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Absorption Tuning of Monosubstituted Triazatruxenes for Bulk Heterojunction Solar Cells

Thomas Bura,[†] Nicolas Leclerc,[‡] Sadiara Fall,[§] Patrick Lévêque,[§] Thomas Heiser,[§] and Raymond Ziessel*,[†]

Laboratoire de Chimie Organique et Spectroscopies Avancées (LCOSA), CNRS, Ecole de Chimie, Polymères, Matériaux de Strasbourg (ECPM), 25 rue Becquerel, 67087 Strasbourg, Cedex 02, France, Laboratoire d'Ingénierie des Polymères pour les Hautes Technologies (LIPHT), Université de Strasbourg, Ecole Européenne de Chimie, Polymères et Matériaux, 25 rue Becquerel, 67087 Strasbourg, France, and Institut d'Electronique du Solide et des Systèmes (InESS), Université de Strasbourg-CNRS, 23 rue du Loess, 67037 Strasbourg, France

ziessel@unistra.fr

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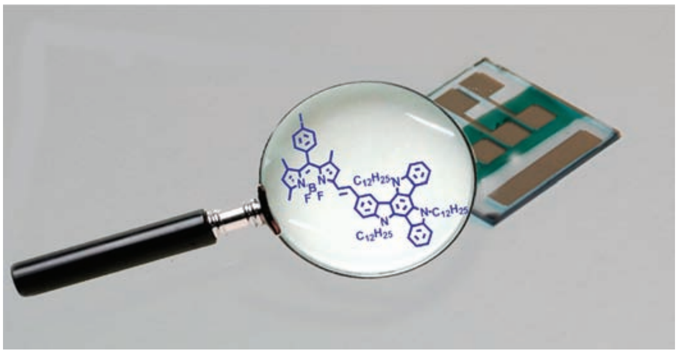
ABSTRACT



A series of triazatruxene (TAT)-functionalized Bodipy dyes were prepared by a sequence of reactions involving either cross-coupling reactions promoted by Pd complexes or a Knoevenagel reaction leading to a vinyl linker. The new dyes show large absorption coefficients and fluorescence quantum yields as well as interesting electrochemical properties. The blue dyes of this series exhibit interesting photovoltaic effects (V_{OC} = 0.83 V, J_{SC} = 3.6 mA/cm^2, efficiency 0.9%) in bulk heterojunction solar cells, due to the good hole mobility imported by the TAT entity.

Flat π-conjugated platforms such as triphenylene, benzohexacoronenes, perylene, and other rylenes have been extensively explored in organic electronics for applications including energy conversion devices.[1] In this context, we became interested in the preorganized truxene platform from the point of view of linking various photoactive modules to promote directional energy transfer.[2] The replacement of the three methylene groups at the 5, 10, and 15 positions of truxene by three nitrogen atoms endows the resultant triazatruxene (TAT) core, which consists of a C_3 symmetry of fused carbazole trimer and also presents a flat aromatic surface.

The three indolic NH centers can be functionalized with flexible side chains and the core by bromo groups at the periphery.[3] Star-shaped octupolar TAT derivatives are known to be efficient in two-photon absorption spectroscopy,[4]

[†] Ecole de Chimie, Polymères, Matériaux de Strasbourg (ECPM).

[‡] Université de Strasbourg, Ecole Européenne de Chimie, Polymères et Matériaux.

[§] Université de Strasbourg-CNRS.

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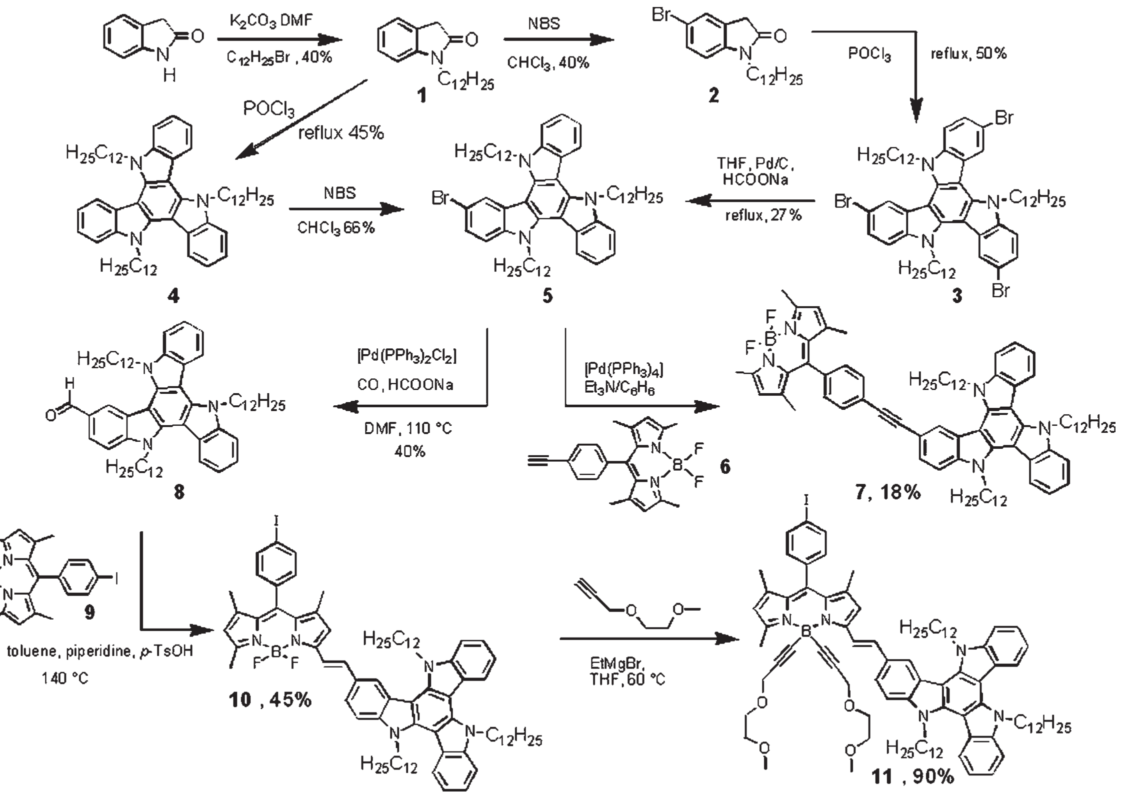
Scheme 1. Synthesis of the Triazatruxene-Linked Bodipy Derivatives



and organic-light-emitting diodes[5] and self-assembled hexafunctionalized TAT frameworks can be used to produce electroactive discotic liquid−crystalline materials with high hole mobility.[6] Surprisingly, despite these various applications, the chemistry of TAT is limited largely to that of homohexa- and homotrisubstituted derivatives, and applications in solar cells have not been demonstrated up to now, probably due to the limited absorption in the visible portion of the solar spectrum. Our choice of TAT was motivated by its high charge carrier mobilities in thin films and its semiconductor character, attractive redox properties, and strong fluorescence.[7] Here, we report that monosubstituted TAT derivatives can be prepared in a controlled manner and cross-linked to boron−difluorodipyrromethene (Bodipy) dyes to produce photoactive layers in bulk heterojunction (BHJ) solar cells. As simple Bodipy derivatives themselves are active materials in dye-sensitized solar cells (DSSC)[8] and BHJ solar cells,[9] it was tempting to try to link the photosensitizer (Bodipy) to TAT while conserving the charge carrier mobility. Two strategies were devised for the preparation of 3-bromo-5,10,15-triazatruxene. The first requires the preparation of 3,8,15-tribromo-5,10,15-triazatruxene and subsequent dehalogenation, and the second necessitates monohalogenation of 5,10,15-triazatruxene (Scheme 1). As a first synthetic approach, a four-step protocol starting from 2-oxindole, followed by alkylation with bromododecane giving **1**, followed by a selective bromination in the 5-position affording **2** was developed. A final trimerization in neat $POCl_3$ provided the target compound **3**. Such cyclocondensation is the most common route to triazatruxene derivatives.[10,5] The use of reductive dehalogenation was based on previous work[4b] and was performed in refluxing THF using formate salts as the reducing agent and Pd supported on charcoal as catalyst. The reaction was not selective but provided the target monobromo derivative **5** and the dibromo compound in 27 and 20% yields, respectively. Cross-coupling of **5** with

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the alkyne-Bodipy **6** (Bodipy = borondipyrromethene) afforded the truxene derivative **7** in modest yield (Scheme 1).

In a second synthetic approach, the monobromo derivative **5** was prepared in two steps from *N*-dodecane-2-oxindole **1** using the protocol described above for **3**, followed by a relatively selective (66%) bromination at the 3-position. Then, a carboformylation reaction promoted by a Pd-catalyst was performed in hot DMF under a flux of CO at atmospheric pressure. The stable formyl derivative **8** was allowed to react with the simple Bodipy **9** in the presence of piperidine and trace amounts of *p*-TsOH. The proton NMR spectrum is diagnostic for the monosubstituted compound due to the presence of two β-pyrrolic proton peaks at the expected chemical shifts (δ 6.06 and 6.73 ppm).[11,12] Finally, substitution of the boron fluoro groups using the Grignard reagent of 2,5-dioxaoct-7-yne[13] led to dye **11** in excellent yield.

Data defining the photophysical properties of the new monobromo and monoaldehyde triazatruxene and Bodipy dyes are gathered in Table S1, Supporting Information.

The absorption spectra of **5** and **8** exhibit a major absorption peak around 317 nm characteristic of triazatruxene derivatives (Figure S1, Supporting Information).[4] Moderately efficient fluorescence of both truxene derivatives was observed. The absorption spectra of the mixed Bodipy/truxene dyes **7**, **10**, and **11** are typical of boradiazaidacene π systems, showing peaks at the expected wavelength for unsubstituted dyes (for **7**, λ_{abs} 501 nm, ε 87000 $M^{-1}cm^{-1}$) and monostyryl dyes (for **10**, λ_{abs} 609 nm, ε 112000 $M^{-1}cm^{-1}$, for **11**, λ_{abs} 607 nm, ε 125000 $M^{-1}cm^{-1}$).[14] These absorptions are safely assigned, in light of previous accounts, to $S_0 \rightarrow S_1$ transitions typical of singlet excited states. Interestingly, excitation in the truxene module result in quantitative energy transfer to the Bodipy fragment, which is the unique emitting species (Figure 1). The Bodipy fluorescence quantum yields lie in the range of 37–46% for dyes **7**, **10**, and **11** (Table S1, Supporting Information).

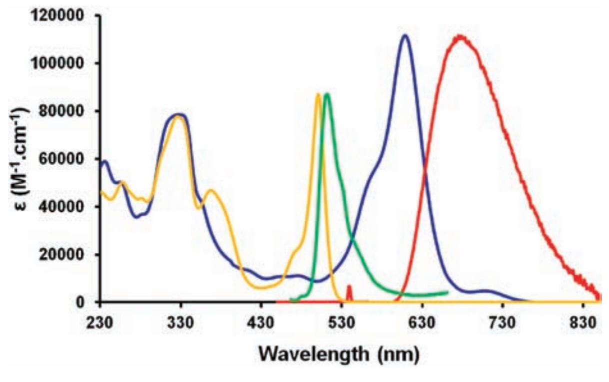

Figure 1. Absorption and emission spectra of **7** in THF (orange and green lines) and of **10** in benzene (blue and red lines), at rt, concentration ca. 1 × 10^{-6} M, excitation wavelength 460 nm for **7** and 550 nm for **10**.

The electrochemical properties of the dyes were evaluated by cyclic voltammetry, and compounds **5**, **6**, and **8** were used as reference. The TAT substrates exhibit two reversible monoelectronic oxidations about +0.80 and +1.36 V, in keeping with literature data (Figure 2).[6c] The simple Bodipy **6** exhibits two reversible monoelectronic processes at +1.16 and −1.24 V, assigned to the π-radical cation and π-radical anion, respectively.[15] Linking covalently both subunits together, providing dye **7**, gives a cyclic voltammogram reflecting a combination of the electroactivity of the TAT and Bodipy units (Figure 2a and Table S2, Supporting Information).

For the second set of dyes **10** and **11**, the first oxidation potential around +0.62 V is assigned to the Bodipy oxidation while the second and third reversible one electron oxidation waves define successive TAT oxidations. The reversible reduction wave is most reasonably assigned to the reduction of the Bodipy to the radical anion. Note that for **11** the reduction potential is cathodically shifted by 140 mV, a situation expected based on the increase of the electron density imported by the alkyne moieties. In contrast, the oxidation potential of **11** is shifted by 50 mV with respect to that of dye **10**.

The hole mobilities in thin films of the new Bodipy dyes were extracted from the transfer characteristics in the saturation regime of bottom contact field effect transistors. Commercial, highly doped oxidized silicon was used as substrate and gate electrode, while a hexamethyldisilazane (HMDS)-treated, 200 nm thick, SiO_2 layer was used as gate dielectric. Gold source and drain electrodes were obtained by photolithography. Bulk heterojunction solar cells were composed of a standard ITO/PEDOT:PSS/active layer/Al structure.

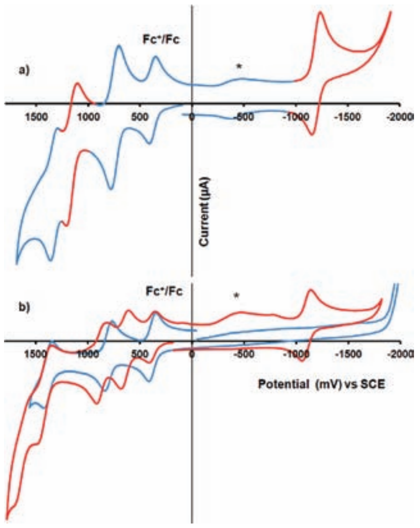

Figure 2. (a) Cyclic voltammetry of dye **7** and added ferrocene in CH_2Cl_2 and $TBAPF_6$. The red line corresponds to the redox processes associated with the Bodipy part. (b) Cyclic voltammetry of TAT derivative **8** (blue trace) and dye **10** (red trace), in both cases with added ferrocene. *Residual water present in the sample.

Table 1. Measured Hole Mobility for Different Bodipy Dyes and the Best Photovoltaic Parameters Obtained for Bodipy/$PC_{61}BM$ Blend Photovoltaic Cells[a]

	bodipy/PCBM ratio	cathode	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	thick-ness (nm)	μ_h (cm^2/V·s)
7	1:2	Al	0.57	0.5	28	0.08		
10	1:1	Al	0.71	2.9	29	0.66	55	1×10^{-4}
11	1:1	Al	0.71	2.0	29	0.40	50	4×10^{-3}
10	1:1	Ca/Al	0.83	3.6	29	0.90	55	1×10^{-4}

[a] J_{SC} for short-circuit current densities; FF for fill factors; PCE for power conversion efficiencies; μ_h for hole mobility; and V_{OC} for open circuit voltage.

The elaboration procedure (except for the active layer deposition) has been described elsewhere.[16] The active layer was obtained by spin-coating chloroform solutions of compounds **7**, **10**, and **11** with $PC_{61}BM$ in various ratios. The best photovoltaic parameters for each compound are listed in Table 1 together with the hole mobility of the pure material.

Compound **7** with the triazatruxene linked in the meso position gave negligible PCE, and the hole mobility could not be measured due to the absence of a transistor effect. The presence of a marked tilt angle between the Bodipy and the TAT engendered by the phenyl ring is probably detrimental for the π-stacking ability of the molecule.

In strong contrast, all other molecules have a reasonable hole mobility. Photovoltaic devices exhibit short-circuit current densities (J_{sc}) above 2.0 mA/cm^2, fill factors (FF) around 30%, and power conversion efficiencies (PCE) around 0.5%. This significant increase in J_{sc} and PCE, in comparison to compound **7**, is mainly due to the acceptable hole mobility values even if a small contribution of the enhanced absorption ability of the monostyryl compounds can not be completely neglected. The open circuit voltage (V_{oc}) increases also for compounds **10** and **11** to reach a value around 0.7 V (when Al is used as cathode) in good agreement with the HOMO levels determined by CV measurements.[17] For compound **10**, we also performed measurements on cells with a bilayer Ca(20 nm)/Al(120 nm) cathode, characterized by a lower work function. This time, the V_{oc} reaches 0.83 V and the PCE a promising 0.9%. However, the (J−V) characteristics under standard AM1.5 (100 mW/cm^2) illumination conditions shown in Figure 3 (characterized by a low fill factor and a low parallel resistance at 0 V) indicate that the charge carrier extraction is not efficient enough, even with the acceptable hole mobility measured in the pure material.

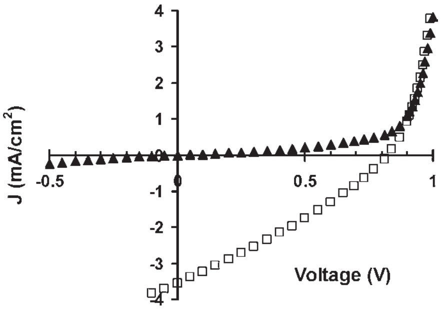

Figure 3. J−V characteristics measured in a photovoltaic device using compound **10** blended with $PC_{61}BM$ (1:1 wt ratio) as active layer. The solar cell structure is IT0/PEDOT:PSS/active layer/Ca/Al, and the measurements were performed in the dark (closed triangles) and under standard AM1.5 (100 mW/cm^2) illumination conditions (open squares).

In summary, a series of TAT-functionalized Bodipys have been prepared and their optical and electrochemical properties have been investigated and processed in BHJ solar cells. Further work is in progress to improve the active layer morphology as well as the charge carrier mobilities in the blend.

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Supporting Information Available. Synthetic procedures and analytical data reported herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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