Aggregate formation and its effect on (opto)electronic properties of guest-host organic semiconductors

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We quantify guest molecule aggregation and its effect on the photoconductive properties of guest-host thin films, depending on the guest concentration and host material. A high-performance anthradithiophene (ADT) derivative served as a guest, while functionalized benzothiophene (BTBTB) and polymethylmethacrylate (PMMA) were chosen as hosts. Aggregates exhibited redshifted optical absorption and photoluminescence (PL) spectra, as well as reduced PL quantum yields. Propensity toward guest aggregation differed for PMMA and BTBTB hosts. Photocurrents dramatically increased as the percentage of aggregated guest molecules increased due to considerably higher charge carrier mobility in the aggregates. At low guest concentrations, BTBTB films outperformed PMMA films. © *2010 American Institute of Physics*. [doi:10.1063/1.3505493]

Organic (opto)electronic materials present a promising system due to their tunable properties and low cost.[1] Solution processable materials provide further advantages as they can be deposited using various thin-film solution deposition technologies.[2] Additionally, such materials can be easily doped to create blends with properties tailored for specific applications. Functionalized fluorinated anthradithiophene (ADT) derivatives are particularly interesting as their solution-deposited thin films exhibit charge carrier (hole) mobilities of >1.2 $cm^2/(V\,s)$,[3,4] fast charge carrier photogeneration, high photoconductivity, and relatively strong photoluminescence (PL).[5–7] These molecules form π-stacked arrangements with short interplanar spacings of 3.2–3.4 Å,[8] conducive to molecular aggregate formation.[9] Thus, the optical and electronic properties of ADT thin films and crystals are highly sensitive to molecular packing and intermolecular interactions,[5,8,10] which are currently not well understood. In this letter, we seek to establish properties of ADT aggregates and conditions of their formation. In particular, we embedded ADT molecules at various concentrations into two different inert host materials and measured optical absorption, PL spectra, time-resolved PL decay dynamics, and photoconductivity upon photoexcitation of the ADT guest. These were then compared to properties of pristine ADT films.

The materials used in our studies are a fluorinated ADT derivative functionalized with triethylsilylethynyl (TES) side groups, ADT-TES-F (inset of Fig. 1),[3,5] as a guest, and functionalized benzothiophene (6,12-bis[2-(t-butyl)ethynyl]-benzo[1,2-b:4,5-b']bis(1)benzothiophene, t-bu BTBTB in the inset of Fig. 1) or polymethylmethacrylate (PMMA) as hosts. PMMA (Polysciences, Inc., 75,000 MW) and t-bu-BTBTB were dissolved in toluene and in tetrahydrofuran (THF), respectively, at concentrations of 10^{-3} M and 10^{-2} M, respectively. ADT-TES-F 10^{-5} M stock solutions in toluene or THF were used to add an appropriate amount of ADT-TES-F to PMMA or t-bu BTBTB solutions. PMMA (t-bu BTBTB) samples were spin coated at 600 (1000) rpm for 50 s onto clean glass substrates. Samples with several concentrations of ADT-TES-F in host matrices (PMMA and t-bu BTBTB) were prepared, with average distances r between ADT-TES-F molecules ranging from $r=1$ nm to $r=15$ nm, denoted as P_r and B_r, respectively, with r in nanometers (nm). The distance r was determined according to $r=[M/(N_A\rho_m c)]^{1/3}$, where ρ_m is the mass density, M is the molar mass of the host material, N_A is Avogadro's number, and c is the molar fraction of guest to host.[11–13] Pristine ADT-TES-F films were spin coated from a 10^{-2} M toluene solution. The choice of host materials was based upon following two considerations: (1) both t-bu BTBTB and PMMA have considerably higher highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps (5.6 eV and 3.52 eV, respectively)[14,15] than that of ADT-TES-F (2.3 eV),[5] which minimized guest-to-host charge and energy transfer, and (2) these hosts provided different environments for embedded ADT-TES-F molecules. In particular, a t-bu BTBTB solid exhibits π-stacking properties similar to those of ADT-TES-F, which could impose packing constraints on embedded ADT-TES-F guest molecules. Additionally, pristine t-bu BTBTB thin films were shown to be photoconductive under 355 nm excitation.[15] In contrast, PMMA is not conductive and, additionally, ADT-TES-F molecules in PMMA are expected to be randomly oriented.[12,16] Guest concentrations in both PMMA and t-bu BTBTB hosts corresponding to $r=1$ nm, 2 nm, 3 nm, 5 nm, 10 nm, and 15 nm are 1.6 mol/l, 0.2 mol/l, 0.059 mol/l,

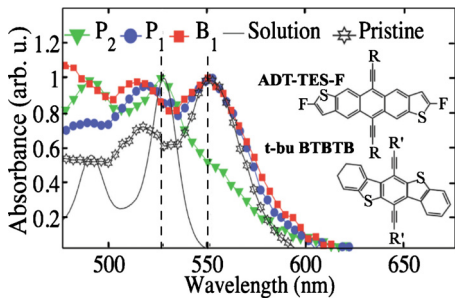

FIG. 1. (Color online) Absorbance of P_1, B_1, and pristine ADT-TES-F films normalized by their values at 553 nm and of P_2 and of ADT-TES-F solution in toluene normalized by their values at 528 nm. Dashed lines indicate dominant peak positions for the pristine film and solution. Insets show molecular structures of ADT-TES-F and t-bu BTBTB.

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0.0128 mol/l, 0.0016 mol/l, and 4.74×10^{-4} mol/l, respectively.[12] Optical densities in all films did not exceed 0.25 at the absorption maximum. For studies of photoconductivity, films were prepared on glass substrates with photolithographically deposited 5 nm/50 nm thick Cr/Au interdigitated electrode pairs. Electrodes consisted of ten pairs of 1 mm long fingers with 25 μm finger width and 25 μm gaps between the fingers of opposite electrodes. All experiments were carried out in air at room temperature.

Figure 1 shows optical absorption spectra of ADT-TES-F molecules in dilute toluene solution and in P_1, P_2, and B_1, as well as pristine ADT-TES-F films. Spectrum of isolated ADT-TES-F molecules exhibits a $0\rightarrow0$ transition at 528 nm with a full width at half maximum (FWHM) of ~550 cm^{-1} and vibronic progression with a wave number of ~1410 cm^{-1} corresponding to a C–C stretching mode.[17] Upon increase in guest concentration, effects of intermolecular interactions between ADT-TES-F molecules started contributing to absorption spectra.[18,19] In particular, an absorption band, redshifted by ~760 cm^{-1}(~25 nm) with respect to $0\rightarrow0$ transition in solution, develops. This suggests an increased conjugation path leading to a higher degree of exciton delocalization.[20] For example, in the P_2 film in Fig. 1, the band due to ADT-TES-F aggregates is seen as a shoulder at ~550–555 nm, which then develops into a well-resolved peak in the P_1, B_1, and pristine ADT-TES-F samples, while spectral features pertaining to noninteracting ADT-TES-F molecules disappear. The ADT-TES-F aggregate absorption spectrum retains exciton-phonon coupling features of isolated ADT-TES-F molecules, although most coupling occurs to a different vibrational mode with a wave number of ~1240 cm^{-1} with vibronic peaks broadened (FWHM of ~900 cm^{-1} and ~1000 cm^{-1} in P_1 and B_1, respectively) due to disorder and coupling to additional vibrational modes,[21,22] as compared to isolated ADT-TES-F molecules.

PL spectra of films were obtained using a 532 nm $Nd:YVO_4$ cw laser or 355 nm frequency-tripled neodymium-doped yttrium aluminum garnet pulsed excitation. In PMMA films, PL spectra did not depend on the excitation wavelength. In t-bu BTBTB films, only a 532 nm excitation was used to ensure excitation of ADT-TES-F exclusively.[15] Emission was collected with a parabolic mirror and detected with a fiber coupled spectrometer (Ocean Optics USB2000) calibrated against a 3100 K black-body emitter. PL lifetimes were obtained under 400 nm 80 fs excitation (frequency-doubled Ti:sapphire laser) using time-correlated single-photon counting board and an avalanche photodiode with an instrument response time of ~250 ps.[5] Figure 2(a) shows PL spectra, corrected for self-absorption, of P_{15}, B_5, P_2, B_2, and P_1 films. In PMMA films at ADT-TES-F concentrations corresponding to $r>5$ nm, PL properties were similar to those of isolated (noninteracting) ADT-TES-F molecules in solution: a dominant $0\rightarrow0$ transition at ~535 nm followed by a vibronic progression [e.g., P_{15} in Fig. 2(a)], single-exponential PL decays [e.g., P_{10} in Fig. 2(b)], and high PL quantum yields (QYs) approaching 0.9. In similar t-bu BTBTB films, the shape of the PL spectra was similar to that in PMMA ones, except for a redshift by ~180 cm^{-1} due to a difference in refractive indices of PMMA and t-bu BTBTB. Upon increase of ADT-TES-F concentrations, a redshifted PL band with a dominant peak at ~585 nm appeared due to ADT-TES-F aggregates. For example, in Fig. 2(a),

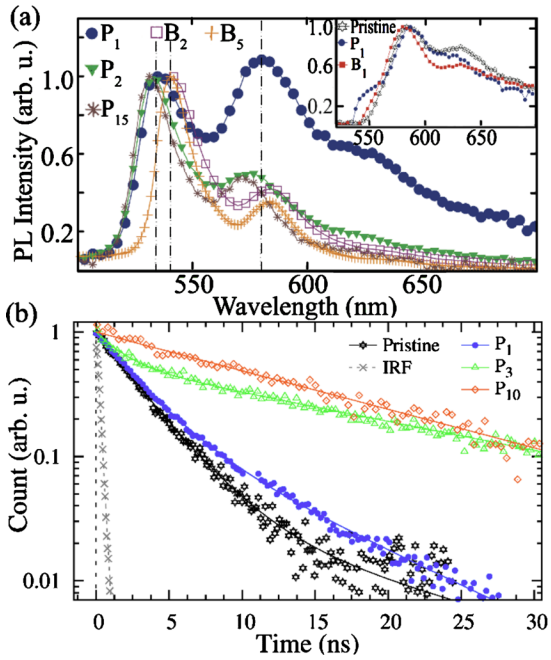

FIG. 2. (Color online) (a) PL spectra from P_1, P_2, P_{15}, B_2, and B_5 films, normalized by their peak values at 535–540 nm. Dashed lines indicate PL peak positions of noninteracting ADT-TES-F molecules and ADT-TES-F aggregates in a P_1 film and of noninteracting ADT-TES-F molecules in a B_2 film. Inset shows PL spectra from pristine ADT-TES-F film plotted with the aggregate PL spectra from P_1 and B_1. (b) Normalized time-resolved PL decays in P_{10}, P_3, P_1, and pristine ADT-TES-F films. Lines correspond to a single-exponential fit in P_{10} and biexponential fits in other films. Instrument response function (IRF) is also included.

contributions both from noninteracting ADT-TES-F molecules and from ADT-TES-F aggregates can be seen in the PL spectra of P_2, B_2, and P_1 films. Inset of Fig. 2(a) shows PL spectra of aggregates in P_1 and B_1 films, obtained by subtraction of the portion of PL spectra due to noninteracting molecules (taken here as normalized PL spectra measured in P_{15} and B_{10} films for PMMA and t-bu BTBTB films, respectively) from the total PL spectra. Spectra of the aggregates in the P_1 and B_1 films, as well as in films with lower guest concentrations, were similar to those from a pristine ADT-TES-F film [inset of Fig. 2(a)], which suggests similar nature of the aggregates in all films. More studies, however, are needed to establish the exact type of these aggregates, as their optical and PL properties exhibit features of both H- and J-aggregates.[9] The PL spectral changes upon aggregation were accompanied by a change from a single-exponential decay with a lifetime of ~10–13 ns to biexponential PL decays with lifetimes of ~2–3 ns and ~8–13 ns, with a contribution of the shorter lifetime increasing as the concentration of the guest molecule increased [Fig. 2(b)]. For example, in biexponential PL decays in P_3, P_1, and pristine ADT-TES-F films in Fig. 2(b), the shorter lifetime, which we attribute to ADT-TES-F aggregates,[12] had relative weights of 0.44, 0.78, and 0.96, respectively. From absorption and PL spectra of films, we estimated a radiative lifetime of 11.4 ns and PL QY of 0.23 in ADT-TES-F aggregates.[23] Similarity between radiative lifetimes of ADT-TES-F aggregates and of noninteracting ADT-TES-F molecules (13.4 ns) (Ref. 5) suggests that aggregation enables nonradiative decay pathways which reduce PL QYs without significantly impacting radiative processes.

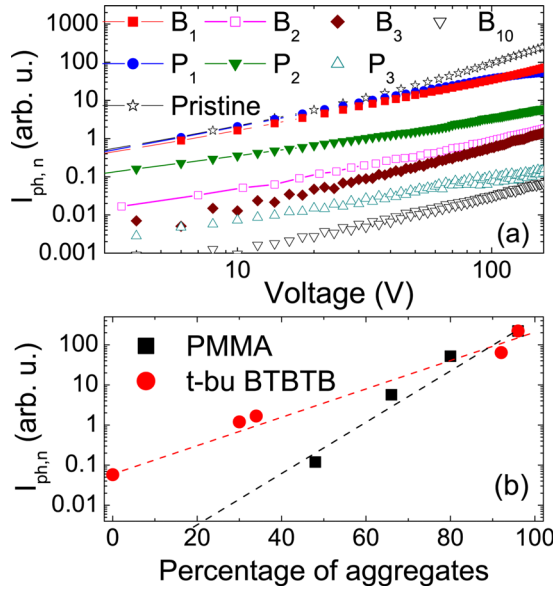

FIG. 3. (Color online) Photocurrent normalized by the number of absorbed photons, $I_{ph,n}$, measured at 5 mW/cm^2 532 nm cw illumination: (a) as a function of applied voltage in B_{10}, P_3, B_3, P_2, B_2, P_1, B_1, and pristine ADT-TES-F films and (b) at 150 V as a function of percentage of aggregated molecules calculated from the PL data from the same films. No aggregation (0%) was assumed for B_{10}. Lines in (b) provide a guide for the eye.

The propensity for ADT-TES-F aggregation was significantly different in PMMA and t-bu BTBTB hosts. While 92% of ADT-TES-F molecules were in the aggregated state in a B_1 film, the percentage of aggregated molecules was only about 34% and 30% in B_2 and B_3 films, respectively. In contrast, 80%, 66%, and 48% of ADT-TES-F molecules were in the aggregated state in P_1, P_2, and P_3 films, respectively.[23] This suggests that structural similarity of ADT-TES-F guest and t-bu BTBTB host molecules provided effective dispersion of the ADT-TES-F guest molecules in the host matrix until high guest concentrations, in contrast to ADT-TES-F in PMMA. In films with $r \geq 5$ nm, the percentage of aggregates was below 5% in both hosts.

For photocurrent measurements, samples were illuminated from the substrate side with ~5 mW/cm^2 cw 532 nm light, which excited only ADT-TES-F molecules, and not t-bu BTBTB or PMMA. Currents in the dark and under photoexcitation as functions of applied voltage were measured using a Keithley 237 source-measure unit, and the photocurrent was calculated as the difference between the two. No photocurrent was observed upon excitation of pristine t-bu BTBTB or PMMA films. Figure 3(a) shows photocurrent normalized by the number density of absorbed photons ($I_{ph,n}$) obtained in various films. Aggregate formation established via optical and PL measurements was correlated with an increase in the $I_{ph,n}$ due to increase in charge carrier mobility in aggregates as compared to isolated guest molecules [Fig. 3(b)].[24] An increase in percentage of aggregated molecules in the $P_2(P_1)$ with respect to the P_3 film led to a ~5-(45-)fold increase in the $I_{ph,n}$. B_2 and B_3 films, which had similar percentages of aggregates, had similar values of $I_{ph,n}$. These increased by a factor of ~70 in the B_1 film that had a significantly higher percentage of aggregated molecules. At lower concentrations of ADT-TES-F guest molecules ($r \geq 3$ nm), t-bu BTBTB films outperformed the PMMA ones [Fig. 3(b)],[15] most likely due to additional conductive pathways via t-bu BTBTB molecules.[11] These would contribute if holes photoexcited on ADT-TES-F guest molecules overcame a ~0.4 eV potential barrier between HOMO levels of ADT-TES-F and t-bu BTBTB, enabling charge transport in the t-bu BTBTB,[15] as evidenced by a detectable photocurrent in a B_{10} film. In PMMA, conduction path through host molecules is inefficient, resulting in no measurable photocurrents in PMMA films at $r \geq 5$ nm under our experimental conditions.

In summary, aggregation of ADT-TES-F guest molecules, quantified using optical and PL properties of films, was more pronounced in PMMA as compared to t-bu BTBTB host. Aggregates were characterized by redshifted optical absorption and PL spectra, as well as reduced PL QYs. Photocurrents dramatically increased as the aggregate content increased due to considerably higher charge carrier mobility in the ADT-TES-F aggregates. At low ADT-TES-F guest concentrations, t-bu BTBTB films exhibited significantly higher photocurrents than PMMA films due to additional conductive pathways via host molecules.

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