



Charge transport, doping and luminescence in solution-processed, phosphorescent, air-stable tellurophene thin films



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ABSTRACT

Recently synthesized small molecule tellurophenes containing ring-appended pinacolboronate (BPin) side groups possess remarkable guest-free air-stable solid-state phosphorescence, structure-based color-tunability and aggregation induced enhanced emission. The charge transport, doping and luminescence behavior of thin transparent films of a tellurophene with BPin groups positioned at the 2,5-positions (**B-Te-6-B**) was investigated. Film formation played a critical role in determining the hole mobility and the photoluminescence (PL) lifetime. Drop-coated films showed the strongest crystallinity, the highest PL quantum yields and a hole mobility (μ_p) of $1.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which places tellurophenes in a select group of high mobility phosphorescent emitters. **B-Te-6-B** was also found to spontaneously form high aspect-ratio microwires upon drop-casting from supersaturated solutions. Oxidative doping in solution by a $\text{N}(\text{C}_6\text{H}_4\text{Br})_3[\text{SbCl}_6]/\text{LiNTf}_2$ reagent combination ($\text{Tf} = \text{SO}_2\text{CF}_3$) increased conductivity by 2–4 orders of magnitude without inducing a color change in the films, while exposure to iodine vapor induced a dramatic change in color together with a 4–6 order of magnitude change in the conductivity. The optical transparency, facile electrical doping and relatively high hole mobilities of **B-Te-6-B** in solution processed thin films offer promise for the use of tellurophenes as host-free emissive layers and hole transport layers in organic optoelectronic devices.

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1. Introduction

Oligothiophenes and polythiophenes are among the most widely studied organic semiconductors due to the combination of high absorption coefficients, good charge transport properties in solution-processed thin films and good performance in electronic devices such as organic field effect transistors and organic photovoltaics (OPV) [1–7]. Some drawbacks of solution processed neat films of oligothiophenes and polythiophenes include low

luminescence quantum yields rendering them unacceptable as emissive layers in organic light emitting diodes (OLEDs), hole mobilities lower than acene-type organic semiconductors, and poor absorption of red and infrared photons (needed for high efficiency solar cells). With a view toward modifying and improving upon the optoelectronic properties of oligothiophenes – siloles, germales and selenophenes have been synthesized and tested [8–11]. Π -conjugated organic small molecules containing one or more carbon atoms in the ring substituted by a heavier atom such as Si, Ge and Se have received significant attention in recent years due to the beneficial effects expected from the high polarizability of the heavy atom [12–17]. These effects include a higher dielectric constant (and refractive index) that follow directly from the Clausius-Mosotti equation as well as more red-shifted optical transitions. Substitution of the S atom in thiophenes with their heavier element congeners selenium and tellurium has also been found to result in a tripling of the value of

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the non-resonant electronic second hyperpolarizability (γ) compared to thiophene, which is of interest for non-linear optics [18]. A wider electronic band-width and improved carrier transport parameters are also expected due to the higher polarizability and the stronger electronic coupling resulting from intermolecular Te-Te interactions [19,20].

In 2014, our team reported on the bright room temperature phosphorescence from a tellurophene containing ring-appended pinacolboronate (BPin) side groups (**B-Te-6-B**; Fig. 1), and extended this in 2015 to a broader class of tellurophenes and benzotellurophenes with color-tunability of the emission [21,22]. The photoluminescence behavior in these compounds was rendered unusual by the observation of the still-rare aggregation-induced enhanced phosphorescence (AIEP) (a special case of aggregation-induced enhanced emission) [23–27], the high ambient stability of the observed phosphorescence emission to oxygen and the essential participation of the boron-based BPin groups in the emission process. The rarity of room temperature solid-state phosphorescent organic compounds [28,29] is underscored by the relatively few examples of organic compounds known to show this effect. The ambient-stability, solution-processability, solid-state phosphorescence and optical transparency of tellurophenes renders them particularly attractive for use as undoped, singlet-doped and triplet-doped phosphorescent matrix emitters in OLEDs [30], and as triplet exciton transporters in bulk heterojunction OPVs to overcome the exciton diffusion bottleneck [31–33]. We report herein on the film formation, charge transport behavior and dopability of the **B-Te-6-B** tellurophene.

2. Experimental section

B-Te-6-B was synthesized according to procedures reported elsewhere [34], while all other reagents were obtained from commercial sources and used as received. In this work, we examined three different processing schemes for preparing tellurophene thin films, namely, thermal evaporation, spin coating, and drop coating. Evaporation was performed in a PVD-75 system from Kurt J. Lesker equipped with 4 ceramic crucibles surrounded with tungsten filaments. Evaporation of **B-Te-6-B** started at 65 °C and thin film deposition was completed at 80 °C at a chamber pressure of 2.5×10^{-6} Torr. For both spin coating and drop coating, tetrahydrofuran (THF) (99.5%, Fisher Scientific) was used as the solvent to dissolve the **B-Te-6-B**. Different concentrations of tellurophene were tested ranging from 40 mg mL⁻¹ to 72 mg mL⁻¹ with a typical volume of 50 μ L used for both spin-coating and drop-coating. Fluorine-doped tin oxide (FTO) coated glass slides with a conductivity of 8 Ω sq⁻¹, bare single crystal Si wafers and thermal oxide-coated heavily doped Si wafers were adopted as substrates for film formation and electrical studies. For some of the samples, a spin-coated and dehydrated film of Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (1.3 wt % dispersion in H₂O, conductive grade, Sigma Aldrich) was coated on the FTO substrates prior to tellurophene deposition. For both two-terminal and three-terminal electrical measurements, a back-gated field effect transistor configuration was employed using the tellurophene film as the active layer, thermally grown SiO₂ as the gate dielectric and n^{++} -Si as the gate electrode. The oxide thickness was 200 nm, the channel length was 50 μ m and the channel width was

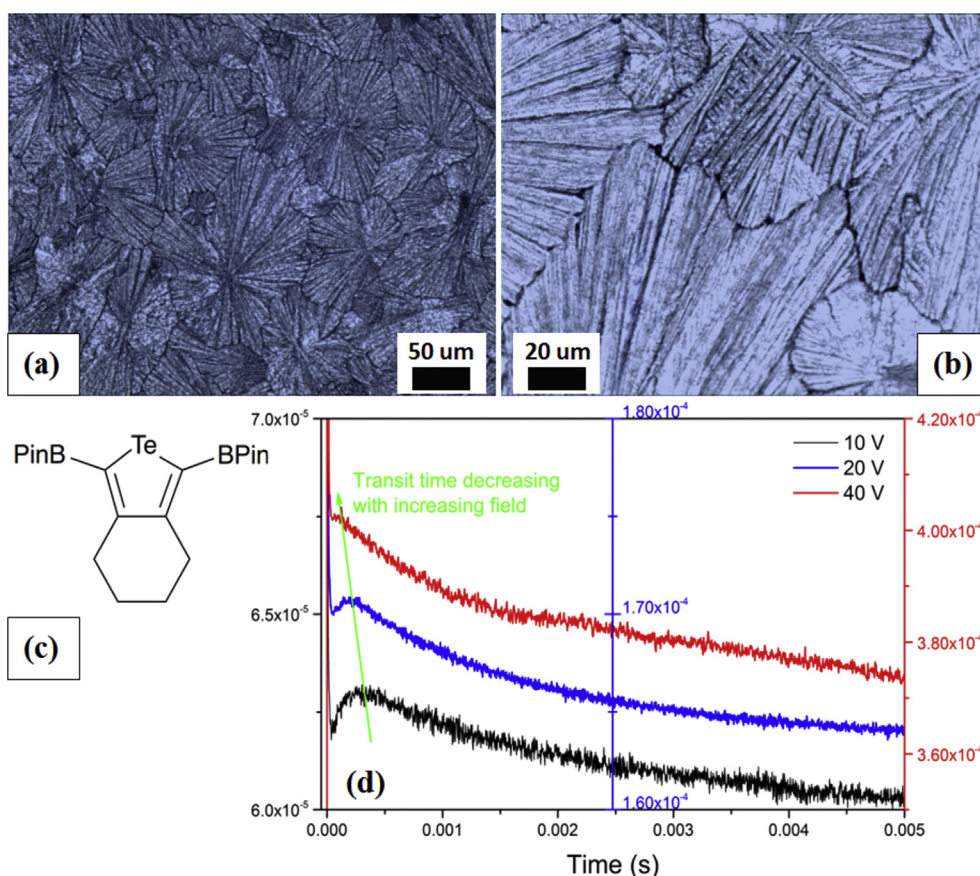


Fig. 1. Optical images for drop coated **B-Te-6-B** films (cast at 40 mg mL⁻¹) taken at magnifications of (a) 25 \times and (b) 50 \times ; (c) shows the molecular structure of the **B-Te-6-B** tellurophene and (d) dark injection transients for drop coated **B-Te-6-B** films measured at three different voltages.

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