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Pairing of α-fused BODIPY, towards panchromatic n-type semi-conducting materials.

Quentin Huaulmé,[a]* Sadiara Fall,[b] Patrick Lévêque,[b] Gilles Ulrich[a]* and Nicolas Leclerc[a]*

Abstract: We report herein a chemical strategy to efficiently perform the dimerization of α-fused BODIPY. The straightforward synthesis of one of this dimer is described and its properties are investigated through UV-Vis spectroscopy, cyclic voltammetry, DSC and charge carriers mobility measurements using organic filed effect transistors and space-charge limited current diodes. Those results allowed us to identify a chemical strategy to decrease simultaneously the tendency of α-fused BODIPY to crystallize, to increase its light-harvesting properties and to promote isotropic charge carriers transport. Moreover, the disclosed approach is also a way to maintain the deep LUMO level of α-fused BODIPY, making this class of materials highly desirable for optoelectronic applications.

Introduction

Thanks to their peculiar optoelectronic properties, some natural and synthetic organic dyes have found several applications in the field of organic electronics, including organic electroluminescent diodes (OLED),[1] biological labelling,[2] bioelectronics,[3] lasers,[4] and organic photovoltaics (OPV).[5] For this latter, in addition to their optical properties, the selected dyes may exhibit high charge carriers mobilities in solid state to allow efficient photo-generated charges extraction.

Polyaromatic dyes have emerged recently as promising candidates for optoelectronic applications, because of their extended π-delocalization that generally combines intensive visible-Near Infra-Red (NIR) absorption as well as high planarity leading to high charge carrier mobilities.[6] However, this high planarity is in general responsible of a very pronounced material tendency to crystallize. Therefore, these dyes are often difficult to blend and to process from solution.

To overcome this critical issue, the so-called dimerization strategy, using short conjugated linkages or even direct C-C bonds between two π-conjugated and hindered sub-units, has been introduced.[7] The short linkage insures a high steric hindrance between the two polycyclic plans leading to a dihedral angle with an amplitude depending on the steric hindrance range. The perylene diimide (PDI) core is a perfect example of the application of such chemical engineering strategy, used in the bulk heterojunction (BHJ) OPV field.[8] Indeed, this small polyaromatic unit exhibits several desirable optoelectronic properties, including a high electron affinity (similar to the fullerene derivatives), a high electron mobility and a high extinction coefficient around 550 – 600 nm in the solid state. However, its use in solution-processed BHJ OPV devices has been limited by its strong π-π stacking ability leading to micrometer-size crystallites, which prevent an accurate blending with the electron donor component for OPV applications. Hence, recently, dimerization of PDI units has been applied, mainly through its bay bridge positions, in order to disrupt the planar nature of the PDI and to avoid its crystallization tendency.[9] Doing so the PDI unit has become one of the most famous and efficient Non Fullerene Acceptor (NFA) used in fullerene-free BHJ OPV devices.[10]

We reported recently the highly versatile, straightforward and selective synthesis of α-fused boron dipyrromethene (BODIPY).[11] With nine fused and coplanar aromatic cycles, these α-fused BODIPYs can be considered as polycyclic aromatic units. They exhibit really promising optoelectronic properties, with an intense absorption in the UV-visible-NIR range, high electron affinity and, can exhibit a good and balanced ambipolar charge carriers mobilities. In addition and as opposed to PDI for instance, their properties are easy to tune thanks to the highly versatile chemistry of the BODIPY core. However, similarly to the PDI core, α-fused BODIPY are highly planar and highly crystalline, and consequently difficult to process from solution. Therefore, in the present manuscript we report a chemical strategy leading to the dimerization of the α-fused BODIPY, with the challenge of keeping the straightforward and selective nature of the previously published synthetic route.

Results and Discussion

a. Synthesis.

Despite the very rich chemistry developed around the BODIPY core, rather few BODIPY dimers have been reported so far.

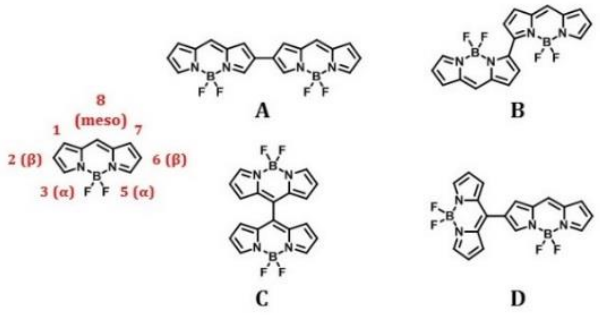

Figure 1. Left, BODIPY chemical structure and reactive positions; right, chemical structures of representative BODIPY-dimers.

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Among them we could consider two classes of materials *i.e.* the directly linked BODIPY dimers[12] and the conjugated[13] or non-conjugated[14] short linker-based BODIPY dimers. Due to the numerous reactive positions of the BODIPY core, different types of dimers have been reported including the ß-linked dimers[15] (linked in the 2,2'-positions, compound **A** in fig. 1 for example), the α-linked dimers[16] (linked in the 3,3'-positions, see compound **B** in fig. 1 for example), the *meso*-linked dimers[17] (linked in the 8,8'-positions, see compound **C** in fig. 1 for example) or the unsymmetrical *meso*-ß-linked dimers[18] (linked in the 2 and 8'-positions respectively, see compound **D** in fig. 1 for example).

The synthetic procedure, that we recently reported for the synthesis of α-fused BODIPYs, required the free-access to the 2,3,5,6-positions of the BODIPY core,[11] excluding *de facto* the α- and ß-linked dimers. In addition, the relative steric hindrance around the *meso*-position, due to the substituents in the 1,7-positions, is known to lead to a relative rotation of the aryl groups grafted in this *meso*-position.[19] This main-plan twisting is a rather good feature considering our wish to decrease the final compound crystallinity. Therefore, herein, we targeted the challenging synthesis of α-fused BODIPY dimers linked together in their *meso*-positions.

Before starting the synthesis, we performed some Density Functional Theory (DFT) calculations using the Gaussian 09 program at the B3LYP/6-311 + G* level of theory in vacuum in order to check if the targeted design, using thiophene unit as linker in *meso*-position, would lead to the expected 3D material with the fused BODIPY main-planes presenting a high torsion angle (see Fig. 2).

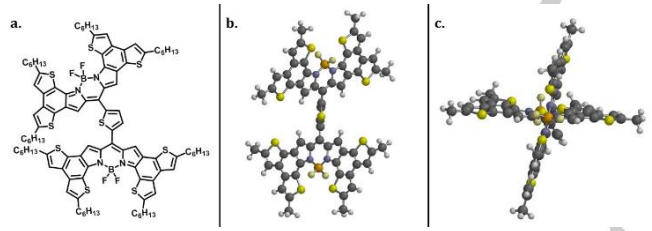

Figure 2. a. Chemical structure of the targeted BODIPY dimer with thiophene linker; **b.** DFT optimized structure of the BODIPY dimer; **c.** Side-view of the same DFT optimized structure highlighting the 85° angle between the fused BODIPY main planes (DFT calculations has been performed using DFT calculations have been performed using the Gaussian 09 program at the B3LYP/6-311 + G* level of theory in vacuum).

As seen in the Figure 2, by using the thiophene unit as linker between two α-fused BODIPY cores, the calculated torsion angle between BODIPY mean planes is of 85°, leading thus to a 3D molecule. The calculated HOMO and LUMO confirmed this 3D nature, as the HOMO level is completely localized on one α-fused BODIPY core, despite the identical electronically features of both BODIPY units involved in the dimer (see Fig. 3). The LUMO level, usually more localized around the 1,7 and *meso*-positions of the BODIPY core, seems to be equally delocalized on both side of the thiophene linker.

The direct comparison with a simple α-fused BODIPY (half of a dimer) carrying a thiophene in meso-position demonstrates that if not completely broken, the conjugation between both BODIPY units in the dimer is really weak and obviously limited to the LUMO level. Consequently, the HOMO values calculated for both molecules are really similar, of about -5.06 and -5.03eV for the dimer and the α-fused BODIPY, respectively. On the other hand, the calculated electron affinity increases slightly when going from the α-fused BODIPY unit to the BODIPY dimer, with a LUMO level of -3.01eV and -3.23eV, respectively.

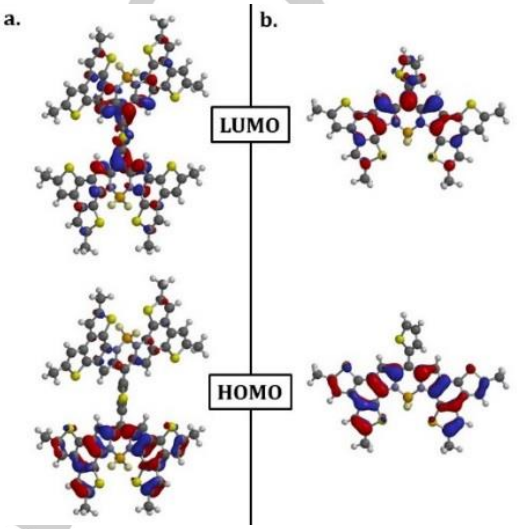

Figure 3. a. Top, dimer LUMO surface; bottom, dimer HOMO surface; b. Top, α-fused BODIPY LUMO surface, bottom, α-fused BODIPY HOMO surface.

To opposite synthetic approaches could be considered to obtain the targeted α-fused BODIPY dimer. A convergent approach is consisting in a first synthesis of the α-fused BODIPY molecules that are in a second time paired together through their meso positions in order to obtain the dimer. However, the dimerization step, that would take place at the end of the chemical route, is in most cases a low yield reaction (20-40% at maximum). In addition, this dimerization step required a reactive group in meso-position, which could disrupt with the α-fused BODIPY synthesis. These two bottlenecks could be overpassed by using a divergent approach: consisting in a first dimerization of unsubstituted BODIPYs, that will then be transformed in α-fused BODIPY dimer. Despite the challenging octa-bromation and octa-cross-coupling steps required by this divergent route, it seems more accessible. Moreover, this strategy could allow introduction of various subtituents after having built the dimer and hence appeared more versatile.

The followed synthetic route is sketched in the scheme 1. The first step is consisting in the synthesis of a BODIPY unit substituted by a chlorine atom in the meso-position. In order to avoid the pyrrolic polycondensation by-products, we used the pyrrole addition on thiophosgene route developed by Smythe *et al.*,[20] leading to subsequent dipyrrilthione derivative 1 in a rather good yield of 58%. A subsequent oxidation by a H_2O_2-KOH mixture leads to the corresponding dipyrromethanone 2 in 77% yield.[21] Compound **2** is then converted in BODIPY **3** by a two steps in one-pot reaction:

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i) a $POCl_3$ oxidation in dipyrromethenium chloride followed by ii) a $BF_3.OEt_2$ complexation in basic media

The second step consists in elaborating the BODIPY dimer by cross-coupling compound **3** by the meso-position on a di-stannylthiophene derivative. Surprisingly the Stille cross-coupling is highly efficient and leads to the BODIPY-dimer **4** in a very high yield of 98%.

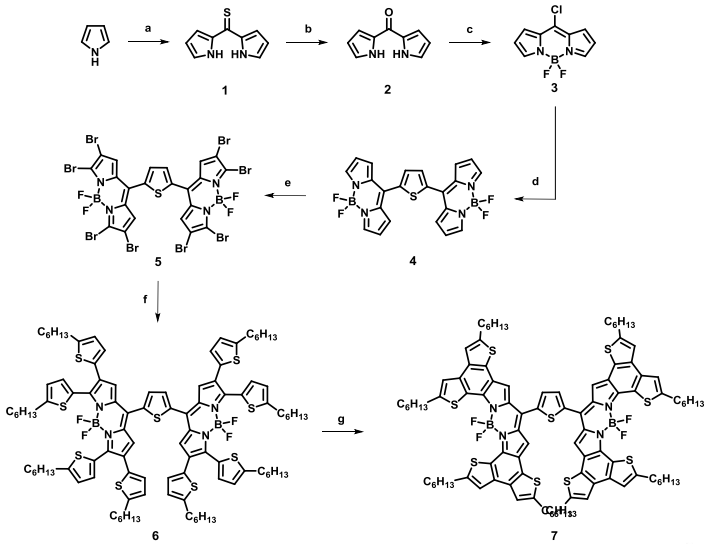

Figure 4: Synthetic route for the targeted α-fused BODIPY dimer. Keys: a. thiophosgene, Et_2O/PhMe, 0°C, 58%; b. H_2O_2, KOH, MeOH/H_2O, 77%; c. $POCl_3$, DCE, 80°C then $BF_3{\cdot}OEt_2$, NEt_3, DCE, 0°C to RT, 56% over two steps; d. 2,5-bis(trimethylstannyl)thiophene, [$Pd(PPh_3)_4$], toluene, 110°C, 93%; e. Br_2, chloroform, 58%; f. tributyl(5-hexylthiophen-2-yl)stannane, [$Pd(PPh_3)_4$], toluene, 51%; g. $FeCl_3$, DCM, 0°C, 56%.(see experimental part for detailed synthetic procedures and analysis).

The regioselective octa-brominated BODIPY dimer **5**, was obtained using a simple and straightforward bromination reaction with an excess of bromine in a chloroform solution. Due to a very poor solubility, compound **5** precipitated out during the reaction, making the purification easier but also render its NMR characterization impossible. Though, a HRMS ESI-TOF analysis confirmed its structure (see Fig. S21 in ESI section), and display the expected and characteristic isotopic repartition of masses. The octa-thiophene substitution is obtained in a pretty good yield of 52% (*circa* 92% per Br substituent) by using an excess of tri-butyl-stannyl-thiophene derivative with $Pd(PPh_3)_4$ as catalyst. Finally, in a presence of an excess of iron(III) chloride (16eq.) as oxidant, the octa-substituted BODIPY dimer **6** quickly undergoes oxidative ring closure leading to the corresponding α-fused BODIPY-dimer **7** in a good yield of 56%. The molecular structures of all the intermediates and final compounds were attributed by ^1H, ^{13}C, ^{11}B, ^{19}F NMR and HR-MS. The regioselectivity of the oxidative ring closure has been previously demonstrated on simple α-fused BODIPY.[11]

b. UV-Visible spectroscopic studies.

The spectroscopic data, absorption and emission measurements, of all the synthetized isomers were investigated and are summarized in Table 1. Only the unsubstituted BODIPY, compound **3**, has shown emissive properties (see emission parameters in ESI section). The other materials are all non-emissive at 25°C in aerated solvent.

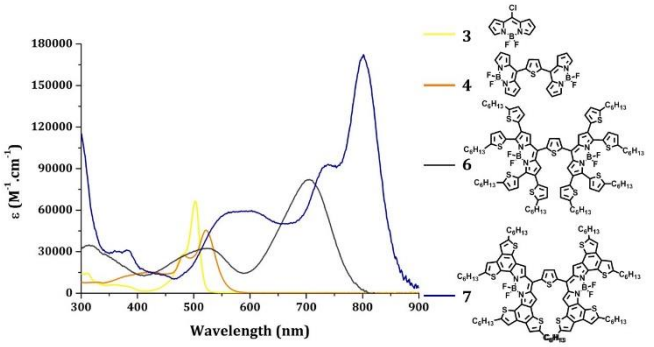

Figure 5. Figure 5. Absorption spectra of compounds 3, 4, 6 and 7 (toluene, 25°C, ∼ 10^{-6} M).

All compounds exhibit a strong absorption in the UV-visible region (see Fig. 5). A first trend appears clearly, i.e. the increase of the conjugation by dimerization of the BODIPY unit (from **3** to **4**) and then by substitution with thiophene units (from **4** to **6**) leads to a bathochromic shift of the absorption bands.

Compound **3** exhibits a narrow absorption band displaying a shoulder at higher energy wavelengths, typically observed for the BODIPY unit.[23] After dimerization, the absorption band of compound **4**, which undergoes a slight bathochromic shift of approximately 15 nm compared with **3**, shows a less common feature with a broader absorption band with two maxima at 483 and 522nm in toluene. This feature could be due either to relative dipole positions of each BODIPY in the dimer, responsible of an intramolecular excitonic coupling and leading to an absorption band splitting,[24] or to a dimer symmetry breaking leading to two different conformations.[25] The octa-substitution of compound **5**,

Table 1. Spectroscopic data recorded in diluted solutions (~10^{-6}M, aerated solvent) at 25°C. a) Quantum yields calculated using the following standard: cresyl violet in ethanol (ϕ_F = 0.50). All ϕ_F are corrected for changes in refractive index. b) kr and knr were calculated using the following equations: kr = ϕ_F/τ, knr = $(1-\phi_F)/\tau$ assuming that the excited state is obtained with unit efficiency. The uncertainties on the lmax, ε(lmax) and QF are 1 nm, 5% and 10 %, respectively.

Compound	λ_{abs} (nm)	ε ($10^4.M^{-1}.cm^{-1}$)	Solvent
3	504	6.60	DCM
	507	6.30	PhMe
4	520,486	4.52, 2.83	DCM
	522, 483	4.55, 2.70	PhMe
6	697	8.95	DCM
	706	8.20	PhMe
7	799	12.1	DCM
	801	17.2	PhMe

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leads to a further absorption band bathochromic shift as can be seen in compound **6**. One can observe two absorption bands; the more intense, at lower energy, is probably due to the $S_0 \rightarrow S_1$ transition, while the second one, broad and located at lower wavelengths could be attributed to a superposition of an internal charge transfer between the electron rich thiophene units and the electron deficient BODIPY unit and some intramolecular excitonic coupling. Finally, after cyclization, the α-fused BODIPY dimer **7** exhibits both hyperchromic and bathochromic effects as compared to the octa-substituted thiophene derivative **6** with an intense absorption band attributed to the $S_0 \rightarrow S_1$ transition shifted to the near-IR. Similar effects have been observed previously during the characterization of simple α-fused BODIPYs.[11] Those effects are attributed to the enhancement of the electronic delocalization all over the α-fused BODIPY backbone induced by the coplanarization of the peripheral substituents and to the stiffening of the structure. The second large broadband could in comparison with other BODIPY dimer be partially attributed to intramolecular excitonic coupling and some ICT contribution. Like the other reported α-fused BODIPY reported so far,[15, 23] this α-fused-BODIPY dimer does not display significant solvatochromism when changing the solvent dielectric constant (see Table 1 and Fig. 6).

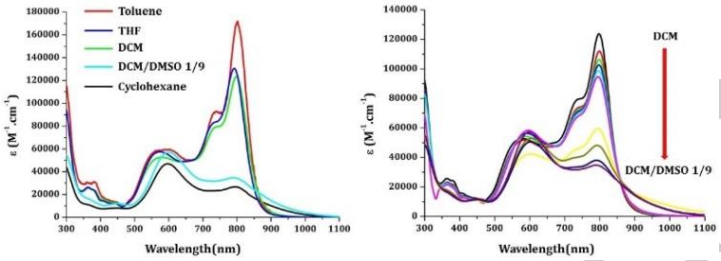

Figure 6. Absorption spectra of compound 7 in solution in various solvents (∼10^{-5}M, 25°C).

However, due to a moderate solubility it forms aggregates in some solvents such as cyclohexane or DMSO. These aggregates in solution exhibit a very broad absorption band from 500 to almost 1000nm with a first maximum at 600nm and a second at 800nm. This compound seems to exhibit various types of aggregates competing with $S_0 \rightarrow S_1$ transition and the internal excitonic coupling (disappearance of the 550nm band to the benefits of the 600nm one and disappearance of the $S_0 \rightarrow S_1$ transition concomitantly the enlargement of the absorption band to 1100nm, see Fig. 6 of increasing amount of DMSO, as countersolvent, in DCM). The 3D character of the molecule and thus the multiple arrangement in the π-stacking and dipoles orientations lead to multiples aggregates features spanning the whole visible to NIR spectrum.[26]

This feature is strongly similar to the one of compound **7** in thin-film (Fig. 7), highlighting thus the solid-state nature of those aggregates in poor solvents. A strong enlargement of the major absorption peak as well as a bathochromic shift compared to the solution absorption spectrum is observed in thin-film. Interestingly, the solid-state absorption is almost panchromatic from 300nm up to 1100 nm (no clear-cut transparency range). An optical band gap of 1.18 eV has been measured for this BODIPY-dimer from the absorption onset in thin-film.

Interestingly, when compared to the previously reported α-fused BODIPY unit (see Fig. 8).[11] the new dimer exhibits an obvious bathochromic and hyperchromic shift of its absorption spectrum.

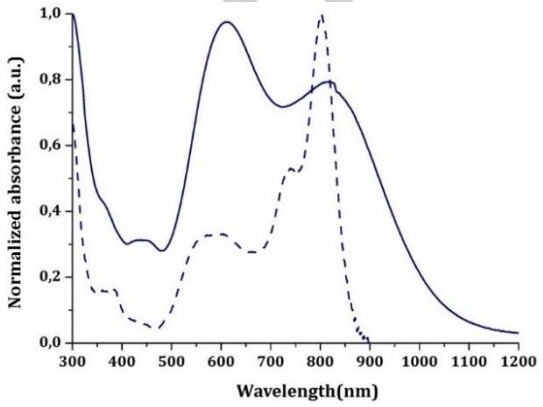

Figure 7. Absorption spectra of compound **7** in toluene (dashed line) and in solid state (full line).

The hyperchromic shift is due to the presence of two α-fused BODIPY units into the dimer, while the bathochromic shift may arise from a slight conjugation of BODIPY units through the thiophene linker and the absorption around 550nm could be attributed to internal excitonic coupling.

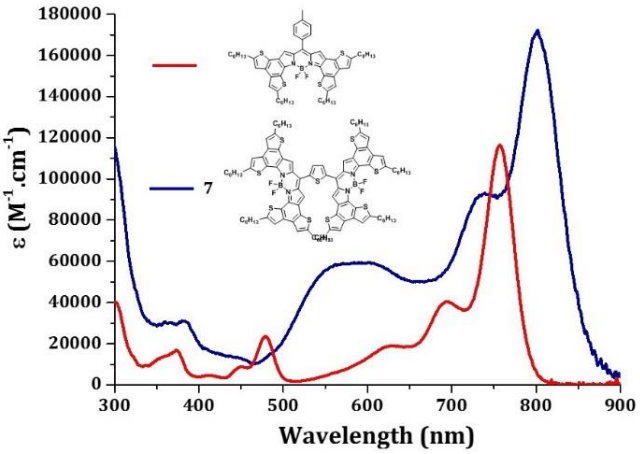

Figure 8. Absorption spectra in toluene solution (∼ 10^{-6}M, 25°C) of the α-fused BODIPY (red line) and of the α-fused BODIPY-dimer (blue line).

c. Electrochemistry.

Cyclic voltammetry (CV) was used to investigate the oxidation and reduction potentials of the fused BODIPY-dimer **7** and thus extrapolate its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. All potentials are referred to the SCE electrode that was calibrated at 0.38 V versus Fc/Fc^+ system.

If the reduction wave is partially reversible, the oxidation process that exhibits two really close maxima is not reversible (see fig. S25 in the ESI section). The onset of the first oxidation process gives a value for the oxidation potential of this BODIPY-dimer of 0.85 V. The reduction occurs at a potential of -0.30 V. When applying the following equations, E_{HOMO} (eV) = - (E_{ox} onset vs SCE) - 4.4 eV and E_{LUMO} (eV) = - (E_{red} onset vs SCE) - 4.4 eV,[27] we calculated HOMO and LUMO levels of -5.25 eV and -4.10 eV, respectively. When compared to the single α-fused BODIPY counterpart previously reported,[11] one can clearly notice that the α-fused BODIPY dimerization impacts mainly the electron affinity with a downshifting of the LUMO energy level of about 0.20eV, from -3.9eV to -4.1eV. The ionization potentials of both derivatives are really similar with HOMO levels of approximately -5.25eV. The relative values of the HOMO and LUMO levels when going from α-fused BODIPY to the fused BODIPY-dimer **7** are consistent with the frontier-energy level surfaces calculated by DFT. An electrochemical band-gap of 1.15eV can be deduced from the CV measurements, which is consistent with the optical band-gap of 1.18eV deduced from the absorption on thin-film

d. Impact of crystallinity on charge transport properties.
Thermal properties of the synthesized BODIPY-dimer **7** have been characterized by differential scanning calorimetry (DSC, see Fig. S28 in the ESI section). In opposite to the really clear melting process observed in the previously published α-fused BODIPY (see Fig. S27 in the ESI section), no thermal event has been observed in the thermogram of the BODIPY-dimer **7**, pointing out that the dimerization strategy did lead to a loose of crystallinity.

In order to get more insight into the impact of the loss of crystallinity on charge transport properties, and to complement the semiconducting properties characterization of this new dimer, its charge-carrier mobilities were investigated. Due to its expected 3D and its demonstrated amorphous natures, we used two different devices to probe their charge transport properties in all directions. The organic field-effect transistor (OFET) device allows to probe the charge transport in the substrate plane, while the space charge limited current (SCLC) device will give an information on the charge transport perpendicular to the substrate plane.

The OFET device allows to investigate both hole and electron mobilities in a single device, by just varying the OFET polarization (see Fig. 9). Doing so, we clearly highlighted the ambipolar nature of this new BODIPY-dimer. Such a feature is not surprising if one consider its really high electron affinity, similar to the one reported for fullerene derivatives. The charge-carriers mobilities are very well balanced, with both hole and electron mobilities of approximately $5x10^{-5}$ $cm^2.V^{-1}.s^{-1}$.

The investigation of the dimer electron mobility by using SCLC devices in electron only configuration leads to interesting pieces of information. Indeed, the dimer exhibits an SCLC electron mobility of approximately $1.3x10^{-6}$ $cm^2.V^{-1}.s^{-1}$. This SCLC electron mobility is roughly 40 times lower than the OFET electron mobility. This value is fully consistent with the variation of charge-carrier

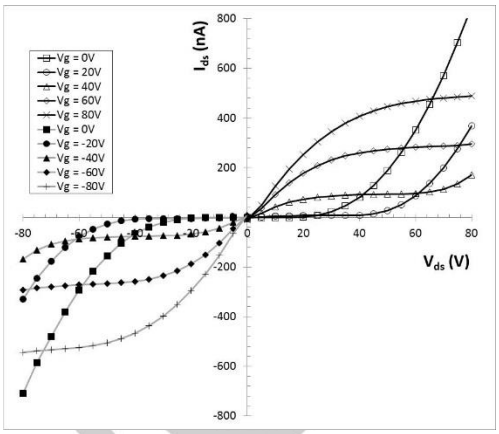

Figure 9. Output characteristics of an OFET annealed at 130°C for 15 minutes. The source-drain current (I_{ds}) is measured as a function of the source-drain voltage (V_{ds}) for different gate voltages (V_g). The open symbols corresponds to positive V_{ds}, V_g and I_{ds} values *i.e*. will probe the electrons in a unipolar material. The closed symbols corresponds to negative V_{ds}, V_g and I_{ds} values i.e. will probe the holes in a unipolar material.

mobility as a function of the carrier concentration in an isotropic organic semiconducting disordered material using standard models as explained in ESI.[28] One could therefore consider that electron mobilities in both directions, parallel and perpendicular to the substrate plane, if they were extracted in the same carrier-concentration regime would be in the same range. In conclusion, the electron transport could be considered as isotropic in the BODIPY-dimer as expected from its 3D nature.

Conclusions

Dimerization of polycyclic aromatic units is a powerful approach to limit their strong tendency to crystallize and to increase substantially their miscibility with complementary materials for BHJ OPV applications for instance.
A highly straightforward synthesis enabling α-fused BODIPY dimerization has been presented. The synthetic strategy relies on the i) dimerization of two BODIPY units through their meso position via a thiophene π-conjugated linker ii) followed by the subsequent building of the α-fused units on each BODIPY core. This second step is based on a very versatile chemical strategy recently reported by our group and should pave the way to an endless and easy fine-tuning of the optoelectronic properties of such dimers, by playing on the aromatic substrates and their regioselective condensations.
Despite the slight conjugation break due to the high dihedral angle between the two BODIPY mean planes, the final dimer exhibits both a hyperchromic and bathochromic absorption spectrum as regards to the simple α-fused BODIPY unit counterpart. Consequently, the dimer shows in solution a broad absorption band from 500 to 900nm with a maximum molar absorption coefficient of more than $170000M^{-1}.cm^{-1}$ at 800nm. The multiple intermolecular interactions induce an even broader absorption in thin-films with a highly desirable panchromatic absorption, for

efficient light harvesting behavior, displaying a cut-off at approximately 1200nm.
Simultaneously, this dimer exhibits a slightly higher electron affinity, really close to the fullerene derivatives ones, without losing its ambipolar feature. Finally, although moderate, the electron charge carrier mobilities are in the same range in all directions *i.e.* the dimer **7** presents isotropic charge-carrier transport properties. All those desirable features make this class of polycyclic BODIPY-dimer attractive and promising organic semiconducting materials for optoelectronic applications.

Experimental Section

Synthesis of compound **1**. To a stirred solution of thiophosgene (2.10g, 18.3mmol, 1.0eq) in anhydrous toluene (50mL) is added via cannula and at 0°C a solution pyrrole (2.45g, 36.5mmol, 2.0eq.) in anhydrous diethyl ether (25mL). The mixture was stirred at 0°C for 10 minutes before a mixture of MeOH/H_2O (4:1, 100 mL) is added. The mixture is further stirred at room temperature for 45min. The reaction mixture is evaporated to dryness under vacuum. Column chromatography on alumina (PhMe/$CHCl_3$ 9:1) afforded 1.86g (10.6mmol, 58%) of pure compound **1** as an orange solid**. ^{1}H NMR (400 MHz, CDCl3)**: δ = 9.77 (b, 2H), 7.21 (s, 2H), 7.05 (s, 2H), 4.40-6.42 (m, 2H). **^{13}C NMR (100 MHz, CDCl3)**: δ = 193.4, 138.5, 127.8, 114.9, 112.6.

Synthesis of compound **2**. To a stirred solution of dipyrromethanethione (900mg, 5.11mmol) in MeOH/H_20 (28.5/1.5mL) are successively added, at 0°C, KOH (1.13g) and H_2O_2 (30% in water, 3.8mL). After the addition is over, the mixture is heated at reflux (80°C) for 10 minutes. The solution turns from deep red to light yellow. After cooling down at room temperature, water (20mL) is added. The solid is collected by filtration and washed with water to afford 545mg (3.40mmol, 66%) of the pure dipyrromethanone as a light yellow solid**. ^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 9.66 (b, 2H), 7.15-7.17 (m, 2H), 7.08-7.09 (m, 2H), 6.35-6.37 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 172.8, 130.6, 124.0, 116.0, 111.2.

Synthesis of compound **3**. To a solution of dipyrromethanone (217mg, 1.35mmol), in anhydrous DCE (7.0mL) is added dropwise $POCl_3$ (415mg, 0.25mL, 2.0eq). The reaction mixture is heated to reflux for 3h. After cooling down to 0°C, TEA (1.37g, 1.9mL, 10eq) and $BF_3.OEt_2$ (2.11g, 1.9mL, 11eq) are successively added. The mixture is stirred 1h30 at R.T. before being poured on water and diluted with Et_2O. The organic layer is washed with water. The aqueous layer is extracted with Et_2O, dried over $MgSO_4$, and evaporated to dryness. Column chromatography on silica gel (DCM/PE 3:2) afforded 173mg (0.764mmol, 56%) of pure compound **3** as a red solid. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.89 (bs, 2H), 7.41 (d, 2H, 3J=4.3Hz), 6.58 (d, 2H, 3J=4.3Hz). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 145.2, 141.3, 134.1, 129.4, 119.2. **^{11}B NMR (128 MHz, $CDCl_3$)**: δ = 0.08 (t, J_{B-F} =28.7Hz). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = -145.6 (q, J_{F-B}=28.7Hz).

Synthesis of compound **4**. A solution of compound **3** (158mg, 0.698mmol, 2.2eq) and 2,5-(trimethylstannane)thiophene (130mg, 0.317mmol, 1.00eq) in dry toluene (5.0 mL) was degassed with argon for 30min. $Pd(PPh_3)_4$ was added (18.4mg, 0.0159mmol, 5.0mol%) and the reaction mixture was heated at 110°C for 3h. The reaction mixture was diluted with DCM, washed with water. The aqueous layer was extracted with DCM, dried over $MgSO_4$, and evaporated to dryness. Column chromatography (PE/DCM 4:6) followed by recrystallization under reduced pressure from DCM/EtOH afforded 138mg (0.297mmol, 93%) of compound **4** as a red solid. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.00 (s, 4H), 7.68 (s, 2H), 7.32 (d, 4H, ^{3}J=4.1Hz), 6.64 (d, 4H, ^{3}J=4.1Hz). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 145.3, 139.5, 137.4, 134.3, 133.0, 131.6, 119.3. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 0.20 (t, J_{B-F} = 28.6Hz). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = -145.1 (q, J_{F-B}=28.4Hz). **HRMS (ESI-TOF)**: calcd for $C_{22}H_{14}B_2F_4N_4S$ [M+K]+,503.0701; found 503.0734.

Synthesis of compound **5**. To a stirred solution of compound **4** (145mg, 0.312mmol, 1.0eq) in $CHCl_3$ (30mL) is added at R.T. Br_2 (0.48mL, 1.50g, 9.37mmol, 30 eq). The mixture is stirred 3h at R.T. EtOH (15mL) is added, and the mixture is stirred 15min at R.T. The solid is collected by filtration and washed with a mixture of $CHCl_3$ and EtOH (7:3, 20mL) to afford pure compound **5** (200mg, 0.182mmol, 58%) as a red solid. The extreme insolubility of the product in common organic solvents only allowed HRMS analysis. **HRMS (ESI-TOF)**: calcd for $C_{22}H_6B_2Br_8F_4N_4S$ $[M+K]^+$,1134.3463; found 1134.3463.

Synthesis of compound **6.** A solution of compound **5** (124.1mg, 0.113mmol) and tributyl(5-hexylthiophen-2-yl)stannane (1.81 mmol, 16 eq) in anhydrous toluene is degassed with Argon. $Pd(PPh_3)_4$ (13mg, 0.0113mmol, 10mol%) is added and the reaction mixture is stirred at 110°C for 16h. The solvent is removed by vacuum distillation. The resulting crude product is purified by column chromatography (PE/DCM 4/1). Trituration in EtOH (20 mL) afforded 104mg of the pure expected product **6** (0.0579mmol, 51%). **^{1}H NMR (400 MHz, C_6D_6)**: δ = 7.93 (d, 4H, ^{3}J=3.7Hz), 7.28 (s, 4H), 7.04 (s, 2H), 6.83 (d, 4H, ^{3}J=3.5Hz), 6.59 (d, 4H, ^{3}J=3.7Hz), 6.56 (d, 4H, ^{3}J=3.5Hz), 2.57 (t, 8H, ^{3}J=7.6Hz), 2.45 (t, 8H, ^{3}J=7.6Hz), 1.41 (t, 8H, ^{3}J=7.5Hz), 1.09-1.21 (m, 48H), 0.87 (t, 12H, ^{3}J=7.2Hz), 0.83 (t, 12H, ^{3}J=7.3Hz). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 151.5, 149.8, 146.8, 139.3, 134.5, 132.9, 132.9, 132.7, 132.3, 128.6, 127.2, 127.2, 126.5, 124.8, 124.4, 34.3, 31.7, 31.7, 31.5, 30.4, 30.3, 28.9, 22.7, 22.7, 22.5, 14.2, 14.2. **^{11}B NMR (128 MHz, C_6D_6)**: δ = 1.74 (t, J_{B-F} = 30.7Hz). **^{19}F NMR (376 MHz, C_6D_6)**: δ = -134.1 (q, J_{F-B}=30.7Hz). **HRMS (ESI-TOF)**: calcd for $C_{102}H_{126}B_2F_4N_4S_9$ [M]+,1793.7627; found 1793.7695.

Synthesis of compound **7**. To a stirred solution of compound **8** (73.7mg, 0.0411mmol, 1.0eq) in anhydrous DCM (100mL) is added at 0°C anhydrous $FeCl_3$ (106mg, 0.657mmol, 16eq). The mixture turns quickly from black to blue. The reaction mixture is stirred at 0°C for 25min. Water (50mL) is added. The organic layer is washed twice with water, dried over $MgSO_4$, filtered off and concentrated under vacuum. Column chromatography (Cyclohexane/DCM 3:2) followed by recrystallization from DCM/EtOH afforded the pure expected product **7** (41.1mg, 0.0230mmol, 56%) as a blue powder. **^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 369K)**: δ = 7.84 (s, 2H), 7.63 (s, 4H), 7.38 (s, 4H), 7.30 (s, 4H), 3.13 (t, 8H, ^{3}J=7.5Hz), 3.00 (t, 8H, ^{3}J=7.4Hz), 1.98 (t, 8H, ^{3}J=7.6Hz), 1.85 (t, 8H, ^{3}J=7.4Hz), 1.56-1.65 (m, 8H), 1.47-1.55 (m, 24H), 1.38-1.44 (m, 16H), 1.02 (t, 12H, ^{3}J=7.2Hz), 0.96 (t, 12H, ^{3}J=7.2Hz). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 154.4, 145.3, 144.8, 139.9, 139.3, 137.1, 131.8, 131.4, 128.2, 126.0, 121.2, 119.8, 119.7, 119.3, 119.1, 30.7, 30.6, 30.4, 30.2, 30.0, 29.7, 28.1, 27.9, 21.7, 21.6. **^{11}B NMR (128 MHz, $CDCl_3$)**: δ = 0.87 (t, J_{B-F} = 32.5Hz). **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = -141.0 (bs). **HRMS (ESI-TOF)**: calcd for $C_{102}H_{118}B_2F_4N_4S_9$ [M]+,1785.7001; found 1785.6989.

Keywords: α-fused BODIPY, panchromatic absorbing materials, high electron affinity material, BODIPY pairing.

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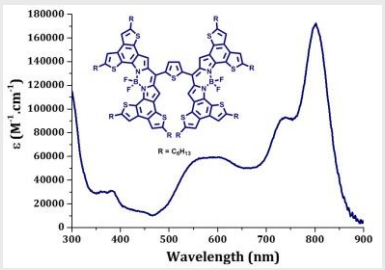

Quentin Huaulmé, Sadiara Fall, Patrick Lévêque, Gilles Ulrich and Nicolas Leclerc**

Pairing of α-fused BODIPY, towards panchromatic n-type semi-conducting materials.

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