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FULL PAPER

Toward sustainable organic semiconductors from a broad palette of green reactions

Alexandre Faurie,[a] Jérémie Grolleau,[a] Frédéric Gohier,[a] Magali Allain,[a] Stéphanie Legoupy*[a] and Pierre Frère*[a]

Abstract: New conjugated materials, based on triphenylamine-thiophene moiety and integrating azomethine bonds with dibenzofuran unit or cyanovinyl bond with phenyl-thiophene and bithiophene units, have been synthesized by using a wide range of green reactions such as direct heteroarylation coupling reaction, Knoevenagel and Schiff base condensations and Stille cross coupling reaction from ionic liquid supported thiophenstannane. The electronic properties of the new molecules were analyzed by using UV/Vis spectroscopy and cyclic voltammetry. The potential use of the molecules as donor materials for photovoltaic conversion were evaluated in simple bilayer solar cells by using C_{60} fullerene as acceptor material.

Introduction

Extended conjugated systems are the focus of extensive researches motivated by their potentials as organic semiconductor materials used for the development of large area, lightweight and flexible optoelectronic devices such as organic field-effect transistors (OFET), organic electroluminescent diodes (OLED) and organic photovoltaic cells (OPC).[1] Currently in the field of organic photovoltaics, a large part of the works focuses on the design of new conjugated materials for increasing the performances of the devices,[2] thus leading to more complex extended molecular structures, polymers or small molecules.[3] The conception of most conjugated materials induces long synthetic routes and the formation of more and more wastes, making difficult to claim the green and low cost criteria for the synthesis of organic-semiconductors. For three years, several reviews emphasized the importance of integrating the green chemistry concepts to the conception of organic semiconductor materials.[4] It has evidenced that cleaner and cheaper routes toward conjugated systems can be achieved by handling: (i) green condensation reactions such as Knœvenagel reactions or Schiff base chemistry allowing to develop ethylenic or imine bonds,[5] (ii) direct C-H arylation reactions for the extension of heterocycle systems by avoiding organometallic coupling reactions.[6] However, to merit the sustainable appellation, the green synthetic procedures must involve all the synthetic steps and do not have to limit to the last step. Moreover, basic concepts must be respected, as the non-use of chlorinated solvents or the non-formation of by-products, especially if toxic, needing laborious purifications using large amounts of solvent.

As a further step in our contribution on the synthesis of organic semiconductors via green approaches,[7] we have explored the synthesis of new conjugated materials by exploiting a wide range of various green reactions. Within the class of conjugated materials, the donor-acceptor (D/A) approach with electron-donating (D) and electron acceptor (A) blocks in the conjugated backbone is currently one of the most widely investigated materials for the development of electronic plastics.[8] Thus we have focused on the synthesis of D/A molecules **I** and **IIa,b** including the triphenylamine (TPA) -thiophene moiety for the donor block (Figure 1). For molecule **I**, the central acceptor part is constituted by an imino-pentafluorobenzodifuran moiety, while for unsymmetrical compounds **IIa,b** the acceptor block corresponds to a cyanovinyl unit. The electronic properties of the new derivatives and the results of prototype of bilayer solar cells performed with **I** and **IIa,b** as donor and C_{60} as acceptor materials are also presented.

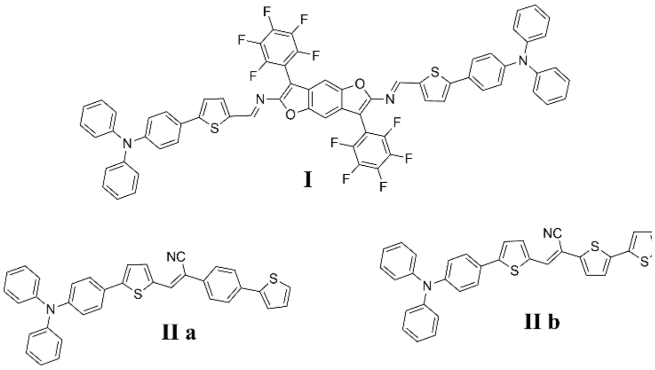

Figure 1. Structures of new conjugated systems **I** and **II** based on TPA moiety.

Results and Discussion

The eco-friendly synthetic pathways for preparing **I** and **IIa,b**, presented in Scheme 1, are based for the first step on the

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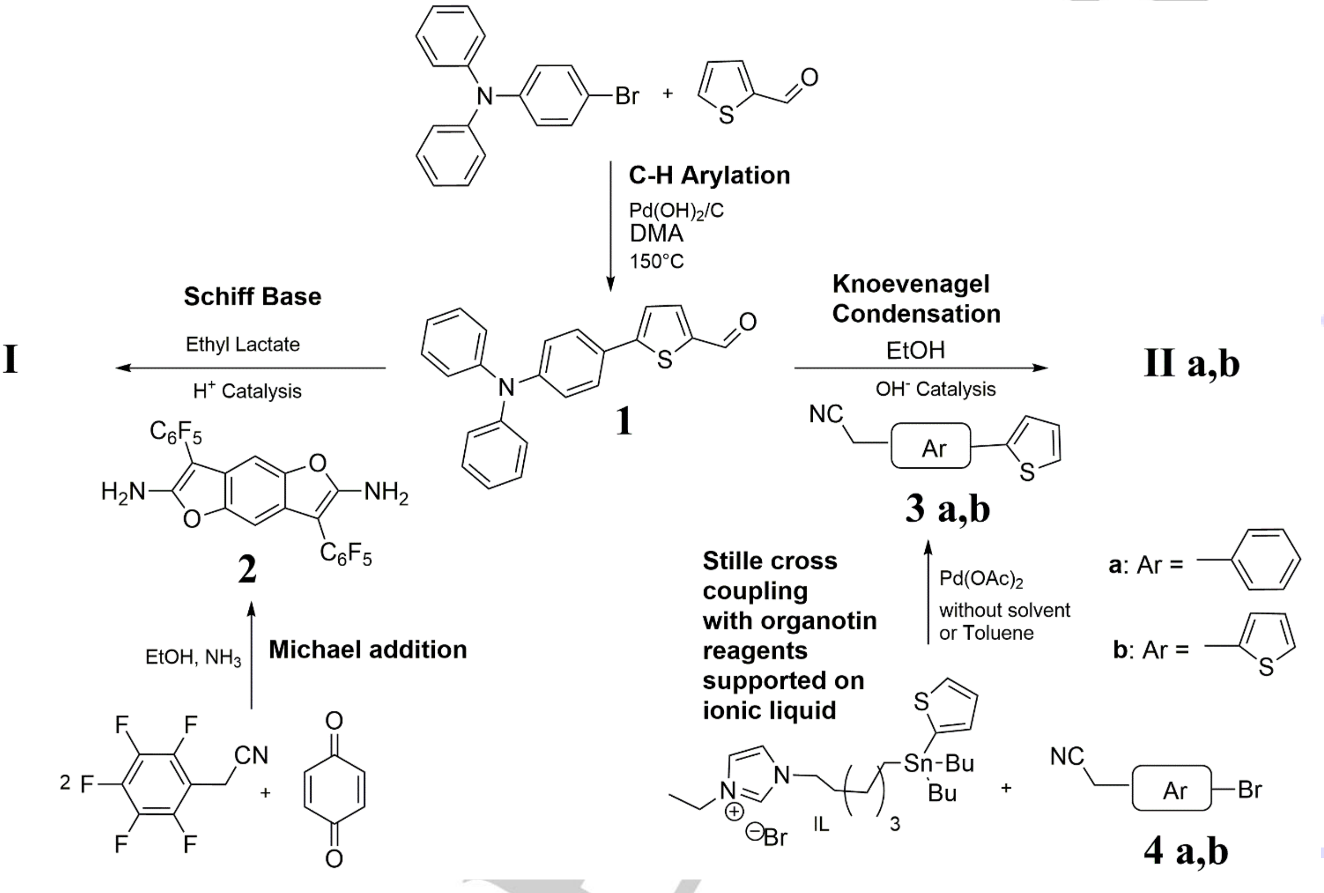
Supporting information, including the electrical characteristic of the solar cells (Figure S1) and NMR spectra of compounds I, IIa,b, is given via a link at the end of the document.

synthesis of aldehyde of the TPA-thiophene unit **1**, easily and rapidly obtained via a direct heteroarylation coupling reaction. The last steps correspond to condensation reactions with diaminobenzodifurane **2** or thiophene-aryl-acetonitrile **3**.



Scheme 1. Synthetic pathways of **I** and **IIa,b** .

These last derivatives are obtained in one step by green reactions; double Michael addition for **2** and Stille cross coupling with ionic liquid supported organotin reagents.

Since the first demonstration of direct arylation of thiophene with aryl-halide by Ohta and coworkers in 1990,[9] this methodology is more and more used for the development of extended conjugated materials based on thiophene moiety for optoelectronic applications. In 2011, Fagnou et al. demonstrated that TPA-Thiophene carbaldehyde **1** could be synthesized by direct arylation route from 2-formyl thiophene[10] instead of Stille[11] or Suzuki[12] reactions. The direct coupling proceeded in 72 % yield by heating at 100°C in toluene for 16h a stoichiometric mixture of Br-TPA and thiophene carboxaldehyde in presence of phosphine derivative $PCy_3.HBF_4$ (10 - 12 mol %), pivalic acid (30 mol %), K_2CO_3 (3 equiv.) and $Pd(OAc)_2$ (6 mol %).[7c] Without phosphine in the same conditions, the yield fell to less of 5%. A column chromatography on silica gel was necessary to purify the aldehyde **1**. We have sought to simplify the procedure by using a heterogeneous catalyst such as $Pd(OH)_2/C$ (Pearlman's catalyst).[7b, 13] Thus by using stoichiometric amount of thiophene carbaldehyde and TPA-Br, potassium acetate (3 equiv.) and palladium hydroxide on carbon (3% mol. in $Pd(OH)_2$) in dimethylacetamide (DMA) at 150 °C, the compound **1** was isolated in 60 % yield after simple filtration on a small plug of silica gel. Between the two methods, on the one hand the use of homogeneous catalysis allows to less heating for obtaining **1** in a slight better yield, on the other hand with the Pearlman's catalyst there is no need to use the expensive phosphine derivative and the purification is easier allowing to handle less solvent.

The first titled compound **I** has been obtained by a double condensation between the diaminobenzodifurane **2** and 2 equiv. of aldehyde **1** performed at room temperature in ethyl lactate as green solvent with acid catalysis (trifluroacetic acid 5% mol.).[7a] Addition of water in the mixture favors the precipitation, then the filtered solid is washed three times with ethanol to give **I** as a red solid in 70 % yield. As already described, the diamino compound **2** is rapidly obtained in one step by a double Michael addition between benzoquinone and 2 equiv. of pentafluoroacetonitrile in the presence of aqueous ammoniac solution in ethanol.[14]

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Single crystal of **I**, obtained by slow evaporation of chloroform solution, has been analyzed by X-ray diffraction. The latter crystallizes in the triclinic P-1 space group. The phenyl of the TPA connected to the thiophene and the azomethine junction in a E configuration are in the plane defined by the benzodifuran systems (Figure 2). Each lateral pentafluorophenyl cycle assumes a torsional angle of 54° with respect to the benzodifuran plane. The molecules stack along the b axe such as the central benzodifurane moiety of a molecule overlaps the iminothiophene part of the molecules above and below. The distance between two consecutive planes formed by BDF units is of 3.80 Å.

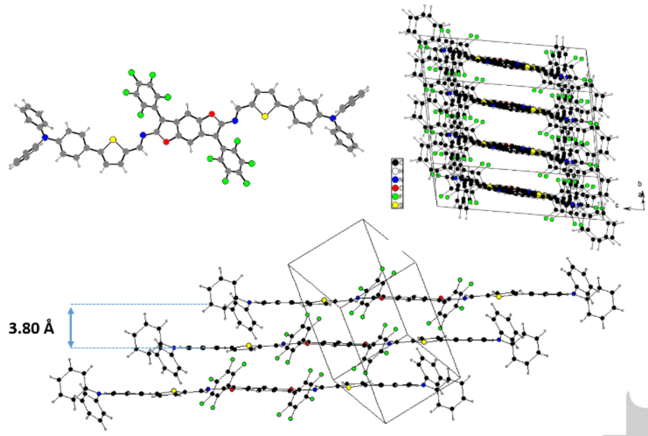

Figure 2. X-ray structure of **I**

The syntheses of the acetonitrile derivatives **3a,b** from bromo-arylacetonitrile **4a,b** have been already reported, either by direct arylation coupling with an excess of thiophene (**3a** in 62% yield)[15] or by Suzuki reaction with the thiophene boronic acid derivative (**3b** in 38% yield).[16] In this work, we have explored the use of thiophenstannane supported on ionic liquid[17] in Stille cross-coupling reaction as a new method for synthesizing **3a,b**. The Stille reaction is extensively used for the synthesis of conjugated materials[18] due to many advantages of the organostannanes compared to other organometallics such as their readily syntheses, their water- and air-stability and their tolerance towards many functional groups. Moreover, the Stille reaction requires mild reaction conditions without additive of expensive ligand to give high yields.[19] However, organic tin chemistry presents disadvantages such as pollution of obtained conjugated materials by tin salts and difficulties of separation. Efforts have been made to overcome these problems, leading, for example, to the development of synthetic methods using organotin reagents supported [20] on polymers [21] or ionic liquids.[22] On the other hand, it has been shown that Stille cross-coupling reactions with organotin reagents supported on ionic liquid could be performed without solvent or additive by using commercially available catalysts.[22-23] The cross-coupling products were obtained by using simple purification techniques and the contamination by tin wastes was limited. Organotin compound was recycled five times with good yield and reused in Stille cross-coupling reactions without loss of reactivity. The Stille reaction with ionic liquid supported thiophenstannane on brominated acetonitrile derivatives **4a,b** have been tested without solvent in presence of $Pd(OAc)_2$ as precatalyst. After 18h heating at 80°C, the target coupling products **3a,b** were obtained by extraction with diethyl ether in 45 % and 50 % yields respectively. The reaction has also been performed by using toluene as solvent at 80 °C. After 18h stirring the solvent was removed and the coupling products **3a,b** were isolated in 50 and 53 % yields respectively, by simple extraction with diethyl ether.

The Knoevenagel condensations between aldehyde **1** and the acetonitrile derivatives **3a,b** were performed in ethanol as solvent in presence of a catalytic amount of ^{t}BuONa. After 18h stirring at room temperature, the precipitate was filtered then washed with ethanol to give the pure target molecules **IIa** and **IIb** as red solids in 70 and 80 % yields respectively.

The electronic properties of the titled molecules have been evaluated by theoretical calculations and analysed by UV-Vis spectroscopy and cyclic voltammetry. Theoretical and experimental data are gathered in Table 1.

Theoretical calculations were performed at the ab initio density functional level with the gaussian09 package by using Becke's three parameter gradient corrected functional (B3LYP) with a polarized 6.31G(d,p) for the HOMO and LUMO determinations. The optimized structures and the contours of the orbitals for the HOMO and LUMO levels are presented in Figure 3.

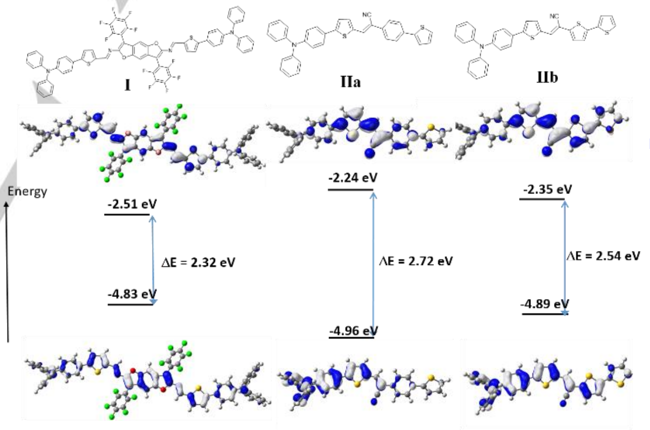

Figure 3. Calculated HOMOs and LUMOs (B3LYP/6-31G(d,p). and energy levels for the compounds **I** and **IIa,b**.

The optimized structure of **I** is very close to that obtained from X-ray, ie good planarity of the conjugated system including the benzodifurane moiety and the two imino-thiophene units while the lateral pentafluorophenyl cycles have a torsional angle of 49° with the benzodifurane plane. The HOMO is allocated on the TPA units and on all the conjugated system. The LUMO is delocalized on the benzodithiophene and the two thiophene-imino units. For the two compounds **IIa,b**, the structures are almost identical and, they present planar structures of the conjugated backbones and a torsion of the outermost phenyl units of TPA. The HOMOs are

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allocated on the TPA – thiophene units and extended to the phenyl or thienyl cyanovinyl units. The LUMOs are mainly delocalized on the central part of the molecules including thiophene-cyanovinyl-thiophene or phenyl units. Compound **I** with the longer extended system presents the lowest band gap ΔE = 2.32 eV. Between **IIa** and **IIb**, the replacement of the external phenyl-thiophene in **IIa** by a bithiophene in **IIb** unit allows both to destabilize the HOMO and stabilize the LUMO leading to a reduction of the band gap of 2.72 to 2.54 eV.

Table 1. Theoretical band gap, experimental absorption data and cyclic voltammetry data of compounds **I** and **IIa,b**.

Cpds	ΔE_{Theo}[a] eV	λ_{max}[b] nm	ΔE_{opt}[c] eV	E_{ox1}[d] V	E_{ox2}[d] V	E_{red}[d] V	ΔE_{Elec}[e] eV
I	2.32	303 536	1.90	0.84	1.26	-1.20	2.04
IIa	2.72	301 431	2.38	1.06	1.24	-1.28	2.34
IIb	2.54	304 451	2.25	0.97	1.05	-1.22	2.19

[a] B3LYP/6-31G(d,p). [b] 2 10^{-5} M in CH_2Cl_2 [c] Optical band gap calculated from the edge of the absorption band. [d]10^{-3} M in 0.1 M Bu_4NPF_6/CH_2Cl_2, scan rate 100 mV s^{-1}, Pt working electrode, ref. SCE. [e] Electrochemical band gap $\Delta E_{Elect} = E_{ox1} - E_{red.}$

The UV-vis absorption spectra of **I** and **IIa,b** in CH_2Cl_2 exhibit two distinct absorption bands (Figure 4). The high-energy band with a maximum around 300 nm could be assigned to the specific transition involving TPA. The second band around 430-450 nm for **IIa**,**b** and at 534 nm for **I** corresponds to the classical π–π*. The smallest band gap calculated from the foot of the absorption band is 1.90 eV for the more extended compound **I**. Between compounds **IIa,b**, the red shift observed for **IIb** corresponds to a better electronic delocalization through thiophene cycle, less aromatic than the phenyl.

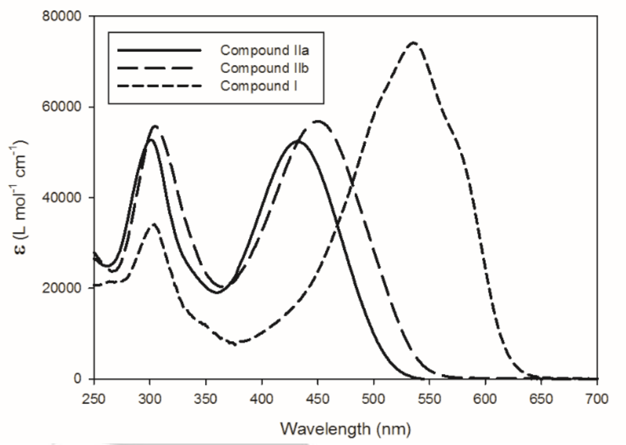

Figure 4. UV-Vis absorption spectra of compounds **I** and **IIa,b** in CH_2Cl_2.

Cyclic voltammetry (CV) was performed in methylene chloride in the presence of 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The CV of **I** (Figure 5 top) presents two oxidation waves with anodic peaks E_{ox1} and E_{ox2} at 0.84 and 1.20 V respectively. The analysis of the oxidation processes shows that the difference between the anodic and the cathodic peaks ($\Delta Ep = Ea_{ox1} - Ec_{ox1}$) of the reversible oxidation waves is 40 mV for the first oxidation process and 70 mV for the second. Considering the theoretical 60 mV expected for a mono-electronic process, we can stipulate for the first oxidation wave, a bi-electronic process giving directly a dication $\mathbf{I}^{++}$,[24] followed by another one-electron oxidation in $\mathbf{I}^{+3\cdot}$. The large extended conjugated structure of compound **I** favours the access to polycationic state. In reduction compound **I** presents an irreversible peak at E_{red} = -1.30 V.

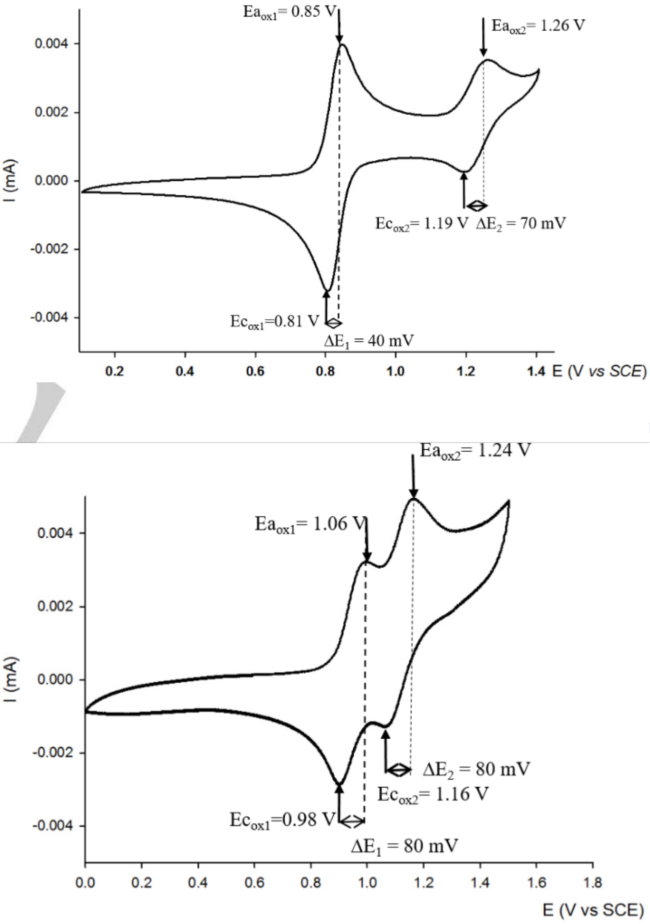

Figure 5. CVs of **I** (top) and **IIa** (bottom) 10^{-3} mol L^{-1} in 0.1 M Bu_4NPF_6 in CH_2Cl_2, v = 100 mV s^{-1}

For the less extended compounds **IIa,b**, the two one-electron oxidation processes (Figure 5 bottom for **IIa**) correspond to the formation of radical cation $\mathbf{II}^{+\cdot}$ and dication $\mathbf{II}^{++}$. Compared to **I**, the

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values of the first oxidation potentials E_{ox1} are positively shifted at 1.06 V and 0.90 V for **IIa** and **IIb** respectively indicating a stabilization of the HOMO level, thus confirming the theoretical calculations. Between **IIa** and **IIb**, the replacement of phenyl by thienyl cycle leads to a slight cathodic shift of 160 mV for **IIb** indicating a better electronic delocalization. Both **IIa,b** show irreversible reduction peaks at -1.28 and -1.22 V respectively.

The potentialities of these molecules as donor materials in photovoltaic devices have been evaluated in basic bilayer planar heterojunction solar cells (PHJ) by using C_{60} as acceptor materials. The cells of 0.28 cm^2 area were fabricated using the classical procedure. The electrical characteristic of the solar cells under AM 1.5-stimulated solar irradiation at 80 mW cm^{-2} are gathered in Table 2 and Figure S1 (in supporting information) presents the plots of current density versus voltage of PHJ cells based on **I** and **IIa**.

Table 2. Photovoltaic characteristics of PHJ cells based on donors **I** and **IIa,b** under 1.5 simulated solar illumination at 80 mW cm^{-2}.

Entry	Cpd	T $_{annealed}$[a] °C	V_{oc} V	J_{SC} mA cm^{-2}	FF	PCE %
1	**I**		0.84	4.13	0.40	1.73
2	**I**	100	0.77	4.36	0.35	1.56
3	**IIa**		0.72	2.85	0.44	1.11
4	**IIa**	130	0.68	4.69	0.48	1.92
5	**IIb**		0.58	3.17	0.30	0.46

[a] After 5 min annealing.

For compound **I**, the cells before annealing (entry 1) present a photovoltaic effect with an open circuit voltage (V_{oc}) of ca 0.84 V, a short-circuit current density (J_{SC}) of 4.13 mA.cm^{-2} and a fill factor (FF) of 0.36, resulting in an average PCE of 1.73 %. Tests of annealing at different temperatures (example at 100 °C, entry 2) showed decreased performances of the cells due to a concomitant decrease of V_{oc} and FF. After prolonged annealing, a significant deterioration of the films was observed. For compounds **IIa,b**, high difference in the photovoltaic effects were obtained. Cells built with **IIb** (entry 5) presented small PCE of 0.46 % with a small fill factor of 0.30 and the smaller V_{oc} of 0.58V. A rapid deterioration of the cells was observed during the tests of annealing. By using **IIa** as donor material, the PCE raised to 1.11 % (entry 3) with a V_{oc} of 0.72 V and a FF of 0.44. For this material, annealing at 130 °C during 5 min allowed to enhance the performance to reach a PCE of 1.92 % due to a large enhancing of the current density that increased from a value of 2.84 to 4.69 mA cm^{-2}. The external quantum efficiency (EQE) spectra for the best cells built with **I** and **IIa** were recorded under monochromatic irradiation (Figure 6). For the cell based on **I**, the spectrum shows a broad wave extending from 350 to 650 nm with a maximum at 390 nm, probably corresponding in part to the contribution of C_{60} to the photocurrent, followed by a shoulder around 600 nm due to the compound **I**. The cell based on **IIa** presents a first peak at 355 nm following by a broad band extending up to 580 nm with the highest contribution for the photocurrent at 420 nm corresponding to the absorption of **IIa**.

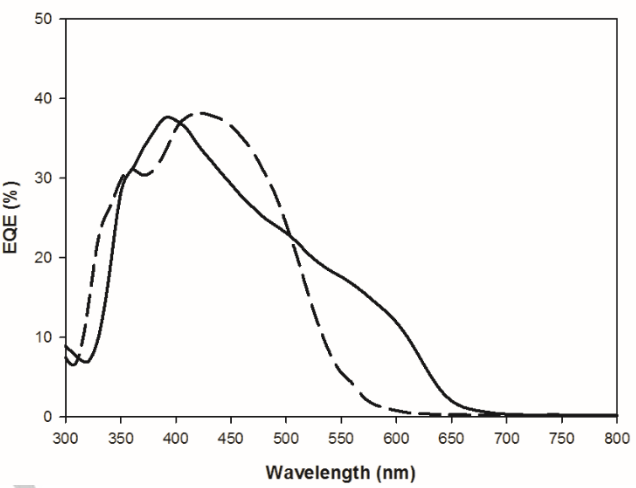

Figure 6. External quantum efficiency (EQE) of the cells produced with donors **I** (solid line) and **IIa** (dashed line).

Conclusions

Two series of conjugated small molecules have been synthesized by exploiting various green reactions. The coupling reactions of heterocycles have been carried out by seeking either to limit the formation or to suppress the diffusion of metallic by-products. For the first case, direct heteroarylation coupling reaction has been realized between TPA and thiophene carbaldehyde using an extremely simple procedure with heterogeneous [Pd] catalysis. For the second case, Stille cross coupling were performed from thiophenstannane supported on ionic liquid, not generating small brominated stannyl byproducts. The synthetic procedures were realized without solvent or in presence of small amount of toluene while the target compounds were purified by a simple extraction with diethyl ether. All the other reactions, Michael addition, Knoevenagel and Schiff base condensations giving only water as by-products were carried out at room temperature and in green solvents such as ethanol or ethyl lactate. Moreover, one the main interest of this approach resides in the ease and rapidity of obtaining the target molecules. The study of the electronic properties shows that these small molecules, based on TPA-thiophene moieties and integrating azomethine bonds with dibenzofuran unit or cyanovinyl bond with phenyl-thiophene and bithiophene units, present optical properties and energy levels adapted to be used as donor materials for photovoltaic conversion. The compatibility of the new small molecules for the OPV has been shown with the first attempts in simple bilayer solar cells by using C_{60} as acceptor materials leading to performances reaching up to 2% of PCE.

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Experimental Section

Synthesis

*Preparation of **1** by Direct C-H heteroarylation with heterogeneous catalysis*

To a solution of 4-bromo-*N*,*N*-diphenylaniline (300 mg, 0.91 mmol), potassium acetate (277 mg, 2.82 mmol, 3.1 eq), palladium hydroxide on carbon (20 wt. % loading) (71 mg, 10% mol) in dimethylacetamide (6 ml) degassed with argon during 20 min was added 2-thiophenecarboxaldehyde (85 µL, 0.91 mmol). The mixture was stirred at 150°C during 16h, cooled and poured into water (50 mL). The organic layer was extracted with ethyl acetate (30 mL), dried over anhydrous $MgSO_4$ and solvent was removed. The residue was purified by a flash chromatography over 2cm silica gel (Hexane/AcOEt: 60/40) to afford a yellow solid (195 mg, yield: 60%).

m.p. 88-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ [ppm] = 9.85 (s, 1H); 7.71 (d, 1H, J=4.0Hz); 7.52 (d, 2H, J=8.8Hz); 7.34-7.26 (m, 5H); 7.17-7.04 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ [ppm] = 182.8, 154.8, 149.4, 147.2, 141.6, 137.9, 129.7, 127.5, 126.4, 125.4, 124.1, 123.1, 122.6; HRMS (FAB) calcd for $C_{23}H_{17}NOS$ [M^+]: 355.1031, found: 355.1028

*Preparation of **I** by Schiff base condensation*

To a solution of **1** (220 mg,0.62 mmol) in ethyl lactate (8 ml) stirred at room temperature was added diaminobenzofuran (150 mg, 0.29 mmol) and a catalytic amount of trifluoroacetic acid (0.1 ml). After a night at RT, water (20 ml) was added and the precipitate was filtered and triturated with methanol to give a red solid (240 mg, yield 70%).

m.p. > 260 °C;^{1}H (300 MHz, $C_2D_2Cl_4$, TMS): δ [ppm] = 8.96 (s, 1H); 7.57 – 7.52 (m, 6H); 7.44 (s,2H); 7.34-7.29 (m, 10H), 7.17-7.05 (m, 16H); ^{19}F ($CDCl_3$): -137.0 (dd, 4F, J=21.8 Hz, J = 7.0 Hz); -154.6 (t, 2F, J=21 Hz), -162.2 (td, 4F, J = 21.8 Hz, J= 7.0 Hz); HRMS (MALDI-TOF) calcd for $C_{66}H_{36}N_4O_2S_2$ [M^+]: 1194.2120, found: 1194.2112.

General procedure for the Stille coupling with ionic liquid supported organotin reagents

1-(6-(Dibutyl(thiophen-2-yl)stannyl)hexyl)-3-ethyl-1H-imidazol-3-ium bromide has been prepared as already described.[17]

Under inert atmosphere, a mixture of ionic liquid (1 equiv.), aryl bromide (1equiv.) and palladium acetate (0.05 equiv.) without toluene or with 5 mL of toluene was heated at 80 °C or 110 °C during 17h. The mixture was cooled, the co-solvent was evaporated in vacuo then the residue was treated with diethyl ether to extract the compound and the crude product was purified via flash chromatography over 2cm silica gel (Hexane/AcOEt: 60/40).

Compound **3a**
M.p. 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ [ppm] = 7.63 (d, 2H, *J* = 8.2 Hz); 7.35-7.30 (m, 4H); 7.10 (dd, 1H *J*= 5.0 Hz, *J*=3.7 Hz), 3.77 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ [ppm] =143.3, 134.4, 128.9, 128.5, 128.2, 126.6, 125.3, 123.6, 117.7, 23.4; HRMS – CI : Calculated for $C_{12}H_9NS$ 199.0456; found 199.0451.

Compound **3b**
M.p. 62 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ [ppm] = 7.24 (dd, 1H, J = 5.1 Hz, *J*=1.0 Hz); 7.13 (dd, 1H J=3.6 Hz, J=1.0 Hz), 7.03 -7.01 (m, 2H); 6.97-6.96 (m, 1H); 3.89 (d, 2H, *J*=1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ [ppm] =138.1, 136.4, 129.5, 127.8, 127.7, 124.9, 124.1, 123.5, 116.6, 18.7; HRMS – CI : Calculated for $C_{10}H_7NS_2$ 205.0020; found 205.0017.

*General procedure for preparation of **IIa** and **IIb** by Knoevenagel reaction*

To a solution of aldehyde **1** (100 mg, 0.28 mmol) and acetonitrile derivative **3a** (56 mg, 0.28 mmol) or **3b** (58 mg, 0.28 mmol) in 10 mL of EtOH was added a catalytic amount of sodium tert-butoxide. After night stirring at RT, the crude was filtered and triturated with cold EtOH to give red powders.

Compound **IIa.** Yield 70 %.
M.P. 187 °C; ^{1}H (300 MHz, $CDCl_3$, TMS): δ [ppm] =7.66 – 7.50 (m, 7H), 7.38 – 7.25 (m, 7H), 7.15-7.05 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ [ppm] = 149.4, 148.5, 147.2, 143.4, 136.2, 134.7,134,4, 133.8, 133.1, 129.9, 129.4, 128.3, 127.0, 126.9, 126.4, 126.0,125.5, 125.0, 123.7, 123.6, 122.9, 122.7, 106.2; HRMS (FAB) calcd for $C_{35}H_{24}N_2S_2$ [M^+]: 536.1375, found: 536.1375.

Compound **IIb.** Yield 80 %.
M.p.: 210 °C; ^{1}H (300 MHz, $CDCl_3$, TMS): δ [ppm] = 7.54 – 7.05 (m, 22 H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ [ppm] = 149.4, 148.5, 147.2, 137.8, 137.6, 136.7, 135.9, 134.1, 130.1, 131.6, 129.5, 128.1, 127.4, 127.0, 125.3 125.0, 124.4, 124.3, 123.6, 122.9, 122.8, 122.6, 101.4; HRMS (FAB) calcd for $C_{33}H_{22}N_2S_3$ [M^+]: found: 542.0945.

Structure Refinement and crystal data for I

Single crystals of **I** suitable for X-ray diffraction analysis were obtained by slow evaporation of a mixture of chlorobenzene - chloroform solution. The compound crystallizes in the triclinic P-1 space group. X-ray single-crystal diffraction data were collected at 150K on an Agilent SuperNova diffractometer equipped with Atlas CCD detector and mirror monochromated micro-focus Cu-K_α radiation (λ = 1.54184 Å). The structure was solved by direct methods and refined on F^2 by full matrix least-squares techniques using SHELX97 programs (G.M. Sheldrick, 1998). All non-H atoms were refined anisotropically and multiscan empirical absorption was corrected using CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.37.35g, 2014). The H atoms were included in the calculation without refinement.

$C_{68}H_{36}F_{10}N_4O_2S_2$, M = 1195.13, brown needle, 0.31 × 0.09 × 0.03 mm^3, triclinic, space group P-1, a = 7.6536(11) Å, b = 12.286(3) Å, c =15.052(2) Å, α = 82.317(15)°, β = 79.867(12)°, γ = 79.896(15)°, V =1364.0(4) $Å^3$, Z =1, ρ_{calc} =1.455 g/cm^3, μ(Cu Kα) = 1.639 mm^{-1}, F(000) = 610, θmin = 3.00°, θmax = 73.11°, 9759 reflections collected, 5184 unique (Rint = 0.0951), parameters/restraints = 388/0, R1 = 0.0825 and wR2 = 0.1885 using 3047 reflections with I > 2σ(I), R1 = 0.1335 and wR2 = 0.2157 using all data, GOF = 0.999, −0.602 < Δρ < 0.457 e.$Å^{-3}$. CCDC- 1530104

Preparation of the solar cells

Indium-tin oxide coated glass slides of 24×25×1.1 mm with a sheet resistance of RS = 10 Ω/sq were purchased from VisionTek Systems Ltd. The substrates were scrubbed using dishwashing soap before being cleaned by a series of ultrasonic treatments for 15 min in distilled water, acetone, and isopropanol. Once dried under a steam of nitrogen, a UV-ozone plasma treatment (UV/Ozone ProCleaner Plus, Bioforce Nanosciences) was performed for 15 min. A filtered aqueous solution of poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate) (PEDOT:PSS; Clevios P VP. AI 4083) through a 0.45 µm RC membrane (Millex®) was spun-cast onto the patterned ITO surface at 5000 rpm for 40 s before being baked at 115°C for 15 min. The films of donor materials **I**, **IIa** or **IIb** were spun-cast from 2-methyltetrahydrofurane[25] solutions containing 8 mg/mL of material then the cells were completed by the successive thermal deposition of C_{60} (30 nm) and aluminum (80 nm) at a pressure of 10^{-6} Torr through a shadow mask defining two cells of 27 mm^2 each. J vs V curves were recorded in the dark and under illumination using a Keithley 236 source-measure unit and a home-made acquisition program. The light source is an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttecknik, equipped with a metal halogen lamp). The light intensity was measured by a broad-band power meter (13PEM001, Melles Griot). EQE was recorded under ambient atmosphere using a halogen lamp (Osram) with an Action Spectra Pro 150 monochromator, a lock-in amplifier (Perkin-Elmer 7225) and a S2281 photodiode (Hamamatsu).

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Keywords: Sustainable Chemistry • Organic photovoltaics • C-H direct Arylation • Schiff Base • Ionic liquids

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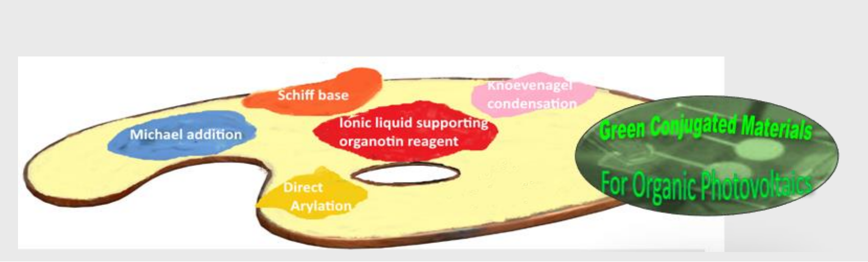

Alexandre Faurie, Jérémie Grolleau, Frédéric Gohier, Magali Allain, Stéphanie Legoupy and Pierre Frère**

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Toward sustainable organic semiconductors from a broad palette of green reactions

New conjugated materials, based on triphenylamine-thiophene moiety and integrating azomethine bonds with dibenzofuran unit or cyanovinyl bond with phenyl-thiophene and bithiophene units, have been synthesized by using a wide range of green reactions