Structure-properties relationships in triarylamine-based donor-acceptor molecules containing naphtyl groups as donor material for organic solar cells

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The effects of replacing the phenyl rings of triphenylamine (TPA) by naphtyl groups are analysed on a series of push-pull molecules containing a 2-thienyl-dicyanovinyl acceptor group. UV-Vis absorption spectroscopy and cyclic voltammetry show that the introduction of one or two naphtyl groups in the structure has limited effects on the optical properties and energy levels of the molecule. On the other hand, the evaluation of the compounds as donor material in bi-layer solar cells with C60 as acceptor shows that the number and mode of linkage of the naphtyl groups exert a marked influence on the power conversion efficiency (PCE) of the cell. Two naphtyl groups lead to a decrease of PCE with respect to TPA, while a single naphtyl group produces opposite effects depending on the linking mode. Compared to TPA, an alpha-naphtyl group leads to a small decrease of PCE while in contrast a beta-naphtyl leads to a 35% increase of PCE due to improved short-circuit current density (Jsc) and fill-factor. The determination of the hole-mobility of these two donors by the space-charge-limited current method shows that these effects are correlated with the higher hole-mobility of the beta-naphtyl compound.

The chemistry of active materials for organic photovoltaics (OPV) is a highly active field of research powered by the exciting technological opportunities offered by the lightness, plasticity and flexibility of organic materials1–9. Besides innovative potential applications, the major motivation for developing OPV remains an expected drastic reduction of the cost and environmental impact of the production of solar cells compared to the established silicon technology. Although soluble conjugated polymers remain a major class of donor materials for solution-processed bulk heterojunction OPV cells1–4, recent years have seen the emergence of small molecules on the forefront of research on OPV materials owing to the obvious advantages of well-defined chemical structures in terms of reproducibility of synthesis, purification, composition and properties of the materials combined with the possibility to develop more reliable analyses of structure-properties relationships.5–9 After seminal work published in 200510 the design of soluble molecular donors has generated considerable research efforts11–13 and solution-processed bulk heterojunction (BHI) cells with power conversion efficiency (PCE) of 8.0–10% have been reported11–13. However, these results have been obtained with fully optimized solar cells of small active areas and with donor materials of relatively complex chemical structure prepared by multi-step syntheses which can pose the problem of the overall yield, cost environmental impact and scalability of the active material. As discussed in some recent reviews, one of the key for a future industrial development of OPV technology lies in the drastic reduction of the cost and environmental impact of the synthesis of active materials14–16. In this context, it appears that beyond an exclusive focus on PCE, the chemistry of OPV should also take into consideration the development of active materials that combine decent efficiency with high yield, clean and scalable synthesis.

Small molecules have been used for a long time in vacuum-deposited OPV cells17–20, and recent work has shown that single-junction cells based on tailored donors of low molecular weight can reach power conversion efficiencies in the range of 6.0–7.0%21,22. It has been shown already that interesting photovoltaic performances can be obtained with small donor-acceptor molecules based on the triphenylamine (TPA) donor block5,7,9,22–26. Some of these compounds that combine low molecular weight, simple structure and good overall synthetic yield present the advantage to be processable from solutions or by thermal evaporation under vacuum23–25. Thus, when used in combination with C60 as acceptor a small structure such as 1 (Scheme 1) leads to a PCE of 2.50% in a simple...
bi-layer cell and 4.00% in a co-evaporated active layer. Based on these promising results, compound 1 has been selected as a working platform for further structural manipulations with the double objective of improving the performances of the donor structure and progressing in our understanding of structure-properties relationships in this class of molecules. In this context, we have shown already that the rigidification of part of the structure by ethylene or o-phenylene covalent bridge can significantly improve the relevant photovoltaic parameters. As a further step, we report here on a series of small donor-acceptor molecules in which the phenyl groups of the TPA block of compound 1 are replaced by one or two naphthyl groups namely α-naphthyl (2a), β-naphthyl (2b), ζ,β-dinaphtyl (3ab), and ζ,β-dinaphtyl (4bb) (Figure 1).

The synthesis and characterization of the electronic properties of the molecules are described and the effects of the number and mode of linkage of the naphtyl groups on the performances of simple bi-layer solar cells with C60 as acceptor material are discussed.

Results and Discussion
The synthesis of the target compounds is described in Figure 2 (see SI). The brominated triarylamines (7) have been synthesized in 45 to 80% yield by coupling diarylamines 5 with p-dibromobenzene (6) in...
the presence a palladium catalyst. The reaction was optimized by varying the ligand of the catalyst and the temperature and duration of the reaction. A Stille coupling of bromo-compounds 7 with 2-(tributylstannyl)thiophene gives the 2-thienyl-derivatized compounds present a slight red shift of the absorption band while the low energy absorption edge lead to estimated band gaps of ~2.00 eV similar to that of compound 1.

Cyclic voltammetry (CV) was performed in dichloromethane in the presence of Bu$_4$NF as supporting electrolyte. All compounds present very similar CVs that exhibit a reversible one-electron oxidation process with an anodic peak potential ($E_{pa}$) in the 0.90–1.05 V vs SCE range corresponding to the formation of the cation-radical (Figure 4) and an irreversible reduction process with a cathodic peak potential ($E_{pc}$) in the −1.10 to −1.30 V region (Table 1 and SI). Replacement of a phenyl ring of compound 1 by a naphtyl group leads to different effects depending on the mode of linkage. Thus, for compound 2a a 20 mV positive shift of $E_{pa}$ is observed. This effect can be assigned to the larger steric demand of the α-naphthyl group vs the phenyl one which results in more twisted structure and hence lower donor strength of the aromatic block. In contrast, for 2b a 40 mV negative shift of $E_{pa}$ occurs due to the increased donor effect of the β-naphtyl group which allows a more coplanar geometry of the molecule.

The introduction of a second naphtyl group produces a further small negative shift of $E_{pa}$ to 0.93 and 0.91 V for 3ab and 4bb respectively. Again the lower oxidation potential of the β,β'-disubstituted compound 4bb compared to the α,β 3ab can be attributed to a lesser steric hindrance. Replacement of one phenyl ring by a naphtyl group produces a ca 100 mV negative shift of $E_{pc}$ while a second naphtyl group produces a further shift of 100–140 mV, these effects are consistent with the stronger donor effect of the naphtyl group compared to the phenyl one (Table 1 and SI).

The optical and electrochemical results show that the introduction of naphtyl groups in the structure of compound 1 has only a small impact on the absorption spectrum of the molecule and hence on its light-harvesting properties. Furthermore, the naphtyl groups exert only a limited influence on the energy level of the frontier orbitals. Thus, a single naphtyl group leads to a ~0.10 eV increase of the HOMO and LUMO level while introduction of two naphtyl groups raises these levels by 0.10–0.20 eV (Table 1). A preliminary evaluation of the new compounds as donor material for OPV cells has been carried out on bi-layer planar heterojunction of 28 mm$^2$ active area cells fabricated by spin-casting ca 20 nm thick films of donor from chloroform solutions containing 5 mg/mL of compound on ITO substrates pre-coated with 40 nm thick films PEDOT:PSS. The substrates were then introduced in a vacuum chamber. A 30 nm thick layer of C$_6$O was deposited by thermal evaporation under a pressure of 2×10$^{-6}$ mbar and the devices were completed by deposition of a 100 nm layer of aluminum. Each batch typically involves six cells. After fabrication the cells were subjected to a ten minutes thermal treatment at 120°C. Although the solubility of the compounds was compatible with the fabrication of solution-processed BHJ cells, no attempt in that direction was made at this stage of the research. Due to a larger dispersion of the results, solution-processed BHJ cells generally require longer optimization implying the fabrication of a larger number of devices than simple PHJ cells. Furthermore, since the purpose of this work is to analyse

**Table 1 | UV-Vis absorption and cyclic voltammetry data for the D-A compounds**

| Compd | $\lambda_{max}$ a [nm] | $\lambda_{max}$ b [nm] | $\varepsilon$ [M$^{-1}$ cm$^{-1}$] | $E_{pa}$ [V vs SCE] | $E_{pc}$ [V vs SCE] | HOMO [eV] | LUMO [eV] | $\Delta E$ [eV] |
|-------|----------------------|----------------------|-------------------------------|-------------------|-------------------|-------------|-------------|--------------|
| 1 a   | 500                  | 523                  | 27000                         | 1.04              | −1.10             | −6.0        | −3.8        | 2.2          |
| 2a    | 498                  | 510                  | 32500                         | 1.06              | −1.19             | −6.0        | −3.8        | 2.2          |
| 2b    | 500                  | 518                  | 36300                         | 1.00              | −1.21             | −5.9        | −3.7        | 2.2          |
| 3ab   | 494                  | 503                  | 27000                         | 0.93              | −1.34             | −5.7        | −3.4        | 2.3          |
| 4bb   | 510                  | 513                  | 31000                         | 0.91              | −1.29             | −5.7        | −3.5        | 2.2          |

*a in CH$_2$Cl$_2$;  
*b on films;  
* using an offset of −4.99 eV vs vacuum level for SCE.  
*from Ref. 23.
structure-properties relationships, simple two-layer devices appear as a more convenient tool as they give more reproducible and more reliable results despite an efficiency inferior to that of BHJ cells.

The photovoltaic characteristics of the bi-layer cells based on the four donors containing napthyl groups are shown in Figure 5 and the corresponding data are listed in Table 2 using compound 1 as reference. A first examination of the current density vs voltage curves of Figure 3 clearly shows that the introduction of naphtyl groups in the donor structure exerts a considerable effect on the performances of the cells. Thus, replacement of two phenyl groups by two naphtyl ones leads to a decrease of PCE from 2.50% for 1 to 1.70 and 1.40% for 3ab and 4bb respectively. This phenomenon results essentially from the decrease of $J_{sc}$ to values inferior to 4.0 mA cm$^{-2}$. Surprisingly, the devices based on the di-naphtyl compounds 3ab and 4bb show slightly higher $V_{oc}$ values than compound 1 although the opposite effect could be anticipated in view of the higher HOMO level of 3ab and 4bb compared to the singly substituted compounds$^{28}$. Such unexpected structural effects on $V_{oc}$ have already been observed and attributed to changes in the interfacial dipole at the D/A heterojunction$^{29}$. Anyway further work is needed to clarify this point. Except for 2b, the J vs V curves present a more or less pronounced S shape. This phenomenon can be attributed to imbalanced mobility of holes and electrons$^{30}$ and/or to problems of charge-transfer at the active material/electrode interface. Based on the relatively small differences among the HOMO and LUMO levels of the various donors, the former explanation appears more plausible. Furthermore, this interpretation is consistent with the observed differences in hole-mobilities (see below).

The results for compound 2a show that replacement of one phenyl group by an α-naphtyl one leads to a small decrease of $V_{oc}$ and fill factor resulting in a decrease of PCE from ca 2.50 to 2.20%. However, when the naphtyl group is connected to the nitrogen atom by its β-position in 2b, a marked increase of PCE is observed due in particular to an increase of $J_{sc}$ up to 7.80 mA cm$^{-2}$ and to an improvement of the filling factor (FF). The best device gave a PCE of ~3.40% with an average value of 3.10% (see SI). Based on the large increase of PCE previously observed upon optimization of cells based on compound 1$^{26}$ the results obtained with 2b suggest that there is still much room for improvement of the performances of cells.

Figure 6 shows the external quantum efficiency (EQE) action spectrum of a device based on 2b under monochromatic irradiation. The first maximum around 360 nm can be attributed to the contribution of C60. This first band is followed by a broad shoulder in the 400 to 600 nm region with a maximum of ~70% in agreement with the absorption spectrum of the donor. These results show that the β-naphtyl D-A molecule can lead to interesting photon/electron con-
The results show that the replacement of a phenyl group deposited by spin-casting from chloroform solutions (22 mg/mL) donor/Au. Films of the donors of 200–300 nm thickness have been measured by the space-charge limited current method mobility of the three representative compounds SCLC on “hole-only” devices of structure: ITO/PEDOT PSS/ been measured by the space-charge limited current method electronic properties of the molecule31.

In a previous work we have shown that the introduction of a 5-hexyl-2,2′-bithienyl hole-transporting group in the meso-position of a BODIPY donor leads to a two-fold increase in the efficiency of the resulting solar cell and that this effect was due exclusively to an increase of hole-mobility without any effect on electronic properties of the molecule31.

In order to test this hypothesis in the present case. The hole-mobility of the three representative compounds 1, 2a and 2b has been measured by the space-charge limited current method (SCLC) on "hole-only" devices of structure: ITO/PEDOT PSS/ donor/Au. Films of the donors of 200–300 nm thickness have been deposited by spin-casting from chloroform solutions (22 mg/mL) (see SI). The results show that the replacement of a phenyl group of compound 1 by an α-naphtyl group leads to a two-fold increase of hole mobility (μ₁₁) from 1.0 × 10⁻⁶ cm² V⁻¹ s⁻¹ for 1 to 4.2 × 10⁻⁶ cm² V⁻¹ s⁻¹ for 2a (Table 2). In contrast, replacement of the phenyl by a β-naphtyl leads to an increase of μ₂₂ by a factor of five (μ₂₂ = 5.5 × 10⁻⁶ cm² V⁻¹ s⁻¹) which results in a difference of more than one order of magnitude between the hole mobility of the α- and β-mono-substituted compounds 2a and 2b. This large difference which clearly confirms the significant role of the mode of grafting of the naphtyl group can be attributed to a molecular packing more propitious to efficient charge transport in the case of 2b due to the already discussed lesser steric hindrance associated with the β-linkage. Finally comparison of these results with the photovoltaic data in Table 2 confirms, in agreement with previous conclusions31, that the structural optimization of the hole-mobility represents an interesting tool for the improvement of the photovoltaic performances of molecular donors.

### Conclusion

A series of donor-acceptor systems based on triarylamine donor blocks in which one or two phenyl rings are replaced by naphtyl groups has been synthesized in good overall yields. Although the introduction of naphtyl groups in the structure has little influence on the light-harvesting properties and energy levels of the molecule, the results obtained on bi-layer OPV cells reveal a large diversity of situations. The introduction of two naphtyl groups through α,β' or β,β' linkages induces a net decrease of conversion efficiency. When linked via an α-position, a naphtyl group produces a small decrease of PCE while in contrast, when attached at a β-position this group produces a significant increase of PCE due in particular to a large increase of Jsc correlated to a parallel increase of hole mobility. These opposite effects are attributed to the consequences of the different intramolecular steric effects associated with the mode of linkage of the naphtyl group on the intermolecular interactions and molecular packing. Based on the strong current interest in TPA-based systems for the design of donor materials for OPV, of non-metal sensitizers for dye-sensitized solar cells32, or of hole-transporting materials for perovskite solar cells33 these results provide a strong incitement to further investigations of structure-properties relationships in this class of D-A systems. Work in this direction is now underway and will be reported in future publications.

### Table 2 | Photovoltaic characteristics of bi-layer solar cells donor/C60 under AM 1.5 simulated solar illumination with a power intensity of 90 mW cm⁻².

| Donor | Jsc (mA cm⁻²) | Voc (V) | FF | PCE (%) | μ (cm² V⁻¹ s⁻¹) |
|-------|---------------|--------|----|---------|----------------|
| 1     | 5.80          | 0.92   | 0.42 | 2.50    | 1.0 × 10⁻⁵     |
| 2a    | 5.90          | 0.80   | 0.40 | 2.10    | 0.70 × 10⁻⁵    |
| 2b    | 6.20          | 0.80   | 0.40 | 2.20    | 0.42 × 10⁻⁵    |
| 3ab   | 7.80          | 0.83   | 0.45 | 3.11    | 5.5 × 10⁻⁵     |
| 4bb   | 4.00          | 0.96   | 0.39 | 1.66    | 1.53           |
| 4bb   | 3.10          | 0.95   | 0.40 | 1.31    |                 |
| 4bb   | 3.30          | 0.92   | 0.40 | 1.35    |                 |

Although these results clearly demonstrate that the introduction of naphtyl groups in the structure of compound 1 exerts a marked influence on the photovoltaic performances of the donor, the origin of these effects is not evident. As shown by optical and electrochemical data, the naphtyl groups have only limited effects on the light-harvesting properties and energy levels of the system. This indicates that the origin of the effects of the naphtyl groups on the performances of the photovoltaic cells is probably related to changes in intermolecular interactions. In a previous work we have shown that the introduction of a 5-hexyl-2,2′-bithienyl hole-transporting group in the meso-position of a BODIPY donor leads to a two-fold increase of the efficiency of the resulting solar cell and that this effect was due exclusively to an increase of hole-mobility without any effect on electronic properties of the molecule31.

### Figure 6 | External quantum efficiency of the cell ITO/PEDOT:PSS/2b/ C60/Al under monochromatic irradiation.

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Author contributions
S.M. synthesized and characterized the materials. D.D. performed device fabrication and characterization, J.R. supervised the project and prepared the manuscript. J.-A.L. and P.B. analysed the data and contributed to revisions.

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