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## Experimental and theoretical studies of quadrupolar oligothiophene-cored chromophores containing dimesitylboryl moieties as $\pi$ -accepting end-groups: Syntheses, structures, fluorescence, one- and two-photon absorption

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**Keywords** Two-photon absorption; Dimesitylboryl; Oligothiophene; Fluorescence; Photophysics

### Abstract

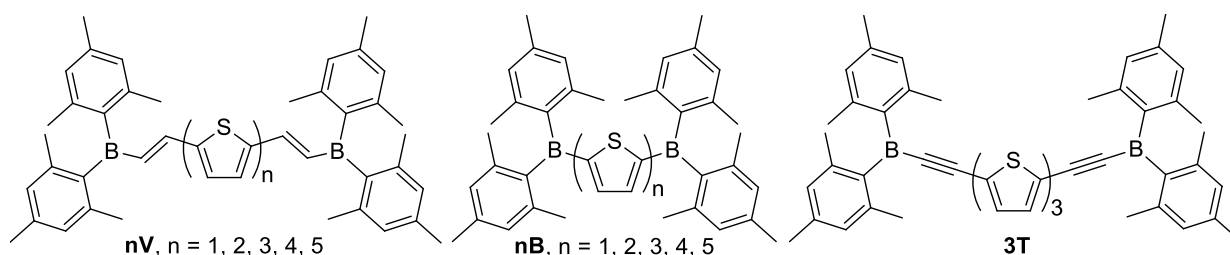
Quadrupolar oligothiophene chromophores with four and five thiophene rings and two terminal (*E*)-dimesitylborylvinyl accepting groups (**4V-5V**), five thiophene rings and two terminal aryl dimesitylboryl groups (**5B**), and an analogue of **5V** with an alternative EDOT

central ring (**5VE**) have all been synthesized via Pd-catalyzed cross-coupling reactions in good to excellent yields (66-89%). Single-crystal X-ray diffraction structures of **4V**, **5V** and **5B**, as well as the structures of the previously reported two-thiophene analogue **2V** and several synthetic intermediates, have been determined. Chromophores **4V**, **5V**, **5B** and **5VE** exhibit moderate photoluminescence quantum yields (0.26-0.29), higher than previously reported analogues with shorter oligothiophene chains [**1V** (0.01), **2V** (0.11) and **3V** (0.20)], while fluorescence lifetimes are quite short, being in the range 0.50-1.05 ns for all chromophores studied. Two-photon absorption cross-sections ( $\sigma_2$ ) have been measured for all chromophores across the range 750-920 nm, allowing comparison of the series **1V-5V**, in which  $\sigma_2$  increases steadily with length up to ca. 1600 GM at the biologically-relevant wavelength of 800 nm. Furthermore, the influence of removing the vinyl groups in **5B** and introducing a central donating group in **5VE** is discussed. DFT and TD-DFT calculations complement the experimental findings and contribute to their interpretation. A comparison to related thiophene and dimesitylboryl analogues indicates that our design strategy is promising for the synthesis of efficient dyes for applications in, *e.g.*, two-photon-excited fluorescence microscopy.

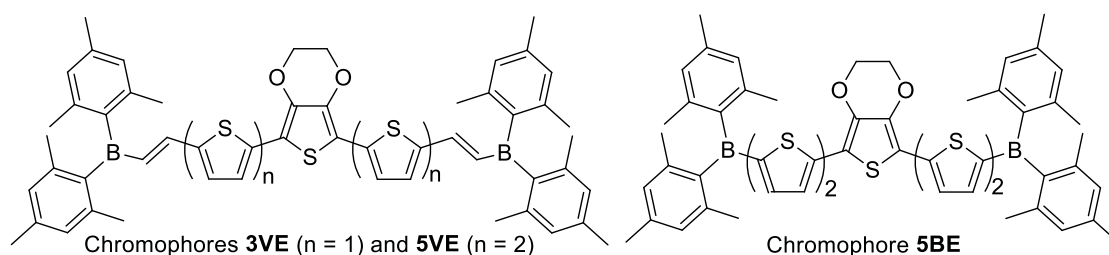
## Introduction

Over the past decade, two-photon absorption (TPA) has attracted a tremendous research effort, especially from synthetic chemists in the quest of designing new chromophores, combining enhanced TPA responses and appropriate properties for particular applications. The latter range from material science to medicine and have prompted a series of review papers in recent years addressing TPA fundamentals, scope in terms of applications, as well as various synthetic strategies implemented for the design of TPA chromophores.<sup>[1]</sup> Among the benefits of TPA over alternative techniques, spatiotemporal control of excitation and/or fluorescence is probably the most prominent. It is a direct byproduct of the simultaneous absorption of a pair of photons that may have different or the same energies. Such fine spatiotemporal control, combined with the use of near-IR photons, meets the prerequisites required for photochemical tools capable of investigating the dynamics of biological processes. Indeed, several recent reviews demonstrate both achievements and needs in matter of sensing, imaging, and uncaging carried out within living cells and tissues or applied to the study of physiological processes.<sup>[2]</sup>

At the same time, boron chemistry has expanded its use from material to medical science where it is believed to provide a new class of molecules for imaging or therapeutic agents.<sup>[3]</sup> Boron chemistry has also contributed to a major advance in the field of molecular machines, with the discovery of a double stranded helicate bridged by two spiroborate moieties capable of undergoing a reversible spring-like motion triggered by inclusion and removal of a sodium ion.<sup>[4]</sup> Unlike four-coordinated boron, three-coordinated boron can be incorporated in  $\pi$ -conjugated molecules where it acts as a  $\pi$ -acceptor due to its vacant p-orbital, while remaining at the same time a strong  $\sigma$ -donor.<sup>[5]</sup> To prevent attack of the three-coordinated boron center by nucleophiles, sterically-shielding substituents, such as mesityl (2,4,6-trimethylphenyl) groups, have proved efficient, limiting, at the same time,  $\pi$ -stacking in condensed phases.<sup>[6]</sup> This has opened the way for the design of conjugated boron-based chromophores with interesting linear and non-linear optical properties. However, despite the numerous studies of structure-property relationship for TPA responses over more than a decade,<sup>[1]</sup> chromophores built from dimesitylboryl  $\pi$ -accepting moieties are still relatively rare<sup>[7-14]</sup> as are those containing oligothiophene moieties.<sup>[8,11,14-20]</sup>



**Scheme 1.** Chromophores **1V-5V** (left), **1B-5B** (middle) and **3T** (right). Single-crystal X-ray diffraction data are available for compounds **1V-4V** and **5B**.



**Scheme 2.** Chromophores **3VE** and **5VE** (left) and **5BE** (right).

This prompted us to investigate further the TPA properties of A-D-A quadrupoles containing both of these electron accepting and donating building blocks, in line with the earlier work by some of us.<sup>[14]</sup> In fact, we have shown that symmetric (*E*)-dimesitylborylvinyl dithiophene (**2V**) and terthiophene (**3V**) (Scheme 1) have promising TPA cross-sections and clear TPA

enhancement upon chain elongation with a concomitant two-fold increase of the radiative quantum yield. To investigate further the structure-properties relationships of this class of chromophores, we report herein our investigations of both the chain length effect with **4V** and **5V** (Scheme 1) and the nature of the conjugated bridge by removing the vinylene spacers (**5B**, Scheme 1). Further diversification was also considered with the inclusion of the electron donating 3,4-ethylenedioxy-thiophene (EDOT) unit (**5VE**, Scheme 2), in a comparable strategy to the one recently developed for D-A-D conjugated oligomers.<sup>[15]</sup>

In the present paper, we present first the synthesis and characterization of the above mentioned compounds and then discuss their crystal structures and molecular geometries as derived from single-crystal X-ray diffraction data and Density Functional Theory (DFT) optimized geometries, respectively. Theoretical calculations were used to extend the scope of the study by investigating all chromophores sketched in Schemes 1 and 2. Next, one-photon absorption (OPA), emission, solvatochromism and TPA are discussed in sequence in the light of TD-DFT calculations relevant for the ground state conformations, and anterior few-state modelling for emission properties.<sup>[21]</sup> Finally, the TPA activity of our quadrupolar chromophores is compared to that of related compounds built from either BMes<sub>2</sub><sup>[8-13]</sup> or oligothiophene moieties,<sup>[15-20]</sup> allowing additional insight into structure-TPA relationships.

## Results and Discussion

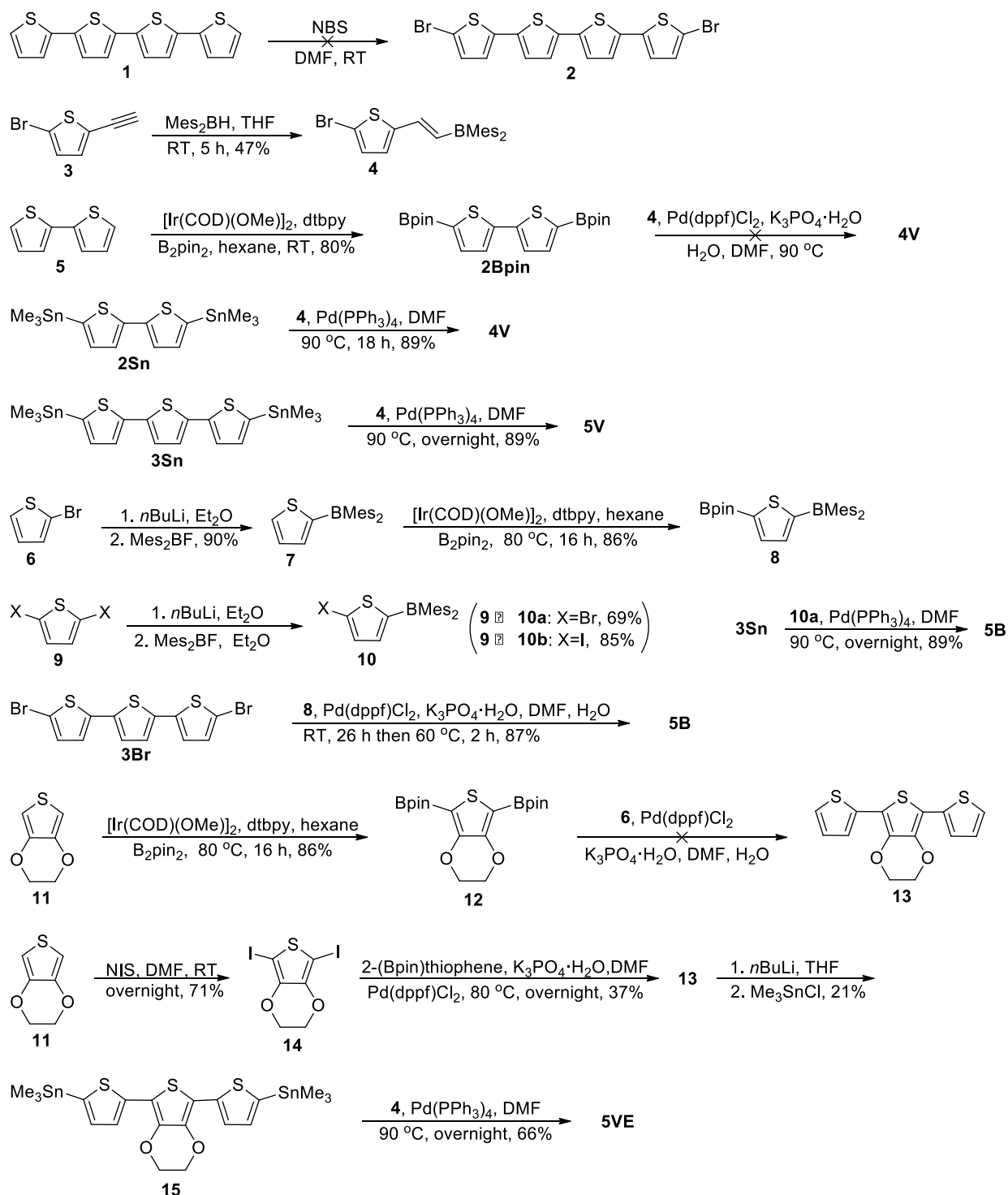
**Synthesis:** The compounds were synthesized as summarized in Scheme 3. Compounds **2V** and **3V** were synthesized by direct hydroboration of the respective diterminal alkynes, according to the published procedure.<sup>[14]</sup>

In the synthesis of compound **4V**, using a similar procedure as for **2V** and **3V**, it proved difficult to isolate the intermediate dibromoquaterthiophene **2** because of its poor solubility. In the synthesis of **2V** and **3V**, we found that the compound 5,5''-diethynyl-2,2':5',2''-terthiophene tended to darken and became insoluble when it was heated to 40 °C under vacuum in a rotary evaporator. Therefore, the solvent must be removed on a vacuum line without heating. The two pure diynes (5,5'-diethynyl-2,2'-bithiophene and 5,5''-diethynyl-2,2':5',2''-terthiophene) turn dark and become insoluble after storage for two weeks. This may be caused by polymerization, which occurs slowly even at room temperature and very fast when heated even under vacuum. Therefore, even if we were able to isolate **2** to prepare 5,5''-diethynyl-2,2':5',2''-5''-quaterthiophene, the latter is not predicted to be a very stable

compound according to the trend observed for its di- and terthiophene analogues. Instead, we prepared the bis(bororate) **2Bpin** via Ir-catalyzed borylation<sup>[22]</sup> of dithiophene **5**. Suzuki-Miyaura coupling of compound **4** and **2Bpin** using  $K_3PO_4 \cdot H_2O$  as base and  $Pd(dppf)Cl_2$  as catalyst at 90 °C in DMF was attempted to synthesize **4V**. However, none of the target compound was isolated, whereas **4** was fully consumed according to TLC analysis, even when it was used in excess. It was reported by Wang and co-workers<sup>[23]</sup> that some ArylBMes<sub>2</sub> compounds can act as mesityl transfer agents in Suzuki-Miyaura coupling reactions under certain conditions. ArylBMes<sub>2</sub> compounds are stable in Sonogashira and Heck reactions when using amine bases,<sup>[12]</sup> so it is likely that only small basic groups such as fluoride and hydroxide ion can attack the bulky boron center causing problems in palladium-catalyzed reactions. It is also possible that some protodeborylation of **2Bpin** occurred under our reaction conditions. With these issues in mind, we then employed a Stille coupling reaction, which does not require added base.

Coupling of **4** with **2Sn**, using  $Pd(PPh_3)_4$  as the catalyst in DMF at 90 °C, resulted in a high yield (89%) of **4V**. Compounds **5V**, **5VE**, and **5B** were synthesized using similar reaction conditions, all with high yields (66-89%). Compound **5B** was also synthesized by Suzuki-Miyaura coupling of **8** with **3Br** in a comparable yield (88%), which suggests that ArylBMes<sub>2</sub> is a more stable group than vinylBMes<sub>2</sub> in Suzuki-Miyaura couplings and that, contrary to our initial concern, thiophene-BMes<sub>2</sub> groups do not necessarily undergo mesityl transfer under Suzuki-Miyaura coupling reaction conditions.

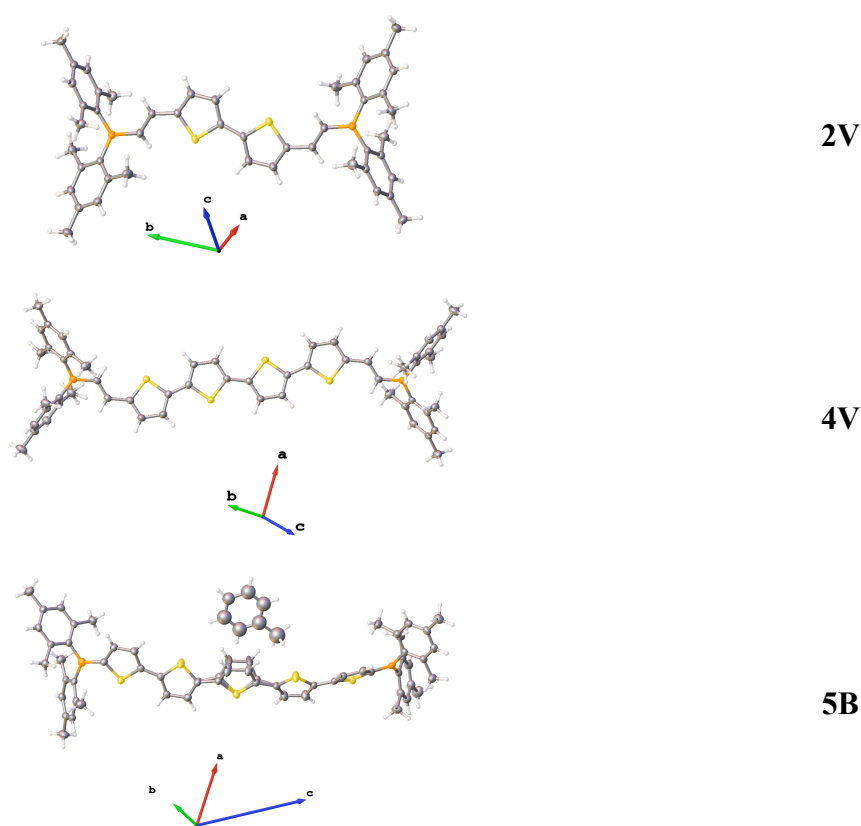
To synthesize compound **13**, Suzuki-Miyaura coupling of **6** and **12** using  $Pd(dppf)Cl_2$  as the catalyst and  $K_3PO_4 \cdot H_2O$  as the base, was initially attempted. However, compound **12** undergoes protodeborylation and polymerization, so we did not obtain **13** via this reaction. Thus, **13** was synthesized via Suzuki-Miyaura coupling of **14** with 2-(Bpin)thiophene.



Scheme 3. Synthesis of 4V, 5V, 5B, and 5VE.

**Crystal structures and molecular geometries:** Structural information has been derived both from single-crystal X-ray diffraction data and calculated optimized geometries in vacuum (experimental section). Although they belong to two extremes regarding the nature and

strength of chromophore interactions with their surroundings, both provide information about the structure-property relationships of the investigated compounds. The molecular structures of compounds **1V** and **3V** have been published previously,<sup>[14]</sup> and we report herein the structures of **2V**, **4V** and the toluene hemisolvate of **5B** (Figure 1). Crystals of **2V** were obtained from hexane, while those of **4V** and **5B** were grown by slow diffusion of methanol into toluene solutions. All bond lengths are in the normal ranges.<sup>[24]</sup> In addition, the crystal structures of synthetic intermediates **4**, **7**, **8**, **10b**, and **12** have been determined (see ESI Figures S1-S5). Crystallographic data of all compounds are listed in Tables S1-S3, while Table 1 summarizes corresponding intramolecular torsional angles and bond lengths, including crystallographic data previously reported for **1V** and **3V** for comparison.<sup>[14]</sup> Similar data for **4**, **7**, **8**, **10b**, and **12** are presented in Table S4.



**Figure 1.** Molecular structures of compounds **2V**, **4V** and **5B** (toluene hemisolvate) as determined by single-crystal X-ray crystallography. Atomic displacement ellipsoids are drawn at 50% probability. The central thiophene ring of **5B** is disordered over two positions, modeled with an occupancy of 50:50. Element (color): carbon (gray), hydrogen (white), sulfur (yellow) and boron (orange).



All new crystal structures containing more than one thiophene ring reveal an *all-trans* conformation with adjacent thiophene rings orientated in opposite directions. B3LYP/6-31G\* optimized geometries support the preference for this conformation and suggest possible coexistence of both *trans* and *cis* conformers in solution at room temperature (RT) only for the compounds with the lowest number of thiophene rings. Concerning the vinyl-containing compounds, both *cisoid* and *transoid* conformers are experimentally evidenced with a preference for the *transoid* conformation when the molecular structure is compatible with inversion symmetry, *i.e.* for an even number of thiophene rings. However, we reported previously that the crystal structure of **1V** contains two symmetry independent molecules realizing both *cisoid* and *transoid* conformers.<sup>[14]</sup> In addition, calculations show that both conformers are energetically close enough to be present in solution at RT.

The crystal structures of the unsolvated compounds **2V** and **4V** confirm the theoretical predictions and show that adjacent thiophene rings are almost, but not fully, co-planar, indicative of conjugation along the oligothiophene backbones. In addition, there is no twist between the terminal thiophene rings (measured as the torsion angle). All crystal structures of the compounds with an odd number of thiophene rings contain solvent of crystallization. Thus, the apparent molecular conformations may be influenced by the incorporated solvent molecules, and, therefore, correlations with the theoretical structures in the gas phase and in solution have to be made bearing this in mind. For the structures **3V** and **5B**, the thiophene backbone arches, presumably caused by the need to accommodate the solvent molecules. In **5B**, this solvent also causes a disorder in the central thiophene ring over two positions (50:50). However, the apparent bending observed from the crystal structures is also noticeable in DFT gas phase calculations (Figure S6). In addition, the crystal structures of **3V** and **5B** show a considerable twist of the backbone compared to the even numbered analogues, which again is apparent in the DFT calculations.

As reported for related structures,<sup>[5e, 25]</sup> the mesityl rings attached to the boron core orient in a propeller-like fashion with a trigonal planar geometry around the boron (sum of angles around boron  $\sim 360^\circ$ ). Thus, conjugation between the boron atom and the mesityl groups is limited, and electron deficiency on the boron atom is maintained. The addition of a vinyl spacer between the  $\text{BMes}_2$  groups and the thiophene backbone introduces a twist of up to  $20^\circ$  between the oligothiophene backbone and the trigonal plane of the boron group, independent of solvate formation. Even though no crystal structures could be obtained to confirm this

finding, no perceptible change in the molecular geometry is predicted by DFT optimizations when the central thiophene ring is substituted by an EDOT moiety.

**Table 1.** Selected structural data from the crystal structures of **1V-4V** and **5B**. M1, M2, M3 and M4 are planes of mesityl substituents of the terminal BMes<sub>2</sub> groups;  $\tau = |180^\circ - \text{torsion angle B-C=C-C(thiophene)}|$ ; V = vinyl moiety B-C=C-C(thiophene);  $\theta$  = torsion angle between terminal thiophene rings.

	<b>1V</b> <sup>[14]</sup> (CH <sub>2</sub> Cl <sub>2</sub> solvate)		<b>2V</b>	<b>3V</b> <sup>[14]</sup> (CH <sub>2</sub> Cl <sub>2</sub> solvate)		<b>4V</b>	<b>5B</b> (0.5 toluene solvate)
B1C <sub>3</sub> /M1 [°]	63.61(8)	48.36(8)	64.15(5)	59.16(8)	56.24(8)	60.1(1)	
B1C <sub>3</sub> /M2 [°]	52.15(9)	62.05(8)	49.48(5)	42.52(8)	60.15(9)	55.0(1)	
B1C <sub>3</sub> /V [°]	14.6(2)	24.6(2)	22.3(1)	28.8(2)	19.4(2)		
B1C <sub>3</sub> /thio1 [°]						10.6(1)	
B2C <sub>3</sub> /M3 [°]	47.71(8)	60.97(8)		58.45(9)		57.3(1)	
B2C <sub>3</sub> /M4 [°]	51.73(8)	57.01(9)		53.65(9)		62.6(1)	
B2C <sub>3</sub> /V [°]	30.0(2)	15.1(2)		23.1(2)			
V/thio1 [°]	7.6(2)/ 10.2(2)	19.8(2)/ 1.1(2)	16.4(1)	12.5(2)/ 3.8(2)	7.9(2)		
thio1/thio2 [°]			0	10.95(8)	2.54(8)	7.8(1)	
thio2/thio3 [°]				6.21(8)	0	A 23.2(2) B 7.7(3)	
thio3/thio4 [°]						A 9.9(2) B 35.3(2)	
thio4/thio5 [°]						25.4(1)	
B2C <sub>3</sub> /thio5 [°]						17.9(1)	
$\tau$ [°]	$\tau_1$ 3.1 $\tau_2$ 0.8	$\tau_1$ 7.4 $\tau_2$ 4.2	13.8	$\tau_1$ 5.1 $\tau_2$ 6.6	5.75	$\tau_1$ 3.98 $\tau_2$ 5.58	
$\theta$ [°]			0	15.4	0	30.6	
thio1/thio3 [°]				15.36(8)			
thio1/thio5 [°]						54.68(9)	
B-C(Mes) [Å]	1.577(4)	1.575(4)	1.578(2)	1.574(3)	1.580(3)	1.578(4)	
B-C(non-Mes) [Å]	1.552(3)	1.552(3)	1.550(2)	1.556(3)	1.548(3)	1.543(5)	

In addition to the comparison between molecular geometries derived from X-ray data and optimizations in vacuum, the bond length alternation (BLA) of carbon-carbon bonds is often used to correlate structural data with NLO properties.<sup>[26]</sup> It is generally believed that the lower the BLA value, the higher the degree of conjugation, which, in turn, is beneficial for increasing the hyperpolarizability of the molecule. Available data are summarized in Tables 2 and S5. The BLA values from DFT calculations show a slight but sizeable decrease for the series **1V-5V**, *i.e.* with an increase in the number of thiophene rings, while it slightly increases for the series **1B-5B**. This is a direct consequence of the absence or presence of the vinylene spacers that have a large BLA. Thus, from the BLA values of the series **1B-5B**, one would expect reduced conjugation and less NLO enhancement when increasing the number of thiophene rings, as compared to series **1V-5V**. Although of high quality, the accuracy of the X-ray crystallographic data does not allow experimental confirmation of these trends.

**Table 2.** Single-crystal X-ray diffraction experimental and DFT-calculated (B3LYP/6-31G\*) carbon-carbon bond length alternation (BLA [Å]).

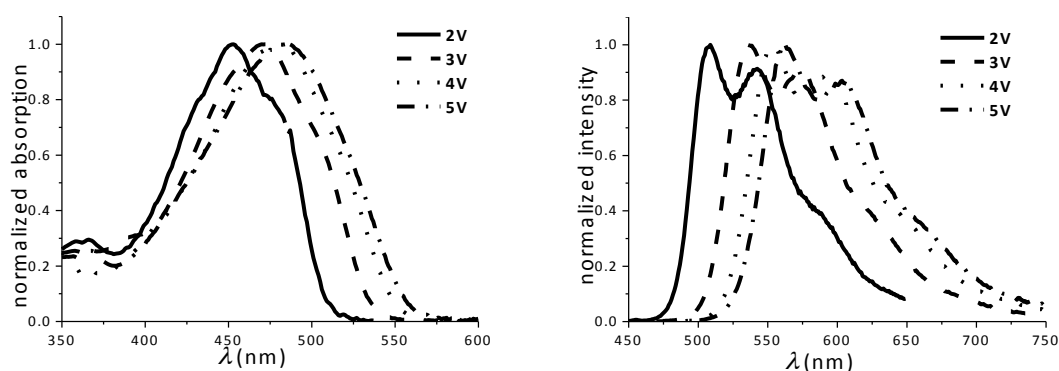
	Solid state (X-ray structure)	Vacuum (DFT)
<b>1V</b>	0.081/0.077 <sup>a</sup>	0.059
<b>2V</b>	0.063	0.053
<b>3V</b>	0.073 <sup>a</sup>	0.050
<b>4V</b>	0.068	0.048
<b>5V</b>		0.047
<b>1B</b>		0.016
<b>2B</b>	0.032 <sup>b</sup>	0.033
<b>3B</b>		0.037
<b>4B</b>		0.038
<b>5B</b>	0.05/0.06 <sup>c</sup>	0.039
<b>3VE</b>		0.047
<b>5VE</b>		0.046

<sup>a</sup> Ref. [14].

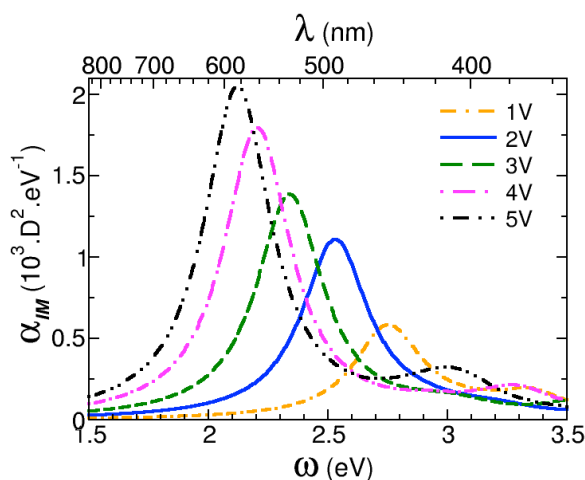
<sup>b</sup> Containing B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> groups replacing BMes<sub>2</sub>.<sup>[27]</sup>

<sup>c</sup> Disordered molecular structure.

**One-Photon Absorption (OPA):** All chromophores of series **1V-5V** and **1B-5B** show an intense absorption band in the blue region of the visible spectrum, and a bathochromic shift upon increasing the number of thiophene rings in the molecular backbone is observed (Figures 2 and 3; Tables 3 and 4). This red shift is accompanied by a hyperchromic effect (Figure 3; Table 4), which is related to the nature of the underlying electronic redistribution upon excitation. Natural transition orbitals<sup>[28]</sup> (NTOs) associated with the vertical transition between the ground state and the lowest excited state are shown for compounds **4B** and **4V** in Figure 4, and are provided in the Supporting Information for all other compounds (Figure S7). They show a close match with the frontier orbitals, and reveal delocalization over the whole molecular backbone of both the holes and the electrons, leading to an increase of transition dipole moments with elongation. The calculated systematic and comparable hyperchromic effect upon elongation for both the **1B-5B** and **1V-5V** series contrasts with the respective increase and decrease of their BLA (Table 2).



**Figure 2.** Normalized absorption (left) and emission (right) spectra of compounds **2V-5V** in toluene.



**Figure 3.** Calculated absorption spectra of compounds **1V-5V** in vacuum (TD-DFT B3LYP/6-31G\*).

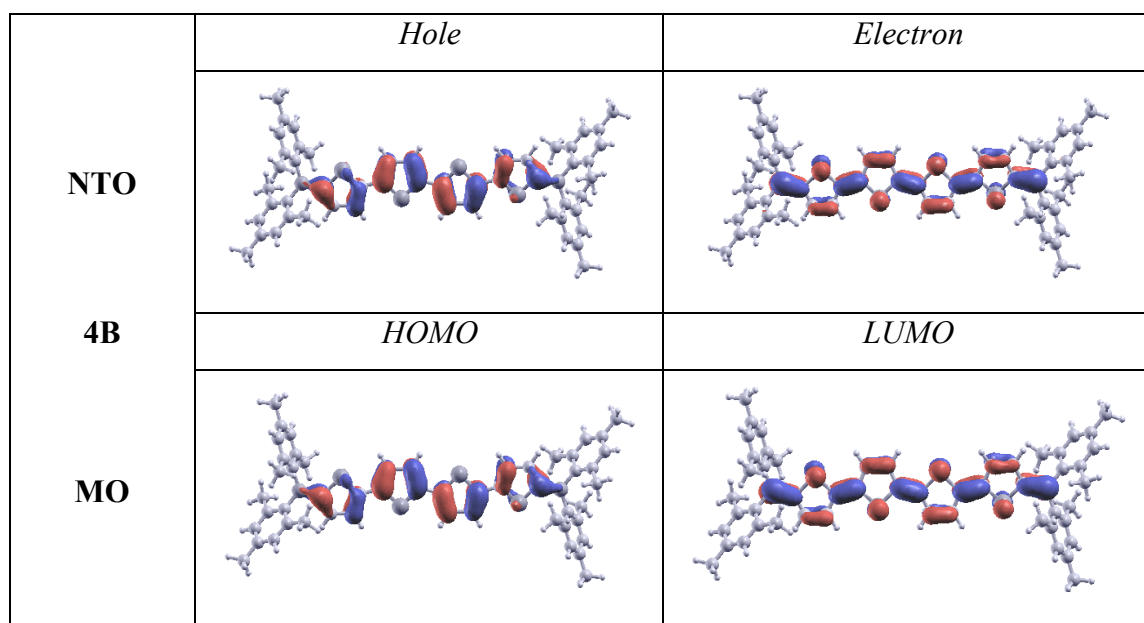
**Table 3.** Photophysical data for chromophores **2V–5V**, **5B**, and **5VE** in toluene.

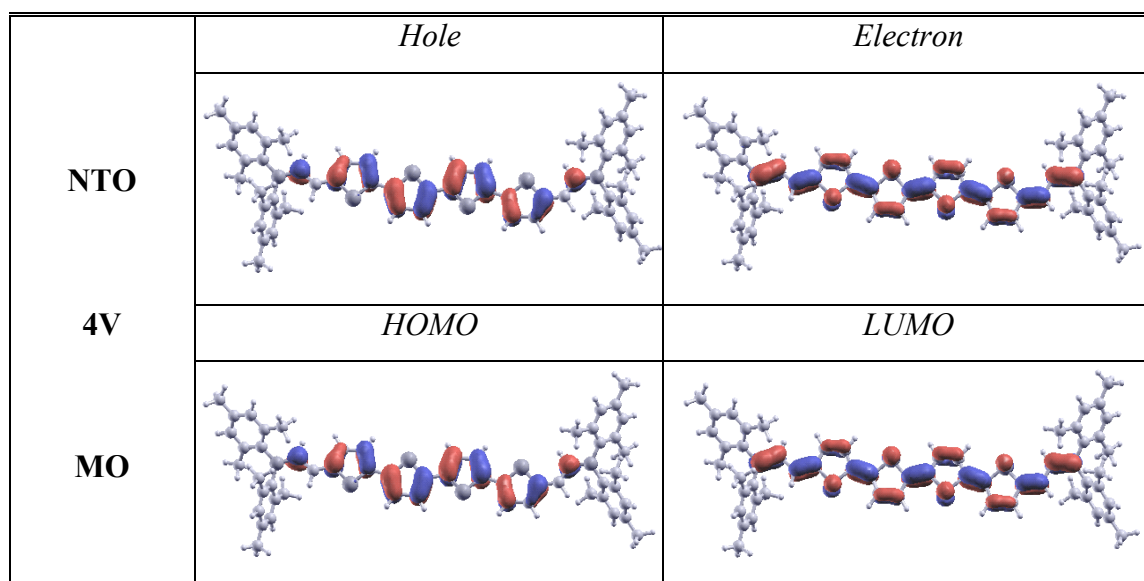
	$\lambda_{\max}[\text{abs}]$ (nm)	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\lambda_{\max}[\text{em}]$ (nm)	Stokes shift ( $\text{cm}^{-1}$ )	$\Phi_f$	$\tau_f$ (ns)	$\tau_0$ (ns)	$k_r$ ( $10^8 \text{ s}^{-1}$ )	$k_{nr}$ ( $10^8 \text{ s}^{-1}$ )
<b>1V</b> <sup>[a]</sup>	411	48 000	452	2200	0.01	0.53	53	0.19	18.7
<b>2V</b>	453	52 000	509	2400	0.11	0.50	4.5	2.2	17.8
<b>3V</b>	470	57 000	536	2600	0.20	0.79	4.0	2.5	10.2
<b>4V</b>	486	70 000	554	2500	0.29	1.05	3.6	2.8	6.7
<b>5V</b>	487	76 000	563	2800	0.26	0.93	3.6	2.8	8.0
<b>5VE</b>	511	100 000	586	2500	0.26	0.98	3.8	2.6	7.6
<b>1B</b> <sup>[b]</sup>			440						
<b>2B</b> <sup>[b]</sup>	402	54 000	440	2100	0.86				
<b>3B</b> <sup>[b]</sup>	437	60 000	488	2400					
<b>5B</b>	467	79 000	540	2900	0.26	0.85	3.3	3.0	8.8

[a] Ref. [14], in cyclohexane. [b]. Ref. [29f], in THF.

**Table 4.** Calculated photophysical properties in vacuum relevant for the first excited singlet state: vertical transition energy ( $\omega_{01}$ ), transition wavelength ( $\lambda_{01}$ ) and oscillator strength ( $f_{01}$ ).

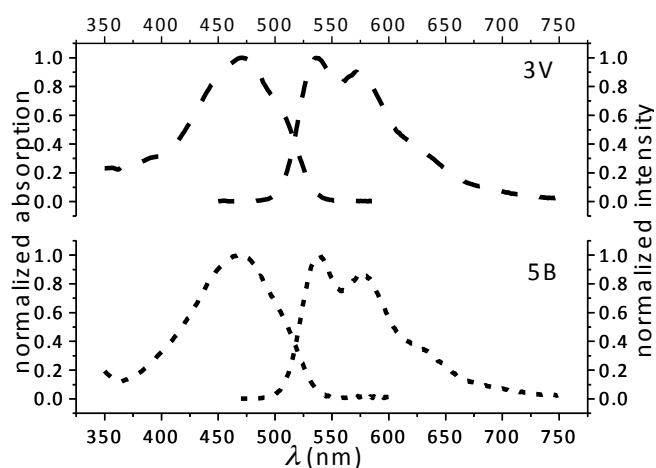
	<b>1V</b>	<b>2V</b>	<b>3V</b>	<b>4V</b>	<b>5V</b>	<b>2B</b>	<b>3B</b>	<b>4B</b>	<b>5B</b>	<b>5BE</b>	<b>3VE</b>	<b>5VE</b>	<b>3T</b>
$\omega_{01}$ (eV)	2.75	2.52	2.34	2.21	2.12	2.90	2.64	2.42	2.30	2.22	2.28	2.05	2.37
$\lambda_{01}$ (nm)	450	492	528	561	585	428	470	512	540	559	543	603	523
$f_{01}$	0.96	1.79	2.09	2.55	2.79	1.00	1.61	2.05	2.42	2.45	2.15	2.81	2.24



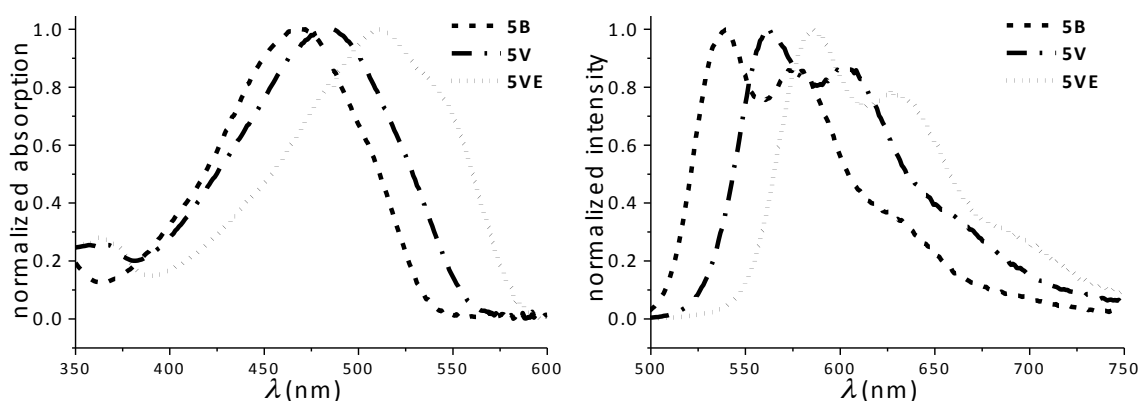


**Figure 4.** Natural transition orbitals (NTO: Hole/Electron) associated with the first excited state of chromophores **4B** and **4V** compared to frontier molecular orbitals (MO: HOMO/LUMO).

Chromophore **5B** shows a significant blue shift compared to its vinylene analogue **5V** ( $800\text{ cm}^{-1}$ , Table 3), leading to a normalized absorption band almost identical to that of **3V** (Figure 5). However, as indicated in Table 3, **5B** has a significantly larger molar extinction coefficient than **3V**, comparable to that of **5V** with the slight gain being compensated by a narrower bandwidth. These trends are confirmed by a theoretical investigation of the whole series **2B-5B** (Table 4, Figure S8). Thus, removal of the two vinylene spacers leads to blue-shifted bands of reduced oscillator strength; however, the larger the chromophore, the smaller this effect becomes. Calculations show that replacement of the vinylene spacers of **3V** by ethynylene groups (**3T**) leads to a reduction in the blue shift of the absorption band and a slight oscillator strength enhancement (Table 4, Figure S9). Excited-state lifetimes were measured using the Time-Correlated Single-Photon Counting (TCSPC) technique. The data fit satisfactorily by a single exponential decay function in each case, with values in the range 0.50–1.05 ns (Table 3, Figure S10 for a representative example).

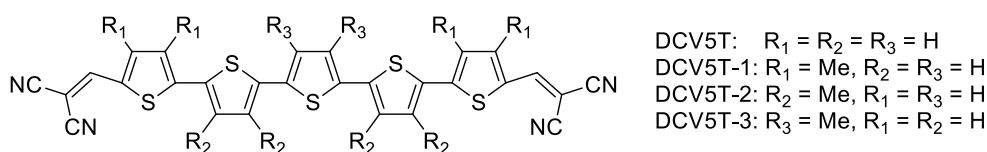


**Figure 5.** Normalized absorption and emission spectra of **3V** and **5B** in toluene.



**Figure 6.** Normalized absorption (left) and emission (right) spectra of **5B**, **5V** and **5VE** in toluene.

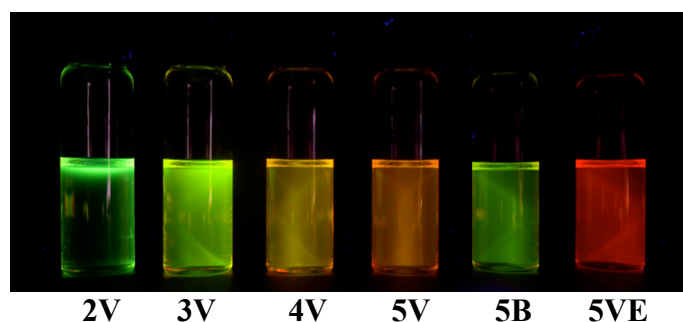
Replacement of the central thiophene ring of **5V** by the electron-rich EDOT moiety (**5VE**) gives rise to a significant increase of the molar extinction coefficient (*ca.* 30%) and a further red shift of more than  $700\text{ cm}^{-1}$  (Table 3, Figure 6). However, as a result of the narrower bandwidth, the oscillator strength shows little enhancement for the values calculated in vacuum (Table 4). Nevertheless, both the bathochromic shift and hyperchromic effect introduced by the EDOT moiety are theoretically confirmed for compounds **3VE** and **5BE** (Table 4, Figures S8 and S9).



**Scheme 4.** Structure of DCV5T and its analogues.

The large molar extinction coefficients and broad absorption bandwidths of our compounds indicate their potential for application in organic solar cells. Indeed, Bäuerle and co-workers have recently reported dicyanovinyl-capped quinquethiophene (DCV5T) analogues (Scheme 4), whose structures are similar to our compounds **5V** and **5VE**, as donor materials for bulk heterojunction solar cells with high power conversion efficiencies (4.6-6.9%).<sup>[30]</sup> The shapes and positions of the absorption bands of the DCV5T analogues are almost the same as those of compound **5VE**, but **5VE** shows a larger molar extinction coefficient ( $10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) than DCV5T ( $7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**Emission:** Table 3 includes the photoluminescence data for all of the chromophores investigated experimentally. With the exception of **1V**,<sup>[14]</sup> all compounds exhibit moderate fluorescence quantum yields of 0.11-0.29 and sizeable Stokes shifts in toluene. The fluorescence can be tuned from deep green to red (Figure 7). Indeed, consistent with the red shift in absorption, increasing the oligothiophene length of the vinylene-based mesitylboryl compounds (**2V-5V**) induces a significant bathochromic shift in the emission of more than  $1900 \text{ cm}^{-1}$ . Replacement of the central thiophene ring by an EDOT moiety provides a further bathochromic shift, resulting in red emission (Figures 6 and 7), while maintaining a similar emission quantum yield (Table 3). Both **5B** and **5V** have the same quantum yield of 0.26, revealing that the incorporation of vinylene spacers does not influence this parameter. However, unlike the substitution by the EDOT ring, the absence of vinylene spacers does give rise to a noticeable hypsochromic shift, leading to overlapping emission spectra of **5B** with **3V**. A similar overlap is observed in the absorption spectra (Figure 5), *vide supra*. These findings, and theoretical predictions for the series **2B-5B** (Table 4), suggest that reducing the size of the oligothiophene unit offers a route to extend the emission range further to the blue end of the spectrum while maintaining sizeable radiative quantum yields.

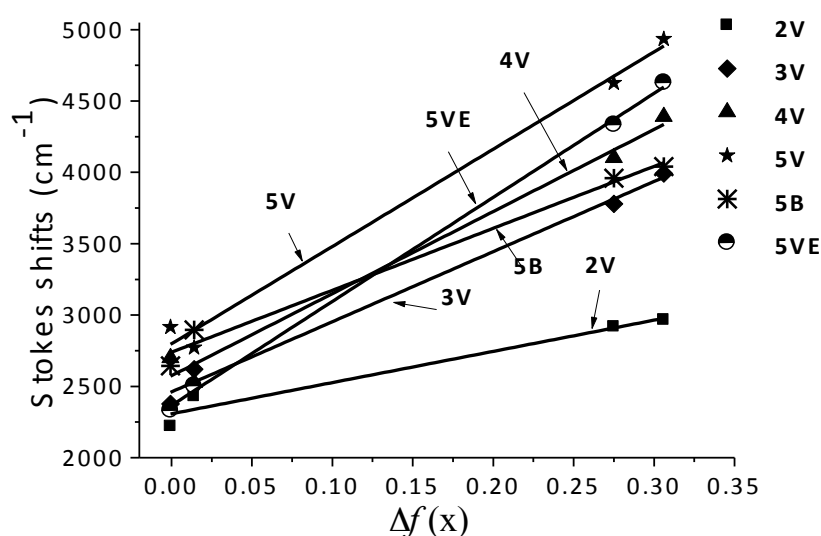


**Figure 7.** Fluorescence of  $10^{-5} \text{ M}$  toluene solutions excited at 365 nm.



**Solvatochromic behavior:** All of the new chromophores reported here exhibit a weak positive solvatochromic absorption behavior (Table S6). This behavior is similar to that previously reported for dipolar analogues,<sup>[5i,25c]</sup> and is consistent with earlier findings on **2V**, **3V** and other quadrupolar A- $\pi$ -A systems containing  $\pi$ -accepting (*E*)-dimesitylborylvinyl groups.<sup>[14]</sup> These measurements reveal that the chromophores have non-polar ground states with small, if not vanishing, dipole moments as a result of an inversion center of symmetry in the molecules. In contrast, emission solvatochromism is much more pronounced (Table S6), suggesting polar emitting states as a consequence of significant reorganization of the excited state prior to emission.<sup>[21,31-32]</sup>

Such a behavior has been reported for both quadrupolar and octupolar chromophores, and has been rationalized *via* the few-state model of Terenziani and co-workers.<sup>[21,31]</sup> These models predict unconditional symmetry breaking for octupolar dyes, so that excitation localization on a single branch occurs after excitation and prior to emission for any solvent, whereas the intramolecular charge transfer taking place upon excitation (absorption) is delocalized over the whole molecular backbone.<sup>[31]</sup> Lambert and co-workers have attributed this type of symmetry breaking in octupolar triarylboranes to the degeneracy of the excited state being lifted by a Jahn-Teller distortion.<sup>[32a]</sup> They also demonstrated that the excitation energy can be transferred among the three branches, which was rationalized by transition dipole-dipole interactions between chromophore subunits. Due to the unconditional nature of the multistability in the case of octupoles, such a behavior is well described by state-of-the-art quantum mechanical approaches.<sup>[32b-d]</sup>



**Figure 8.** Lippert-Mataga plots for chromophores **2V**, **3V**, **4V**, **5V**, **5B**, **5VE**, using the standard definition of the orientation polarizability,  $\Delta f(x)$ .<sup>[32d]</sup>

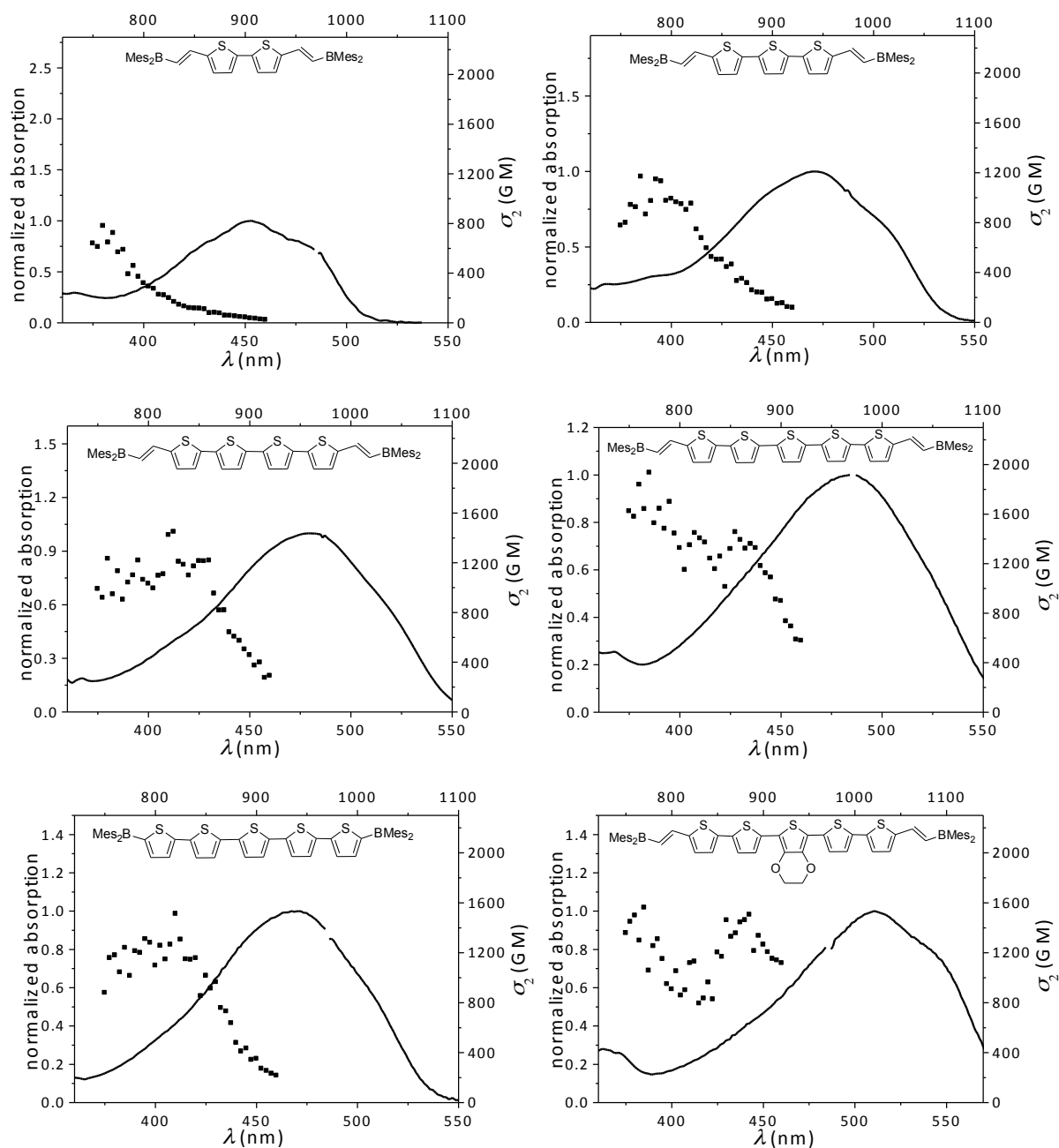
In contrast, quadrupolar chromophores may show distinctly different behavior depending on the nature of their charge distribution in the ground state and have been placed into three different classes.<sup>[21]</sup> Given that all quadrupoles of the present work show small and significant solvatochromic shifts in absorption and fluorescence, respectively, we assign them as belonging to Class I according to ref. [21]. For quadrupoles of this class, the potential energy surface relevant to the first excited state exhibits conditional bistability, with the possible appearance of two degenerate minima, corresponding to asymmetric deformations of the molecule that lead to a broken symmetry and localization of the excited state on either of two portions of the chromophore. This conditional bistability is related to the strength of electron-phonon coupling, and symmetry breaking is induced by relaxation of the solvation coordinate. At least in high polarity solvents, we expect our quadrupoles to undergo stabilization of the broken symmetry state, similar to that reported for fluorene-based quadrupoles,<sup>[21,32b-d]</sup> leading to polar relaxed excited states. Unfortunately, due to the conditional nature of the bistability, excited-state geometry optimizations are not yet capable of reproducing this phenomenon,<sup>[32b-d]</sup> thus, making such calculations mostly irrelevant.

The Lippert-Mataga plots shown in Figure 8 illustrate the overall solvatochromic behavior and offer a way to estimate the variation of the *effective* dipole moment difference between the ground and excited states, provided that a relevant cavity radius is available. From **2V** to **5V**, the gradient steadily increases with the length of the conjugated backbone from  $2.2 \times 10^3$  to  $6.2 \times 10^3 \text{ cm}^{-1}$ . The similarities between compounds **3V** and **5B** in toluene, *vide supra*, are maintained in more polar solvents, as both compounds exhibit comparable gradients. The substitution of the central thiophene ring of **5V** by an EDOT group in **5VE** leads to an additional rise in the Lippert-Mataga slope, reaching a value of  $6.7 \times 10^3 \text{ cm}^{-1}$ . The evolution of the fluorescence energy with the solvent polarity is also instructive.<sup>[21]</sup> In fact, the energy shift between cyclohexane and toluene is almost the same for all compounds (ca.  $600 \text{ cm}^{-1}$ ), while it increases steadily with the chromophore length in more polar solvents. This reveals two distinct behaviors, and it may be an indication of vanishing or limited localization in non-polar environments and true symmetry breaking in high polarity solvents, again similar to that which has been observed in fluorene-based quadrupoles.<sup>[32d]</sup>

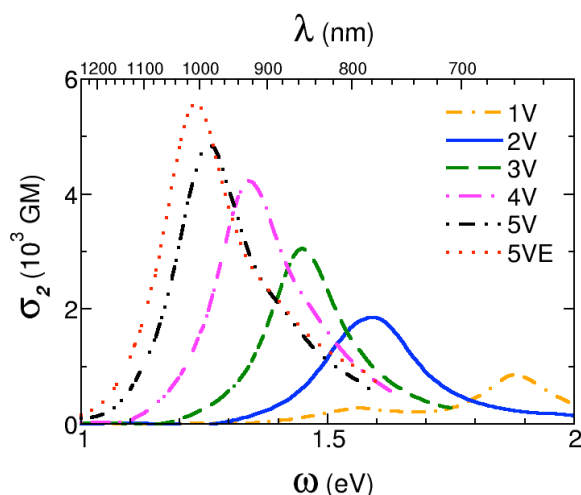
**Two-Photon Absorption (TPA):** Prior to discussing the TPA responses of our chromophores in detail, let us briefly comment on some technical issues to prevent incorrect inferences on

TPA structure-property relationships to be drawn. To measure the TPA cross-sections ( $\sigma_2$ ), we used the well-known two-photon excited fluorescence (TPEF) method proposed by Xu and Webb,<sup>[33]</sup> based on measurements relative to reference compounds with known  $\sigma_2$  values. Thus, the reliability of the derived  $\sigma_2$  values will be adversely affected by any lack of precision in the reference data, which results from the involved experiments required for the determination of their TPA cross-sections by absolute methods. For one of the most widely used standards, namely fluorescein, comparison of data obtained with different experimental setups, spectrally overlapping, and computed values has already revealed repercussions of imprecise data close in the vicinity of 700 nm<sup>[32c]</sup> and in the 900-1000 nm range.<sup>[34]</sup> Using fluorescein as a reference with the original data by Xu and Webb,<sup>[33]</sup> as was done previously for **2V** and **3V**,<sup>[14,35]</sup> we noticed an intriguing increase of the TPA response of **5VE** on the red edge of the spectrum, while using the more recent value of Makarov, Drobizhev and Rebane<sup>[36]</sup> led to overall consistent  $\sigma_2$  values (further details in Supplementary Information. See also Figures S11 and S12). Thus, all TPA cross-sections reported in the manuscript are calculated using the latter data for fluorescein as the reference.

Experimental TPA spectra of series **2V-5V** and compounds **5B** and **5VE** are reported in Figure 9 and compared to their respective normalized one-photon absorption spectra. A quadratic dependence of the integrated emission intensity on excitation power was observed, which confirms a two-photon process (Figure S13). For **2V-3V**, and to a lesser extent **4V-5V** and **5B**, it is clear that the TPA maximum is significantly blue shifted from twice the one-photon absorption band maximum. This systematic blue shift is confirmed by the calculated TPA spectra for **1V-5V** and **5VE** (compare Figures 3 and 10), **2B-5B** and **5BE** (compare Figures S8 and S14), and **3T** (compare Figures S9 and S15). This is a direct consequence of the quadrupolar nature of the investigated chromophores, for which inversion symmetry usually leads to a one-photon allowed and TPA forbidden first excited state and a one-photon forbidden and TPA allowed second excited state. X-ray crystallographic data have indeed evidenced inversion symmetry for molecules based on an even number of thiophene rings, whereas the other chromophores show structural features close to it (*vide supra*). Even so, this inversion symmetry and the coexistence of different conformations in solution at ambient temperature will induce a partial breakdown of the selection rules, their reminiscence remains sufficient to be conspicuous, such as that observed for symmetric or slightly asymmetric fluorene based quadrupoles.<sup>[1d,32b-d]</sup>

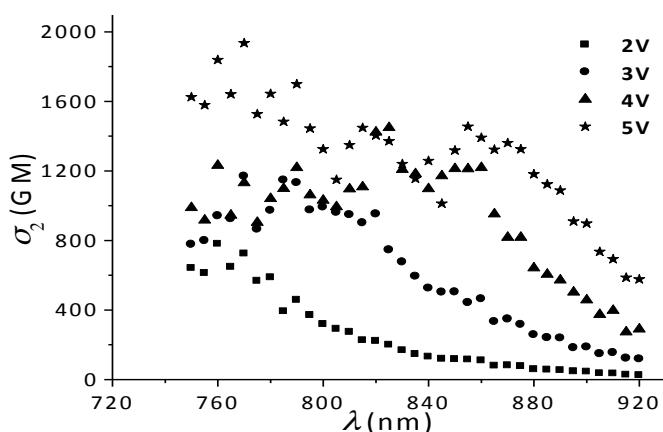


**Figure 9.** Experimental TPA spectra (squares) and normalized absorption spectra (solid lines) of molecules **2V-5V**, **5B** and **5VE** in toluene.



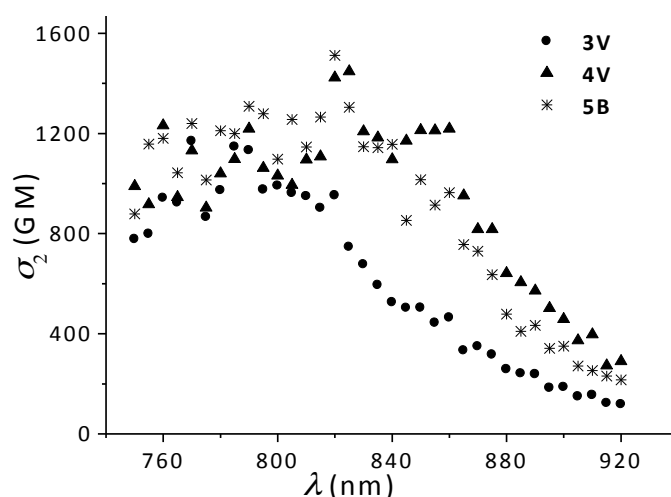
**Figure 10.** Calculated TPA spectra of molecules **1V-5V** and **5VE** in vacuum.

The overall agreement between experiment and theory is good (Figure S16), given that the calculations do not take into account either solvent effects or vibrational contributions and include a fixed bandwidth for all chromophores (Table S7). More importantly, the overestimation of the calculated TPA cross-sections is to be related to the use of B3LYP/6-31G\* level of theory for both geometry optimization and properties, which is well known to overestimate conjugation, resulting in reduced BLA values (Table 2). This is illustrated within the well-known 3-state model in which  $\sigma_2$  is proportional to the fourth power of transition dipole moments.<sup>[1d]</sup> Indeed, overestimation of transition dipole moments by only 15% leads to TPA cross-sections twice as large. Nevertheless, while absolute transition energies are theoretically underestimated, both for absorption and TPA maxima, the corresponding blue shifts of the TPA maximum relative to double the OPA maximum correlate well between experiment and theory (Figure S16) and give confidence for further discussion of the TPA responses.



**Figure 11.** Experimental TPA spectra of **2V-5V** in toluene.

The general trends of TPA responses obtained upon elongation of the oligothiophene unit are in accord with those discussed for one-photon absorption: systematic red shift and increase of the TPA amplitude with increasing size (Figures 10 and 11). Calculated spectra for the whole series **2B-5B** (Figure S14) show similar trends. A systematic blue shift and reduced amplitudes compared to their vinylene analogues having the same number of thiophene rings is observed (Figure 9). Interestingly, while the one-photon spectra of **5B** were almost identical to that of **3V**, their TPA spectra are noticeably different with a good correspondence between **5B** and **4V** (Figure 12). Indeed, calculations confirm that compounds **nB** and **(n-1)V** have comparable TPA spectra, evidencing an interrelationship between these two series in which the TPA properties of compounds that have an identical number of carbon-carbon double bonds are similar. Thus, the overall behavior is identical for both series and does not manifest any correlation with the different trends observed for the BLA (Table 2).

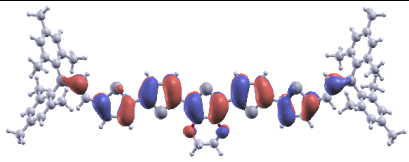
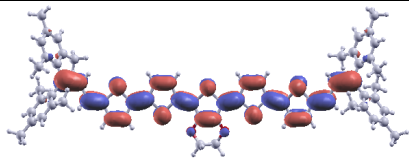
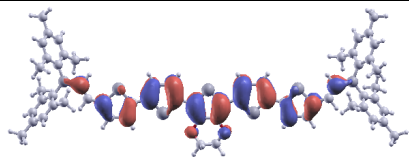
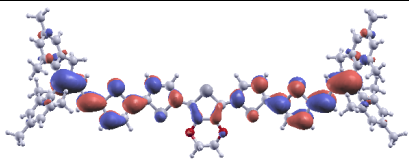


**Figure 12.** Experimental TPA spectra of **3V**, **4V** and **5B** in toluene.

Experimentally, replacement of the central thiophene ring by an EDOT moiety leads to comparable TPA amplitudes, within experimental uncertainty, and suggests a slight red shift of the first TPA band (Figure 9). Indeed, comparison of calculated TPA spectra of **5V/5VE** (Figure 10), **5B/5BE** (Figure S14) and **3V/3VE** (Figure S15) indicate moderate TPA enhancement of 10% or less, *i.e.* lower than experimental error, with a weak red shift of about  $240\text{ cm}^{-1}$ . These trends are consistent with those stated for their one-photon responses (*vide supra*). Interestingly, substitution of the vinylene spacers by ethynylene ones are predicted to induce a significantly larger TPA enhancement, about 20%, accompanied by a very small blue

shift (Figure S15). However, unfortunately, in our experience, alkynylBMes<sub>2</sub> compounds can be less stable towards hydrolysis than their vinyl analogues.

All chromophores experience similar electronic redistribution upon excitation in the first (low energy) TPA band. This electronic redistribution is illustrated in Figure 13 for **5VE** by the plot of the NTOs associated with the second excited state. Comparison to NTOs relative to the first excited state, relevant for linear absorption (*vide supra*), reveals both the different symmetry and the larger component on the boron atom for the electron whereas the hole remains identical. In terms of molecular orbitals, the electron shows a good correspondence with the LUMO+1. The extensive delocalization of both electron and hole over the molecular backbone translates into TPA enhanced responses upon elongation. For the smallest compounds, up to **2V** and **3B**, the main contributions arise from higher lying excited states with similar electronic redistribution and possible involvement of the mesityl groups.

<b>5VE</b>	<i>Hole</i>	<i>Electron</i>
S <sub>1</sub> 2.1 eV 2.8		
S <sub>2</sub> 2.5 eV 0.0		

**Figure 13.** Natural transition orbitals (NTO: Hole/Electron) of chromophores **5VE** associated with the first (S<sub>1</sub>) and second (S<sub>2</sub>) excited singlet states, relevant for the first one-photon and two-photon absorption bands, respectively. The left column lists in sequence the excited state, associated vertical transition energy and oscillator strength.

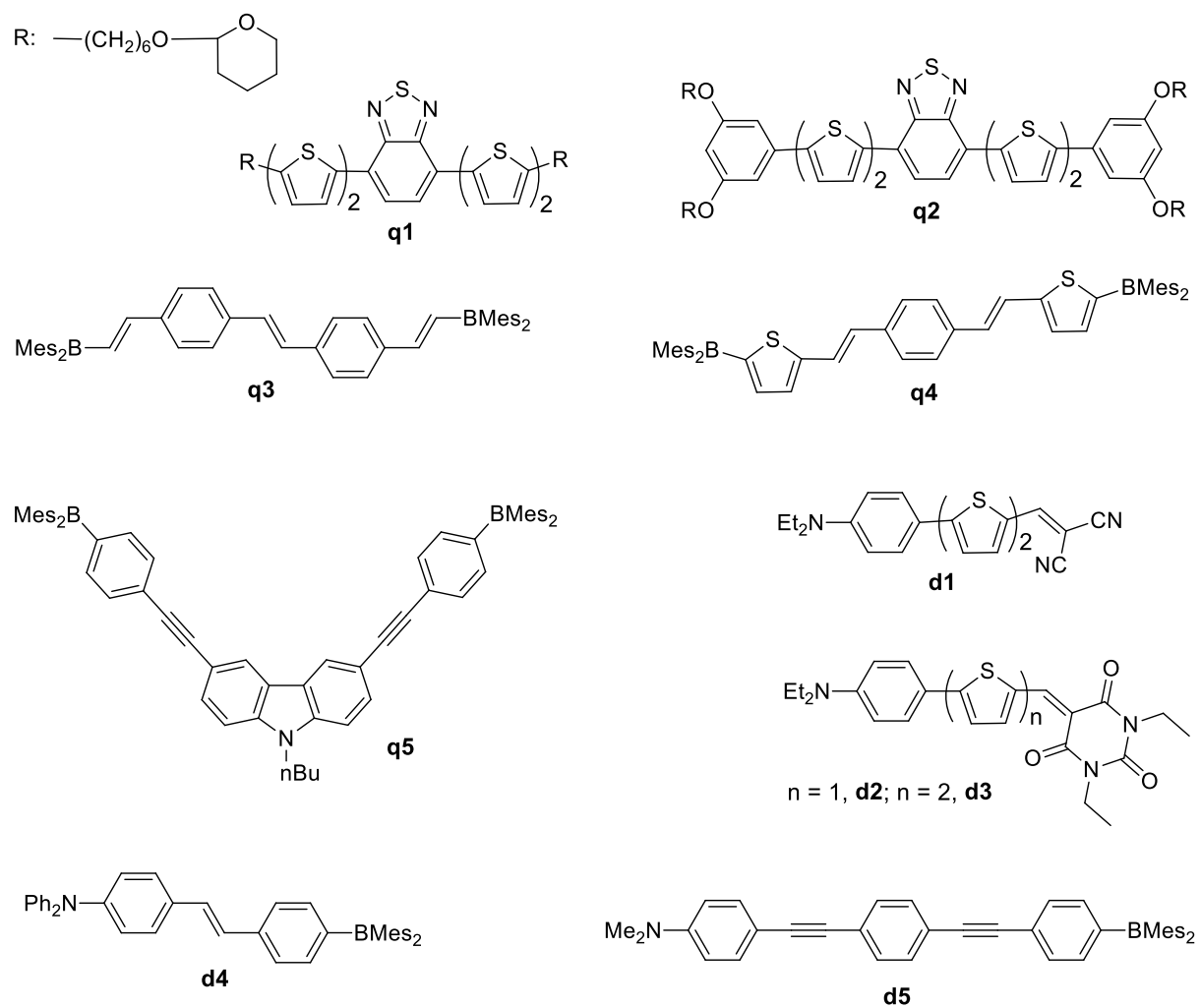
Comparison of the TPA activity of our quadrupolar chromophores to related chromophores built from either BMe<sub>2</sub><sup>[8-13]</sup> or oligothiophene moieties<sup>[15-20]</sup> may be informative to investigate further the structure-TPA relationships. To do so, we choose the normalization procedure based on the molecular weight and collect, to the best of our knowledge, the best-performing related TPA chromophores in Table 5. Corresponding molecular structures are illustrated in Schemes 5 and 6. To ensure appropriate comparison, we have excluded all

reported responses that may be affected by preresonance enhancement, *i.e.* where the excitation wavelength has been tuned close to the lowest energy one-photon resonance. This is particularly important for the oligomers described in Ref. [15], for which it did not seem reasonable to retain EDOT analogues while data for other oligomers were extracted from the low energy part of the reported TPA spectra.

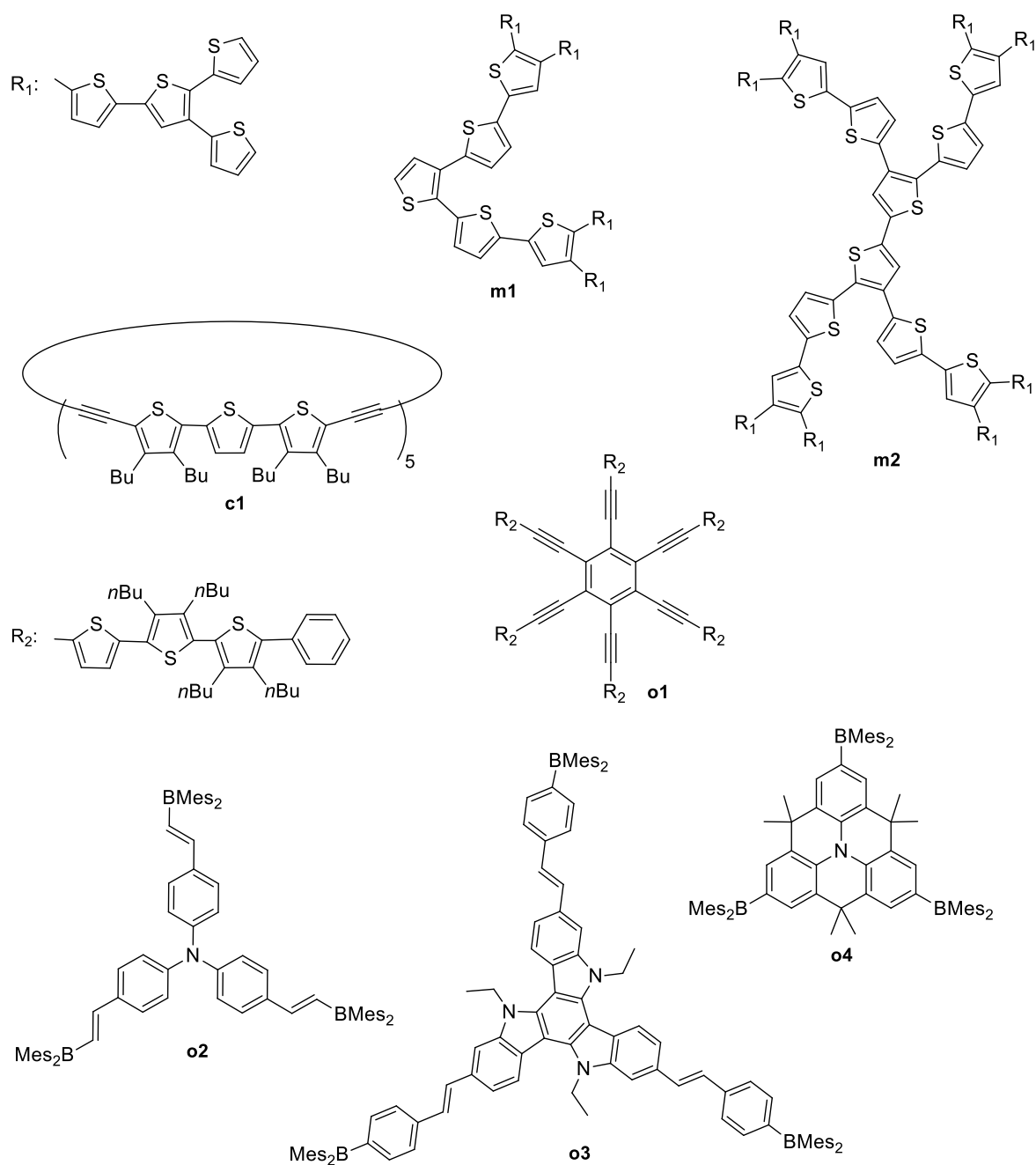
From Table 5 it is clear that, compared to related quadrupoles, our synthetic strategy combining BMes<sub>2</sub> with oligothiophenes proves efficient. In fact, all normalized TPA cross-sections ( $\sigma_2/\text{MW}$ ) are comparable (**2V**) or larger than those previously reported in the literature while the quantum yields remain sizeable. The increase in the length of the oligothiophene spacer appears to be particularly relevant. This prompts comparison to extended oligothiophene-based compounds, such as the all-thiophene dendrimers and the macrocyclic oligothiophenes of Bäuerle and co-workers.<sup>[17-19]</sup> While leading to sizeable absolute TPA amplitudes with increasing size, the absence of an electron-accepting moiety appears to hinder normalized performances. Further comparison to star-shaped oligothiophenes<sup>[20]</sup> leads to similar conclusions.

When compared to the branching strategy applied in Ref. [10,12-13] or to both quadrupolar<sup>[8-10]</sup> and dipolar<sup>[10,11]</sup> analogues, the effectiveness of our BMes<sub>2</sub>-based compounds is clearly evident. The compounds reported herein have normalized TPA cross-sections approaching that of the best-performing bithiophene push-pull chromophores,<sup>[16]</sup> despite the large contribution to the molecular weight of the mesityl groups required for stability and applications. Further comparison of  $\sigma_2/\text{MW}$  values of our oligothiophene-BMes<sub>2</sub> chromophores to other reported BMes<sub>2</sub> containing compounds<sup>[8-13]</sup> (Table 5), shows red-shifted fluorescent maximum, *i.e.* closer to the biological transparency window, especially for the elongated compounds. This makes our oligothiophene-BMes<sub>2</sub> good candidates to use in two-photon excited fluorescence microscopy of living cells.





**Scheme 5.** Structures of the dipolar (**d**) and quadrupolar (**q**) molecules in Table 5.



**Scheme 6.** Structures of the dendrimers (**m**), cyclic (**c**) and octupolar (**o**) molecules in Table 5.

**Table 5.** Comparison of the reported photophysical data for the best-performing ( $\sigma_2$ /MW) chromophores of different shape and size based on BMe<sub>2</sub> and/or oligothiophene moieties. Corresponding molecular structures are given in Scheme 1, 2, 5 and 6.

Class	Quadrupoles						
Moieties	oligothiophene and BMe <sub>2</sub>						
Compound	2V <sup>[a]</sup>	3V <sup>[a]</sup>	4V <sup>[a]</sup>	5V <sup>[a]</sup>	5B <sup>[a]</sup>	5VE <sup>[a]</sup>	
$\lambda_{\text{abs}}(\text{nm})$	453	470	486	487	467	511	
$\varepsilon (10^4 \text{ M}^{-1} \text{ cm}^{-1})$	5.2	5.7	7.0	7.6	7.9	10	
$\lambda_{\text{em}}(\text{nm})$	509	536	554	563	540	586	
$\Phi_{\text{F}}$	0.11	0.20	0.29	0.26	0.26	0.26	
$\sigma_2$ (GM)	780	1170	1450	1930	1510	1500	
@ $\lambda$ (nm)	760	770	825	770	820	760	
$\sigma_2$ (GM)/MW	1.1	1.5	1.6	2.0	1.7	1.5	
Moieties	oligothiophene			BMe <sub>2</sub>			
Compound	q1 <sup>[15][b]</sup>	q2 <sup>[15][b]</sup>		q3 <sup>[8][c]</sup>	q4 <sup>[9][d]</sup>	q5 <sup>[10][a]</sup>	
$\lambda_{\text{abs}}(\text{nm})$	517	528		399	435	385	
$\varepsilon (10^4 \text{ M}^{-1} \text{ cm}^{-1})$	3.0	4.2		7.0	9.3	5.8	
$\lambda_{\text{em}}(\text{nm})$	651	676		447	515	417	
$\Phi_{\text{F}}$	0.85	0.44		0.55	NA	0.85	
$\sigma_2$ (GM)	1200	750		377	850	350	
@ $\lambda$ (nm)	850	850		705	800	770	
$\sigma_2$ (GM)/MW	1.4	0.5		0.5	1.1	0.45	
Class	dipoles						
Moieties	oligothiophene			BMe <sub>2</sub>			
Compound	d1 <sup>[16][b]</sup>	d2 <sup>[16][b]</sup>	d3 <sup>[16][b]</sup>	d4 <sup>[11][d]</sup>		d5 <sup>[10][a]</sup>	
$\lambda_{\text{abs}}(\text{nm})$	551.5	571.5	587.5	402		367	
$\varepsilon (10^4 \text{ M}^{-1} \text{ cm}^{-1})$	3.9	6.2	4.6	NA		4.7	
$\lambda_{\text{em}}(\text{nm})$	727	669	781	522		466	
$\Phi_{\text{F}}$	0.34	0.09	0.06	0.91		0.89	
$\sigma_2$ (GM)	780	1240	1600	300		375	
@ $\lambda$ (nm)	790	800	1170	800		780	
$\sigma_2$ (GM)/MW	2.5	3.0	3.2	0.5		0.7	
Class	cyclic	dendrimers		octupoles			
Moieties	oligothiophene				BMe <sub>2</sub>		
Compound	c1 <sup>[17][a]</sup>	m1 <sup>[18][d]</sup>	m2 <sup>[19][d]</sup>	o1 <sup>[20][c]</sup>	o2 <sup>[10][a]</sup>	o3 <sup>[12][d]</sup>	o4 <sup>[13][d]</sup>
$\lambda_{\text{abs}}(\text{nm})$	433	382	387	490	440	427	420
$\varepsilon (10^4 \text{ M}^{-1} \text{ cm}^{-1})$	NA	NA	NA	19.8	8.5	11	6.4
$\lambda_{\text{em}}(\text{nm})$	541	542	570	603	480	543	453
$\Phi_{\text{F}}$	0.12	0.05	0.07	0.31	0.73	0.40	0.4
$\sigma_2$ (GM)	1470	300	620	2400	1000	2500	260
@ $\lambda$ (nm)	750	760	800	750	740	820	686
$\sigma_2$ (GM)/MW	0.7	0.2	0.2	0.7	0.95	1.7	0.2

[a] in toluene; [b] in CHCl<sub>3</sub>; [c] in CH<sub>2</sub>Cl<sub>2</sub>; [d] in THF.

### Conclusions:

We have designed and studied experimentally and theoretically quadrupolar chromophores composed of dimesitylboryl  $\pi$ -accepting end-groups, oligothiophene-based donating cores and vinylene spacers. They reveal intense absorption bands (molar extinction coefficient up to  $10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the blue region of the visible spectrum and sizeable quantum yields (0.11–0.29) with a bathochromic shift upon elongation of both absorption and emission. The latter can be tuned from deep green to red. Removal of vinylene spacers allows for further blue shift. Systematic and comparable hyperchromic effects upon elongation with or without vinylene spacers contrast with the trends observed in their BLA. Substitution of a thiophene ring by an EDOT moiety leads to a slight bathochromic shift and hyperchromic effect, evidencing interesting features for potential application in organic solar cells when compared to the DCV5T analogues reported by Bäuerle and co-workers.

Non-linear TPA responses show similar trends with substantial cross-sections (up to 2000 GM) in the infrared transparent window of biological samples and tissues. This, combined with the red-shifted fluorescence maximum of our oligothiophene-BMes<sub>2</sub> chromophores when compared to other reported BMes<sub>2</sub> containing compounds, suggest that they may be good candidates to use in two-photon excited fluorescence microscopy of living cells.

### Experimental Section:

**General manipulations and synthetic techniques:** All chemicals were purchased from Sigma-Aldrich, Alfa Aesar, and Acros. B<sub>2</sub>pin<sub>2</sub> was kindly provided by AllyChem Co. Ltd. (Dalian, China). All compounds were used without further purification. THF, hexane, Et<sub>2</sub>O and DMF were dried using an Innovative Technology solvent purification system (SPS). Solvents for chromatography and recrystallization were GPR grade and used without further purification. Dimesitylborane and dimesitylboron fluoride were prepared via literature procedures.<sup>[37]</sup> NMR experiments were performed on Bruker Avance-400, Varian Mercury-400, Inova-500, VNMRS-600 or VNMRS-700 instruments. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to residual protiated solvent. MS and HRMS analyses were obtained on Agilent 6890 GC with a 5973 Inert mass Detector (EI), Bruker Daltonics Autoflex II TOF/TOF (MALDI), Waters LCT Premier XE equipped with an Acquity UPLC and a lock-mass electrospray ion source, and Waters Xevo QTOF equipped with an Atmospheric Solids Analysis Probe (ASAP). Elemental analyses were carried out on an Exeter Analytical CE-440

analyzer at Durham University. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. As is often the case with related  $-BMe_2$  compounds, many compounds gave carbon analysis which were several percent below calculated value. This has previously been ascribed to formation of boron carbide.<sup>[10]</sup>

Precursors **3**,<sup>[38]</sup> **7**,<sup>[39]</sup> **8**,<sup>[39]</sup> **2Sn**,<sup>[40]</sup> **3Sn**,<sup>[41]</sup> **3Br**,<sup>[42]</sup> and 2-(Bpin)thiophene<sup>[43]</sup> were synthesized according to literature procedures. Other known compounds **2Bpin**,<sup>[41, 44]</sup> **10a**,<sup>[45]</sup> **13**,<sup>[46]</sup> and **14**<sup>[47]</sup> were synthesized using alternative methods.

#### **(E)-[2-(5-bromo-thien-2-yl)vinyl]dimesitylborane (4)**

In a glove box, dimesitylborane (400 mg, 1.6 mmol) in THF (50 mL) was added to **3** (180 mg, 0.1 mmol). The solution was stirred for 5 h under nitrogen. After evaporating all of the solvent, the target compound was purified by column chromatography on silica gel with hexane as eluent to give the title compound as a yellow solid (196 mg, 47%). Light yellow crystals were obtained via recrystallization from ethanol. m.p. 130-132 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.09 (d,  $J$  = 17 Hz, 1 H), 7.03 - 6.95 (m, 2 H), 6.84 (m, 5 H), 2.31 (s, 6 H), 2.19 ppm (s, 12 H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 146.3, 143.8, 140.8, 138.7, 131.2, 130.0, 128.4, 115.8, 23.4, 21.3 ppm; MS(EI<sup>+</sup>):  $m/z$ : 436 [ $M^+$ ]; elemental analysis calcd. (%) for C<sub>24</sub>H<sub>26</sub>S: C 65.93, H 5.99; found: C 66.05, H 6.04.

#### **5,5'-bis(Bpin)-2,2'-bithiophene (2Bpin)**

Inside a nitrogen-filled glove box, B<sub>2</sub>pin<sub>2</sub> (2.67 g, 10.5 mmol), [Ir(COD)(OMe)]<sub>2</sub> (0.100 g, 0.15 mmol), dtbpy (0.08 g, 0.30 mmol) and hexane (30 mL) were added to a Schlenk tube. The tube was taken out of the glove box and 2,2'-bithiophene (1.46 g, 8.8 mmol) was added under a stream of nitrogen. After 30 min of stirring at RT, the stirrer stopped due to sudden precipitation; thus, additional hexane (60 mL) was added. The resulting suspension was stirred at RT for another 15 h before the solvent was removed in vacuum to give a light brown residue. The residue was filtered through a plug of silica using 1:1 CH<sub>2</sub>Cl<sub>2</sub>:hexane to give the title compound as a pale green solid (2.91 g, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.52 (d,  $J$  = 4 Hz, 2 H), 7.29 (d,  $J$  = 4 Hz, 2 H), 1.35 ppm (s, 24 H), <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 143.9, 138.0, 125.6, 84.2, 24.7 ppm; MS(EI<sup>+</sup>):  $m/z$ : 418 [ $M^+$ ].

### (5-bromothiophen-2-yl)dimesitylborane (10a)

Under nitrogen, 2,5-dibromothiophene (1.2 mL, 10 mmol) in dry Et<sub>2</sub>O (50 mL) was cooled to -78 °C. *n*BuLi (1.6 M in hexane, 6.5 mL, 11 mmol) was then added under nitrogen. The mixture was stirred for 0.5 h at -78 °C and then 2 h at room temperature. Then the solution was cooled to -78 °C again, and Mes<sub>2</sub>BF (2.7 g, 10 mmol) was added. The solution was stirred for 0.5 h at that temperature and then overnight at room temperature. Water (1 mL) was added to quench the reaction. After removing the solvent, the remaining solid was then purified by column chromatography on silica gel with hexane as eluent to give the title compound as a white solid (2.81 g, 69%). m.p. 136-138 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.21 (d, *J* = 4 Hz, 1 H), 7.17 (d, *J* = 4 Hz, 1 H), 6.83 (s, 4 H), 2.31 (s, 6 H), 2.13 ppm (s, 12 H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 141.0, 140.7, 139.0, 132.6, 128.4, 126.5, 23.6, 21.4 ppm; MS(EI<sup>+</sup>): *m/z*: 413 [*M*<sup>+</sup>]; elemental analysis calcd. (%) for C<sub>22</sub>H<sub>24</sub>BBrS: C 64.26, H 5.88; found: C 64.23, H 5.92.

### (5-iodothiophen-2-yl)dimesitylborane (10b)

To a Schlenk flask charged with 1,4-diiodothiophene (5.0 g, 15 mmol) in 50 mL of dry THF, *n*BuLi (1.6 M in hexane, 10 mL, 16 mmol) was added dropwise via a syringe at -78 °C. The reaction was allowed to warm to room temperature for 1 h and was cooled to -78 °C again and a solution of dimesitylboron fluoride (4.0 g, 15 mmol) in Et<sub>2</sub>O (10 mL) was added. The reaction was allowed to warm to room temperature with stirring overnight. The reaction was quenched with HCl<sub>aq</sub> (1 M, 10 mL), extracted into CH<sub>2</sub>Cl<sub>2</sub>, dried over Mg<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with hexane:CH<sub>2</sub>Cl<sub>2</sub> 4:1 as eluent to give the title compound as a pale yellow solid (5.8 g, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.28 (d, *J* = 4 Hz, 1 H), 7.01 (d, *J* = 4 Hz, 1 H), 6.75 (s, 4 H), 2.23 (s, 6 H), 2.03 ppm (s, 12 H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 141.3, 140.9, 139.3, 138.9, 128.3, 89.4, 23.5, 21.2 ppm; MS (ESI<sup>+</sup>): *m/z*: 458 [*M*<sup>+</sup>], 338 [*M*-mes<sup>+</sup>], 211 [*M*-mes-I<sup>+</sup>]; elemental analysis calcd. (%) for C<sub>22</sub>H<sub>24</sub>BIS: C 57.27, H 5.28; found: C 57.77, H 5.29.

### 2,5-bis-Bpin-EDOT (12)

Inside a nitrogen-filled glove box, B<sub>2</sub>pin<sub>2</sub> (0.51 g, 2 mmol), [Ir(COD)(OMe)]<sub>2</sub> (10 mg, 0.015 mmol), hexane (15 mL), and dtbpy (8 mg, 0.030 mmol) were added to a Young's tap tube. The tube was then sealed and taken out of the glove box and 3,4-ethylenedioxy-thiophene (EDOT) (0.142 g, 1 mmol) was added under a stream of nitrogen. The reaction mixture was

stirred at room temperature for 15 h. After filtration and washing with hexane, the title compound was obtained as a white crystalline solid. Yield (0.3 g, 76 %).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.30 (s, 4 H), 1.35 ppm (s, 24 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.2, 110.9, 84.2, 64.9, 25.0 ppm;  $^{11}\text{B}\{^1\text{H}\}$  NMR (225 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 28.1 ppm; HRMS calcd. for  $^{13}\text{C}_{18}\text{H}_{28}\text{B}_2\text{O}_6\text{S}$ : 415.1758, found: 415.1749; elemental analysis calcd. (%) for  $\text{C}_{18}\text{H}_{28}\text{B}_2\text{O}_6\text{S}$ : C 54.86, H 7.16; found C 54.67, H 7.09.

### 2,9-diiodo-EDOT (14)

*N*-Iodosuccinimide (NIS) (3.87 g, 15 mmol) was added to a solution of EDOT (1.07 g, 7.5 mmol) in DMF (50 mL). The mixture was then stirred overnight before being poured into water (150 mL), causing precipitation of a solid. After filtration, a light brown solid was obtained. Recrystallization from  $\text{CH}_2\text{Cl}_2$  gave the title compound as light brown crystals (2.09 g, 71%). m.p. 179–184 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.26 ppm (s, 4 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.0, 65.3, 51.9 ppm; MS(EI<sup>+</sup>): *m/z*: 394 [*M*<sup>+</sup>]; elemental analysis calcd. (%) for  $\text{C}_6\text{H}_4\text{I}_2\text{O}_2\text{S}$ : C 18.29, H 1.02; found: C 18.43, H 0.91.

### 5,7-di(thiophen-2-yl)-EDOT (13)

Compounds 2-(Bpin)thiophene (2.1 g, 10 mmol), **14** (1.96 g, 5 mmol), Pd(dppf) $\text{Cl}_2$  (0.28 g, 0.34 mmol), and  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  (4.2 g, 20 mmol) were added to a Schlenk flask, followed by dry DMF (60 mL) and distilled water (8 mL) under a stream of nitrogen. The mixture was then heated to 80 °C and stirred overnight. Water (300 mL) was added to quench the reaction, and the mixture was extracted first with  $\text{Et}_2\text{O}$  (150 mL x 3), then  $\text{CHCl}_3$  (400 mL). After evaporating all of the solvent, the remaining oil was then purified by chromatography on silica gel with  $\text{Et}_2\text{O}$ -petroleum ether 1:9 as eluent to give the title compound as a yellow solid (0.57 g, 37%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.23–7.22 (m, 4 H), 7.03 (dd, *J* = 5, 4 Hz, 2 H), 4.39 ppm (s, 4 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 137.6, 134.6, 127.3, 124.1, 123.1, 109.7, 65.1 ppm; MS(EI<sup>+</sup>): *m/z*: 306 [*M*<sup>+</sup>]; elemental analysis calcd. (%) for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}_3$ : C 54.88, H 3.29; found: C 54.27, H, 3.42.

### 5,7-bis(5-(trimethylstannyl)thiophen-2-yl)-EDOT (15)

Under nitrogen, compound **13** (0.31 g, 1 mmol) was dissolved in dry THF (10 mL) in a Young's tube. After cooling to -78 °C, *n*BuLi (1.6 M in hexane, 1.3 mL, 2.1 mmol) was added and the mixture was then stirred for 15 min at that temperature. The solution became cloudy and it was then warmed to room temperature and stirred at RT for 2 h. The reaction mixture

was then cooled to  $-78\text{ }^{\circ}\text{C}$  and  $\text{Me}_3\text{SnCl}$  (0.41 g, 2.05 mmol) was added and the mixture was warmed to room temperature and stirred overnight. Water (100 mL) was added to quench the reaction. It was then extracted into  $\text{CHCl}_3$  (100 mL x 2), and the organic layer was washed with water (100 mL). After evaporating all of the solvent, the remaining solid was recrystallized from ethanol to give the title compound as a light green crystalline solid (130 mg, 21%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.32$  (m, 2 H), 7.10 (d, 84 %,  $^3J(\text{H,H}) = 3$  Hz; dd, 16%,  $^3J(^{117}\text{Sn,H}) = ^3J(^{119}\text{Sn,H}) = 26$  Hz,  $^3J(\text{H,H}) = 3$  Hz, 2 H), 0.38 ppm (s, 84%; d, 16%,  $^2J(^{117}\text{Sn,H}) = 55$  Hz and d,  $^2J(^{119}\text{Sn,H}) = 58$  Hz, 18 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 139.9, 137.2, 136.6, 135.3, 124.0, 109.6, 65.0, -8.2$  ppm; MS(ASAP<sup>+</sup>):  $m/z$ : 634 [ $M^+$ ]; HRMS (ASAP<sup>+</sup>): calcd. for  $\text{C}_{20}\text{H}_{27}\text{O}_2\text{S}_3^{119}\text{Sn}_2$  [ $M+\text{H}$ ]<sup>+</sup>: 632.9214; found: 632.9199.

#### **5,5'''-bis((E)-2-(dimesitylboryl)vinyl)-2,2':5',2'':5'',2''':5''',2''''-quaterthiophene (4V)**

Compound **2Sn** (50 mg, 0.105 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (4 mg, 0.003 mmol) and compound **4** (94 mg, 0.210 mmol) were dissolved in dry DMF (5 mL). The mixture was heated at  $90\text{ }^{\circ}\text{C}$  and stirred for 18 h. Water (50 mL) was added to quench the reaction. Then it was extracted into  $\text{CHCl}_3$  (50 mL x 3) and the organic layer was washed with water (50 mL x 3), followed by chromatography on silica gel using hexane as eluent to give the title compound as an orange powder (84 mg, 89%). m.p.  $250\text{ }^{\circ}\text{C}$  (dec.);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.19$ -7.01 (m, 12 H), 6.84 (s, 8 H), 2.31 (s, 12 H), 2.21 ppm (s, 24 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 144.6, 143.8, 140.9, 139.6, 138.6, 136.7, 136.4, 131.2, 128.4, 125.4, 124.9, 124.8, 23.40, 21.35$  ppm; MS(MALDI<sup>+</sup>):  $m/z$ : 878 [ $M^+$ ]; HRMS (ASAP<sup>+</sup>) calcd. for  $\text{C}_{56}\text{H}_{56}^{10}\text{B}_2\text{S}_4$ : 876.3524, found: 876.3516; elemental analysis calcd. (%) for  $\text{C}_{56}\text{H}_{56}\text{B}_2\text{S}_4$ : C 76.53, H 6.42, found: C 73.85, H 6.62.

#### **5,5''''-bis((E)-2-(dimesitylboryl)vinyl)-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (5V)**

Compound **3Sn** (56 mg, 0.1 mmol), **4** (94.0 mg, 0.210 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (4 mg, 0.003 mmol) were dissolved in dry DMF (5 mL). After degassing, the mixture was heated at  $90\text{ }^{\circ}\text{C}$  and stirred overnight under nitrogen. The solution was added to water (20 mL), and then extracted into  $\text{CHCl}_3$  (20 mL x 3) and dried over  $\text{MgSO}_4$ . After filtration and evaporating all of the solvent, **5V** was purified by chromatography on silica gel starting with petroleum ether, and increasing the polarity to  $\text{CHCl}_3$ :petroleum ether 1:4 as eluent, to give the title compound as an orange powder (86 mg, 89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.20$ -7.02 (m, 14 H), 6.84 (s, 8H), 2.31 (s, 12 H), 2.21 ppm (s, 24 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.6, 143.7, 142.2, 140.8, 139.7, 138.6, 136.8, 136.3, 136.2, 131.2, 128.4,$



125.4, 124.9, 124.8, 23.5, 21.4 ppm; MS(MALDI<sup>+</sup>): *m/z*: 960; HRMS (ASAP<sup>+</sup>): calcd. for C<sub>60</sub>H<sub>58</sub><sup>10</sup>B<sub>2</sub>S<sub>5</sub>: 958.3401, found: 958.3403; elemental analysis calcd. (%) for C<sub>60</sub>H<sub>58</sub>B<sub>2</sub>S<sub>5</sub>: C 74.98, H 6.08; found: C 73.49, H 6.21.

### 5,7-bis(5'-((*E*)-2-(dimesitylboryl)vinyl)-[2,2'-bithiophen]-5-yl)-EDOT (5VE)

Compound **15** (63 mg, 0.1 mmol), **4** (50 mg, 0.23 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mg, 0.003 mmol) were dissolved in DMF (5 mL) in a Young's tube in a nitrogen-filled glove box. The tube was sealed, taken out the glove box, and heated at 90 °C with stirring overnight. The reaction solution was poured into water (40 mL), which caused precipitation of a solid. After filtration, the solid was purified by chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether 1:3 as eluent to give the title compound as a red powder (62 mg, 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.19-7.01 (m, 12 H), 6.84 (s, 8 H), 2.31 (s, 12 H), 2.21 ppm (s, 24 H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.8, 143.3, 142.3, 140.8, 140.2, 138.6, 138.2, 137.5, 135.7, 134.4, 131.3, 128.4, 124.9, 124.3, 123.9, 110.1, 65.2, 23.4, 21.3 ppm; MS(MALDI<sup>+</sup>): *m/z*: 1018; HRMS (ASAP<sup>+</sup>) calcd. for C<sub>62</sub>H<sub>60</sub><sup>10</sup>B<sub>2</sub>O<sub>2</sub>S<sub>5</sub>: 1016.3456, found: 1016.3427; elemental analysis calcd. (%) for C<sub>62</sub>H<sub>60</sub>B<sub>2</sub>O<sub>2</sub>S<sub>5</sub>: C 73.07, H 5.93; found: C 70.89, H 6.17.

### 5,5''''-bis(dimesitylboryl)-2,2': 5',2'': 5'',2''': 5''',2''''-quinquethiophene (5B)

Compound **3Sn** (86 mg, 0.15 mmol), **10a** (150 mg, 0.34 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (4 mg, 0.004 mmol) were dissolved in DMF (5 mL) in a Young's tube in a nitrogen-filled glove box. Then the Young's tube was sealed, heated at 90 °C and stirred overnight. Water (100 mL) was added to quench the reaction, causing precipitation of a solid. After filtration, the residue was purified by chromatography on silica gel first using petroleum ether and then CHCl<sub>3</sub>:petroleum ether 1:5 as eluent to give the title compound as a red solid (118 mg, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.36 (d, *J* = 4 Hz, 2H), 7.29 (d, *J* = 4 Hz, 2H), 7.18 (d, *J* = 4 Hz, 2H), 7.08 (m, 4H), 6.84 (s, 8H), 2.32 (s, 12H), 2.15 ppm (s, 24H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 149.51, 149.45, 141.8, 141.3, 141.1, 138.8, 137.3, 136.5, 136.4, 128.4, 126.0, 124.9, 124.9, 23.7, 21.5 ppm; MS(MALDI<sup>+</sup>): *m/z*: 908 [*M*<sup>+</sup>]; HRMS (ASAP<sup>+</sup>) calcd. for C<sub>56</sub>H<sub>54</sub><sup>10</sup>B<sub>2</sub>S<sub>5</sub>: 906.3088, found: 906.3064; elemental analysis calcd. (%) for C<sub>56</sub>H<sub>54</sub>B<sub>2</sub>S<sub>5</sub>: C 74.00, H 5.99; found: C 71.03, H 5.81.

### Alternative method for the synthesis of **5B**

Dibromoterthiophene **3Br** (40 mg, 0.1 mmol), **8** (92 mg, 0.2 mmol) and K<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O (85 mg, 0.4 mmol) were added to a Young's tube. The tube was taken in to the glove box where

Pd(dppf)Cl<sub>2</sub> (33 mg, 0.004 mmol) and DMF (2 mL) were added. The tube was sealed and taken out of the glove box where H<sub>2</sub>O (0.2 mL) was added under a stream of N<sub>2</sub>. The tube was sealed and stirred at room temperature for 26 h and then heated to 60 °C for 2 h. Water (40 mL) was added to the reaction, the mixture was then extracted with diethyl ether (5 x 20 mL) and ethyl acetate (3 x 20 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated yielding a dark red oily solid which was purified by flash chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>:hexane 1:19 as the eluent to give the title compound as a red solid (80 mg, 88%).

**X-ray crystallography:** Crystals of **2V** were obtained from hexane, while those of **4V** and **5B** were grown by slow diffusion of methanol into toluene solutions. Crystals were selected, coated in perfluoropolyether oil, and mounted on glass fibers. Data were collected on a Bruker SMART CCD 6000 diffractometer utilizing Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 120 K. The crystal structures were integrated using Bruker SAINT and solved and refined using Olex.solve and Olex.refine of the Olex2 software package.<sup>[48]</sup> All non-hydrogen atom positions were located from the Fourier maps and refined anisotropically. Hydrogen atom positions were calculated using a riding model in geometric positions and refined isotropically.

**One-photon absorption and emission spectroscopy, fluorescence quantum yields and lifetimes:** The UV-visible absorption spectra were measured in standard 1 x 1 cm quartz cuvettes using an Agilent 8453 diode-array UV-visible spectrophotometer. Fluorescence spectra and quantum yields were measured using a Horiba Jobin-Yvon Fluoromax-3 spectrophotometer, with a concentration of *ca.* 10<sup>-6</sup> M to minimize reabsorption. The fluorescence quantum yield of **3V** was measured using an integrating sphere on a Horiba Jobin-Yvon Fluorolog-3-22-tau spectrophotometer by a previously reported method,<sup>[49]</sup> to be 0.18, which matches within experimental error (*ca.*  $\pm 10\%$ ) the value reported previously ( $\Phi_F = 0.20$ ).<sup>[14]</sup> The fluorescence quantum yields of all other compounds were measured against the reported value of **3V** in toluene ( $\Phi_F = 0.20$ ) for easier comparison with earlier data. The emission band of **3V** overlaps most of the emission spectra of the compounds measured in this work, which minimizes the error of the measurements.

The fluorescence lifetimes were measured in optically dilute ( $A < 0.15$ ) toluene solution by time-correlated single-photon counting (TCSPC) using 450 nm excitation. The excitation

source used was the 2<sup>nd</sup> harmonic of a mode-locked (900 nm), cavity dumped (APE Pulse switch) Ti:sapphire laser (Coherent MIRA), pumped by the 2<sup>nd</sup> harmonic (532 nm) of a continuous wave Nd:YAG laser (Coherent Verdi V6) at a power of 4.5 W. The pulse characteristics were: a temporal full width at half maximum (FWHM) of ~150 fs at a repetition rate of 4 MHz. The fluorescence emission was collected at right angles to the excitation source, with the emission wavelength selected using a monochromator (Jobin Yvon TRIAX 190) and detected under magic-angle conditions by a cooled photomultiplier-tube module (IBH TBX-04). The power of the laser was modulated to give a detector count rate <20 kHz. The instrument response function (IRF) was measured using pure toluene as the scattering sample, giving an IRF of ~200 ps FWHM. Iterative reconvolution of the IRF with a decay function and non-linear least-squares analysis were used to analyze the data. The quality of the fit was judged by visual inspection of the residuals and autocorrelated residuals, and by the calculated values of  $\chi^2$  and the Durbin-Watson parameter. Fitting with a single decay function gave acceptable results in all cases. Estimated error  $\pm 5\%$ .

**Two-photon absorption (TPA) spectroscopy:** Two-photon cross-sections were measured using the femtosecond two-photon-excited fluorescence method.<sup>[33]</sup> The tunable fundamental output of the same Ti:sapphire laser described above for TCSPC measurements was used as an excitation source. The pulse characteristics were: a temporal full width at half maximum (FWHM) of ~150 fs; average power 5-35 mW at a repetition rate of ~2.5 MHz, giving average energies of 2-14 nJ per pulse. A variable ND filter (Edmund Optics) mounted on a translation stage was used to control the light intensity incident on the sample, with the power monitored by splitting the beam to a photodiode of known response, calibrated against a free standing power meter. Gold mirrors, highly reflective of NIR radiation, were used with a 20x objective (Olympus LWD C A20) to focus the source onto the sample. Samples were prepared with  $A = 0.2$ - $0.3$  at their absorption maximum (concentrations: ca.  $10^{-6}$  M) in quartz cuvettes of path length,  $l = 1$  cm. The two-photon excited fluorescence emission was collected with a dichroic mirror (Semrock FF735) and detected with a 100  $\mu\text{m}$  core fiber-optic cable coupled CCD spectrograph (Avantes Avaspec 2048FT) fitted with a 670 nm narrow band pass filter to remove extraneous laser light. TPA cross-sections ( $\sigma_2$ ) were measured relative to a reference, as per the standard methodology of Rebane and co-workers<sup>[36]</sup> (*vide supra* and Supplementary Information), using the equation:

$$\sigma_2^S = \frac{\sigma_2^R \Phi_F^R c^R n^S F^S(\lambda)}{\Phi_F^S c^S n^R F^R(\lambda)}$$

The superscripts  $R$  and  $S$  refer to the reference and sample respectively,  $\Phi_F$  is the one-photon photoluminescence quantum yield,  $c$  is the concentration,  $n$  is the solvent refractive index and  $F(\lambda)$  is the integrated two-photon emission spectrum. The sample and reference were recorded under identical pulse conditions. The concentration of the reference fluorescein was measured by UV-visible spectroscopy using  $\epsilon_{492\text{ nm}} = 88\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  and interpolated literature values<sup>[36,50]</sup> of  $\sigma_2$  for fluorescein in 0.1 M NaOH with  $\Phi_F = 0.9$  were used. The wavelength of the laser was tuned step-wise to allow the full TPA spectrum to be obtained in 5 nm steps in the range 750 to 920 nm. The system was calibrated to correct for the dark noise of the detector and the photoluminescence spectrum was typically averaged over 100 measurements of 100 ms integration time. In-house software written in Labview 8.6 (National Instruments) was used for data collection and analysis. Estimated error  $\pm 20\%$ .

**Computational details:** We used quantum chemical approaches, as implemented in the Gaussian 03 or 09 packages,<sup>[51]</sup> to model all chromophores. Calculations were performed in vacuum and were limited to properties related to the ground state geometry: geometry optimization and related ground state (GS) properties, one and two-photon absorption related to the electronically excited states (ES). Optical spectra were obtained employing the density matrix formalism for non-linear optical responses as proposed by Tretiak and Chernyak.<sup>[52]</sup> We did not model relaxed excited states to simulate fluorescence as they are expected to undergo localization prior to emission (vide supra) that cannot be reproduced yet by state-of-the-art quantum chemical approaches.<sup>[32b-d]</sup> This rules out any modern approaches, such as that proposed by Jacquemin and co-workers,<sup>[53]</sup> aiming at computing accurate transition energies in solution for quantitative comparison with experimental data. Furthermore, accounting for solvent effects when calculating TPA spectra is not straightforward as the local field correction is not properly described by a simple local field factor to the fourth power.<sup>[1d]</sup> Given the approximations introduced by the use of inexact DFT functionals, one may reach better quantitative results with low cost calculations in vacuum, as has been shown for the hybrid B3LYP functional.<sup>[1d]</sup>

Different levels of theory and starting conformations have been tested for geometry optimization in vacuum using the 6-31G\* basis set. As our main purpose was to investigate NLO properties, we used the bond length alternation as a quality factor. As expected, Hartree-Fock calculations significantly overestimate the BLA, whereas DFT calculations with the BP86 functional, used in previous work on mesitylboryl-based chromophores,<sup>[14]</sup> significantly

underestimate this parameter (Table S4). DFT with the hybrid functional B3LYP was found to lead to a good compromise; even so, the smaller BLA, as compared to that derived from X-ray diffraction structures, highlights its tendency to overestimate conjugation (Table 2 and S4). This could be partly cured using long-range corrected hybrids, such as the CAM-B3LYP functional (Table S5), but we preferred keeping the same level of theory both for geometry optimization and optical properties and to concentrate on overall trends.

The crystal structures reveal both *cisoid* and *transoid* conformers, with a preference for *transoid* when inversion symmetry matches molecular structure (*i.e.* even number of thiophene rings for all *trans* conformation). We have verified, in the case of **2V**, that both conformers are energetically close enough to coexist in solution at room temperature. In addition, the all *trans* conformers, where adjacent rings of the oligothiophene backbones have opposite orientations, have been compared to their all *cis* analogues. While for the shortest compound, namely **2V**, the energy difference is within the energy of thermal activation at RT ( $k_B T_{RT}$ ), it increases with the number of thiophene rings up to about  $10 k_B T_{RT}$  for **5V** and **5VE** in favor of the all *trans* conformation. Thus, for consistency, we retained conformations with all *trans*-thiophene backbones and *cisoid*-vinylBMes<sub>2</sub>/thiophene end groups for all chromophores of interest. Calculations were performed in vacuum at the (TD-)B3LYP/6-31G\*//B3LYP/6-31G\* level of theory, in conventional quantum chemical notation “single point//optimization level”. Natural transition orbitals<sup>[28]</sup> (NTO) analysis has been used to characterize electronic transitions. NTOs offer a compact representation of excited states, particularly useful when there is no dominant amplitude of a pair of occupied and empty individual molecular orbitals (*e.g.* HOMO and LUMO) to the total electronic transition. NTO pairs consist of an excited particle (or electron-orbital) and empty hole (or hole-orbital) illustrating the electronic redistribution upon (de-)excitation. Excited-state electronic-structure analyses, both optical response and NTOs, were performed for 20 singlet excited states (ES). Comparison of 20 and 60 ES at the TD-B3LYP/6-31G\*//B3LYP/6-31G\* level of theory showed that 20 ES are sufficient, especially for the calculations of TPA spectra (Figure S17). All theoretical TPA spectra have been computed following the computational scheme introduced in Ref. [1d]. The damping factor, introduced to simulate the finite linewidth in the resonant spectra, has been fixed to 0.17 eV, derived from the experimental bandwidths (Table S7). Figures visualizing molecular geometries and NTOs were obtained with XCrySDen.<sup>[54]</sup>

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