



Single-molecule imaging of organic semiconductors: Toward nanoscale insights into photophysics and molecular packing



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ABSTRACT

Photophysical properties of functionalized anthradithiophene (ADT) and pentacene (Pn) derivatives, as well as energy and charge transfer properties of donor–acceptor (D/A) pairs of these derivatives, are presented. The molecules studied were imaged on the single-molecule level in a polymeric and in a functionalized benzothiophene (BTBTB) crystalline host using room-temperature wide-field epifluorescence microscopy. The BTBTB host imposed orientational constraints on the guest molecules, depending on their functionalization. Flexibility of functionalization of both guest (ADT, Pn) and host (BTBTB) molecules can be used for systematic studies of nanoscale morphology and photophysics of D/A organic semiconductor bulk heterojunctions using single-molecule fluorescence microscopy.

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1. Introduction

Organic semiconductors have attracted attention due to their potential applications in a variety of (opto)electronic devices including organic thin-film transistors (TFTs), light-emitting diodes, solar cells, photorefractive (PR) holographic displays, and many others [1]. A large subset of these applications, such as solar cells, photodetectors, and PR devices relies on efficient charge carrier photogeneration. Most successful materials for such applications involve donor–acceptor (D/A) bulk heterojunctions (BHJs), properties of which rely on photoinduced D/A interactions. These include charge transfer (CT) and Förster resonant energy transfer (FRET) that depend both on the photophysical properties of donor and acceptor molecules and on their packing at the D/A interface [2–7]. However, nanoscale morphology of D/A BHJs [8], as well as the effect of local nanoenvironment on the molecular photophysics

of donor and acceptor molecules and on their interactions, are difficult to study systematically, due to inherent inhomogeneity of BHJs and lack of necessary spatial resolution. Therefore, it is important to develop the capability that enables such systematic studies, and to identify suitable model systems that utilize technologically relevant organic semiconductors.

Single-molecule fluorescence spectroscopy (SMFS) has been widely utilized in probing nanoscale interactions and local nanoenvironments in a variety of media including biological systems, polymers, and crystals [9–11]. Single molecules (SMs) have been used as sensitive probes of local changes in polarity, viscosity, relaxation dynamics of the host, and acoustic resonances [12–14] in various heterogeneous environments. SM-level imaging of molecular orientations has provided key nanoscale information on the molecular packing in the solid and on the interfaces [15–19]. Additionally, there has been considerable interest in utilizing SMs as probes of conduction and exciton dynamics in organic semiconductors [20–23]. However, difficulties in finding a suitable model system that meets requirements of SMFS (which include high photostability and high fluorescence quantum yield (QY) of the guest molecules and absence of guest–host interactions, such as intermolecular intersystem crossing, that lead to fluorescence quenching) [24] and provides tunable properties of the molecule and of the environment necessary for systematic studies, limits SMFS studies to only a handful of materials of relevance to organic semiconductor devices [16,20,21,23].

In this letter, we present photophysical properties of functionalized acene and acene–thiophene derivatives (Figure 1) suitable for

Abbreviations: ADT, anthradithiophene; BHJ, bulk heterojunction; BTBTB, benzothiophene; CT, charge transfer; D/A, donor–acceptor; DCDHF, dicyanomethylenedihydrofuran; FRET, Förster resonant energy transfer; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; NODIPS, (n-octyldiisopropylsilyl)ethynyl; QY, quantum yield; PMMA, poly(methyl) methacrylate; Pn, pentacene; PR, photorefractive; SM, single molecule; SMFS, single molecule fluorescence spectroscopy; TCHS, (tricyclohexylsilyl)ethynyl; TES, (triethylsilyl)ethynyl; TFT, thin film transistor; TIPS, (triisopropylsilyl)ethynyl; XRD, X-ray diffraction.

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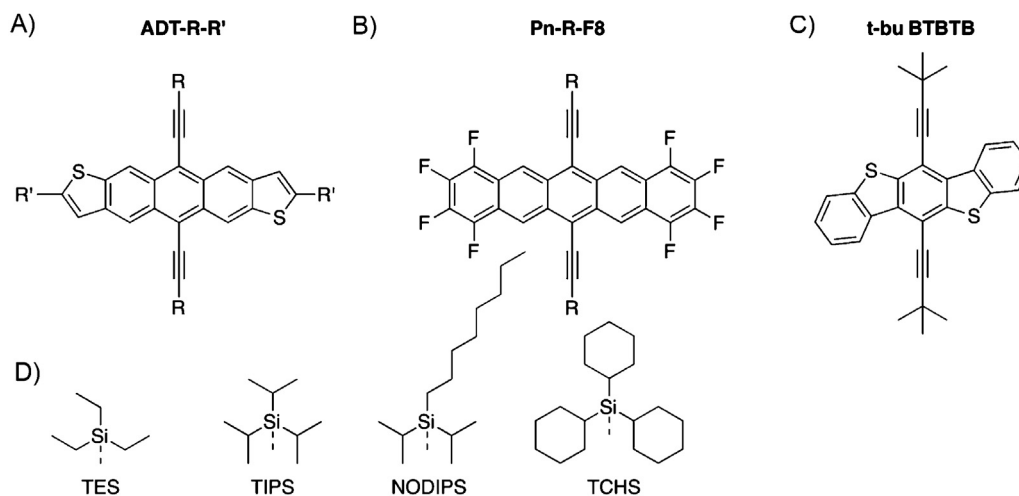


Figure 1. Molecular structures of (a) ADT-R-R', (b) Pn-R-F8, and (c) t-bu BTBTB molecules used in our studies. In (a), R' = F for ADT-TES-F and R' = CN for ADT-TIPS-CN. (d) Structures of the side groups R (R = TES, TIPS, NODIPS, TCHS).

systematic SMFS studies of processes pertinent to nanoscale-level understanding of D/A BHJs: molecular photophysics, molecular packing, and photoinduced intermolecular interactions. These derivatives are of interest due to the following reasons: (1) they are solution-processable organic semiconductors that have been extensively studied in TFTs and solar cells [6,25–27], (2) they can be functionalized to either tune photophysical parameters of the molecule itself or to change the molecular packing in the solid state (e.g. by changing R' and R groups, respectively, Figure 1) [3,5,6], thus enabling systematic studies of effects of substitutions and of local nanoenvironment on the molecular photophysics and packing, and (3) D/A combinations of these molecules exhibit FRET and/or emissive CT state formation (exciplex) [2,5,28,29], which could be utilized in probing nanoscale D/A morphology and effects of local nanoenvironment on photoinduced D/A interactions [8], using SMFS techniques.

2. Experimental

2.1. Materials

Molecules used in our studies as donors and acceptors, and as guests embedded in a solid host for SMFS, are functionalized anthradithiophene (ADT) derivatives with (triethylsilyl)ethynyl (TES) and (triisopropylsilyl)ethynyl (TIPS) side groups (ADT-TES-F and ADT-TIPS-CN, Figure 1a) and pentacene (Pn) derivatives (Figure 1b) with TIPS, NODIPS ((n-octyldiisopropylsilyl)ethynyl), or TCHS ((tricyclohexylsilyl)ethynyl) side groups (Figure 1d). The ADT-TES-F derivative is a high-performance organic semiconductor, solution-deposited films of which exhibit charge carrier mobilities of $>1.5 \text{ cm}^2/(\text{Vs})$ in spin-cast TFTs [25,30], high photoconductive gains, and fast charge carrier photogeneration [3,29,31]. In pristine films of the Pn-TIPS-F8 derivative, ambipolar TFT mobilities of up to $0.33 \text{ cm}^2/(\text{Vs})$ were obtained [32,33]. Both ADT-TIPS-CN and Pn-R-F8 (R = TIPS, NODIPS, TCHS) derivatives have been utilized as acceptors in D/A BHJs with polymer or ADT-TES-F donors [2,4,5,27–29]. In pristine films, ADT-R-R' and Pn-R-F8 derivatives under study exhibit π -stacking² with R-groups controlling the packing motif [6].

As host matrices, we chose a functionalized benzothienothiophene (BTBTB) derivative t-bu BTBTB (6,12-bis[2-(t-butyl)ethynyl]benzo[1,2-b:4,5-b']bis(1)benzothienothiophene) (Figure 1c) and poly(methyl) methacrylate (PMMA) which were previously utilized in our studies of photoconductivity in

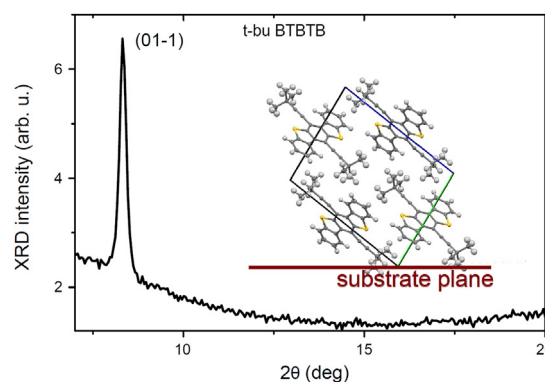


Figure 2. XRD results for out-of-plane structures in spin-cast t-bu BTBTB films. Inset shows alignment of the t-bu BTBTB molecules on the substrate consistent with the (0 1 –1) crystallite orientation as revealed by the XRD.

ADT-TES-F-doped thin-film devices [31]. Both t-bu BTBTB and PMMA hosts have considerably larger HOMO-LUMO gaps (3.52 eV and 5.6 eV, respectively) [31] than ADT and Pn guest molecules (1.9–2.3 eV, depending on the derivative) [5], and no guest-to-host FRET or CT were observed in either guest–host system (Figure S2). The t-bu BTBTB derivative exhibits 1D “slip-stack” π -stacking and crystallizes in a triclinic structure with unit cell parameters $a = 6.3 \text{ \AA}$, $b = 12.6 \text{ \AA}$, $c = 15.9 \text{ \AA}$, $\alpha = 96.1^\circ$, $\beta = 98.5^\circ$, and $\gamma = 102.3^\circ$ (inset of Figure 2). Spin-cast t-bu BTBTB films exhibit crystalline order with a dominant (0 1 –1) crystallite orientation, confirmed by X-ray diffraction (XRD), Figure 2. The lowest-energy absorption/fluorescence maxima in thin t-bu BTBTB films are at 405/415 nm [34], which enables the utility of t-bu BTBTB as a non-emissive host for SM imaging at 532 nm and 633 nm. Functionalized BTBTB derivatives [35] are photoconductive under UV excitation [34], and they have been utilized in solution-deposited field effect transistors exhibiting charge carrier mobilities reaching $1.7 \text{ cm}^2/(\text{Vs})$ [36], $7 \text{ cm}^2/(\text{Vs})$ [37], and $31.3 \text{ cm}^2/(\text{Vs})$ [38], depending on functionalization of the molecule and on device fabrication.

2.2. Sample preparation

For our studies, several types of spin-cast films were prepared: (i) ADT-R-R' or Pn-R-F8 guest molecules at 10^{-10} M concentrations in the PMMA or t-bu BTBTB hosts, for SMFS; (ii) same as (i), but

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