nm), respectively. Fluorescence lifetimes were recorded by exciting the samples with 200 fs pulses centered at 400 nm. The pulses were generated using a 40 kHz regeneratively amplified Ti:Sapphire laser system and frequency doubling in a Type I BBO crystal. The fluorescence emission of liquid samples was collected at 90° relative to the excitation, whereas for film samples the incident angle of the exciting laser beam was about 10° relative to the film surface normal. The excitation pulses exhibited linear polarization, and the angle between the polarization of the collected fluorescence light and that of the excitation light was adjusted to 54.7° (magic angle), using a thin film polarizer, in order to eliminate time-dependent effects due to molecular reorientation. The fluorescence light was directed into a monochromator attached to a picosecond streak camera (Hamamatsu C4334 Streakscope), which provides both time- and wavelength-resolved fluorescence data, with resolutions of 15 ps and 2.5 nm, respectively.

3. Results and discussion

The steady state absorption and fluorescence spectra of tetracene and bistetracene in room temperature benzene are shown in Fig. 2. The tetracene absorption peaks at 475 nm, while that of bistetracene peaks at 487 nm. The bistetracene fluorescence also occurs at lower energy: 495 nm versus 477 nm for tetracene. Along with a slightly larger Stokes shift, there is also a decrease in the intensity

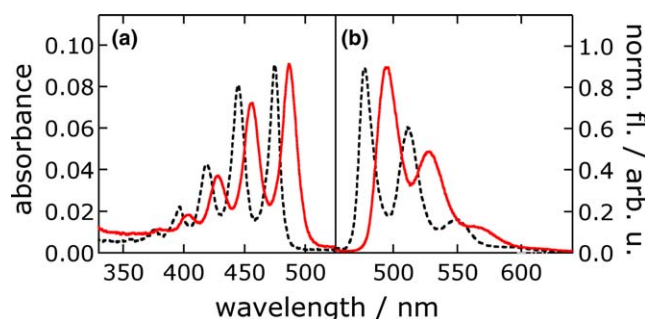


Fig. 2. (a) Absorption and (b) steady-state fluorescence spectra of solutions of tetracene (dashed black lines) and bistetracene (solid red lines) in benzene. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

of the 0–1 vibronic peak relative to the 0–0 peak. Both tetracene and bistetracene undergo a small solvatochromic shift as the solvent polarity is increased, but even going from cyclohexane to DMF, there was only a 5–6 nm red-shift, and no change in spectral shape for either molecule. The fluorescence lifetimes in bistetracene also remained essentially unchanged, so there was no indication of a charge transfer state similar to that observed in bianthryl. The fluorescence quantum yield of tetracene in benzene is 0.17 ± 0.01 , while that of bistetracene is 0.31 ± 0.02 , both measured relative to anthracene in ethanol. Both molecules have single exponential fluorescence decays over the first 2.5 decades of fluorescence intensity. For tetracene, the decay time is (3.8 ± 0.1) ns, while for bistetracene it is (6.3 ± 0.1) ns. These values are obtained by analyzing the data within a 20 ns window. The quantum yields and fluorescence decay times can be used to obtain the radiative lifetimes for the two molecules: 23 ns for tetracene and 20 ns for bistetracene. The value of 23 ns for tetracene is in reasonable agreement with our previously measured value of 27 ns in tetrahydrofuran [14], and with literature values ranging from 27 to 32 ns in other solvents [10,15], especially after the higher refractive index of benzene is taken into account [16,17]. The weakened vibronic progression and enhanced radiative decay rate in bistetracene are less pronounced than what is observed for bianthryl in nonpolar solvents [3], indicating a weaker electronic interaction across the phenylene linker group. In summary, the spectral properties of bistetracene are consistent with it being composed of a pair of weakly interacting tetracene molecules.

The most significant divergence in the behaviors of tetracene and bistetracene occurs in the behavior of their long time (20 ns–1 μ s) fluorescence decays. Fig. 3 shows a comparison of bistetracene and tetracene fluorescence decays obtained for molecules embedded in polyethylene, under vacuum at room temperature. Bistetracene possesses a second low-amplitude decay component that is absent in tetracene. The time constant of this second component is (109 ± 8) ns, much longer than the radiative lifetime obtained for bistetracene in solution. Therefore this component cannot originate directly from the initially excited

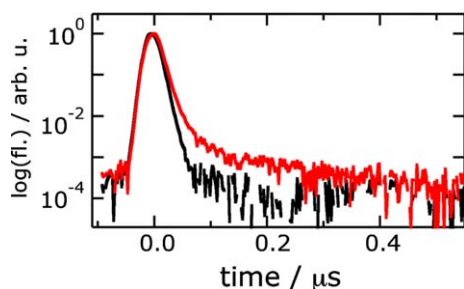


Fig. 3. Time-resolved fluorescence decays of tetracene (black line) and bistetracene (red line) in polyethylene under vacuum at room temperature. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

singlet state. There is considerable evidence that this long-lived component reflects delayed fluorescence resulting from the intramolecular recombination (fusion) of two triplets formed within the same bistetracene molecule. First, the long-lived component disappears when the sample is cooled to 40 K, where the fluorescence decay becomes indistinguishable from that of tetracene. This is consistent with the temperature dependence observed for exciton fission and fusion in solid tetracene [9,18]. Second, the long-lived component in bistetracene was also present in liquid solutions, as long as the solutions had been thoroughly degassed. Fig. 4a shows how the long-lived decay is enhanced by degassing a dilute benzene solution, where its decay time is ~ 115 ns, but is completely absent in an oxygenated solution. This is consistent with triplet quenching by O_2 molecules, which prevents fusion. Third, Fig. 4b shows that the spectrum of the long-lived emission measured in the 100–300 ns window is identical to the bistetracene singlet spectrum measured in the 0–20 ns window in degassed benzene; therefore it does not result from an unknown low-lying state in the molecule. Other possible explanations are less likely. Intermolecular triplet–triplet annihilation due to diffusive encounters between different molecules can be ruled out based on the fact that the long-lived decay is observed for bistetracene in both rigid and fluid media, but never for tetracene. Furthermore, the relative amplitude of the long-lived component does not depend on laser intensity. If the delayed fluorescence was the result of intermolecular triplet fusion, then the long-lived component should depend on the square of the laser intensity and its amplitude, relative to the peak, should change with laser power [17]. Since the signal is so small, there is a concern that fluorescent impurities at concentrations below the level specified by NMR and MS analysis could contribute to the signal. However, it is unlikely that the emission from such species would be identical to that of bistetracene, or that it would disappear at low temperatures.

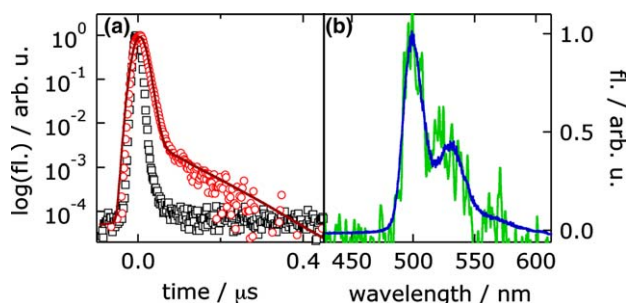


Fig. 4. (a) Time-resolved fluorescence decays of bistetracene dissolved in degassed (red circles) and oxygenated (black squares) benzene. Also shown is a fit (solid line) to the data taken in degassed benzene with a function that contains the measured Gaussian instrument response convoluted with a biexponential decay. (b) Fluorescence emission spectra of bistetracene in degassed benzene in the 0–20 ns time window (blue) and the 100–300 ns time window (green). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

The observations summarized in Figs. 3 and 4 can be explained using a simple model for exciton fission and fusion, which has previously been applied to solid tetracene [19]. We assume that the photophysics of bistetracene is described by the kinetic scheme outlined in Fig. 5. This scheme results in the following three coupled differential equations, which describe the excited state behavior:

$$\frac{\partial N_{S_1}}{\partial t} = -(k_{ISC} + k_{rad} + k_{fiss})N_{S_1} + k_{fus}N_{2T_1} \quad (1)$$

$$\frac{\partial N_{T_1}}{\partial t} = -k_{trip}N_{T_1} + k_{ISC}N_{S_1} \quad (2)$$

$$\frac{\partial N_{2T_1}}{\partial t} = -(k_{trip} + k_{fus})N_{2T_1} + k_{fiss}N_{S_1} \quad (3)$$

Note that there are two types of triplet populations, N_{T_1} and N_{2T_1} , in addition to the singlet population N_{S_1} . In this scheme the total fluorescence decay of the S_1 state is due to the sum of the fission, intersystem crossing, and radiative decay rates (k_{fiss} , k_{ISC} and k_{rad} , respectively), but the singlet population can be regenerated from the triplet pair population N_{2T_1} via k_{fus} . These two processes are reflected in the two-component fluorescence decays seen in Figs. 3 and 4. In order to extract the rate constants of interest from the data, we first make use of the measured quantum yield Q.Y. and the measured fast component of the fluorescence decay, k_{fl} ,

$$Q.Y. = \frac{k_{rad}}{k_{fl}} \quad (4)$$

$$k_{fl} = k_{rad} + k_{ISC} + k_{fiss} \cong k_{rad} + k_{ISC} \quad (5)$$

From the measured quantum yield and k_{fl} , and the assumption that $k_{fiss} \ll (k_{ISC} + k_{rad})$ which is justified below, we can extract both $k_{rad} = 0.049 \text{ ns}^{-1}$ and $k_{ISC} = 0.106 \text{ ns}^{-1}$. The triplet lifetime of tetracene in solution is several hundred μs and can be neglected in these calculations [10,15]. We determine k_{fiss} and k_{fus} by numerically solving the system of Eqs. (1)–(3) for various values of k_{fiss} and k_{fus} to reproduce the bistetracene data. These variables affect the data in different ways, and can be varied independently. For example, k_{fiss} determines the fission yield, which is basically the relative amplitude of the long-lived component in the observed fluorescence signal, while k_{fus} determines the lifetime of the triplet pair and thus the decay

rate of the long-lived component of the fluorescence signal. The best simulation, convoluted with the instrument response, is shown in Fig. 4a, where it is overlaid with the room temperature bistetracene decay in degassed benzene. The values obtained for the triplet dynamics are $k_{fiss} = 2.5 \times 10^6 \text{ s}^{-1}$ (which is consistent with our earlier assumption that $k_{fiss} \ll (k_{ISC} + k_{rad})$) and $k_{fus} = 5.5 \times 10^6 \text{ s}^{-1}$. Literature values for k_{fiss} in solid tetracene range from $1.2 \times 10^8 \text{ s}^{-1}$ to $8 \times 10^9 \text{ s}^{-1}$ [18,20–24]. Despite this large range of values, it is clear that fission is much slower in the bistetracene dimer than in the solid. We were unable to find a value for k_{fus} in solid tetracene, probably due to the fact that the delayed fluorescence rate in the solid depends on many ill-defined variables (triplet diffusion, initial excitation density, reaction radius) and thus it is difficult to extract the intrinsic fusion rate for triplets located on neighboring tetracene molecules in the crystal. The fact that our fission channel shows the same disappearance at low temperatures as observed for solid tetracene suggests that in both cases fission is a thermally activated process [25].

The main question is why the fission rate in bistetracene is so slow relative to solid tetracene. The fact that the two tetracene moieties are covalently bonded via a conjugated phenylene linker might lead one to expect stronger coupling between them and thus enhanced fission. In this context, however, it should be pointed out that intermolecular coupling in the solid is also quite strong, as evidenced by the existence of a Davydov splitting in the absorption spectrum [26]. Recent experiments on polycrystalline tetracene have shown that the singlet state in this material is actually a superradiant intermolecular exciton which is delocalized over ~ 10 molecules at 4 K [14]. These types of excitonic states, where the electronic wave function is spread over several molecular sites, may couple very strongly to the doubly excited triplet state which spans two molecules. In the case of bistetracene, where the intermolecular coupling is weaker than in the solid as evidenced by the smaller perturbation to the steady state spectra, the initially excited state is expected to be mostly localized on a single tetracene, and its overlap with a wave function which involves excitation on both tetracenes may be much smaller than that of the delocalized excitonic state in the crystal. If we were to increase the intermolecular coupling in bistetracene, for example by shortening the linker group, we run two risks. One is that the increased coupling will lead to an increased k_{fus} as well as an increased k_{fiss} . The way to avoid this rapid recombination is to mimic the solid by attaching additional tetracene moieties, so the newly-created triplet states can rapidly separate across larger distances. The triplet hopping time in a tetracene crystal is estimated to be less than 1 ps [27], much faster than the fusion time seen in our data. When the triplet states are unable to diffuse away from each other, as is the case in bistetracene and in solid tetracene doped with inert barrier molecules [21], the recombination will be enhanced. A second problem with increasing the electronic interaction

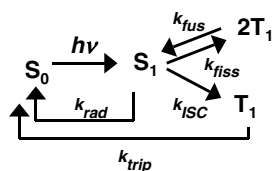


Fig. 5. Kinetic scheme for the photophysics of bistetracene. The parameters are defined as follows: S_0 = ground singlet state, S_1 = excited singlet state which decays by fluorescence (k_{rad}), fission into a pair of triplets (k_{fiss}) and intersystem crossing to T_1 (k_{ISC}), T_1 = singly excited triplet state which is formed by k_{trip} and which cannot reform the S_1 state, $2T_1$ = doubly excited triplet state which is formed by k_{fiss} and recombines back into the S_1 state by k_{fus} .

between the tetracenes is that at some point electron transfer across the linker will become significant, and rather than undergoing fission, the excited singlet state will relax irreversibly to a low energy charge transfer state, as in bianthryl.

In conclusion, we have investigated the photophysical properties of a novel covalent tetracene dimer. Although its steady-state spectroscopy is remarkably similar to that of monomeric tetracene, our data shows that a small (<1%) fraction of the singlet excited states undergoes fission into two triplet states. These triplet pairs recombine on the order of 100 ns, leading to a delayed fluorescence signal which is absent in monomeric tetracene. Unfortunately, this fission channel is so small that it cannot lead to an appreciable enhancement in the triplet quantum yield for this molecule. Nevertheless, its existence suggests that it may be possible to optimize various aspects of the molecule's structure in order to enhance the fission rate and achieve triplet quantum yields greater than one. Such photon splitting molecules could have wide applications, for example in increasing the efficiency of solar cells [28,29].

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