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WWW.TSC.Org/njc Registered Charity Number 207890 In a series of solution-processable small molecules, the optoelectronic and photovoltaic properties are strongly impacted by the way of assembling the chemical building blocks.

DAD Crystal 🖪 Nematic ADA

C8H17 C8H11

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Impact of the arrangement of functional moieties within small molecular systems for solution processable bulk heterojunction solar cells

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5 Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

A series of molecules based on thienofluorene derivatives as electron donating (D) and benzothiadiazole as electron accepting (A) moieties have been assembled into a **DAD** and an **ADA** architectures in order to investigate the influence of the way of assembling the D and A units along the conjugated backbone, on the photovoltaic performances of bulk heterojunction solar cells. It was found that the major difference

from going from ADA to DAD architecture is the change of molecular organization (nematic to crystalline) which increases the charge transport mobility and probably also affects the structural organization in blends with PCBM that ultimately leads to higher photovoltaic performances.

Introduction

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- ¹⁵ Recently, organic small molecules have attracted a great interest for their promising photovoltaic properties [1,2]. Reported power conversion efficiencies (PCE) of solution processed small molecules bulk heterojunction (BHJ) solar cells have increased considerably over the last two years reaching values over 7% [2 the base over 7%]
- 20 [3,4]. In regards to their polymer counterparts, small molecules present some advantages. Among them are the better batch-tobatch reproducibility due to their monodisperse nature and the easier purification achievable by using classical chemical techniques such as column chromatography and recrystallization.
- ²⁵ The chemistry of organic semiconducting small molecules for organic photovoltaic (OPV) applications is extremely dense and diversified. Indeed, this field benefits from the remarkable progress in synthetic organic chemistry tools allowing a wide variety of conjugated aromatic moieties and pro-quinoid units.
- ³⁰ Unfortunately, it is very difficult to anticipate the properties of a new class of organic semiconductors due to the lack of systematic studies. Indeed, numerous parameters influence the optoelectronic properties of an organic semiconductor. Some are obvious, such as the choice of the chemical subunits that
- ³⁵ constitute the material [5-9]. On the other hand some parameters are more elusive, such as the nature and the position of solubilizing side chains [10,11], or the way the chosen subunits are assembled [1,12].
- The purpose of this paper is to investigate how properties are ⁴⁰ influenced by the way the specific moieties are assembled into a molecular structure designed for OPV applications. A classical molecular architecture, composed of alternating electron-rich (acceptor **A**) and electron-poor (donor **D**) units, known for leading to low bandgap organic materials has been chosen as
- ⁴⁵ model system. In the present study, the molecular structure was modified so as to obtain donor-acceptor-donor (DAD) or

acceptor-donor-acceptor (**ADA**) conjugated molecules, while maintaining the same aromatic units and approximately the same number of double bonds. The number and nature of the solubilizing alkyl chains were also kept constant in order to minimize related changes in material properties [10,11]. The molecules are made of dioctylfluorene (F) and benzothiadiazole (Bz) units as electron-rich and electron-poor moieties, respectively, and are associated to thiophene (T) units. 55 Thieno(dialkyl)fluorene derivatives are well-known for their high electron donating ability, their good solubility and for promoting the formation of well-ordered films [13,14]. Benzothiadiazole

(Bz) is a good electron acceptor, relatively easy to synthesize and

intensively used with success for OPV applications [15]. ⁶⁰ Using these moieties, two different assemblies were then designed: FT-TBzT-TF for the **DAD** architecture, and the reverse TBzT-TFT-TBzT assembly for the **ADA** architecture. It is fair to notice that comparable **DAD** molecular structures have been reported in the literature but were used as electroluminescent ⁶⁵ materials [16], chemosensors [17] or for morphological studies [18]. The structures of the investigated molecules are presented in figure 1.



DAD Figure 1: Chemical structures of DAD and ADA molecules.

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Figure 2: Synthetic routes for the preparation of the molecules.

Results and discussion

Synthesis and characterizations

The molecules have been prepared using synthetic routes *s* presented in figure 2.

All molecules are based on the same aromatic units using thiophene and fluorene derivatives as electron-rich moieties and benzothiadiazole as electron-deficient moiety. Bromofluorene derivative **1** is condensed by Stille reaction onto a 2-10 trimethyltinthiophene to obtain the corresponding compound **2**. A subsequent bromination at the 5-position of thiophene by using NBS in chloroform solution led to the brominated derivative **3**. The final **DAD** molecule is synthesized by cross-coupling of previous brominated compounds with the TBzT trimer 15 functionalized with two trimethyltin groups: 4,7-bis-(5-(trimethylstannyl)thiophen-2-yl) benzo[1,2,5]thiadiazole [19].

The ADA molecule has been synthesized following another synthetic route, starting from the synthesis of the unsymmetrical bithiophene-benzothiadiazole compound 4, by Stille cross-

- ²⁰ coupling between the 4,7-dibromobenzothiadiazole unit and 5trimethylstannyl-2,2'-bithiophene [21]. After purification by column chromatography, compound **5** is condensed to 5-octyl-2trimethylstannylthiophene [22] to give compound **6**. The latter is then iodinated by adding with 1 equivalent of NIS in a mixture of ²⁵ chloroform and acetic acid to give the iodide compound **7**.
- Finally, the **ADA** molecule is obtained by a Suzuki crosscoupling of compound **6** and the commercially available 2,7diboronic acid-9,9-dioctylfluorene. All molecules have been characterized by ¹H and ¹³C NMR, and the final molecules were
- ³⁰ additionally analyzed by MALDI-TOF technique (see Experimental section).

Thermal and structural properties

Differential scanning calorimetry (DSC) and polarized optical

microscopy (POM) have been performed to investigate the thermal properties of the molecules. The results reveal a very different thermal behavior and a different type of organization for ⁴⁰ both molecules. Indeed, a crystalline state is observed for the **DAD** molecule, with a melting point at 134°C. On the other hand, a nematic liquid crystal phase is observed for the **ADA** molecule, as evidenced by the characteristic Schlieren texture obtained by POM observation (Fig. 3). The nematic phase in **ADA** is quite ⁴⁵ stable and extends up to $T_{iso} = 206$ °C. At low temperatures, a crystalline state, only present during the first heating ramp ($T_m = 102$ °C), leaves out a glassy state at low temperature, *ca* $T_g = 38$ °C (Fig. 3).



Figure 3: DSC thermograms of ADA (heating and cooling run at 10 and 5°C.min⁻¹, respectively) with the image of the nematic texture as observed by polarized optical microscopy at 100°C (inset). Once melted, the nematic phase is limited at room temperature by a glassy state.

55 Optical and electrochemical properties

UV-vis absorption spectra of the molecules in chloroform solution and in thin films are given in Fig. 4. Values are presented in Table 1.



Figure 4: UV-visible spectra of the molecules recorded at 10⁻⁵ mol.L⁻¹ in chloroform solution (straight lines), and in thin film (dashed lines). **DAD** spectra in bold lines and **ADA** spectra in thin lines. Measurements in films are normalized.

Table 1. Optical absorption properties of the molecules

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Molecule	Solution	Solid state		
	λ_{max} (nm) [ϵ (M.cm ⁻¹)]	$\lambda_{max}\left(nm\right)$	E_{\Box}^{opt} (eV)	
DAD	392 [77000]	405	1 78	
	535 [59000]	557	1.76	
ADA	418 [59000]	412	1.85	
	510 [70000]	552		

Both molecules exhibit a two bands feature spectrum as usually 10 observed for an alternating D-A molecule [23]. The high energy band is attributed to a π - π * transition while the low energy one is ascribed to an internal charge transfer (ICT) band. In solution, the **ADA** UV-visible spectrum presents an interesting feature with a significant merging of both bands in comparison to the **DAD** 115 analogue. The red-shift of about 26 nm of the π - π * band could be explained by a conjugation extension of the electron-donating segment in the **ADA** molecule compared to the **DAD** one (i.e. 6 aromatic units in the unique donor segment of **ADA** vs only 4

aromatic units per donor segment in **DAD**). On the other hand, ²⁰ the origin of the 25 nm blue-shift of the ICT band remains unclear.

In solid state, both **DAD** and **ADA** molecules show a red-shift of their maximum absorption wavelengths. The red-shift of both absorption peaks points out enhanced π -stacking interactions in

- ²⁵ the solid state for every investigated molecule. The **DAD** molecule presents a red-shift of 22 nm leading to an optical bandgap of 1.78 eV which has been estimated from the absorption peak onset in the solid state. In agreement with the DSC analysis previously described, this red-shift indicates clearly
- ³⁰ a rather good solid-state organization for the **DAD** molecule (crystalline). The **ADA** molecule shows a stronger red-shift of around 42 nm in solid state, leading to an optical band gap of 1.85 eV. It remains unclear why the **ADA** molecule leads to such a bathochromic effect in its nematic phase, far exceeding what is
- ³⁵ observed in the DAD counterpart in its crystalline state (22 nm). Finally, it is worth noting that the ADA thin solid film presents very broad absorption spectrum with an almost complete merging

of the π - π * and ICT bands.

Furthermore, extinction coefficients have been measured for both ⁴⁰ molecules in solution. **DAD** presents a slightly higher extinction coefficient of 77000 M⁻¹cm⁻¹ compared to 70000 M⁻¹cm⁻¹ in the case of **ADA**. This could be due to a higher molecular orbital HOMO and LUMO overlap in the **DAD** molecule. In order to better understand this specific point, we performed Density ⁴⁵ Functional Theory (DFT) calculations (in vacuum) using Spartan 10 on each molecule [24]. The structures obtained for the two molecules are presented in Fig. 5. To keep the calculation time reasonable, the alkyl side-chains were substituted by methyl groups.



Figure 5: Conformation and electronic structures of the conjugated core of molecules DAD and ADA, with the frontier molecular orbital surfaces HOMO (left) and LUMO (right).

The results clearly show that both the HOMO and LUMO orbitals ⁵⁵ are localized in the central part of the molecule in **DAD**, explaining the higher extinction coefficient measured for this latter molecule. The HOMO orbitals in **ADA** are similarly localized in the central part. In this case however, the LUMO orbitals is more localized onto the two benzothiadiazole moieties.

⁶⁰ The lower molecular orbital overlap, resulting from this unsymmetrical nature, might therefore be responsible for the slightly lower absorption coefficient in the **ADA** molecule.

Cyclic voltammetry investigations were performed in solid state in order to measure the redox potentials and subsequently 65 determine the HOMO and LUMO energy levels of the molecules.

The redox potentials as well as the corresponding HOMO and LUMO levels for all molecules in the solid state are summarized in Table 2.

70 Table 2. Electrochemical properties and energy levels of the molecules.

Molecules	E _{ox} ^{onset} (V)	E _{red} ^{onset} (V)	HOMO (eV)	LUMO (eV)
DAD	1.07	-	5.47	3.69
ADA	0.96	-0.86	5.36	3.51

In solid state, no reduction wave could be detected for the **DAD** molecule. However, it presents a reversible oxidation wave. The HOMO levels have been calculated by using the following ⁷⁵ equation: HOMO (eV) = E_{ox}^{onset} (V) + 4.4 eV (with the assumption that the energy level of ferrocene is 4.4 eV below vacuum level), while the LUMO levels have been calculated by adding the optical bandgap E_{\Box}^{opt} previously measured to the former HOMO value.

⁸⁰ The **ADA** molecule presents both quasi-reversible oxidation and reduction waves. The oxidation potential is observed for a lower

voltage than for **DAD**, leading to a HOMO level value of 5.36 eV. Despite the presence of two electron-accepting benzothiadiazole units in the **ADA** molecule, the electronic affinity is only slightly decreased in comparison to the **DAD** ⁵ molecule. The LUMO level is located at 3.51 eV.

Charge transport and photovoltaic properties

The charge transport was investigated by means of field-effect transistors (FET). The hole mobility value measured for the ¹⁰ nematic **ADA** molecule is 1.4×10^{-5} cm².V⁻¹.s⁻, which is low value but is typical of nematic compounds of low molecular weight [25]. The hole mobility measured for the crystalline **DAD** molecule gives only a slightly higher value of 4×10^{-5} cm².V⁻¹.s⁻¹. This last value is surprisingly low, when considering the ¹⁵ crystalline nature of the corresponding compound. However, since in FET devices charge transport takes place parallel to the substrate plane along the interface with the dielectric layer, this result may point out that the preferential charge transport axes (along the π - π stacking) for the **DAD** molecule is oriented out of ²⁰ plane.

The photovoltaic performances of the two molecules were investigated through their application in classical BHJ solar cells using [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) as electron-accepting component. The devices were fabricated using ²⁵ a glass/ITO/PEDOT:PSS/molecule:PC₆₁BM blend/Al structure, with various molecule:PC₆₁BM weight ratios. The best performances achieved for each molecule are reported in Table 3, together with the corresponding blend ratio.

 $_{30}$ Table 3. Photovoltaic performance of devices based on blends of the molecules and PC_{61}BM, under AM 1.5G illumination of 100 mW.cm^2.

Molecule	Ratio ^a	V _{oc} (V)	J_{sc} (mA.cm ⁻²)	FF (%) ^b	PCE (%)		
DAD	1:1	0.73	7.3	46	2.19		
ADA	1:1	0.68	2.5	33	0.55		
Molecule:PC ₆₁ BM weight ratio ; ^b Fill factor							

The highest power conversion efficiency (PCE) of 2.2% was 35 obtained on a device using a DAD:PC₆₁BM blend with a 1:1 weight ratio and a 180 nm thick active layer (measured by profilometer). This active layer has been obtained by spin-coating a **DAD** solution in chlorobenzene (15 mg.mL⁻¹) using spincoating parameters listed in the experimental part. Under 40 identical experimental conditions (but differing in optimal blend weight ratio with $PC_{61}BM$), a surprisingly low PCE of 0.55% was achieved with the ADA molecule, despite its relevant optoelectronic properties, and the good V_{oc} value of 0.68 V in accordance with the HOMO level measured by cyclic 45 voltammetry [26]. This result most likely arises from the liquid crystalline nature of the ADA molecule that prevents suitable bulk morphology when blended with $PC_{61}BM$. Despite the longrange molecular organization in the nematic phase that should be beneficial for charge transport, its high fluidity is thought to be 50 detrimental by favoring the expulsion of PC₆₁BM out of the

nematic **ADA** medium. This assumption is supported by the rapid collapse of the short circuit current density J_{sc} of the devices with

a relatively low temperature thermal annealing (below 80°C). It is worth mentioning that BHJ solar cells based on blends of ⁵⁵ PC₆₁BM with (smectic) liquid crystal polymers have already been reported in the literature. In most cases, moderate to low PCEs were measured due to poor nanoscale morphology and/or poor exciton dissociation, thus strongly corroborating the fullerene eviction phenomenon from the liquid crystal medium [27-31]. ⁶⁰ This peculiarity should be amplified in the case of **ADA** molecules because of the quite higher fluidity of the nematic

phase (*vs* smectic phase) and the lower molecular weight of the system. The experimental results obtained in the present study constitute therefore a good example of how morphology can ⁶⁵ dominate over frontier orbital energy position in such a complex system as a bulk heterojunction solar cell. A similar conclusion was furthermore drawn from another recent study on donor-acceptor based small-molecules [32].

70 Conclusions

We synthesized molecules made of thieno(dioctyl)fluorene derivatives as electron donating (D) units and benzothiadiazole as electron-accepting (A) units, assembled in DAD and ADA architectures in order to investigate the structure-property 75 relationships of small molecules for solution processable bulk heterojunction solar cells. Surprisingly, both molecules present similar optical properties as well as electronic properties. However, a major difference is observed in their structural behaviors. While **DAD** molecule presents a crystalline nature, ⁸⁰ ADA is a nematic liquid crystal. This structural difference results in deep morphological variations in both molecules in when blended with PC₆₁BM. Indeed, the DAD molecule showed the highest PV performances with a PCE of 2.2% against only 0.5% for the ADA molecule. This indicates that if the optoelectronic 85 properties are strongly dependent on the nature of the chemical sub-unit and less to the way they are assembled along the conjugated backbone, the molecular architecture has also a considerable impact on the solid-state structure and ultimately on the PV performances. Other series of molecules based on the 90 DAD architecture are currently being investigated as solution processable small-molecules for photovoltaic applications.

Experimental section

Materials

All reagents and chemicals were purchased from commercial ⁹⁵ sources (Aldrich, Across, Fluka) and used without further purification. All reactions were carried out in an argon atmosphere. All solvents were distilled over appropriate drying agent(s) prior to use and were purged with nitrogen. The starting 2-bromo(dioctyl)fluorene derivate 1 was prepared by classical ¹⁰⁰ reaction alkylation of the commercial 2-bromofluorene [33].

Characterizations

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 and a Bruker 400 UltrashieldTM NMR spectrometers, with an ¹⁰⁵ internal lock on the ²H-signal of the solvent (CDCl₃). UV-visible

Downloaded by University of Hong Kong Libraries on 23/04/2013 19:46:59. Published on 22 April 2013 on http://pubs.rsc.org | doi:10.1039/C3NJ00218G absorption spectroscopy measurements were performed using a Hitachi U-3000 spectrophotometer. Differential scanning calorimetry (DSC) experiments were performed on a DSC Q2000 from TA Instrument. Optical microscopy observations were made s with a polarizing Leitz Weitzlar microscope equipped with a

- Mettler FP82 heating stage. Cyclic voltammetry analyses were carried out with a BioLogic VSP potentiostat using platinum electrodes at scan rates of 20 mV.s⁻¹. The measurements were performed on thin films drop-casted from chloroform solutions
- ¹⁰ onto a platinum working electrode. A Pt wire was used as counter electrode and Ag/Ag⁺ as reference electrode in acetonitrile containing 0.1 mol.L⁻¹ of tetrabutylammonium tetrafluoroborate. Ferrocene was used as internal standard to convert the values obtained in reference to Ag/Ag⁺ to the saturated calomel ¹⁵ electrode scale (SCE).
- Field Effect Transistors in bottom-contact configuration were elaborated on commercially available pre-patterned test structures whose source and drain contacts were composed of a 30 nm thick gold layer on top of a 10 nm thick Indium Tin Oxide (ITO) layer.
- ²⁰ A 230 nm thick silicon oxide was used as gate dielectric and ndoped $(3x10^{17} \text{ cm}^{-3})$ silicon as gate electrode. The channel length and channel width were 20 µm and 10 mm respectively. The test structures were cleaned in acetone and isopropyl alcohol and subsequently for 15 minutes into an ultra-violet ozone system.
- ³⁰ 60s and 2000 rpm for 120s, acceleration: 200 rpm.s⁻¹) to complete the FET devices. The samples were then left overnight under vacuum (<10⁻⁶ mbar) to remove residual solvent traces. The output and transfer transistor characteristics were measured using a Keithley 4200 Semiconductor Characterization System. All
- $_{35}$ measurements were performed under a controlled (N₂) atmosphere and the charge carrier mobility was extracted from the saturation regime of the transistors transfer characteristics.
- Bulk heterojunction devices were elaborated using the different synthesized molecules as electron donor and $PC_{61}BM$ as electron ⁴⁰ acceptor. The standard device structure was the following:
- ITO/PEDOT:PSS(~40 nm)/small molecules:PC₆₁BM/Al(~120 nm). ITO-coated glass with a surface resistance lower than 20 Ω .sq⁻¹ was used as transparent substrate. Substrates were cleaned sequentially by ultrasonic treatments in acetone, isopropyl cleaked and deisning during a definition of Ω .sq⁻¹
- ⁴⁵ alcohol, and deionized water. After an additional cleaning for 30 minutes under ultra-violet generated ozone, a 40 nm thick PEDOT:PSS layer was spin coated (1550 rpm for 180 s with an acceleration of 500 rpm.s⁻¹) from an aqueous solution and dried for 30 minutes at 120°C under vacuum before being transferred to
- ⁵⁰ the nitrogen filled glove box. The chlorobenzene small molecules: $PC_{61}BM$ solutions were stirred for at least 24 hours at 70°C before spin-coating. An extra stirring for 30 minutes at 100°C was added just before the active layer deposition. The molecule concentration of the solution was varied from 5 mg.mL
- ^{55 1} up to 20 mg.mL⁻¹ in order to obtain different active layer thicknesses (see ESI). The small molecules:PC₆₁BM weight ratio was also varied from 1:0.5 to 1:3. The active layer spin-coating conditions were made in a two-step procedure: step 1 for 180

seconds (speed: 2200 rpm, acceleration: 600 rpm.s⁻¹), then step 2 for 120 seconds (speed: 2500 rpm, acceleration: 600 rpm.s⁻¹). Finally, a 120 nm thick aluminum layer was thermally evaporated and used as cathode. The device active area was 9 mm², while each sample included four independent diodes. The photovoltaic devices were characterized in a controlled (N₂) atmosphere. The 65 light source was a class A Lot-Oriel solar simulator fitted with a AM1.5G filter. The standard 100 mW.cm⁻² illumination power was checked before the photovoltaic measurements using a single-crystal calibrated silicon solar cell. The current *vs* voltage measurements were performed using a Keithley 2400 Source 70 Measurements Unit.

Synthesis

Compound 2: Compound 1 (1 eq.) and 2-(trimethylstannyl)thiophene (1 eq.) were dissolved in toluene 75 (0.05 M). Then, tris(dibenzylideneacetone) dipalladium (0) (Pd₂dba₃) (0.03 eq) and tris(2-methylphenyl)phosphine (P-(otolyl)₃) (0.12 eq) were added. The reaction was degassed and stirred at 110°C for 2 days under argon atmosphere. The mixture was filtered through a celite pad and the solution was 80 concentrated under high vacuum. The crude product was purified

- by column chromatography on silica gel (petrolum ether:CH₂Cl₂) providing the desired compound as a white solid. Yield: 92%. ¹H NMR (300 MHz, CDCl₃), δ : 7,75-7.69 (m, 2H), 7.66-7.58 (m, 2H), 7.41-7.27 (m, 5H), 7.11 (dd, 1H, J = 3.5 Hz, 1.5 Hz), 2.04-1.02 (m, 4U), 1.20.04 (m, 2010), 0.81 (f, 6U, J = 6.0 Hz), 0.72
- ⁸⁵ 1.93 (m, 4H), 1.29-0.94 (m, 20H), 0.81 (t, 6H, J = 6.9 Hz), 0.73-0.55 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ: 151.5, 150.9, 145.3, 140.7, 140.6, 133.2, 128.0, 127.1, 126.9, 124.9, 124.5, 122.9, 120.2, 120.0, 119.7, 55.2, 40.4, 31.8, 30.0, 29.2, 23.7, 22.6. *Compounds 3*: Compound 2 (1 eq) was solubilized in chloroform
- $_{90}$ (0.02 M) at -50°C under argon. Then, NBS (1 eq) was added in one portion and the mixture was stirred over night at room temperature. The organic phase was washed with H₂0 (×3), dried over MgSO₄ and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum
- ⁹⁵ ether:CH₂Cl₂) to provide compound 4 as a green solid. Yield: 94%. ¹H NMR (300 MHz, CDCl₃) δ: 7.72-7.66 (m, 2H), 7.53-7.44 (m, 2H), 7.38-7.29 (m, 3H), 7.18 (d, 1H, *J* = 3.8 Hz), 7.12 (d, 1H, *J* = 3.8 Hz), 2.02-1.91 (m, 4H), 1.32-0.96 (m, 20H), 0.81 (t, 6H, *J* = 7.1 Hz), 0.73-0.59 (m, 4H). ¹³C NMR (75 MHz, 100 CDCl₃) δ: 152.1, 151.3, 147.1, 141.6, 140.8, 132.7, 131.3, 127.7, 127.2, 124.8, 123.4, 123.3, 120.4, 120.3, 120.2, 111.1, 55.6, 40.6,
- 32.1, 30.3, 29.5, 24.1, 22.9, 14.2. 4,7-bis-(5-(trimethylstannyl)thiophen-2-Compounds DAD: vl)benzo[1,2,5]thiadiazole [19] (1 eq) and compound 3 (1.2 eq) ¹⁰⁵ were dissolved in dry toluene (0.05 M). Then, Pd₂dba₃ (0.03 eq) and P-(o-tolyl)₃ (0.12 eq) were added and the reaction was stirred at 120°C for 2 days under argon atmosphere. Then, the mixture was filtered through a celite pad and the solution was concentrated under high vacuum. The crude product was purified ¹¹⁰ by column chromatography on silica gel (petrolum ether:CH₂Cl₂) providing the desired final compound as a purple solid. Yield: 63%.¹H NMR (300 MHz, CDCl₃,) δ: 8.09 (s, 2H), 7,90 (s, 2H), 7.76-7.74 (m, 4H), 7.66-7.63 (m, 4H), 7.47-7.27 (m, 12H), 2.18-1.98 (m, 8H), 1.38-1.03 (m, 40H), 0.84 (t, 12H, J = 6.7 Hz), 0.77-115 0.58 (m, 8H). ¹³C NMR (75 MHz, CDCl₃) δ: 152.5, 151.6, 150.9, 144.5, 141.0, 140.5, 139.0, 137.9, 136.1, 132.7, 128.3, 127.2,

126.8, 125.5, 125.1, 124.9, 124.5, 124.3, 123.6, 122.9, 120.1, 119.8, 119.7, 55.2, 40.3, 31.8, 30.0, 29.2, 23.7, 22.6, 14.0. MS (Maldi-TOF): m/z calcd 1240.586; found 1240.644 [M⁺].

- Compound 4: To a solution of 4,7-dibromobenzothiadiazole [20] 5 (7.32 g, 26.52 mmol) and 5-trimethylstannyl-2,2'-bithiophene [21] (8.73 g, 26.52 mmol) in toluene (200 mL), P-(o-tolyl)₃ (0.65 g, 2.12 mmol) and Pd₂dba₃ (0.49 g, 0.53 mmol) were added. The reaction mixture was degassed and heated at 110°C during 2 days. After cooling, the reaction mixture was filtered through a
- 10 silica pad and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether with gradual introduction of CH₂Cl₂) to give the product as a red-orange solid (2.92 g, 29 %). ¹H NMR (300 MHz, CDCl₃,) δ : 8.03 (d, 1H, J = 3.9 Hz), 7.86 (d, 1H, J = 7.815 Hz), 7.71 (d, 1H, J = 7.8 Hz), 7.33-7.24 (m, 3H), 7.06 (dd, 1H, J = 3.6 Hz, J = 5.1 Hz).
- Compound 5: To a solution of bromide 4 (2.92 g, 7.69 mmol) and trimethyl(5-octyl-2-thienyl)-stannane [22] (4.15 g, 11.55 mmol) in toluene (70 mL), P-(o-tolyl)3 (0.18 mg, 0.62 mmol) and 20 Pd2dba3 (0.14 mg, 0.15 mmol) were added. The reaction mixture was degassed and heated at 110°C during 2 days. After cooling, the reaction mixture was filtered through a silica pad and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether with 25 gradual introduction of CH₂Cl₂) and by recrystallization (CH₂Cl₂:methanol) to give the product as a red solid (2.73 g, 72 %). ¹H NMR (300 MHz, CDCl₃,) δ : 8.02 (d, 1H, J = 3.9 Hz), 7.95 (d, 1H, J = 3.7 Hz), 7.84 (d, 1H, J = 7.7 Hz), 7.79 (d, 1H, J = 7.7 Hz), 7.32 – 7.24 (m, 3H), 7.06 (dd, 1H, J = 3.6 Hz, 5.1 Hz), $_{30}$ 6.88 (d, 1H, J = 3.4 Hz), 2.89 (t, 2H, J = 7.6 Hz), 1.83-1.68 (m, 2H), 1.48-1.19 (m, 10H), 0.89 (t, 3H, J = 6.9 Hz). ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3) \delta$: 152.7, 152.6, 148.3, 138.7, 138.3, 137.5, 136.8, 128.1, 127.8, 126.4, 125.5, 125.4, 125.1, 124.9, 124.7, 124.1, 32.0, 31.8, 30.5, 29.5, 29.4, 29.3, 22.8, 14.3.
- 35 Compound 6: NIS (231 mg, 1.027 mmol) was added in 2 portions at room temperature to a solution of compound 5 (0.48 g, 0.98 mmol) in a mixture of chloroform (22 mL) and acetic acid (13 mL) under argon and in darkness. The reaction mixture was stirred overnight, then water was added (30 mL). The organic
- ⁴⁰ phase was washed with $H_2O(\times 3)$, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether:CH₂Cl₂; 8:1) to provide the final compound as an orange solid (0.55 g, 91%). ¹H NMR (300 MHz, CDCl₃) δ : 7.98 (d, 1H, J = 3.9 Hz), 7.95 (d,
- 45 1H, J = 3.7 Hz), 7.83 (d, 1H, J = 7.6 Hz), 7.78 (d, 1H, J = 7.6 Hz), 7.19 (d, 2H, J = 3.8 Hz), 6.95 (d, 2H, J = 3.8 Hz), 6.88 (d, 2H, J = 3.7 Hz), 2.87 (dd, 2H, J = 7.5 Hz, 7.6 Hz), 1.83-1.67 (m, 2H), 1.49-1.18 (m, 10H), 0.89 (t, 3H, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 152.7, 152.6, 148.4, 143.4, 138.9, 138.0, 137.4,
- 50 136.8, 128.0, 127.9, 126.7, 125.7, 125.5, 125.4, 125.1, 125.0, 124.9, 32.0, 31.8, 30.5, 29.5, 29.4, 29.3, 22.8, 14.3. Compound ADA: THF (4 mL) and water (1 mL) were added to a
- stirred, degassed mixture of iodide 6 (0.20 g, 0.32 mmol), 9,9dioctylfluorene-2,7-diboronic acid (0.07 g, 0.14 mmol) and
- 55 potassium carbonate (0.08 mg, 0.56 mmol). The mixture was degassed and P-(o-tolyl)₃ (7 mg, 0.02 mmol) and Pd₂dba₃ (5 mg, 0.0056 mmol) were added. The reaction mixture was degassed again and heated at 80°C for 3 days. Then the solution was

cooled to room temperature and water was added. The crude 60 product was extracted from CH₂Cl₂ (3×5 mL). The combined dichloromethane extracts were washed with brine and dried over Na₂SO₄. The desiccant was filtered off, the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel (petroleum ether with gradual 65 introduction of CH₂Cl₂) and recrystallization (CH₂Cl₂:methanol) to give ADA compound as a red solid (0.13 mg, 65 %). ¹H NMR $(300 \text{ MHz}, \text{CDCl}_{3}) \delta$: 7.99 (d, 2H, J = 3.9 Hz), 7.94 (d, 2H, J =3.6 Hz), 7.82 (d, 2H, J = 7.6 Hz), 7.76 (d, 2H, J = 7.6 Hz), 7.64 (d, 2H, J = 8.4 Hz), 7.59 – 7.53 (m, 4H), 7.34 (d, 2H, J $_{70} = 3.7 \text{ Hz}$, 7.29 (d, 2H, J = 3.7 Hz), 7.26 (d, 2H, J = 3.6 Hz), 6.87 (d, 2H, J = 3.6 Hz), 2.88 (t, 4H, ${}^{3}J = 7.6$ Hz),), 2.12-1.96 (m, 4H), 1.83-1.67 (m, 4H), 1.49-0.99 (m, 40H), 0.94-0.65 (m, 16H). ¹³C NMR (75 MHz, CDCl₃) δ :152.7, 152.6, 152.0, 148.2, 144.4, 140.6, 138.8, 138.2, 136.9, 136.5, 133.0, 128.2, 127.8, 75 126.4, 125.4, 125.2, 124.8, 124.5, 123.9, 120.5, 119.8, 55.5, 40.5, 32.04, 31.96, 31.7, 30.5, 30.2, 29.8, 29.5, 29.5, 29.2, 24.0, 22.8, 22.7, 14.25, 14.21. MS (Maldi-TOF): m/z calcd 1374.493; found

Acknowlegments

1374.508 [M⁺].

⁸⁰ The research was supported by the French government via the ANR grant (PICASSO project ANR-11-BS08-0009) and the European Community via the Interreg IV-A program (C25, Rhin-Solar, www.rhinsolar.eu). The authors are grateful to Dr. Benoît Heinrich for carrying out the DSC analyses and Nicolas 85 Zimmermann for his contribution to device elaborations.

Notes and references

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