# Small D-π-A Systems with *o*-Phenylene-Bridged Accepting Units as Active Materials for Organic Photovoltaics

### Antoine Leliège, Jérémie Grolleau, Magali Allain, Philippe Blanchard,\* Dora Demeter, Théodulf Rousseau, and Jean Roncali\*<sup>[a]</sup>

**Abstract:** Donor-acceptor  $(D-\pi-A)$  systems that combine triarylamine donor blocks and dicyanovinyl (DCV) acceptor groups have been synthesized. Starting from the triphenylamine (TPA)-thiophene-DCV compound (1) as a reference system, various synthetic approaches have been developed for controlling the light-harvesting properties and energy levels of the frontier orbitals in this molecule. Thus, the introduction of methoxy groups onto TPA, the replacement of one phenyl ring of TPA by a thiophene ring, or the exten-

sion of the  $\pi$ -conjugating spacer group lead to the modulation of the HOMO level. On the other hand, the fusion of the DCV group onto the vicinal thiophene ring by an *ortho*-phenylene bridge allows for a specific fine-tuning of the LUMO level. The electronic properties of the molecules were analyzed by using UV/Vis spectroscopy

**Keywords:** bridging ligands • chromophores • cyclic voltammetry • donor-acceptor systems • solar cells and cyclic voltammetry and the compounds were evaluated as donor materials in basic bilayer planar heterojunction solar cells by using  $C_{60}$  as acceptor material. The relationships between the electronic properties of the donors and the performance of the corresponding photovoltaic devices are discussed. Bilayer planar heterojunction solar cells that used reference compound **1** and  $C_{70}$  afforded power-conversion efficiencies of up to 3.7%.

#### Introduction

Over the past few years, we have witnessed the emergence of small conjugated molecules at the forefront of research on solution-processed and vacuum-deposited donor-acceptor heterojunction organic solar cells (OSCs).<sup>[1]</sup> Whilst bulk heterojunction (BHJ) OSCs<sup>[2]</sup> that are based on soluble, low-band-gap π-conjugated co-polymers and PC71BM fullerene have reached conversion efficiencies exceeding 9.0%,<sup>[3]</sup> the inherent polydispersity of polymers is a source of variability in the composition, molecular weight, and electronic properties of the final material and, thus, of the performance of the resulting OSCs.<sup>[1]</sup> In this regard, the use of conjugated molecules in OSCs presents several advantages. Besides straightforward synthesis and purification processes and, hence, more-reproducible photovoltaic performance, well-defined chemical structures allow a more precise analysis of the structure-property relationships that remain a

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major tool for the definition of guidelines for the molecular engineering of new active materials.<sup>[1]</sup>

Over the past few years, this molecular approach has led to the synthesis and evaluation of many classes of donor materials that are based on a wide range of chemical structures, such as triphenylamines,<sup>[4]</sup> oligothiophenes,<sup>[5]</sup> squaraines,<sup>[6]</sup> quinacridones,<sup>[7]</sup> cyanines,<sup>[8]</sup> diketopyrrolopyrroles,<sup>[9]</sup> borondipyrromethenes,<sup>[10]</sup> indigo,<sup>[11]</sup> porphyrins,<sup>[12]</sup> and various tailored 1D, 2D, or 3D architectures,<sup>[1,13]</sup>

Intensive research effort that focused on the design of new active materials and on the optimization of the fabrication of OSCs by, for example, the application of thermal treatments,<sup>[9]</sup> the introduction of additives,<sup>[14]</sup> or the insertion of additional intermediate buffer layers,<sup>[3a,5]</sup> has led to rapid progress and conversion efficiencies (*PCEs*) exceeding 7.0% for BHJ cells that are based on hybrid oligothiophenes as donors and PC<sub>71</sub>BM as an acceptor.<sup>[14]</sup> These results demonstrate that molecule-based OSCs are now capable of rivaling their parent polymer-based devices. Moreover, in addition to solution processes, small molecules can also be deposited by using vacuum techniques.<sup>[5a-d,15,16]</sup>

The structure of efficient molecular donors typically involves a combination of donor (D) and acceptor (A) groups to create an internal charge-transfer, which produces an extension of the spectroscopic response of the OSC, an increase in the open-circuit voltage, and enhanced stability of the molecule against oxidation.<sup>[4a,17]</sup> Over the past few years, many donor materials that are based on D–A combinations have been synthesized, including symmetrical D–A–D or A–D–A systems, star-shaped molecules, or more-complex mo-

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lecular architectures.<sup>[1,4-14]</sup> In spite of their efficiency, some of these systems contain a sophisticated molecular structure, thereby requiring relatively complex syntheses, and their molecular weights sometimes exceed 1500 g mol<sup>-1</sup>. In this context, the question of the minimization of the complexity, size, and molecular weight of donor molecules represents an interesting problem. In fact, beyond being a challenge for experimental and theoretical chemists, these various points could have important implications in terms of the cost and environmental impact of future industrial synthesis, purification, and processing of active materials for OSCs.<sup>[18]</sup> In this regard, recent work has shown that interesting photovoltaic performances can be achieved with donors of relatively small spatial extension and low molecular weight.<sup>[8a,15,16]</sup>

A few years ago, we reported the first examples of starshaped triphenylamine (TPA)-based molecules with peripheral dicyanovinyl (DCV) acceptor groups and we showed that these systems could lead to efficient solution-processed or vacuum-deposited OSCs with high open-circuit voltages.<sup>[1e,4a]</sup> More recently, we have shown that unsymmetrical TPA-based systems with two (or even only one) DCV groups can produce interesting results.<sup>[4c]</sup> Herein, considering the **DA**<sub>3</sub> molecule<sup>[4a]</sup> as a starting model (Scheme 1), we



have synthesized a simple D-A molecule (1) as a reference system for an analysis of the structure-property relationships of a series of parent compounds (2-6) in which the energy levels of the frontier orbitals have been modulated by using various synthetic principles. Thus, the modification of the HOMO level has been achieved by the introduction of methoxy groups onto the TPA block, by replacement of one phenyl group of TPA by a thiophene cycle, or by extension of the  $\pi$ -conjugating spacer. On the other hand, control of the LUMO level has been sought through the modulation of the electron-withdrawing effect of the DCV group by covalent bridging. We have extensively investigated rigidification as an efficient approach for the synthesis of low-bandgap  $\pi$ -conjugated systems or push-pull chromophores for nonlinear optics.<sup>[19]</sup> In the specific case of molecular donors, this approach can represent an interesting tool for the control of electronic properties at a moderate cost in terms of increasing the molecular weight.

Preliminary results along this line were recently reported in a short communication.<sup>[20]</sup> Herein, we present a more-extended account of the synthesis and electronic properties of molecules that were designed according to these synthetic principles. Moreover, their potential as donor materials in organic solar cells is discussed with an emphasis on structure–property relationships.

#### **Results and Discussion**

The synthesis of compounds 2-6 is described in Scheme 3 and Scheme 4. Reference compound 1 was prepared according to a literature procedure.<sup>[20,21]</sup> All of these compounds were prepared by Pd-catalyzed cross-coupling reactions as initially reported by Effenberger et al. for analogous donor-acceptor-substituted oligothiophenes.<sup>[22]</sup>

Scheme 2 shows the synthesis of the *ortho*-phenylenebridged acceptor units. Ketone  $7^{[20,23]}$  was brominated at the free  $\alpha$  position of the thiophene ring by using bromine as a reagent. Lower yields were obtained with NBS. A Knoevenagel condensation reaction of compound **8** with malonodinitrile gave dicyano compound **9** in 98% yield. Bromination of ketone  $10^{[24]}$  with NBS gave compound **11** in 77% yield.



Scheme 2. Synthesis of the acceptor building blocks: i)  $Br_2/NaHCO_3$ , CHCl<sub>3</sub> (87%); ii) CH<sub>2</sub>(CN)<sub>2</sub>, NaOAc, EtOH (98%); iii) NBS/DMF (77%). NBS = *N*-bromosuccinimide.

Scheme 1. Structures of the D–A molecules.

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Scheme 3. Synthesis of compounds **2** and **3**: i) *n*BuLi, -78 °C then Bu<sub>3</sub>SnCl, THF; ii) compound **9**, [Pd(PPh<sub>3</sub>)<sub>4</sub>], toluene, reflux (87% yield from compound **12**); iii) *n*BuLi, -78 °C then isopropoxytetramethyldioxaborolane, THF (42%); iv) compound **8**, [Pd(PPh<sub>3</sub>)<sub>4</sub>], Aliquat 336, Na<sub>2</sub>CO<sub>3</sub>, toluene/water 1:1, reflux (88%); v) CH<sub>2</sub>(CN)<sub>2</sub>, Et<sub>3</sub>N, CHCl<sub>3</sub> (90% yield for compound **2**, 67% yield for compound **3**); vi) compound **11**, [Pd(PPh<sub>3</sub>)<sub>4</sub>], Aliquat 336, Na<sub>2</sub>CO<sub>3</sub>, toluene/water 1:1, reflux (86%).

Compound 2 was synthesized by a Suzuki coupling of bromoketone 8 with the boronic ester of TPA 14, followed by a Knoevenagel condensation reaction of extended carbonyl compound 15 with malonodinitrile (Scheme 3). Interestingly, a Stille coupling reaction between the stannyl derivative of TPA 13 and bromo compound 9 led to a more-straightforward route to compound 2.<sup>[20]</sup> Compounds 13 and 14 were obtained from compound 12 after lithium/bromine exchange with *n*BuLi at low temperatures, followed by the addition of Bu<sub>3</sub>SnCl and isopropoxytetramethyldioxaborolane, respectively. Isomeric compound 3 was prepared in an analogous manner by treating compound 14 with bromoketone 11, thus giving the intermediate ketone (16), which was subjected to a Knoevenagel condensation reaction with malonodinitrile.

The synthesis of compounds **4–6** is described in Scheme 4. Selective deprotonation at the  $\alpha$  position of the thiophene ring of compounds **17**,<sup>[25]</sup> **18**,<sup>[26]</sup> and **23**<sup>[27]</sup> with *n*BuLi, followed by the addition of Bu<sub>3</sub>SnCl, gave stannyl derivatives **19**, **20**, and **24**.<sup>[28,29]</sup> These compounds were directly employed in a Stille coupling reaction with bromoketone **8** in the presence of catalytic amount of [Pd(PPh<sub>3</sub>)<sub>4</sub>], thus leading to the formation of extended ketones **21**, **22**, and **25** in 75–79% yields. Finally, Knoevenagel condensation reactions of compounds **21**, **22**, and **25** with malonodinitrile led to compounds **4**, **5**, and **6**, respectively.

Single crystals suitable for X-ray diffraction were grown by the slow evaporation of solutions of bridged compounds 2, 3, and 4 in  $CH_2Cl_2$ . The slow diffusion of MeOH into a solution of compound 1 in  $CH_2Cl_2$  led to the growth of



Scheme 4. Synthesis of compounds 4, 5, and 6: i) *n*BuLi, -78 CC then Bu<sub>3</sub>SnCl, THF; ii) compound 8, [Pd(PPh<sub>3</sub>)<sub>4</sub>], toluene, reflux (75% yield for compound 21 from compound 17, 79% yield for compound 22 from compound 18, and 78% yield for compound 25 from compound 23); iii) CH<sub>2</sub>(CN)<sub>2</sub>, Et<sub>3</sub>N, CHCl<sub>3</sub> (75% yield for compound 4, 75% yield for compound 5, and 92% yield for compound 6).

single crystals of sufficient quality for X-ray analysis. Notably, the preparation of single crystals of open-chain compound **1** was much more tedious. This result is not surprising considering the well-known tendency of TPA derivatives to form amorphous materials.<sup>[30]</sup> These results also suggest that rigidification by covalent bridging improves their aptitude for crystallization.

Figure 1 shows the molecular structures of compounds **1**, **2**, **3**, and **4** (see the Supporting Information, Table S1).<sup>[39]</sup> The DCV group of compound **1** adopts a *cis* conformation relative to the sulfur atom of the vicinal thiophene, as previously observed for  $\alpha, \omega$ -oligothiophenes that were end-capped with DCV groups.<sup>[5b]</sup> With the exception of the two outermost phenyl rings of the TPA unit, the rest of the molecule adopts a quasi-planar conformation, as shown by a dihedral angle of 3.1° (C7-C8-C9-C10) between the inner benzene ring of TPA and the thiophene unit and a dihedral angle of 2.9° between the thiophene ring and the DCV group (C6-C1-C2-C3).

For compounds **2** and **4**, the *cis* conformation of the DCV group relative to the sulfur atom of the vicinal thiophene group is imposed by the covalent bridging. Compared to compound **1**, the dihedral angle (C2-C1-C15-C20) between the inner benzene ring of TPA and the thiophene unit decreases to 0.2°, whereas the dihedral angle (C3-C4-C5-C6) exhibits a value of 0.9°. As expected, the indenothiophene moiety is completely planar. All of these data indicate slightly better planarity of compound **2** compared to reference compound **1**.



Figure 1. Molecular structures of compounds 1, 2, 3, and 4 as obtained by X-ray diffraction.

One major difference between the structures of compounds **2** and **3** is the considerably larger dihedral angle (C2-C1-C15-C20) in compound **3** (15.4°), which leads to a less-planar  $\pi$ -conjugated system. In compound **4**, the two adjacent thiophene rings generate rotational conformers in the unit cell with the thiophene rings in *anti* (**4a**) or *syn* conformations (**4b**) and dihedral angles smaller than 4°.

The electronic properties of compounds **1–6** have been analyzed by using cyclic voltammetry and UV/Vis spectroscopy. The cyclic voltammograms (CVs) in  $CH_2Cl_2$ in the presence of  $Bu_4NPF_6$  as a supporting electrolyte show that all of these compounds can be reversibly oxidized (Figure 2). On the other hand, the reduction process that leads to the formation of the radical anion is reversible for bridged compounds **2–6**, whereas this process appears to be irreversible for open-chain compound **1** (Figure 2).

The CV of compound **1** exhibits a reversible oxidation wave with an anodic peak potential  $(E_{pa})$  at 1.01 V and an irreversible reduction wave with a maximum at  $E_{pr} = -1.23$  V (Table 1). A comparison of the data of compounds **1** and **2** shows that the bridging of the DCV unit leads to a small decrease

in  $E_{\rm pa}$  (10 mV), but a large positive shift in  $E_{\rm pr}$  (430 mV). These results show that the *ortho*-phenylene bridge has a small influence on the HOMO level, but leads to a large decrease in the LUMO level. The large positive shift of the  $E_{\rm pr}$ value and the transition from an irreversible to a reversible reduction process as observed for all of the bridged compounds can be interpreted by stabilization of the reduced state that is associated with the formation of an aromatic cyclopentadienyl anion radical upon reduction (Scheme 5).

Table 1. Cyclic voltammetry data for compounds  $1\!-\!6$  versus SCE in  $0.10\,{\rm M}$   $Bu_4NPF_6/$   $CH_2Cl_2$  (scan rate:  $100~mV\,s^{-1}$ ).

Compd	E <sub>pa</sub> 1 [V/SCE]	E <sub>pr</sub> 1 [V/SCE]	$\Delta E$ [V]	$E_{\rm HOMO}^{[a]}$ [eV]	$E_{\text{LUMO}}^{[a]}$ [eV]	$E_{\rm HOMO} - E_{\rm LUMO}$ [eV]
1	1.01	-1.23 <sup>[b]</sup>	2.24	-5.89	-4.06	1.83
2	1.00	-0.80	1.80	-5.87	-4.33	1.54
3	0.92	-0.83	1.75	-5.79	-4.29	1.50
4	0.81	-0.78	1.59	-5.67	-4.34	1.33
5	0.70	-0.79	1.49	-5.56	-4.32	1.24
6	0.85	-0.76	1.61	-5.75	-4.36	1.39

[a] The energy levels of the HOMO and LUMO were determined from the onset of the oxidation and reduction waves, respectively, by using an offset of  $4.99 \,\text{eV}$  for the SCE versus the vacuum level.<sup>[31]</sup>

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Figure 2. Cyclic voltammograms of compounds 1 (0.5 mm), 2 (1 mm), 3 (0.5 mm), 4 (1 mm), 5 (1 mm), and 6 (<0.5 mm) in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> (scan rate: 100 mVs<sup>-1</sup>).



Scheme 5. Formation of a cyclopentadienyl anion upon electrochemical reduction.

A comparison of the CV data for compounds **1** and **3** shows that, when connected at the 3-position of the thiophene ring, the DCV group leads to a moderate decrease in

the  $E_{\rm pa}$  value (90 mV) but still produces a positive shift of the  $E_{\rm pr}$  value of 400 mV. This former observation can be related to an extension of the whole  $\pi$  system, which results from a connection of the terminal phenyl ring on the 2-position of the thiophene ring.

On the other hand, the significant positive shift in the  $E_{\rm pr}$  value of compound **3** shows that, although the DCV group is not directly conjugated to the donor part of the molecule, thereby generating a much weaker internal charge transfer (as shown by the UV/Vis data discussed below), the bridging DCV group still exerts a strong influence on the LUMO level. In fact, as in the case of its isomer (**2**), the reduced state of compound **3** can be also stabilized by the formation of an aromatic cyclopentadienyl radical anion (Scheme 5). This result confirms the strong localization of the LUMO on the acceptor part of the molecule.

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As expected, the replacement of the TPA moiety of compound **2** by a diphenylthienylamine unit (compound **4**) and the further introduction of methoxy groups (compound **5**) produce negative shifts in the  $E_{\rm pa}$  value of 190 and 300 mV, respectively, whereas the  $E_{\rm pr}$  values are positively shifted by only 10–20 mV. These results are consistent with a HOMO that is essentially localized on the donor part of the molecule.

Finally, the CV data for compound **6** show that the insertion of an additional thiophene ring into the conjugating spacer of compound **2** produces a 0.15 V decrease in the  $E_{\rm pa}$  value but has almost no effect on the  $E_{\rm pr}$  value, thus further confirming the strong localization of the LUMO on the acceptor part of the molecule.

To summarize, these CV results show that the introduction of methoxy groups or the replacement of a phenyl group by a thienyl group in the TPA block significantly increases the HOMO level, with little or no effect on the LUMO level. Conversely, the *ortho*-phenylene bridging of the DCV group has practically no effect on the HOMO, but essentially affects the LUMO level. All of these results are consistent with strongly localized HOMO and LUMO, the energy levels of which can be specifically tuned by using appropriate synthetic approaches.

The optical properties of these D–A compounds have been investigated by using UV/Vis spectroscopy in solution and as thin films that were spin-cast onto glass from their solutions  $(10 \text{ mgmL}^{-1})$  in CHCl<sub>3</sub>. Table 2 lists the main opti-

Table 2. UV/Vis absorption data for compounds  $1\!-\!6$  as solutions in  $CH_2Cl_2$  or as thin films that were spin-cast onto glass from solutions in  $CHCl_3$  and thermal data.

Compd	$\lambda_{\max}$ (ICT) [nm]	$\varepsilon$ (ICT) [ $M^{-1}$ cm <sup>-1</sup> ]	$\lambda_{\max}$ (film) [nm]	$E_{ m g} [ m eV]^{[a]}$	М.р. [°С]	Τ <sub>d</sub> [°C]
1	501	33 900	523	1.98	178	292
2	610	16200	633	1.58	249	334
3	600	500	392 (644) <sup>[b]</sup>	2.70 (1.70) <sup>[b]</sup>	262	338
4	664	17600	688	1.42	228	324
5	710	23100	738	1.28	200	379
6	621	17100	638	1.50	$>\!260$	397

[a]  $E_g$  was estimated from the onset of absorption at low energies. [b] Values in parentheses correspond to the weak ICT band.

cal properties of the various compounds, together with their melting points and decomposition temperatures, as measured by using TGA. These data show that all of these compounds present a relatively high decomposition temperature. The spectra of all of these D–A compounds show a first absorption band within the region 300–400 nm and a second band at longer wavelengths, which is assigned as an internal charge transfer (ICT).<sup>[4a, 32]</sup>

Figure 3 shows the UV/Vis spectra of compounds 1, 2, and 3. A comparison of the spectra of compounds 1 and 2 clearly shows that the *ortho*-phenylene bridge produces a large bathochromic shift of the maximum of the ICT band (about 100 nm). However, this shift is accompanied by a substantial decrease in the molecular absorption coefficient



Figure 3. UV/Vis absorption spectra in  $CH_2Cl_2$ . Dotted line (1), solid line (2), and dashed line (3).

( $\varepsilon$ ). For compound **3**, the ICT band is hardly discernible. This result can be explained by the fact that, when connected at the 3-position of the thiophene ring, the DCV group is no longer directly conjugated with the donor part of the molecule, which results in an almost-complete annihilation of the ICT, even if the absorption onset can still be discerned at about 700 nm. This result provides further indirect confirmation of the ICT origin of the long-wavelength absorption band for this class of D–A compounds.

The spectra of compounds **2**, **4**, and **5** (Figure 4) show that replacing the inner phenyl ring of TPA by a thiophene unit



Figure 4. UV/Vis absorption spectra in  $CH_2Cl_2$ . Solid line (2), dotted line (4), and dashed line (5).

leads to a 54 nm red-shift of  $\lambda_{max}$ , whilst a further 46 nm red shift is obtained by the introduction of methoxy groups at the *para* positions of the two phenyl rings. Furthermore, these changes are accompanied by a significant increase in the intensity of the ICT band relative to the  $\pi$ - $\pi$ \* electronic transition. On the other hand, a comparison of the data for compounds **2** and **6** shows that the extension of the conjugating spacer by the insertion of an additional thiophene ring only has a minor influence on the optical gap (see the Supporting Information, Figure S1). In agreement with the CV data, the narrowing of the optical gap in compounds **4** and **5** compared to compound **2** is due to an increase in the HOMO level (Table 1).

The optical band gap in these compounds ( $E_g$ ) was estimated from the long-wavelength absorption edge of the spectra of their spin-cast thin films on glass substrates. For most of these compounds, their solid-state spectra present a broadening of the absorption band and a red-shift of  $\lambda_{max}$  (Table 2 and the Supporting Information, Figure S2). The  $E_g$  values follow the same trend as indicated by the  $\lambda_{max}$  values and show that gaps smaller than 1.50 eV are reached for compounds **4–6**.

To gain further insight into the effects of covalent bridging on the electronic properties of these compounds, theoretical calculations based on density functional methods were performed with the Gaussian 09 program for the nonbridged compound (1) and *ortho*-phenylene-bridged compounds 2 and  $3^{[33]}$  Becke's three-parameter<sup>[34]</sup> gradient-corrected functional (B3LYP) with the 6-31G(d,p) basis set were used to optimize their geometries and to compute their electronic structures at the observed minima.

Apart from the two outermost phenyl units of TPA, all of the molecules exhibit a quasi-planar structure. In agreement with the X-ray data, the DCV moiety of compound 1 adopts a *syn* conformation relative to the sulfur atom of the thiophene ring, whereas this conformation is imposed by the bridging in compound 2. Figure 5 shows the HOMO and



Figure 5. HOMO and LUMO energy levels and their representations for compounds 1, 2, and 3 after optimization with Gaussian 09 at the B3LYP/ 6-31G(d,p) level of theory.

LUMO energy levels of these molecules. The *ortho*-phenylene bridge leads to a small increase in the HOMO level of compounds 2 and 3, but to a large decrease in the LUMO level. As already discussed, this result agrees well with the significant positive shift of the  $E_{\rm pr}$  value as observed by cyclic voltammetry for compounds 2 and 3 compared to compound 1. The HOMO level of compound 3 increases slightly compared to that of compound 2, in agreement with the lower  $E_{\rm pa}$  value for compound 3. Figure 5 also shows that, whereas the HOMO of compounds 1–3 is essentially present on the TPA-thiophene moiety, the LUMO is strongly localized on the thiophene–DCV block for compound 1 and is further extended onto the *ortho*-phenylene ring in compounds 2 and 3.

To summarize, these theoretical results are in full agreement with the experimental data, that is, the *ortho*-phenylene bridges specifically affect the LUMO level of the D–A systems, thus confirming the interest in this synthetic approach for the fine-tuning of the energy levels of D–A systems.

These D–A compounds have been evaluated as donor materials in basic bilayer planar heterojunctions by using  $C_{60}$  as an acceptor. Although solution-processed molecular BHJs that incorporate  $C_{70}$  derivatives as acceptor molecules and some additives can achieve high *PCE* values,<sup>[14]</sup> the optimization of the multiple experimental variables that are involved in such cells is a rather tedious task that requires large amounts of the donor compound and, therefore, this kind of devices does not appear to be the most convenient for the analysis of structure–property relationships in a large series of compounds.

The donor layer (thickness  $\approx$  35 nm) was spin-cast from a solution of the compound in  $CHCl_3$  (10 mgmL<sup>-1</sup>) onto ITO slides that were pre-coated with a PEDOT:PSS film (thickness: 40 nm). Then, the slides were introduced in a glove box that was equipped with a vacuum chamber, a layer of  $C_{60}$  (thickness: 30 nm) was deposited by thermal evaporation, and the devices were completed by the vacuum deposition of an aluminum electrode (thickness: 100 nm). Each batch comprised two or three slides with two cells of size  $0.28 \text{ cm}^2$  on each slide. For all of these compounds, thermal treatment for 5 min was found to significantly improve their PCE values through increasing their short-circuit current densities  $(J_{sc})$ , open-circuit voltages  $(V_{oc})$ , or filling factors (FFs; Table 3 and the Supporting Information, Table S2). Figure 6 and the Supporting Information, Figure S3 show the effect of thermal treatment on the plot of current density versus voltage of the of PHJ cells that were based on compounds 1-5. However, attempts to detect some thermally induced material reorganization with eventual crystallization by using X-ray diffraction and UV/Vis absorption spectroscopy of spin-cast films of the donors were unsuccessful. Although reorganization, such as reorientation of push-pull molecules upon thermal treatment, as has been recently reported,<sup>[35]</sup> cannot be ruled out, this result suggests that the observed increase in the PCE might be due to a thermally induced extension of the area of the D/A interfacial contact zone, thus leading to an enhanced interpenetration of the donor and acceptor materials.<sup>[36]</sup> This hypothesis needs to be confirmed, although it is consistent with the higher efficiency of mixed co-evaporated cells compared to simple bilayer cells.<sup>[15b, 16, 37]</sup>

Table 3 lists the photovoltaic parameters of the devices under AM 1.5 simulated solar illumination. A comparison of the data for the cells that were based on donors **1** and **2** shows that the *ortho*-phenylene bridge produces an improvement in the *FF* value from 0.43 to 0.52 and in the  $V_{oc}$ value from 0.92 to 0.97 V, which result in an increase in the

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Figure 6. Left: Plots of current density versus voltage of PHJ cells that were based on donors 1 (top) and 2 (bottom) with C<sub>60</sub> in the dark (white circles) and under white-light illumination with an incident power light of 90 mWcm<sup>-2</sup> before (gray circles) and after thermal treatment (black circles). Right: External quantum efficiency of the cells under monochromatic irradiation after thermal treatment (solid line) and UV/Vis spectra of thin-films of the donors (dashed lines).

Table 3. Photovoltaic parameters after 5 min thermal treatment of bilayer donor/acceptor cells based on donors 1-5 under white-light illumination at a power density of 90 mW cm<sup>-2</sup>.

Donor/	V <sub>oc</sub>	$J_{ m SC}$	FF	PCE
acceptor	[V]	$[mA cm^{-2}]$	[%]	[%]
1/C <sub>60</sub> <sup>[a]</sup>	0.92	5.77	43	2.53
2/C <sub>60</sub> <sup>[a]</sup>	0.97	5.32	52	2.97
3/C <sub>60</sub> <sup>[b]</sup>	0.71	2.07	35	0.57
4/C <sub>60</sub> <sup>[a]</sup>	0.73	3.83	44	1.35
5/C <sub>60</sub> <sup>[c]</sup>	0.55	4.97	52	1.57
1/C <sub>70</sub> <sup>[a]</sup>	0.81	7.52	35	2.37
2/C <sub>70</sub> <sup>[a]</sup>	0.83	6.20	43	2.46

[a] Thermal treatment at 120°C. [b] Thermal treatment at 150°C. [c] Thermal treatment at 140 °C.

PCE value from about 2.50 to 3.00%. However, this increase in efficiency is essentially due to a spectroscopic extension of the photoresponse, as shown by the EQE spectrum of compound 2 in Figure 6. This latter EQE spectrum also shows the contribution of the ICT absorption band of films of compound 2 to the photocurrent. As expected, compound 3, in which the ICT is almost eliminated, leads to the lowest PCE among this series. Finally, a comparison of the results that were obtained with compounds 2, 4, and 5 shows that, despite their lower band gap, compounds 4 and 5 lead to lower PCE values. Besides lower  $J_{sc}$  values, this result is

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due to the large decrease in  $V_{\rm oc}$  value (for example, to 0.55 V for compound 5), which is caused by an increase in the HOMO level, owing to the introduction of thiophene and methoxy groups into the structure.

On the basis of the best performance of the compounds reported above, compounds 1 and 2 were chosen for the preparation of bilayer planar heterojunctions with C<sub>70</sub> as acceptor material under the same conditions. After thermal treatment at 120 °C for 5 min, the cells gave PCE values of 2.37 for compound 1 and 2.46 for compound 2 (see the Supporting Information, Figure S4). As presented in Table 3, the replacement of  $C_{60}$  by  $C_{70}$  significantly increased the  $J_{sc}$ value, which could be related to the better absorption properties of C70 over C60. [38] However, the Voc value decreased by 110 mV and 140 mV for compounds 1 and 2, respectively, thus leading to PCEs that were comparable to those measured with C<sub>60</sub>.

All of these results show that, in spite of their simple structures, these small D-A compounds can lead to efficient photovoltaic conversion. To gain further information on the potential of this class of compounds, some device optimization was performed by using the simplest compound (1) as a donor. To this end, a layer of the donor (thickness: 25 nm) and a layer of C<sub>70</sub> (thickness: 20 nm) were successively deposited by thermal evaporation onto an ITO slide that was coated with PEDOT:PSS. The simple aluminum cathode



Figure 7. Top: Plots of current density versus voltage of a PHJ cell that was based on ITO/PEDOT-PSS/donor  $1/C_{70}/Ca/Al$  in the dark (white circles) and under white-light illumination with an incident power light of 100 mW cm<sup>-2</sup> before (gray circles) and after thermal treatment (black circles). Bottom: External quantum efficiency of the cells before (gray circles) and after thermal treatment (black circles).

was replaced by calcium (thickness: 40 nm) and aluminum (thickness: 100 nm).

After thermal treatment at 100 °C for 30 min, the *EQE* spectrum of the cell presents a broad spectroscopic response with a maximum of about 65 % at 540 nm (Figure 7). The plot of *J* versus *V*, recorded under AM 1.5 simulated solar illumination, affords a  $J_{sc}$  value of 9.81 mA cm<sup>-2</sup>, which, combined with a  $V_{oc}$  value of 0.96 V and a *FF* of 40 %, leads to a *PCE* of 3.70 %.

#### Conclusion

To summarize, small D–A conjugated systems that were based on triarylamine and DCV groups have been synthesized. The simplicity of their structures, combined with the strong localization of the frontier orbitals, make these molecules interesting model systems for the analysis of structure– properties relationships and, thus, for the definition of some synthetic guidelines for the selective tuning of the energy levels of frontier orbitals. Thus, it has been shown that the bridging of the DCV group can significantly narrow the optical band gap, owing to a strong decrease in the LUMO level, whereas a modulation of the HOMO level can be achieve by using some more-classical synthetic principles.

The potential use of these molecular donors for photovoltaic conversion has been evaluated in basic planar heterojunction solar cells by using  $C_{60}$  fullerene as an acceptor. The photovoltaic results have shown that some of these simple compounds can lead to efficiencies that are comparable to those obtained with more complex heavier molecules, a conclusion that is supported by some preliminary attempts at device optimization.

Work that is aimed at the design and synthesis of new series of molecular donors of smaller size, taking into account the conclusions of the above analyses of structure– property relationships, is underway.

#### **Experimental Section**

**General:** NMR spectra were recorded on Bruker AVANCE III 300 (<sup>1</sup>H: 300 MHz, <sup>13</sup>C: 75 MHz) or Bruker AVANCE DRX 500 spectrometers (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz). Chemical shifts are given in ppm relative to TMS. IR spectra were recorded on a Bruker Vertex 70 spectrometer and UV/Vis spectra were recorded on Perkin–Elmer Lambda 19 or 950 spectrometers. Melting points are uncorrected. Matrix-assisted laser-desorption/ionization mass spectrometer y was performed on a Bruker Daltonics BIFLEX III spectrometer by using dithranol as the matrix.

Cyclic voltammetry was performed in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> (HPLC grade) on a Biologic SP-150 potentiostat with positive feedback compensation. Solutions were degassed by nitrogen bubbling prior to each experiment. The experiments were carried out in a one-compartment cell that was equipped with a platinum electrode (diameter: 2 mm) as working electrode, a platinum wire counter electrode, and a silver wire in a 0.01 m solution of AgNO<sub>3</sub> in MeCN as a reference electrode. The ferricinium/ferrocenium couple was used as internal reference ( $E^{\circ}(Fc^+/Fc) = 0.405 \text{ V/SCE}$  in 0.1 m Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> and the potentials were expressed versus a saturated calomel electrode (SCE) as a reference. Elemental analysis was performed on a thermoelectron instrument. Purification by column chromatography was carried out on Acros silica gel Si 60 (35–70 mm). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on instruments from TA Instruments.

Device preparation: Glass slides (24×25×1.1 mm<sup>2</sup>) that were coated with indium tin oxide with a surface resistance of  $10 \Omega/\Box$  were purchased from Praezisions Glas & Optik GmbH. Part of the ITO layer was etched away with a 37% aqueous solution of HCl and Zn. Then, the ITO electrodes were successively cleaned in an ultrasound bath with Deconex (VWR international GmbH), distilled water (15.3 M $\Omega$  cm<sup>-1</sup>), acetone, EtOH, and distilled water again for 10 min each and dried in an oven at 100°C. Then, the electrodes were modified by spin-casting a layer of PE-DOT:PSS (Clevios P VP. AI 4083, HC-Starck; filtered through a 0.45 µm membrane just prior to use) at 5000 rpm (r=10 s, t=60 s) and the electrode was dried at 130 °C for 15 min. Films of the donor materials (thickness: 30-35 nm) were spin-cast under atmospheric conditions from 10 mg mL<sup>-1</sup> solutions of the donors in CHCl<sub>3</sub> (6000 rpm for 3 s and 10000 rpm for 9 s). CHCl<sub>3</sub> (HPLC grade) was distilled over P<sub>2</sub>O<sub>5</sub> before use. After film deposition, the devices were introduced in an Ar-filled glove box (200B, MBraun) that was equipped with a vacuum chamber and a film of  $C_{60}$  fullerene (>99%, thickness: 30 nm, MER Corporation) and an aluminum electrode (thickness: 100 nm) were thermally evaporated on top of the donor film under a pressure of  $2 \times 10^{-6}\,\rm mbar$  through a mask that defined two cells (diameter: 6.0 mm, 0.28 cm<sup>2</sup>) on each ITO electrode. C<sub>70</sub> (>99%) was purchased from MER Corporation and used as received.



The plots of J versus V of these devices were recorded in a glove box in the dark and under illumination by using a Keithley 236 source-measure unit and a home-made acquisition program. The light source was an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttecknik) that was equipped with a metal-halogen lamp. The light intensity was measured by a broad-band power meter (13PEM001, Melles Griot). The devices were illuminated through the ITO electrode side. The efficiency values reported herein are not corrected for the possible spectroscopic mismatch of the solar simulator. External quantum efficiency (EQE) was measured by using a halogen lamp (Osram) on an Action Spectra Pro 150 monochromator, a lock-in amplifier (Perkin–Elmer 7225), and a S2281 photodiode (Hamamatsu).

Synthesis: 2-Bromo-8H-indeno[2,1-b]thiophen-8-one (8): Br<sub>2</sub> (0.19 mL, 3.70 mmol) was added dropwise into a solution of ketone 7 (0.5 g, 2.68 mmol) and NaHCO<sub>3</sub> (241 mg, 2.87 mmol) in CHCl<sub>3</sub> (20 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 7 h. After the addition of water, the mixture was extracted with CH2Cl2. The organic phase was washed with a saturated aqueous solution of NaHCO3 and water, dried over MgSO4, and concentrated under vacuum. Column chromatography on silica gel (petroleum ether/CH2Cl2, 1:1) gave a yellow-orange powder (0.62 g, 87%). M.p. 135-136°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47 (ddd, J = 7.2, 1.2, 0.7 Hz, 1 H), 7.34 (td, J=7.2, 1.2 Hz, 1H), 7.19 (td, J=7.2, 1.0 Hz, 1H), 7.17 (s, 1H), 7.13 ppm (ddd, J = 7.2, 0.9, 0.7 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta =$ 184.7, 157.7, 139.2, 136.8, 136.5, 133.9, 128.8, 128.1, 124.5, 123.6, 119.9 ppm; IR (neat):  $\tilde{\nu} = 1726$ , 1685 cm<sup>-1</sup> (C=O); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  $(\varepsilon) = 408 \text{ nm} (800 \text{ Lmol}^{-1} \text{ cm}^{-1}); \text{ MS (EI): } m/z: 263.6/266.0 [M]^+; \text{ elemen-}$ tal analysis calcd (%) for C<sub>11</sub>H<sub>5</sub>BrOS: C 49.83, H 1.90; found: C 49.76, H 2.06.

2-(2-Bromo-8H-indeno[2,1-b]thiophen-8-ylidene)malononitrile (9): Malononitrile (124 mg, 1.88 mmol) was added to a solution of compound **8** (250 mg, 0.94 mmol) and CH<sub>3</sub>COONa (100 mg, 1.22 mmol) in EtOH (10 mL). The reaction mixture was heated at reflux for 1.5 h and cooled in an ice bath. The precipitate was recovered by filtration and washed with EtOH to give a brown powder (290 mg, 98%). M.p. 254–258°C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =8.12 (d, *J*=7.7 Hz, 1H), 7.39 (td, *J*=7.5, 1 Hz, 1H), 7.29 (d, *J*=7.4 Hz, 1H), 7.27 (s, 1H), 7.24 ppm (td, *J*=7.6, 1.3 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =157.9, 154.4, 138.2, 136.7, 136.1, 134.1, 129.0, 128.8, 127.1, 124.1, 121.4, 114.2, 113.0, 74.0 ppm; IR (neat):  $\bar{\nu}$ =2220 cm<sup>-1</sup> (C≡N); MS (EI): *m/z*: 311.7 [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>32</sub>H<sub>19</sub>N<sub>3</sub>S: C 53.69, H 1.61, N 8.95; found: C 53.23, H 1.61, N 8.83.

2-Bromo-4H-indeno[1,2-b]thiophen-4-one (11): In the absence of light, a solution of NBS (110 mg, 0.61 mmol) in DMF (2 mL) was added dropwise to a solution of ketone  $10^{[24]}$  (100 mg, 0.54 mmol) in DMF (4 mL) at 0°C. The reaction mixture was stirred 12 h at room temperature. After the addition of an aqueous solution of HCl (10%), the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with a saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and water, dried over MgSO<sub>4</sub>, and concentrated under vacuum. Column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1) gave an orange powder (0.11 g, 77%). M.p. 104–105°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.43 (d, *J*=7.2 Hz, 1H); 7.32 (t, *J*=7.8 Hz, 1H); 7.18 (t, *J*=7.8 Hz, 1H); 7.11 ppm (s, 1H); 7.06 (d, *J*=7.2 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =186.1, 158.6, 140.7, 138.5, 134.7, 134.1, 128.8, 124.0, 123.9, 119.3, 115.5 ppm; IR (neat):  $\tilde{\nu}$ = 1710 cm<sup>-1</sup> (C=O); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ =273, 435 nm; MS (ESI): *m/z*: 264.8/266.8 [*M*+H]<sup>+</sup>.

N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (14): Under an argon atmosphere, a 1.6 m solution of *n*BuLi in *n*-hexane (1.15 mL, 1.84 mmol) was added dropwise into a solution of 4-bromo-N,N-diphenylaniline (400 mg, 1.23 mmol) in anhydrous THF (2 mL) in a Schlenk flask at -78 °C. After stirring for 0.5 h at this temperature, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.38 mL, 1.86 mmol) was added dropwise and the stirring was continued for a further 1.5 h at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 4 h. The solvent was evaporated and the resulting oil was purified by column chromatography on silica gel (*n*-hexane/ EtOAc, 5:1) to give compound **14** as a yellow oil (190 mg, 42%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=7.66 (d, *J*=8.6 Hz, 2H), 7.28–7.24 (m, 4H), 7.14–7.06 (m, 6H), 7.05–7.01 (m, 2H), 1.33 ppm (s, 12 H).

2-(4-(Diphenylamino)phenyl)-8H-indeno[2,1-b]thiophen-8-one (15): A solution of Na<sub>2</sub>CO<sub>3</sub> (540 mg, 5.1 mmol) in water (5 mL) and Aliquat 336 (200 mg) were added to a solution of ketone 8 (130 mg, 0.51 mmol) and boronate ester 14 (190 mg, 0.51 mmol) in a Schlenk tube. The mixture was degassed with argon for 15 min, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (60 mg, 0.05 mmol, 5% mol) was added, and the mixture was heated at reflux under an argon atmosphere for 48 h. After the addition of water (20 mL) at room temperature, the mixture was extracted with toluene (2×20 mL). The organic phases were washed with a saturated aqueous solution of  $NH_4Cl$  (20 mL) and water (3×20 mL), dried over MgSO<sub>4</sub>, and concentrated to dryness. The product was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to give compound 15 as a red solid (190 mg, 88%). M.p. 210–212°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.51$  (d, J =8.9 Hz, 2H), 7.47 (d, J=6.6 Hz, 1H), 7.36-7.27 (m, 5H), 7.24 (s, 1H), 7.21–7.04 ppm (m, 10H);  $^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 185.6, 159.7, 159.6, 149.2, 147.1, 139.7, 138.1, 133.8, 133.5, 129.6, 128.4, 127.0, 126.7, 125.3, 124.0, 123.7, 122.5, 119.6, 114.9 ppm; IR (neat):  $\tilde{\nu} = 1721$ , 1684 cm<sup>-1</sup> (C=O); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ ) = 484 nm (12700 L mol<sup>-1</sup> cm<sup>-1</sup>); MS (EI): m/z: 428.8 [M]<sup>+</sup>; HRMS (ESI): m/z calcd for  $C_{29}H_{19}NOS$ : 430.12601; found: 430.12589; elemental analysis calcd (%) for C29H19NOS: C 80.09, H 4.46, N 3.26, C 80.32, H 4.57, N 3.12.

2-(4-(Diphenylamino)phenyl)-4H-indeno[1,2-b]thiophen-4-one (16): A solution of Na2CO3 (290 mg, 2.7 mmol) in water (2.5 mL) and Aliquat 336 (100 mg) were added to a solution of bromoketone 11 (70 mg. 0.27 mmol) and Suzuki reagent 14 (100 mg, 0.27 mmol) in a Schlenk tube. The mixture was degassed with argon for 15 min. [Pd(PPh<sub>2</sub>)<sub>4</sub>] (30 mg. 0.026 mmol, 5 mol%), and the mixture was heated at reflux under an argon atmosphere for 48 h. After the addition of water at room temperature, the mixture was extracted with toluene. The combined organic phases were washed with a saturated aqueous solution of NH<sub>4</sub>Cl, water, dried over MgSO<sub>4</sub>, and concentrated to dryness. Column chromatography on silica gel (petroleum ether/EtOAc, 1:5) gave a red solid (100 mg, 86%). M.p. 212–214°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47–7.39 (m, 3H), 7.37–7.26 (m, 5H), 7.22 (s, 1H), 7.20–7.03 ppm (m, 10H); <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{CDCl}_3): \delta = 187.9, 156.7, 149.1, 148.2, 147.3, 142.7, 139.3, 136.0,$ 134.1, 129.6, 128.5, 127.3, 126.5, 124.9, 123.6, 123.2, 119.2, 115.7 ppm; IR (neat):  $\tilde{\nu} = 1701 \text{ cm}^{-1}$  (C=O); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\varepsilon$ ) = 488 nm  $(1600 \text{ Lmol}^{-1} \text{ cm}^{-1}); \text{ MS (EI): } m/z: 428.5 [M]^+; \text{ MS (MALDI-TOF): } m/z:$ 429.2 [M]+; HRMS (ESI): m/z calcd for C<sub>29</sub>H<sub>19</sub>ONS: 429.11819; found: 429.11849.

2-(5-(N,N-Diphenylamino)thiophen-2-yl)-8H-indeno[2,1-b]thiophen-8-one (21): Under an argon atmosphere, a 2.5 M solution of *n*BuLi in *n*-hexane (0.35 mL, 0.87 mmol) was added dropwise to a solution of compound 17<sup>[25]</sup> (200 mg, 0.79 mmol) in anhydrous THF (15 mL) in a Schlenk flask at -78°C in the dark. The reaction mixture was stirred at this temperature for 0.5 h before the addition of Bu<sub>3</sub>SnCl (0.27 mL, 0.99 mmol). After 5 min at -78°C, the mixture was allowed to warm to room temperature and then stirred for 2 h. After dilution with Et<sub>2</sub>O (50 mL), the organic phase was washed with a saturated aqueous solution of NaF, water, dried over MgSO<sub>4</sub>, and evaporated to give Stille reagent 19 as a light-yellow oil, which was directly used in the next step. A mixture of compounds 19 and 8 (200 mg, 0.80 mmol) in toluene (10 mL) in a Schlenk flask was degassed with argon for 15 min before the addition of [Pd(PPh<sub>3</sub>)<sub>4</sub>] (46 mg, 0.04 mmol). The reaction mixture was heated at reflux for 14 h under an argon atmosphere. After the addition of water, the mixture was extracted with toluene. The organic phase was washed with a saturated aqueous solution of NH4Cl, water, dried over MgSO4, and evaporated. Column chromatography on silica gel (CH2Cl2) gave a purple solid (260 mg, 75%). M.p. 170–172°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.45$  (d, J =7.2 Hz, 1 H), 7.36-7.27 (m, 5 H), 7.24-7.08 (m, 9 H), 7.01 (s, 1 H), 6.55 ppm (d, J = 4.0 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 185.2$ , 159.4, 154.4, 152.9, 147.3, 139.4, 138.2, 133.4, 132.8, 129.6, 128.5, 127.9, 125.1, 124.3, 123.7, 123.6, 119.6, 118.8, 114.8 ppm; IR (neat):  $\tilde{v} = 1715$ ,  $(\varepsilon) = 516 \text{ nm}$  $1666 \text{ cm}^{-1}$ (C=O); UV/Vis  $(CH_2Cl_2)$ :  $\lambda_{\max}$  $(12700 \text{ Lmol}^{-1} \text{ cm}^{-1});$  MS (MALDI-TOF): m/z: 435.2 [M]<sup>+</sup>; HRMS (ESI): *m*/*z* calcd for C<sub>27</sub>H<sub>17</sub>ONS<sub>2</sub>: 435.07461; found: 435.07480.

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 $2\-(5\-(Bis(4\-methoxyphenyl)amino)thiophen\-2\-yl)\-8H\-indeno[2,1\-b]thio-2+yl)\-8H\-indeno[$ 

*phen-8-one* (22): Compound 22 was prepared according to the same procedure as for compound 21, starting from compound  $18^{[26]}$  (300 mg, 0.96 mmol), a 2.5 m solution of *n*BuLi (0.4 mL, 1 mmol), Bu<sub>3</sub>SnCl (0.27 mL, 0.99 mmol), and compound 8 (250 mg, 0.94 mmol), as a purple solid (370 mg, 79%). M.p. 153–154°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.42 (d, *J* = 7.1 Hz, 1 H), 7.34–7.24 (m, 2 H), 7.21–7.11 (m, 5 H), 7.10–7.04 (m, 2 H), 6.92 (s, 1 H), 6.87 (d, *J* = 9.0 Hz, 4 H), 6.27 (d, *J* = 4.1 Hz, 1 H), 3.81 ppm (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 185.1, 159.5, 156.9, 153.6, 140.4, 139.4, 138.427, 133.2, 131.8, 128.4, 126.0, 125.6, 124.3, 123.5, 119.5, 114.9, 113.9, 113.5, 55.7 ppm; IR (neat):  $\tilde{v}$  = 1713, 1666 cm<sup>-1</sup> (C= O); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 542 nm (15700 Lmol<sup>-1</sup> cm<sup>-1</sup>); MS (MALDI-TOF): *m/z*: 495.3 [*M*]<sup>+</sup>; HRMS (ESI): *m/z* calcd for C<sub>29</sub>H<sub>21</sub>O<sub>3</sub>NS<sub>2</sub>: 495.09574; found: 495.09544.

2-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-8H-indeno[2,1-b]thiophen-8-one (25): Under an argon atmosphere, a 2.5 M solution of *n*BuLi in *n*hexane (0.28 mL, 0.7 mmol) was added dropwise to a solution of *N*,*N*-diphenyl-4-(thiophen-2-yl)aniline (23,<sup>[27]</sup> 190 mg, 0.58 mmol) in anhydrous THF (8 mL) in a Schlenk flask at -78 °C. After stirring for 1 h at this temperature, Bu<sub>3</sub>SnCl (95% of purity, 0.20 mL, 0.7 mmol) was added dropwise. After 5 min, the reaction mixture was allowed to warm to room temperature and stirred for a further 1 h. After evaporation of the solvent, EtOAc (25 mL) was added and the organic layer was washed with a saturated aqueous solution of NaF, a saturated aqueous solution of NaCl, dried over MgSO<sub>4</sub>, and concentrated to dryness to give an orange oil that corresponded to compound 24, which was used in the next step without further purification.

In a Schlenk flask, a mixture of stannyl derivative **24** (430 mg, 0.7 mmol) and compound **8** (200 mg, 0.75 mmol) in toluene (30 mL) was degassed with argon for 15 min. After the addition of  $[Pd(PPh_3)_4]$  (45 mg, 0.04 mmol), the Schlenk flask was sealed and the reaction mixture was stirred at 110 °C for 3 days. After the addition of water, the organic phase was separated and the aqueous phase was extracted with toluene. The organic phases were combined, washed with a saturated aqueous solution of NaCl, dried over MgSO<sub>4</sub>, and concentrated under vacuum. Column chromatography on silica gel (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub>, 7:3) gave a red powder (300 mg, 78%). M.p. 210–212 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.50–7.43 (m, 3H), 7.37–7.26 (m, 6H), 7.22–7.11 (m, 8H), 7.11–7.03 (m, 4H); IR (neat):  $\tilde{\nu}$ =1720, 1681 cm<sup>-1</sup> (C=O); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ )=499 nm (10500 Lmol<sup>-1</sup>cm<sup>-1</sup>); MS (MALDI-TOF): *m/z*: 510.6 [*M*]<sup>+</sup>; HRMS (ESI): *m/z* calcd for C<sub>33</sub>H<sub>21</sub>ONS<sub>2</sub>: 511.10591; found: 511.10526.

2-(2-(4-(Diphenylamino)phenyl)-8H-indeno[2,1-b]thiophen-8-ylidene)malononitrile (2): Route 1: Under an argon atmosphere, a 2.5 M solution of *n*BuLi in *n*-hexane (0.50 mL, 1.25 mmol) was added dropwise to a solution of compound 12 (250 mg, 0.77 mmol) in anhydrous THF (15 mL) in a Schlenk flask at -78 °C in the dark. The reaction mixture was stirred at this temperature for 0.5 h before the addition of Bu<sub>3</sub>SnCl (0.25 mL, 0.92 mmol). After 5 min at -78 °C, the mixture was allowed to warm to room temperature and then stirred for a further 2 h. After dilution with Et<sub>2</sub>O, the organic phase was washed with a saturated aqueous solution of NaF and water and dried over MgSO<sub>4</sub>. Evaporation of the solvent gave compound 13 as slightly yellow oil, which was directly used in the next step.

To a mixture of compound **13** and compound **9** (240 mg, 0.77 mmol) in toluene (10 mL) in a degassed Schlenk flask was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (50 mg, 0.04 mmol) and the mixture was heated at reflux for 12 h under an argon atmosphere. After the addition of water, the mixture was extracted with toluene. The organic phase was washed with a saturated aqueous solution of NH<sub>4</sub>Cl and water, dried over MgSO<sub>4</sub>, and evaporated under vacuum. The residue was purified twice by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to give a dark-blue solid (320 mg, 87%). Route 2: Two drops of Et<sub>3</sub>N were added to a mixture of compound **15** (90 mg, 0.21 mmol) and malonitrile (28 mg, 0.42 mmol) in CHCl<sub>3</sub> (15 mL). The reaction mixture was heated at reflux for 14 h. The solvent was evaporated under vacuum and the crude product was triturated with hot EtOH (10 mL), filtered, and washed with EtOH (2 × 10 mL) to give compound **2** as a dark-blue powder (90 mg, 90%). M.p. 249–251°C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =8.07 (d, J=7.6 Hz, 1H), 7.55 (d, J=

8.8 Hz, 2 H), 7.40–7.27 (m, 7 H); 7.21 (m, J=7.3, 1.7 Hz, 1 H), 7.19–7.09 (m, 6 H), 7.04 ppm (d, J=8.8 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 161.5, 157.5, 156.3, 149.9, 146.8, 138.2, 138.1, 133.2, 132.8, 129.7, 128.4, 127.2, 126.3, 125.9, 125.6, 124.4, 121.9, 120.8, 114.7, 114.4, 113.5, 70.7 ppm; IR (neat):  $\tilde{\nu}$ =2219 cm<sup>-1</sup> (C=N); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ )= 610 nm (16200 Lmol<sup>-1</sup> cm<sup>-1</sup>); MS (EI): m/z: 477.1 [M]<sup>+</sup>; HRMS (ESI): m/z calcd for C<sub>32</sub>H<sub>20</sub>N<sub>3</sub>S: 478.13724; found: 478.13720; elemental analysis calcd (%) for C<sub>32</sub>H<sub>19</sub>N<sub>3</sub>S: C 80.48, H 4.01, N 8.80, S 6.71; found: C 80.08, H 3.99, N 8.72, S 6.61.

2-(2-(4-(*Diphenylamino*)*phenyl*)-4*H*-*indeno*[1,2-*b*]*thiophen*-4*ylidene*)*ma*lononitrile (**3**): Two drops of Et<sub>3</sub>N were added to a mixture of compound **16** (100 mg, 0.23 mmol) and malonitrile (30 mg, 0.46 mmol) in CHCl<sub>3</sub> (15 mL). The reaction mixture was heated at reflux for 14 h. The solvent was evaporated under vacuum and the crude product was triturated with hot EtOH (10 mL), filtered, and washed with EtOH (2×10 mL) to give compound **3** as a dark green powder (90 mg, 67%). M.p. 262–264°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=8.08 (d, *J*=8.3 Hz, 1H), 7.61 (s, 1H), 7.43 (d, *J*=8.9 Hz, 2H), 7.36–7.27 (m, 5H), 7.19–7.04 ppm (m, 10H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=157.9, 151.9, 149.5, 148.6, 147.2, 140.7, 138.1, 136.4, 134.2, 129.6, 128.2, 126.7, 126.6, 126.6, 125.0, 123.8, 123.0, 120.2, 117.1, 113.5, 113.0, 75.2 ppm; IR (neat):  $\bar{\nu}$ =2224 cm<sup>-1</sup> (C=N); UV/ Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε)=600 nm (500 L mol<sup>-1</sup> cm<sup>-1</sup>); MS (MALDI-TOF): *m/z*: 477.2 [*M*]<sup>+</sup>; HRMS (ESI): *m/z* calcd for C<sub>32</sub>H<sub>20</sub>N<sub>3</sub>S: 478.13724; found: 478.13752.

2-(2-(5-(Diphenylamino)thiophen-2-yl)-8H-indeno[2,1-b]thiophen-8-ylidene)malononitrile (4): Two drops of Et<sub>3</sub>N were added to a mixture of malonitrile (25 mg, 0.36 mmol) and compound 21 (60 mg, 0.14 mmol) in CHCl<sub>3</sub> (15 mL). The reaction mixture was heated at reflux overnight. The solvent was evaporated and the residue was purified four times by column chromatography on silica gel (CH2Cl2) to give a green solid (50 mg, 75 %). M.p. 228–231 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.95$  (d, J=7.3 Hz, 1H), 7.40-7.30 (m, 4H), 7.29-7.07 (m, 10H), 6.87 (s, 1H), 6.48 ppm (d, J = 4.0 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 156.7$ , 156.3, 156.1, 146.9, 138.3, 137.8, 132.9, 131.4, 129.8, 128.5, 126.7, 126.2, 126.0, 125.0, 124.4, 120.7, 117.1, 114.7, 114.2, 113.7, 69.7 ppm; IR (neat):  $\tilde{v} = 2217 \text{ cm}^{-1}$  (C=N); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{
m max}$  $(\varepsilon) = 664 \text{ nm}$  $(17600 \text{ Lmol}^{-1} \text{ cm}^{-1});$  MS (MALDI-TOF): m/z: 483.3 [M]<sup>+</sup>; HRMS (ESI): *m*/*z* calcd for C<sub>30</sub>H<sub>17</sub>N<sub>3</sub>S<sub>2</sub>: 483.08584; found: 483.08534.

2-(2-(5-(Bis(4-methoxyphenyl)amino)thiophen-2-yl)-8H-indeno[2,1-b]thiophen-8-ylidene)malononitrile (5): Three drops of Et<sub>3</sub>N were added to a mixture of compound 22 (205 mg, 0.41 mmol) and malonitrile (54 mg, 0.82 mmol) in CHCl<sub>3</sub> (30 mL). The reaction mixture was heated at reflux for 12 h. The solvent was evaporated under vacuum and the crude product was triturated with hot EtOH (10 mL), filtered, and washed with EtOH  $(2 \times 10 \text{ mL})$  to give compound 5 as a green powder (200 mg, 90%). M.p. 200–202 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.03$  (d, J = 8.3 Hz, 1H), 7.30-7.11 (m, 8H), 6.93-6.85 (m, 5H), 6.24 (d, J=4.2 Hz, 1H), 3.83 ppm (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 159.0$ , 157.5, 156.3, 155.7, 140.0, 139.8, 138.6, 137.7, 132.6, 128.4, 127.6, 126.6, 125.8, 124.4, 120.6, 115.0, 114.7, 114.0, 113.3, 113.3, 112.1, 68.3, 55.7 ppm; IR (neat):  $\tilde{\nu} = 2211 \text{ cm}^{-1}$  $(C \equiv N);$  UV/Vis  $(CH_2Cl_2):$   $\lambda_{max}$  $(\varepsilon) = 710 \text{ nm}$  $(23100 \text{ Lmol}^{-1} \text{ cm}^{-1});$  MS (MALDI TOF): m/z: 543.0 [M]<sup>+</sup>; HRMS (ESI): *m*/*z* calcd for C<sub>32</sub>H<sub>21</sub>O<sub>2</sub>N<sub>3</sub>S<sub>2</sub>: 543.10697; found: 543.10593.

2-(2-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-8H-indeno[2,1-b]thiophen-8-ylidene)malononitrile (6): Four drops of Et<sub>3</sub>N were added to a mixture of malonitrile (60 mg, 0.90 mmol) and compound **25** (200 mg, 0.39 mmol) in CHCl<sub>3</sub> (15 mL). The reaction mixture was heated at reflux overnight. The solvent was evaporated under vacuum and the crude product was triturated with hot EtOH (10 mL), filtered, and washed with EtOH (2×10 mL) to give compound **6** as a green powder (180 mg, 83%). M.p. > 260 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.12 (d, *J*=7.5 Hz, 1H), 7.47 (d, *J*=8.7 Hz, 2H), 7.39 (d, *J*=4.0 Hz, 1H), 7.36–7.18 (m, 11H), 7.17–7.03 ppm (m, 6H); IR (neat):  $\tilde{\nu}$ =2213 cm<sup>-1</sup> (C=N); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ )=620 nm (17100 Lmol<sup>-1</sup> cm<sup>-1</sup>); MS (MALDI-TOF): *m*/*z*: 558.6 [*M*]<sup>+</sup>; HRMS (MALDI-TOF): *m*/*z* calcd for C<sub>36</sub>H<sub>21</sub>N<sub>3</sub>S<sub>2</sub>: 559.1177; found: 559.1186.





**CHEMISTRY** 

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### CHEMISTRY

#### A EUROPEAN JOURNAL

#### **Donor-Acceptor Systems**

- A. Leliège, J. Grolleau, M. Allain,
- P. Blanchard,\* D. Demeter,
- T. Rousseau, J. Roncali\*....

Small D-π-A Systems with *o*-Phenylene-Bridged Accepting Units as Active Materials for Organic Photovoltaics



**Good things in small packages**: The bridging of a dicyanovinyl group to the vicinal thiophene by an *ortho*-phenylene bridge leads to a new electronwithdrawing building block, which has been used for the synthesis of small donor– $\pi$ –acceptor molecular donors with tailored electronic properties. Efficient planar heterojunction solar cells based on these donors of reduced molecular size and C<sub>60</sub> or C<sub>70</sub> are reported.