

# Design of Linear and Star-Shaped Macromolecular Organic Semiconductors for Photonic Applications

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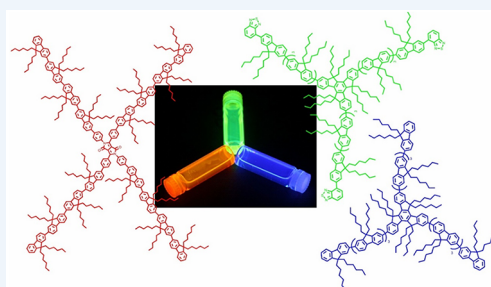
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**CONSPECTUS:** One of the most desirable and advantageous attributes of organic materials chemistry is the ability to tune the molecular structure to achieve targeted physical properties. This can be performed to achieve specific values for the ionization potential or electron affinity of the material, the absorption and emission characteristics, charge transport properties, phase behavior, solubility, processability, and many other properties, which in turn can help push the limits of performance in organic semiconductor devices. A striking example is the ability to make subtle structural changes to a conjugated macromolecule to vary the absorption and emission properties of a generic chemical structure.

In this Account, we demonstrate that target properties for specific photonic applications can be achieved from different types of semiconductor structures, namely, monodisperse star-shaped molecules, complex linear macromolecules, and conjugated polymers. The most appropriate material for any single application inevitably demands consideration of a trade-off of various properties; in this Account, we focus on applications such as organic lasers, electrogenerated chemiluminescence, hybrid light emitting diodes, and visible light communications. In terms of synthesis, atom and step economies are also important. The star-shaped structures consist of a core unit with 3 or 4 functional connection points, to which can be attached conjugated oligomers of varying length and composition. This strategy follows a convergent synthetic pathway and allows the isolation of target macromolecules in good yield, high purity, and absolute reproducibility. It is a versatile approach, providing a wide choice of constituent molecular units and therefore varying properties, while the products share many of the desirable attributes of polymers. Constructing linear conjugated macromolecules with multifunctionality can lead to complex synthetic routes and lower atom and step economies, inferior processability, and lower thermal or chemical stability, but these materials can be designed to provide a range of different targeted physical properties. Conventional conjugated polymers, as the third type of structure, often feature so-called “champion” properties. The synthetic challenge is mainly concerned with monomer synthesis, but the final polymerization sequence can be hard to control, leading to variable molecular weights and polydispersities and some degree of inconsistency in the properties of the same material between different synthetic batches. If a champion characteristic persists between samples, then the variation of other properties between batches can be tolerable, depending on the target application. In the case of polymers, we have chosen to study PPV-type polymers with bulky side groups that provide protection of their conjugated backbone from  $\pi$ – $\pi$  stacking interactions. These polymers exhibit high photoluminescence quantum yields (PLQYs) in films and short radiative lifetimes and are an important benchmark to monodisperse star-shaped systems in terms of different absorption/emission regions. This Account therefore outlines the advantages and special features of monodisperse star-shaped macromolecules for photonic applications but also considers the two alternative classes of materials and highlights the pros and cons of each class of conjugated structure.



## 1. INTRODUCTION

Organic semiconductors are  $\pi$ -conjugated systems with a hugely diverse range of structural possibilities. Historically, linear conjugated polymers were first investigated for their high conductivities and subsequently for their electronic and photonic properties as components in semiconductor devices.<sup>1</sup> Starburst or star-shaped monodisperse macromolecules often feature attributes that combine desirable characteristics of polymers (e.g., solution processability and excellent film-

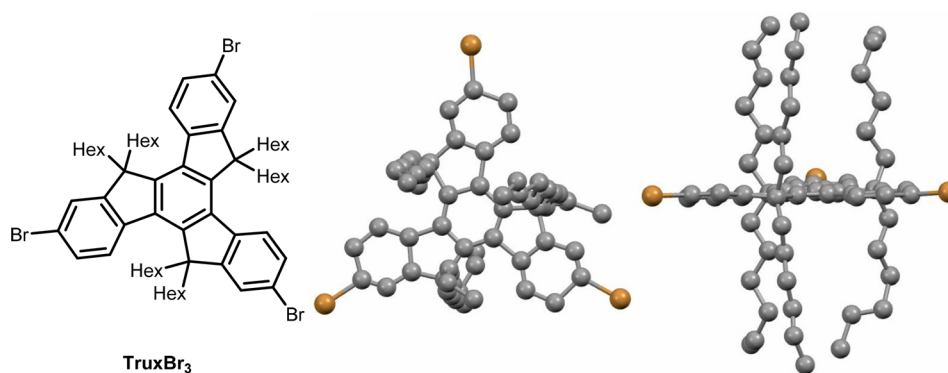
forming properties) but retain the well-defined physical properties of discrete molecules and the ability to be isolated in high purity.<sup>2</sup>

In this Account, we review the progress of our work on conjugated macromolecules as high performance, bespoke materials for a range of photonic devices.

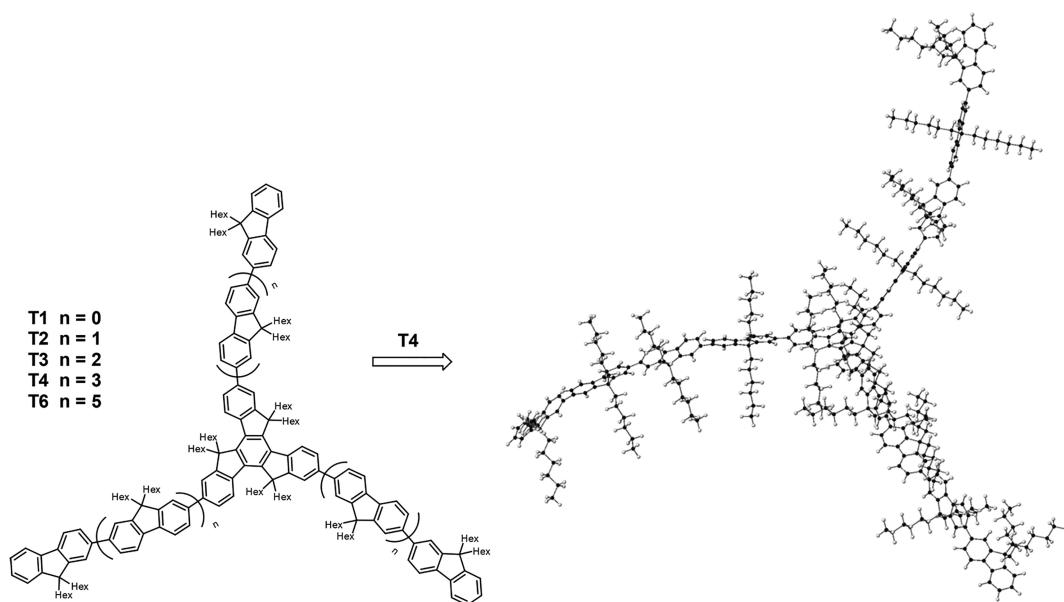
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**Figure 1.** Chemical structure of TruxBr<sub>3</sub> and views of the molecule from above and side-on with respect to the central benzene unit.



**Figure 2.** Chemical structures of the  $T_n$  series of truxenes. The dimensions for T4 (right) are 1.7 nm for the height of the molecule and 3.9 nm for the radius.

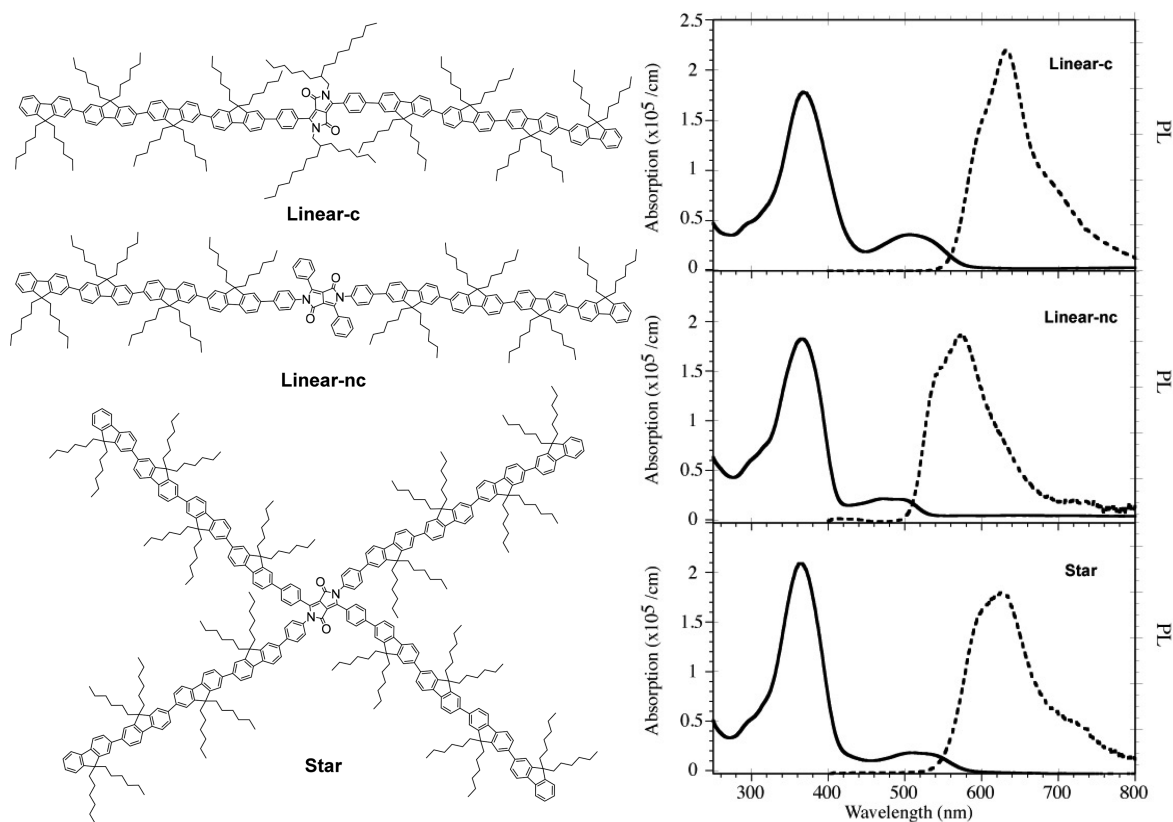
By introduction, the star-shaped conjugated macromolecules under discussion essentially possess two structural features that can be altered to tune the physical properties of the resulting molecule, the core and the conjugated units (arms) attached to it. The core typically consists of a rigid and multifunctional aromatic unit, and in our earlier work we chose the truxene derivative TruxBr<sub>3</sub> as a central scaffold (Figure 1).<sup>3</sup> Our decision to apply this core in the first instance was based on the substitution pattern of the hexyl chains. The alkyl chains reside perpendicular to the plane of the rigid core and across the molecule, and this perturbs the molecules from strongly aggregating through the benzene rings. This is a key feature of the hexa-alkylated truxene core in the design of highly emissive materials for photonic applications, since aggregation through  $\pi$ – $\pi$  intermolecular interactions and excimer formation upon photoexcitation can lead to emission quenching.<sup>4</sup>

Attaching conjugated chains to the core through the bromo functionalities of TruxBr<sub>3</sub> is completed in one step. This can be accomplished following Negishi or Suzuki coupling protocols. Figure 2 shows a family of truxene derivatives, T1–T4 and Ti–6, with one to four or six fluorenes in each arm, respectively. The various oligomer arms were each synthesized and functionalized with bromine or boronic ester groups prior to

coupling to the core, such that the final assembly of the target molecule was completed via a single-step convergent strategy. This is the preferred method for the assembly of hyperbranched oligofluorenes in star-shaped macromolecules, since a divergent approach makes purification difficult because partly substituted side products are similar in size and physical properties.<sup>5</sup> The truxene family of compounds can be regarded as discrete nanosized organic semiconductors, as shown in Figure 2.

## 2. STRUCTURE AND PROPERTIES

The  $T_n$  series of compounds are blue emitters (400–475 nm) and have featureless absorption bands in the range 343–374 nm, typically 20–30 nm blue-shifted with respect to poly(9,9-dialkylfluorene)s.<sup>6</sup> The energies of the absorption maxima follow a straight line plot with the reciprocal of the number of benzene rings in the arms, resulting in a very small difference between the peak values for T3 and T4 (3 nm), thereby reaching a limit to the effective conjugation length of the arms in the higher truxene.<sup>3</sup> These star-shaped molecules are excellent light harvesters, absorbing across the entire molecule, with extinction coefficients in the range  $9 \times 10^4$  to  $5 \times 10^5$  L mol<sup>−1</sup> cm<sup>−1</sup> for the truxene  $T_n$  series.<sup>7,8</sup> The emissive properties of the truxenes make them desirable candidates for photonic applications with



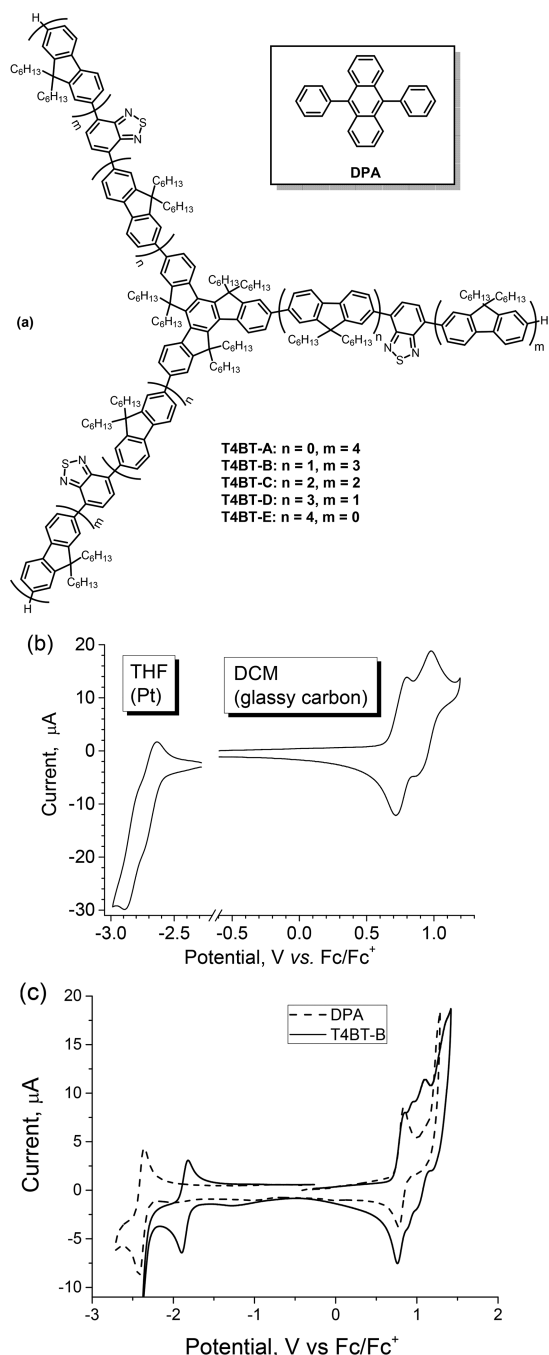
**Figure 3.** Chemical structures of DPP-oligofluorene systems and their absorption/emission characteristics. Reproduced with permission from ref 12. Copyright 2011 Wiley-VCH.

values for the photoluminescence quantum yield (PLQY) up to 60% in the solid state and higher than those for analogous linear oligofluorenes.<sup>8</sup> After photoexcitation, the molecules undergo complex relaxation energy pathways, leading to emission from localized excited states and spectra with fine structure.<sup>9</sup> This indicates that the star-shaped structures can support long-lived delocalized excitons that facilitate efficient energy transfer. Indeed, these absorption and emission characteristics encouraged us to look at star-shaped macromolecules as luminescent solar concentrators in boron-dipyrromethene (BODIPY)-core systems (*vide infra*, section 4), and we found these materials to perform as well as leading nanocrystalline emitters.<sup>10</sup>

Tailoring the structure of the core or arms of the compounds allows tuning of the absorption and emission characteristics. Moreover, providing a design and pathway for energy transfer within the individual molecule creates the opportunity for a large difference between the excitation and emission wavelengths that greatly limits reabsorption, which is a key loss mechanism to avoid in solar concentrators.<sup>11</sup> This can be seen clearly from the family of red-emitting molecules presented in Figure 3, which feature a 1,4-diketo-2,3,5,6-tetraphenyl-pyrrolo[3,4-*c*] pyrrole (DPP) core unit. The quaterfluorene arms absorb strongly at ca. 368 nm, and there is a shallow band at 486–517 nm, which is assigned to an intramolecular charge-transfer component within the DPP unit.<sup>12</sup> The emission spectrum is entirely based on the DPP core, showing highly efficient energy transfer from the fluorene-based arms to the DPP unit. The propensity for such molecules to undergo intramolecular energy transfer has been used to good effect in frequency down-converting applications (*vide infra*). Nevertheless, the DPP core in the compounds in Figure 3 is responsible for aggregation through quadrupole

interactions in solution and solid state, leading to low PLQYs (2–20%). Indeed, in stark contrast to the amorphous nature of the truxene family of compounds, the Linear-c analogue forms films with small crystalline domains; organic field effect transistors comprising this material gave hole mobilities up to  $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>13</sup>

Apart from adapting the core of the parent truxene structures, the photophysical properties can be tuned by altering the molecular structure of the arms. 2,1,3-Benzothiadiazole (BT) is a well-known heterocycle used in molecular systems or as a comonomer in polymers. In the copolymer poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT), a high performance polymer used in organic light emitting diodes (OLEDs), the BT unit changes the emissive properties of the parent polyfluorene from blue to green-yellow.<sup>14</sup> Introducing the BT heterocycle into specific positions in the arms of the truxene T4 gives rise to five possible structural isomers, T4BT-A to T4BT-E (Figure 4), with solid-state PLQY values up to 55%.<sup>15</sup> The positioning of the BT units has an effect on the photophysical properties of the molecules, particularly in the case of the terminally functionalized T4BT-E, which has blue-shifted emission and a lower PLQY compared to its isomers (27%). The BT unit is beneficial to the electrochemical properties of the series since it imparts reversibility in the reduction of the T4BT series, which is irreversible in the truxenes T1–T4. The reversibility of oxidation and reduction processes in the T4BT series is used to good effect in electrogenerated chemiluminescence (ECL), a powerful technique used in sensing applications. ECL relies on the generation of radical anions and radical cations at the working electrode of an electrochemical cell, and subsequent annihilation

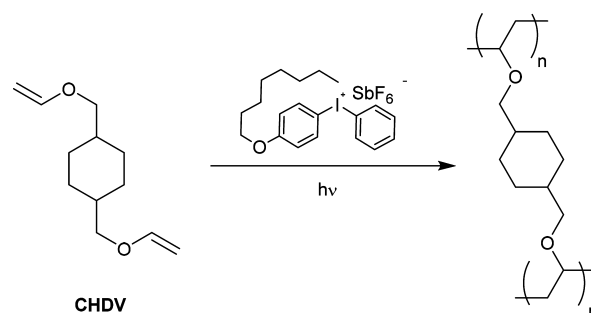


**Figure 4.** (a) Chemical structures of the five isomers of truxene T4BT. Cyclic voltammograms of (b) T3 and (c) T4BT-B and DPA, showing the difference in reversibility for the reduction of the truxene molecules. Panel b reproduced with permission from ref 3. Copyright 2004 American Chemical Society. Panel c adapted with permission from ref 18. Copyright 2015 Royal Society of Chemistry.

of these species to give emissive excited states. While the ECL intensity of the truxene T4 was found to be 80% of the standard ECL emitter 9,10-diphenylanthracene (DPA, Figure 4a),<sup>16</sup> the increased stability of the radical anions in T4BT-B led to the ECL intensity increasing to 7 times that of the DPA standard,<sup>17,18</sup> proving that the BT-containing compounds are highly efficient and superior ECL materials compared to their parent truxene materials.

The star-shaped materials reported above have excellent solubility in organic solvents such as THF, dichloromethane,

and toluene. While the truxene-based compounds form uniform amorphous films through drop-casting or spin-coating, more robust films can be processed as composites with a photoresist material. The monomer 1,4-cyclohexyldimethanol divinyl ether (CHDV) has proven to be a most suitable material that acts as a solvent for the conjugated organic compounds and is cured by UV irradiation with a typical loading of 0.5–1% w/w of the photoacid generator (PAG) [*p*-(octyloxy)phenyl](phenyl)-iodonium hexafluoroantimonate (Figure 5). Using such blends,



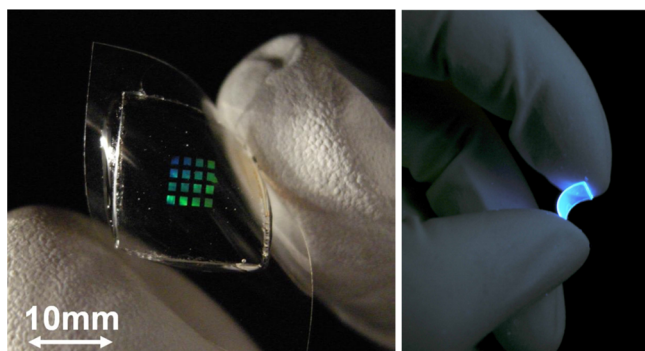
**Figure 5.** Photopolymerization of the monomer CHDV.

one can process films and structures by inkjet printing,<sup>19,20</sup> direct laser writing,<sup>21</sup> and dip-pen nanolithography,<sup>22</sup> with concentrations of the emissive materials in the range 0.5–10% w/w. These processing routes enabled the fabrication of a range of photonic devices, which are discussed below.

### 3. ORGANIC LASERS

Distributed feedback lasers (devices consisting of an optical resonance cavity with a periodic structure that acts as a reflector at the wavelength of laser action) based on truxenes and related structures have shown that star-shaped conjugated molecules are excellent materials with low thresholds for photopumped lasing.<sup>23</sup> The advantages of these structures for lasing applications are demonstrated by their high absorption coefficients, high PLQYs, low optical losses, and high optical gain.<sup>24</sup> At the time of publication, neat films of the truxene T4 demonstrated the lowest reported waveguide loss coefficient for a solution-processed organic semiconductor ( $2.3 \text{ cm}^{-1}$ ).<sup>25</sup> For lasing experiments, a 20 mg/mL solution of T4 in toluene was spin-coated onto a corrugated silica substrate and the assembled distributed feedback (DFB) device was optically pumped to lase at a low threshold of  $270 \text{ W/cm}^2$ . Studies on the truxene T3 showed that this material had a higher threshold for lasing ( $515 \text{ W/cm}^2$ ) but a higher PLQY, higher net gain coefficient, and lower threshold for amplified spontaneous emission (ASE, which is a process closely related to lasing but the amplified emission does not involve a resonant cavity or DFB structure). By altering the thickness of the T3 layer, the laser emission wavelength could be tuned across 51 nm ( $422\text{--}473 \text{ nm}$ ); at the time of publication this represented the broadest tuning range reported for organic deep-blue/blue lasing materials.<sup>26</sup> Due to the amorphous and excellent film-forming properties of the truxene molecules, flexible devices have been produced by spin-coating neat T3 onto an epoxy grating<sup>27</sup> or by applying a soft lithography approach from the reproduction of a silica master grating<sup>28</sup> or a holographic reflection grating (Figure 6).<sup>29</sup> The photostability of these devices can be significantly improved by encapsulating with poly(vinyl alcohol) (PVA).<sup>27</sup> To demonstrate the extent of using neat films, free-standing films of T3





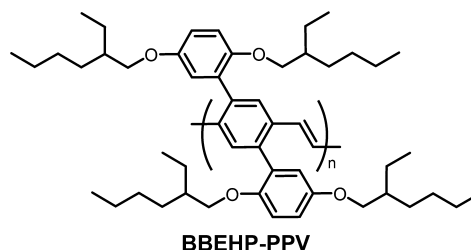
**Figure 6.** Mechanically flexible laser devices under illumination and bending. The picture shows an array of epoxy gratings (left), enabling an array of lasers after coating with T3. Left panel reproduced with permission from ref 28. Copyright 2012 IEEE Photonics Society. Right panel reproduced with permission from ref 29. Copyright 2010 Optical Society of America.

have even been formed on the surface of water and demonstrated ASE with a threshold of ca.  $400 \mu\text{J}/\text{cm}^2$ .<sup>30</sup>

The largest oligofluorene-truxene to be synthesized is T6 ( $n = 5$  in Figure 2), and this material was studied for its two-photon absorption (2PA) properties in comparison to its smaller truxene analogues.<sup>31</sup> The 2PA cross-section for T6 was found to be the highest in the series (2200 GM; T4 = 1600 and T3 = 900 GM). A frequency up-converted laser of T6 demonstrated a threshold as low as  $3.1 \text{ mJ}/\text{cm}^2$ , which is more than an order of magnitude lower than that of any conjugated polymer (pump beam 800 nm, laser peak emission 441 nm).

While a variation in photophysical properties is clearly observed as a function of different arm lengths in the molecules T3, T4, and T6, the significance of the truxene core has also been investigated. Pei et al. synthesized analogues of T1–T4 in which the truxene core is replaced by a benzene ring, substituted with oligofluorene chains at the 1,3, and 5 positions.<sup>32</sup> The minimum lasing thresholds recorded for this benzene-core series were found to be  $1.1 \text{ kW}/\text{cm}^2$  for the tris(terfluorene) material and  $1.2 \text{ kW}/\text{cm}^2$  for the T4 analogue,<sup>33</sup> which are far higher than the thresholds for devices based on the truxene compounds. This was attributed to the fact that there are greater intermolecular interactions for the benzene-core series of compound, and in comparison to the truxenes, this leads to far lower PLQYs in the solid state as well as higher optical losses in waveguides.

A major aspiration in the field of organic lasers is the realization of electrically driven devices, and ideally, this would be accompanied by a cheap manufacturing route. While this has yet to be achieved, advances have been made with indirectly electrically driven organic lasers, in which the gain material is pumped by an inorganic LED. A low lasing threshold is a key material requirement in this case, and the high performance green-emitting polymer poly[2,5-bis(2',5'-bis(2"-ethylhexyloxy)phenyl)-p-phenylenevinylene] (BBEHP-PPV, Figure 7), first synthesized by Swager and co-workers,<sup>34</sup> is an excellent candidate. Using BBEHP-PPV as the gain material, organic lasers have been fabricated from mixed order<sup>35</sup> and substructured second order gratings<sup>36</sup> with lasing thresholds as low as  $15 \text{ W}/\text{cm}^2$ . For indirectly electrically driven organic lasers, BBEHP-PPV devices have been made by nanoimprint lithography (NIL), a technique that is compatible with high-volume, low-cost production of nanostructures but with lower resolution waveguides and threshold excitation densities up to



**Figure 7.** Chemical structure of BBEHP-PPV.

$10 \text{ kW}/\text{cm}^2$ .<sup>37</sup> In our work with BBEHP-PPV,<sup>38</sup> the thresholds ( $770 \text{ W}/\text{cm}^2$ ) were low enough to be driven by commercially available LEDs, which typically have a maximum power output of  $1 \text{ kW}/\text{cm}^2$ . While these achievements are highly significant, it is important to comment on the batch-to-batch reproducibility of BBEHP-PPV. Under the same reaction conditions, four batches of this high performance polymer were prepared.<sup>38</sup> Despite attempts to purify these batches by various means, it was impossible to control or refine the polydispersity and molecular weights of the polymers, which were prepared by the well-known Gilch method. The batches gave different values of PLQY, waveguide losses, and ASE thresholds, which did not correlate at all to the variation of polydispersity and MW. Since the threshold is key to the device being driven by the LED, a batch-to-batch variation with no control is highly undesirable, especially to industry. In this respect, monodisperse conjugated compounds have a huge advantage over polymers such as BBEHP-PPV, since their synthetic reproducibility (and hence their physical properties) is 100%.

#### 4. HYBRID INORGANIC–ORGANIC LEDs AND VISIBLE LIGHT COMMUNICATIONS

Commercial white light LEDs for lighting applications currently work on the principle of frequency down-conversion, in which light emitted from a LED is absorbed by an inorganic phosphor, which in turn re-emits light at a longer wavelength. The combination of emission wavelengths from the LED and the phosphor gives white light, that is, from blue and yellow emission in a two-component system or from red, green, and blue from a more complex device. Organic semiconductors are alternative materials to inorganic phosphors. Compound [BODFluTh]<sub>2</sub>FB was synthesized (Figure 8)<sup>39</sup> to assess the suitability of down-converting organic materials containing the fluorescent molecule 4,4-difluoro-4-borata-3a-azonia-4a-aza-s-indacene (BODIPY). In this molecule, it was anticipated that the central conjugated unit would act as a light-harvesting antenna and, upon photoexcitation under blue light, the chromophore would transfer energy to the BODIPY unit through Förster resonance energy transfer (FRET), which in turn would emit at a much longer wavelength (yellow) than the emission of the central unit.

In order for such a molecule to perform satisfactorily in a white light device driven by a blue LED, the organic material needs to satisfy a number of criteria: (i) precise absorption wavelength (in the range 400–450 nm), (ii) sufficient absorptivity, (iii) high photoluminescence quantum yield (PLQY), (iv) highly efficient internal energy transfer, and (v) precise emission wavelength (550–584 nm) for white light generation from a mixture of blue and yellow light. The compound proved to be an excellent candidate with a PLQY (solid state) of 63% in films using CHDV as a benign host, absorption maxima at 403 and 525 nm, and emission at 550 nm

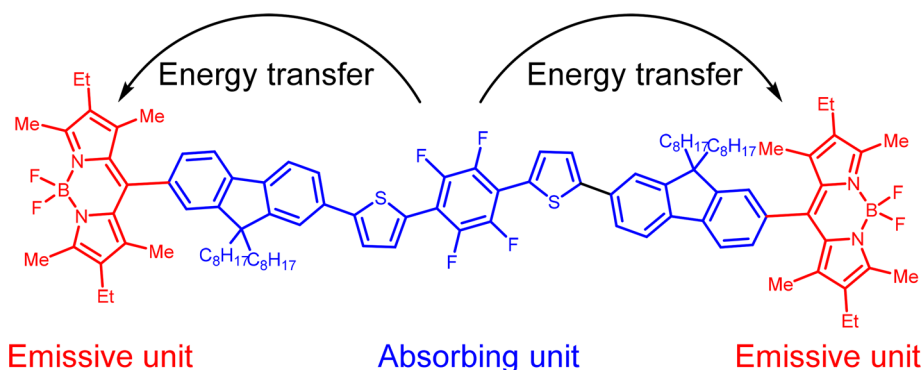


Figure 8. Chemical structure of  $[\text{BODFluTh}]_2\text{FB}$ .

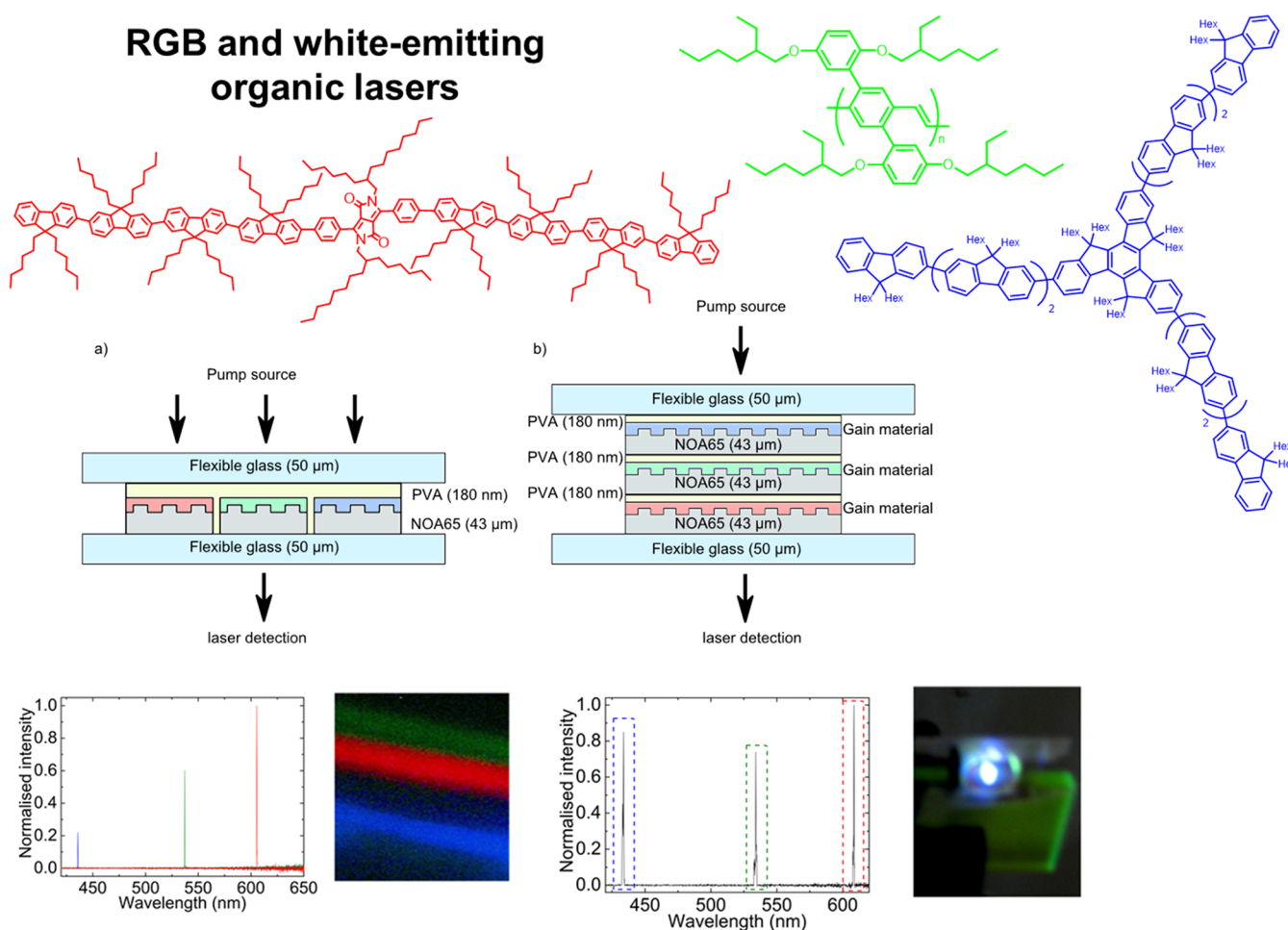
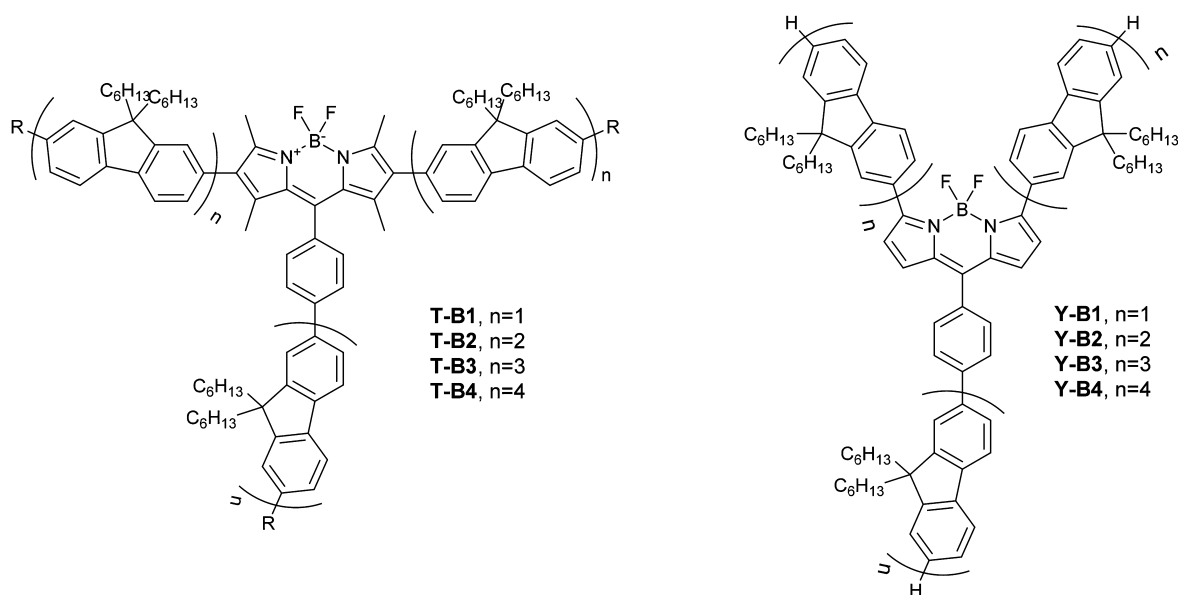


Figure 9. Using a combination of RGB emitters to achieve (a) multicolor and (b) white laser devices. Reproduced with permission from ref 42. Copyright 2016 Optical Society of America.

(excited at 435 nm). It is worth noting that neat films of the emitter were cracked and of poor quality and the solid state PLQY was greatly reduced.  $[\text{BODFluTh}]_2\text{FB}/\text{CHDV}$  coated onto a blue LED chip (445 nm emission) gave cool white light devices with a correlated color temperature (CCT) of 5137 K (0.34, 0.31) and with a luminous efficacy of 13.6 lm/W.<sup>39</sup> Under the concentrations used in these experiments (0.5–1.0% w/v), it is estimated that 1 mg of  $[\text{BODFluTh}]_2\text{FB}$  would be enough to produce 1000 white light LEDs. Interestingly, increasing the amount of the organic emitter decreases the conversion efficiency, due to aggregation effects and subsequent quenching

of emission.<sup>40</sup> Subsequent work involved structural modification of the absorbing unit of the organic converter to give cool to warm white light devices with improved luminous efficacy (368 lm/W).<sup>41</sup>

The high suitability of organic macromolecular conjugated materials for applications involving frequency down-conversion is eloquently demonstrated in a multilayer white light laser device.<sup>42</sup> Combining three of the emissive materials already described in this Account (Linear-c, T3, and BBEHP-PPV) in parallel in a single device provided a RGB vertically emitting distributed feedback laser, and when the materials are aligned in



**Figure 10.** Structures of star-shaped conjugated macromolecules based on a BODIPY core, designed for VLC applications.

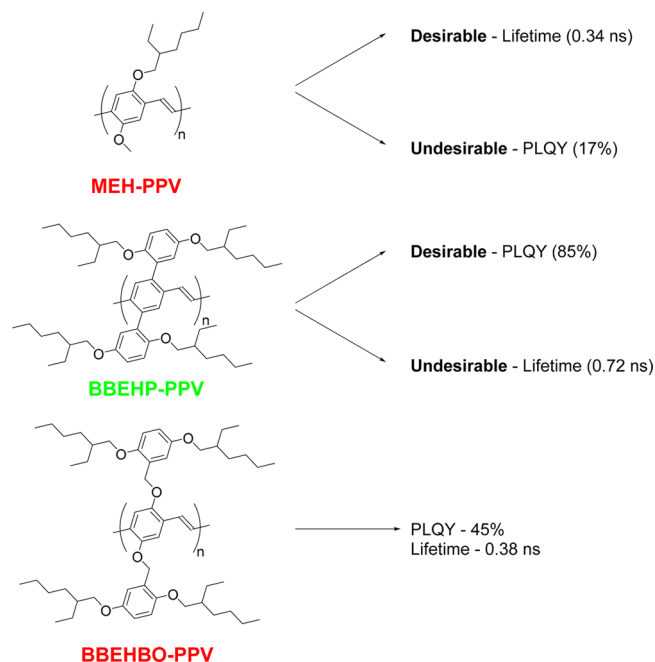
series according to increasing emission wavelength, an optically pumped white light laser is achieved (Figure 9). For the latter, the whole device threshold is  $42 \mu\text{J}/\text{cm}^2$  (when the three lasers emit at the same time). This is an improvement in threshold of  $\sim 100$  times compared to the result shown by Yamashita et al. with three organic dyes.<sup>43</sup>

The characteristics of the down-converters demonstrated above promise great potential for visible light communications (VLC), where data transfer functionality is coupled with illumination.<sup>44</sup> This technology, often referred to as LiFi,<sup>45</sup> is a fascinating alternative to WiFi, which relies on radio frequencies for wireless data transmission. In the case of VLC, the ability to switch light devices on and off gives rise to binary code: 0 when the light is off and 1 when the device emits light. The rate at which this can be done is highly dependent on the luminescence lifetimes of the emissive materials. For inorganic phosphors with lifetimes of milliseconds or microseconds, switching speed will be  $10^3$ – $10^6$  times slower relative to organic emitters that can achieve sub-nanosecond fluorescence lifetimes. Multiplexing a series of signals with a range of wavelengths provided by microLEDs gives LiFi technology the potential to reach data transfer rates far superior to WiFi speeds, demonstrating the enormous interest and high importance in this area as the general demand for data increases rapidly.

In order to develop organic materials for VLC, short fluorescence lifetimes are an additional requirement to the five essential criteria mentioned above for converter materials. Consequently, organic materials design strategies for VLC applications have included this factor, and a series of star-shaped conjugated macromolecules with a BODIPY core were synthesized in which oligofluorene units have been attached to  $\beta$ - and meso-positions of the BODIPY core or to the  $\alpha$ - and meso-positions to give the T-series and Y-series, respectively (Figure 10).<sup>46</sup> Solution state PLQYs for the T-series were higher (up to 75% in solution) than for the Y-series (up to 62%), but there was much greater spectral overlap with the emission of commercially available microLEDs used for VLC (ca. 450 nm). Thus, the Y-series compounds were studied for this application, with solution-state experiments demonstrating data rates of 100 Mb/s<sup>47</sup> and solid-state measurements of 370 Mb/s.<sup>48</sup> The

increased data rate is due to the shorter radiative lifetimes in the solid state compared to solution state (3.2 vs 6.5 ns for Y-B3, which was used for data transmission measurements).

In an attempt to improve on these data rates, binary blends of the green-emitter T4BT-B (Figure 4a) and T-B3 or Y-B3 were investigated. The strategy behind this concept was the greater absorptivity of T4BT-B in the blue and the observed FRET efficiency from T4BT-B to the BODIPY star molecules, which was found to be very high ( $>70\%$  for T-B3 and  $>90\%$  for Y-B3). This led to data rates of  $>200$  Mb/s for both BODIPY materials.<sup>49</sup> Turning instead to a blend of polymers, namely, the green-emitting BBEHP-PPV and MEH-PPV (Figure 11), the same strategy gave transfer rates of  $>350$  Mb/s.<sup>50</sup> Here, the higher radiative rate that MEH-PPV offers was targeted,



**Figure 11.** PPV derivatives for VLC.



alongside the high PLQY of BBEHP-PPV. However, the limiting factor to even higher data transfer rates was the rather low PLQY of MEH-PPV (17%), despite its sub-nanosecond radiative lifetime. Obtaining a single red emitter with a high PLQY and short lifetime, together with good absorptivity at 450 nm, is challenging, but a single component material would be more practical than a blend. To this end, we looked toward a new PPV derivative that would feature the best attributes of MEH-PPV and BBEHP-PPV, namely, BBEHBO-PPV (Figure 11). We speculated that the low PLQY of MEH-PPV was due to aggregation effects, especially in mind of the bulky, twisted side groups featured in BBEHP-PPV, which would act as a sheath over the backbone of the conjugated polymer. Conversely, the oxygen atoms directly attached to the PPV chain in MEH-PPV dictate the red emission and may have an effect on the radiative lifetime as well. Retaining the side groups in BBEHP-PPV and oxygen atoms on the backbone of the PPV chain gave the template for the design of BBEHBO-PPV. This served to good effect, retaining a very short radiative lifetime (0.38 ns) but increasing the PLQY significantly from 17% for MEH-PPV to 45% for BBEHBO-PPV. A data transfer rate of 550 Mb/s for this material was demonstrated,<sup>51</sup> which is 55 times faster than the commercially available and widely studied phosphor CL-840 measured under the same conditions.

## 5. CONCLUSIONS

We have presented and discussed the properties of three different classes of organic semiconductors for photonic applications. Star-shaped structures are excellent gain materials in organic lasers, owing to their synthetic tunability, photophysical properties, and polymer-like characteristics. In principle, they are the ideal type of material, mainly due to their exceptionally high degree of batch-to-batch reproducibility. The low lasing thresholds observed in the truxene family of molecules show that these materials can be used in indirectly electrically pumped organic lasers, powered by a commercial LED. The potential of linear conjugated compounds to deliver a more complex array of properties compared to oligomers and polymers is limited to the ability and imagination of the synthetic chemist. However, these systems do tend to have limitations in forming good quality films. Linear conjugated compounds have a greater tendency to aggregate, and this leads to complex photophysical processes and reduced PLQYs. Star-shaped, monodisperse macromolecules have the right template to be the ideal material, but further work needs to be carried out to design and synthesize structures that will match the performance of the best conjugated polymers reported to date. For example, in relation to VLC, PLQYs can be extremely high in some star-shaped molecules, but emissive lifetimes less than 1 ns have yet to be realized and that would make such materials more suitable for this application. Nevertheless, the future for star-shaped conjugated macromolecules for photonic applications is bright, since the versatility of the synthetic strategies already realized, together with the demonstration of high-performance devices, show a clear route to exploitation of star-shaped conjugated macromolecules. The star-shaped materials out-perform the benchmark inorganic phosphor CL-840 (Intermatix ChromaLit) in VLC applications, while the purely organic nature of these molecules avoids the use of expensive rare-earth metals.

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