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Synthesis and optical properties of a new triphenylamine-*p*phenylenevinylene-small molecule with applications in high opencircuit voltage organic solar cells

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promising

A new oligomer-type *para*-phenylenevinylene end-capped with triphenylamine groups (TPAPV) was synthesised and its optical properties thoroughly investigated. Fluorescence quenching studies showed that an important fraction of the photogenerated excitons formed in TPAPV is quenched by [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) in blend films, therefore indicating efficient exciton dissociation and potential applications in organic photovoltaic (PV) cells. Planar heterojunction organic photovoltaic cells containing TPAPV as electron-donor were fabricated and devices with structure ITO/TPAPV(6nm)/C₆₀(50 nm)/BCP(10 nm)/Ag exhibited an open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), Fill Factor (FF), and power-conversion efficiency (PCE) of 0.92 V, 2.9 mA/cm², 47.8 %, and 1.23 %, respectively.

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Introduction

Triarylamines have been considered one of the best building blocks to design organic semiconductors for a significant number of opto-electronic devices, such as organic lightemitting diodes (OLEDs),^{1,2} organic field effect transistors,^{3,4} electrochromic devices,⁵ etc. Due to the combination of good hole transport properties ($\mu_{\rm h} = 10^{-2} - 10^{-3} \, {\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}$) via radical cationic species arisen from the electron-donating nature of the nitrogen center atom and high light-emitting efficiency typically observed for the arylamine-based oligomers and polymers, a wide variety of chemical structures containing the triarylamine block has been studied as hole-transport layer (HTL) in multilayer OLEDs,⁶⁻⁸ as sensitizers in dye-sensitized solar cells,⁹ and as electron-donor in organic photovoltaic cells (OPVs).^{10,11} In particular, the search for small molecular donors for OPV devices has attracted significant efforts, since they do not hold the drawbacks of polymers, namely batch-to-batch variations and ill-defined chemical structures, which can affect device reproducibility and efficiency. Also, conversely to electroactive polymers, small-molecules, being structurally well-defined and monodisperse, are ideal models to unravel structure-properties relationships. Such benefits of

resolved fluorescence analysis, and show applications in organic photovoltaic devices with a planar heterojunction architecture. Hole mobility of the new compound was also measured through hole-only defices and thin field-effect transistors (TFTs). Time-resolved fluorescence spectroscopy has been shown to be an useful tool for investigating many of the mechanisms involved in energy transfer processes in end-capped oligophenylene-vinylene oligomers, such as solvent relaxation and/or conformational relaxation of the conjugated backbone,¹⁴ intrachain energy transfer in solutions,¹⁵ or interchain energy transfer in solutions,¹⁶ We chose to fabricate planar heterojunction OPVs, since for such architecture, the device operation is not dependent on the intricate morphology of the donor:acceptor blend as for BHJ cells, and therefore they are good prototypes for investigating

investigating electroactive small-molecules-based devices have

driven numerous works and have resulted in device performances up to values well-comparable with most

demonstrated

counterparts. In the particular case of OPVs, small-molecule-

based cells have surpassed already 8% in thermally evaporated

structures,¹² and 9 % in power-conversion efficiency for

optimized solution-processed BHJ PV cells.¹³ The search for

for

polymer-based

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improving PV cells performance has also encouraged studies to understand the processes that govern the photophysical behaviour of the electroactive materials. To this respect, small molecules and oligomers are also the best candidates since they can be model compounds for large molecular weight materials. Here, we present the synthesis of a new π -conjugated triphenylamine-containing small molecule composed of a *para*-phenylene-vinylene trimer as the central unit (Scheme 1), a study on its optical properties with emphasis on timeresolved fluorescence analysis, and show applications in organic photovoltaic devices with a planar heterojunction architecture. Hole mobility of the new compound was also

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materials individual performance. Furthermore, planar heterojunction OPVs are attractive for being easy to fabricate through utilizing thermal evaporation to deposit the organic materials from the gas phase, allowing precise control of layer thicknesses. However, they often show power conversion efficiencies (PCEs) lower than their BHJ counterparts (due to an unfavorable balance between the optical absorption length and the exciton diffusion length) but they potentially exhibit high charge collection efficiencies owing to reduced nongeminated (bimolecular) charge recombination rates.¹⁷ This loss mechanism refers to charge annihilation caused by recombination of polarons of opposite charge meeting on their way towards the electrodes and therefore is minimized in the pure-layers (all donor and all acceptor) of planar heterojunctions.

Experimental

Materials

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All reagents were purchased from commercial suppliers (SIGMA-Aldrich and STREM) and used as received and without further purification unless otherwise stated. All the solvents used under inert atmosphere were dried by refluxing over a suitable drying agent under nitrogen and deoxygenated before use by freeze-pump-thaw cycling.

Synthesis

TPAPV was synthesised through a Suzuki Pd(0)-catalyzed crosscoupling reaction between 4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)triphenylamine and **4** (Scheme 1). 4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine was prepared from 4-bromotriphenylamine following reported procedures¹⁸ and **4** was prepared through a Wittig reaction from 4-bromobenzaldehyde and 1,4-bis((2-ethylhexyl)oxy)-2,5xylenebis(triphenyl)phosphonium bromide (**3**) using the same procedure reported for 1,4-bis((hexyl)oxy)-2,5xylenebis(triphenyl)phosphonium bromide (Scheme 2).^{19,20}

4,4'-[(2,5-(2-ethylhexyl)oxy-1,4-phenylene)di(E)ethene-2,1-

diyl]dibromobenzene (4) 2.5 ml of a 0.8 M NaOEt/EtOH solution, freshly prepared from 0.047 g (2.03 mmol) of Na in 2.5 ml of dried EtOH, were added dropwise to a solution of 3 (0.850 g, 0.81 mmol) and 4-bromobenzaldehyde (0.316 g, 1.71 mmol) in 10 ml of CH₂Cl₂, under N₂. The mixture was stirred at room temperature for 12 h. Then, 10 ml of water were added and the organic layer was extracted with CH₂Cl₂, washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The product was purified by column chromatography with SiO₂ (97/3, v/v, CH₂Cl₂/EtOAc) as a yellow solid (0.340 g). Yield: 60 %. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.50-7.45 (4H, d, *J* = 8.88 Hz + 2H, d, *J* = 16.05), 7.39 (4H, d, *J* = 5.48 Hz), 1.86-1.79 (2H, quint, *J* = 5.95 Hz), 1.62-1.30

(16H, m), 0.99 (6H, t, J = 7.46 Hz), 0.92 (6H, t, J = 6.99 Hz). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.25, 136.97, 131.79, 127.92, 127.60, 126.69, 124.22, 121.09, 110.35, 71.79, 39.77,

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4,4'-[(2,5-(2-ethylhexyl)oxy-1,4-phenylene)di(E)ethene-2,1-

30.97, 29.28, 24.27, 23.13, 14.14, 11.35.

dividibenzotriphenylamine (TPAPV) A flask charged with 4 (0.326 g, 0.47 mmol), and 4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)triphenylamine (0.382 g, 1.03 mmol) was charged with $Pd(PPh_3)_4$ (4 %, mol) in a glove box with nitrogen atmosphere. A degassed mixture of 7.0 ml of toluene and 4.5 ml of Et₄NOH (20 % wt. in H₂O) was added and the mixture was refluxed under vigorous stirring for 12 h, under inert atmosphere (N_2) . The reaction was guenched by adding water and the organic layer was separated with CH₂Cl₂, washed with brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The product was purified by column chromatography with SiO₂ (70/30, v/v, CH₂Cl₂/Hexane) as a yellow solid (0.348 g). Yield: 73 %. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.59 (8H, s); 7.56-7.52 (2H, d, J = 16.56 Hz); 7.54-7.52 (4H, d, J = 8.78 Hz); 7.30-7.26 (8H, m); 7.23-7.19 (2H, d, J = 16.56 Hz); 7.18 (2H, s); 7.13-7.12 (8H, d, J = 1.25 Hz); 7.11-7.10 (4H, d, J = 1.25 Hz); 7.06-7.02 (4H, tt, J = 7.28 and 1.13 Hz); 3.99-3.98 (4H, d, J = 5.52 Hz); 1.87-1.81 (2H, quint, J = 6.02 Hz); 1.65-1.33 (16H, m); 1.02-0.98 (6H, t, J = 7.53 Hz); 0.94-0.91 (6H, t, J = 7.03 Hz). ¹³C NMR (100 MHz, CDCl₃): 206.37, 151.21, 147.64, 139.41, 136.39, 129.26, 128.08, 127.36, 126.83, 126.72, 126.65, 124.44, 123.76, 123.08, 123.01, 39.83, 30.93, 30.58, 29.26, 24.25, 23.13, 13.90, 11.10. MALDI-TOF MS (matrix 2,5-DHB)), m/z (Da): 1025.54 (M⁺). Calcd. for C₇₄H₇₆N₂O₂: 1025.43.



Scheme 1. Synthetic route of TPAPV.

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Scheme 2. Synthetic route to 3: i) NaOHaq., 2-ethylhexylbromide, Hexane, TBABr; reflux, 12 h, ii) HBr, HCHO, AcOH, 70 °C, 4h; iii) PPh₃, DMF, 80 °C, 12 h.

Measurements

NMR spectra were recorded on a Brucker "Advance II" spectrometer (300 MHz or 400 MHz) in CDCl₃ or CD₂Cl₂. ¹H and ¹³C NMR spectra are referenced to the residual solvent impurity peak of the solvents. Multiplicities were abbreviated as: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), doublet of doublets (dd), doublet of triplets (dt), triplet of doublets (td). Matrix-assisted laser desorption ionization (MALDI) mass spectra were performed on a Voyager-DE™ PRO Biospectrometry Workstation MALDI/TOF/MS analyzer (Applied Biosystems) bv LAREQUIMTE. Thermal analysis was performed by Differential Scanning Calorimetry (DSC) in a 2920 Modulated DSC TA Instruments. Cyclic voltammetry (CV) measurements were performed in a Solartron potentiostat using 0.1 M tetrabutylammonium tetrafluorborate (TBABF₄)/CH₃CN supporting electrolyte, at a scan rate of 50 mV/s. A saturated calomel reference electrode (SCE) calibrated against ferrocene, Fc/Fc^{+} (0.41 V), a platinum wire as counter electrode and a platinum disk as working electrode were used. The compound TPAPV was drop cast from toluene solutions onto the working electrode. As the energy level of Fc/Fc^{+} is at 4.80 eV below the vacuum level we calculate HOMO (eV) = $-(E_{onset,ox}(eV) + 4.41)$ and LUMO (eV) = - $(E_{onset,red}$ (eV) + 4.39).²¹ UV/Visible absorption spectra were recorded in a Beckman DU-70 spectrophotometer. Photoluminescence spectra were measured on a SPEX Fluorolog 212I spectrophotometer, at the right angle geometry, S/R mode, and corrected for instrumental wavelength dependence, optics and detector wavelength dependence. Photoluminescence decays were measured using the picosecond time-correlated single-photon counting (TCSPC) technique, and the obtained fluorescence decays analyzed as described in ref. 22. A mode-locked Ti:sapphire Tsunami laser was used as a pulsed excitation source. Measurements were carried out by exciting the samples with vertically polarized light and setting the emission polarizer at the magic angle. Sample signals were collected until 5000 counts had been accumulated at the maximum of the decay.

The optimized ground state geometric structures and frontier levels (HOMO and LUMO) for the molecule TPAPV in the gas phase were determined by density functional theory (DFT, B3LYP method with 6-31G* basis set) using a SPARTAN software (Wave function, Inc.). Atomic Force Microscopy (AFM) analysis were performed on a NanoObserver from Concept Scientific Instruments.

Device fabrication

Thin film transistors of TPAPV were prepared by subliming TPAPV under vacuum (ca. 2×10^{-6} mbar) over a 625 nm thick dielectric layer of silicon dioxide (SiO₂) treated with HMDS (1,1,1,3,3,3-hexamethyldisilazane). Underneath this dielectric, a highly-doped silicon layer acted as gate contact. Source and drain contacts, made of 20 nm-thick molybdenum oxide (MoO₃) coated with a 40 nm thick aluminium layer, were deposited over the TPAPV layer (110 nm thick) using a shadow mask, defining a channel with a length of 100 micron and width of 3.5 mm. Hole-only devices were prepared by subliming TPAPV under vacuum over a glass/ITO substrate coated with a PEDOT:PSS layer (40 nm thick). A top contact of MoO₃/Al was deposited defining pixel areas of 4 mm². Organic PV cells were fabricated with the planar heterojunction architecture ITO(indium tin oxide)(140 nm)/TPAPV/C₆₀/BCP(10 nm)/Ag (120 nm) by depositing the organic layers from vapor in a high vacuum chamber (base pressure < 1 \times 10 $^{\rm 6}$ Torr). The deposition rates for organic layers were kept between 0.1-1.2 Å/s. The active area of the devices was 13 mm². Currentvoltage (I-V) characteristics were measured under inert atmosphere (N_2) . Power conversion efficiencies (PCEs) of the devices were measured with a solar simulator (Abet) with simulated AM 1.5G illumination, calibrated using a Fraunhofer certified cell at 100 mW/cm².

Results and Discussion

Synthesis

The isomer E,E of TPAPV was isolated in good yield (73 %) although other geometric isomers were formed according to NMR-¹H spectra for the mixture. The (E,E) trimer was purified by chromatography in SiO₂ and its structure was confirmed by the presence of two doublets in the NMR-¹H spectrum assigned to the four ¹H of the vinylene groups, at 7.56-7.52 and 7.23-7.19 ppm with J = 16.56 Hz. Thermal analysis of TPAPV (DSC) at a heating rate of 10 K/min in the range of 0-350 °C shows a well-defined melting peak at 183.8 °C and do not show exothermal transitions which could indicate thermal degradation under that temperature range (Figure S1 in Supplementary Info).

Electrochemical properties

TPAPV electrochemical properties were characterised through cyclic voltammetry and optical properties were characterised by UV–Vis absorption and fluorescence spectroscopy. The HOMO and LUMO energies were estimated from the onset values measured for the oxidation (*p*-doping) and reduction (*n*-doping) processes, respectively, by cyclic voltammetry, and compared with values calculated for the optimized ground state geometric structure for TPAPV in the gas phase determined by quantum-chemical methods using density functional theory (DFT). The obtained voltammograms are shown in Figure 1. As the anodic and cathodic peaks are not fully reversible, fresh films were used for the oxidation

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(anodic) and for the reduction (cathodic) scans. The estimates for HOMO and LUMO values are -5.26 eV and -2.54 eV, respectively. The HOMO energy is higher than values found for conjugated polymers based on the triphenylamine monomer units which range at -5.6 – -5.8 eV.²³ This is attributed to the strong contribution of the central block of three phenylene rings for the HOMO, as predicted by DFT calculations (Figure 2).



Figure 1. Cyclic voltammograms of TPAPV in film deposited over the Pt disc working electrode.



Figure 2. Optimized ground-state (S0) geometric structure of TPAPV and respective HOMO and LUMO wavefunctions representations as determined at the B3LYP/6-31G* level of DFT.

Unlike HOMO, the LUMO is more delocalized over the C=C backbones of the central trimer and shows little contribution of triphenylamine end-caps. The HOMO and LUMO energies calculated by DFT, being -4.78 eV and -1.81 eV, respectively, are both higher than those estimated by cyclic voltammetry for TPAPV in solid films. This shift should be mainly related to the orbitals energy differences between the gas phase and

solid films, where in these last packing and ordering effects should lead to π -electron delocalization over neighbour molecular orbitals. To better elucidate the optical properties-structure relationships, we have further investigated the photophysical properties of TPAPV.

Photophysical studies

Figure 3 shows the absorption and fluorescence spectra of TPAPV in dilute toluene solution and in solid film spin cast from concentrated toluene solutions (40 mg/ml). The fluorescence spectrum in solution exhibits vibrational resolution similar to that observed for other related phenylenevinylene trimers end-capped with carbonyl groups instead of triphenylamines.²² This is in accordance with previous works, showing that the first excited singlet state of phenylenevinylene (PV) trimers is not significantly affected by the incorporation of triphenylamine-type end-caps. The fluorescence quantum yield measured for TPAPV in toluene at 293 K was 0.70 ± 0.01 , also very similar to that for the aforementioned PV trimers without TPA end-groups (0.71-0.72).^{16,24}

The absorption spectrum in film is broadened relative to the one in solution, this being probably associated to the presence of a greater variety of conformational species in film with more planar conformations (larger effective conjugation lengths) absorbing at longer wavelengths. The emission spectrum is red-shifted with respect to the solution spectrum, as typically found for conjugated compounds, this being attributed to solid-state interactions and effects of molecular ordering in the solid state.



Figure 3. Normalized absorption and fluorescence spectra of TPAPV in toluene and in solid film, at room temperature. The emission spectra were obtained with excitation at 415 nm.

Solvent effect In order to investigate the variation of electronic distribution from the ground state to the first excited state, a systematic study of the absorption and fluorescence spectra of TPAPV in solvents of different polarizabilities was carried out. The changes in Stokes shifts with the solvent polarizability provides information on the solvent reorganization around the

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excited state and on variations on charge distribution between the electronic states involved in the transitions.²⁵ We found that the solvent effects are less pronounced in the absorption spectra than in the fluorescence spectra (Table 1), although both spectra show clear sensitivity to the solvent. Also, the emission spectra show a progressive red-shift and reduction of the vibronic structure with increasing solvent polarity (Figure 4 and Table 1). Thus, using a Lippert-Mattaga plot,²⁴ we found that the slope of the linear regression used to fit the Stokes shifts as a function of the solvent polarizability was close to zero, indicating a small dipole moment change (< 1 Debye) upon photoexcitation and therefore, a negligible solvent reorganization around the excited state should be expected. Hence, we conclude that the differences between the electronic distribution of the HOMO and the LUMO orbitals, calculated by DFT, should not affect significantly the dipole moment variation nor the solvent reorganization upon photoexcitation.

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Table 1. Maximum absorption and emission wavelengths of TPAPV in different solvents.

Solvent	ε ^a	n_{D}^{b}	η ^ϲ (cP)	λ _{abs} (nm)	λ _{em} * (nm)	Stokes Shift (nm)
DMSO	47.2	1.48	1.991	425	481	56
DMF	36.7	1.43	0.802	422	475	53
Acetone	21.0	1.36	2.415	417	468	51
HF	7.68	1.41	0.575	418	471	53
Chloroform	4.81	1.48	0.580	418	474	56
Toluene	2.38	1.50	0.586	418	471	53
Hexadecane	2.05	1.44	3.351	416	466	50
Tetradecane	2.03	1.44	2.342	415	465	50
MCH	2.02	1.42	0.734	411	464	53
Undecane	2.01	1.44	1.508	413	464	51
Hexane	1.88	1.38	0.313	410	462	52

^aDieletric constant (pure solvent), ^bRefractive Index (pure solvent), ^cViscosity (pure solvent), * Maximum emission wavelength of the first vibronic band, identified through spectra deconvolution with Gaussian functions.



Figure 4. Normalized fluorescence spectra of TPAPV in different solvents, at room temperature ($\lambda_{exc.}$ = 415 nm).

Time-resolved fluorescence studies Time-resolved fluorescence measurements with picosecond time resolution of TPAPV were performed by collecting the fluorescence intensity at the beginning (450 nm), at close to the maximum (490 nm), and at the lower energy side (540 nm) of the emission band, in two solvents, toluene and methylcyclohexane (MCH). Figure 5 shows the fluorescence decays obtained in MCH. For each solvent, the simultaneous analysis of the three decays were fitted to double exponential functions, showing a short component (toluene: 14 ps, MCH: 26 ps) and a long component (toluene: 936 ps, MCH: 926 ps). The pre-exponential coefficients of the longer decay components are positive at the three wavelengths and represent the largest

contribution to the fluorescence decays. Therefore, the longer time is assigned to the lifetime of the compound. The shorter time appears as a decay-time at the beginning of the emission band (positive pre-exponential coefficient) and as a rise-time at the lower energy part of the band (negative coefficients). Similar short components have been observed in other conjugated systems and various explanations have been given, in particular associated to intrachain or interchain energy transfer, solvent relaxation, and conformational relaxation.^{26,27}



Figure 5. Fluorescence decays of TPAPV in MCH at 293 K, measured with excitation at 425 nm and 6.13 ps/channel. From the simultaneous fit of the three decays, the times

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and pre-exponential coefficients at each emission wavelength are obtained. Weighted residuals and autocorrelation functions (AC) are represented together with χ^2 values of the fits. The time resolution of the experimental set-up is ca. 3 ps.

Photophysical studies of TPAPV in blend films with PC61BM To anticipate potential applications of TPAPV in OPV cells as electron-donor, excited state-related processes of TPAPV in solid films, prepared from blends with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) were investigated. For a better understanding of films of blends behaviour, neat films of TPAPV were also studied. For neat films, we found that, when exciting at 415 nm, a strong reabsorption of the first vibronic emission band occurs, as inferred from the observed relative reduction in intensity of this vibronic band when compared with that of the second vibronic peak, at 523 nm (Figure 3). On the other hand, in the low energy region of the emission band, where the reabsorption is absent, the red shift of the spectrum is clear, which should be related with the emission of species of more extended effective conjugated lengths. We also note that photoexcitations at different wavelengths, ranging at the absorption maximum and at the low energy edge of the absorption band, do not induce significant changes in the emission spectrum. Time-resolved fluorescence measurements carried out for films of TPAPV with PC61BM (blend films prepared from 10:1 TPAPV:PC₆₁BM solutions) and without PC₆₁BM (neat films) were compared. The fluorescence decays were measured at 293 K, with excitation at 410 nm and collecting the emission at 550 nm. Since PC₆₁BM does not show emission at 550 nm, only TPAPV contributes for the collected fluorescence. Therefore, fluorescence extinction at this wavelength is only due to quenching of photogenerated excitons in TPAPV. The measurements for the fluorescence decays in neat films were fitted to a sum of two exponential terms, with two decay times, τ_1 = 595 ps and τ_2 = 172 ps, which are well different from those found for TPAPV in toluene solution (936 ps). The pre-exponential coefficients of the decay times in films are: 0.69 (τ_1) and 0.31 (τ_2). This type of variance in excited state dynamics from solution to film has been reported for various conjugated polymers and oligomers, and has been attributed to a combination of photophysical processes involving, for example, interchain and non-radiative energy transfer mechanisms.^{27,28} The fluorescence decays and corresponding fitting curves obtained for films of TPAPV are shown in Supplementary Information (Figure S1). In blend films of TPAPV:PC₆₁BM, prepared from spin casting solutions in toluene, the fluorescence decays required a fit of a sum of three exponential terms, τ_1 = 404 ps (pre-exponential coefficient: 0.04), τ_2 = 112 ps (0.17) and τ_3 = 12 ps (0.79), to obtain a good fitting. While the two first decay times compare well with those observed in the neat film, a new short time appears (12 ps), similar to that found in toluene solution. Such short time cannot be assigned to conformational relaxation, since this is unlikely to occur in solid films. Thus, we assign this component to the dissociation process of the photogenerated excitons in TPAPV phase due to the presence of the electronacceptor PC₆₁BM. Since the HOMO and LUMO levels for PC₆₁BM are estimated as -6.1 eV and -3.75 eV,^{29,30} respectively,

it may perform as electron-acceptor for TPAPV and cause exciton dissociation. Regarding the neat film, the average lifetime for the first excited state is 464 ps (0.69×595 ps + 0.31×172 ps). In comparison, for the blend film, the average lifetime is 45 ps, i.e. an order of magnitude lower. This means that an important fraction of the photogenerated excitons formed in TPAPV is quenched by $PC_{61}BM$ in blend films. We therefore conclude that, similarly, TPAPV may perform as an efficient electron-donor in heterojunction PV cells with the fullerene $PC_{61}BM$ as electron-acceptor.

Hole mobility studies

The hole mobility of TPAPV was determined using two different device structures: a thin film transistor (TFT) and a hole-only device fabricated as described. From the transfer curve measured for TFTs in the saturation regime (V_{sd} =-100 V, V_g down to -100 V), a field-effect hole mobility of 1.3×10^{-5} cm²/V.s was obtained. The hole mobility extracted from hole-only devices was obtained by fitting the current-voltage curves to the equation:

$$J_{SCLC} = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{(V - V_{bi})^2}{L^3}$$

in the space-charge limited current (SCLC) regime.³¹ Assuming $\varepsilon_r = 3$ (a typical value for organic conjugated systems)³² and L= 110 nm (thickness of the TPAPV layer), μ_h was determined as 4.0×10^{-6} cm²/V.s. The difference between the two values of μ_h is attributed to the sample morphology as the measured mobility in the hole-only device is normal to the substrate and in the TFT device the transport is parallel to the dielectric substrate surface. Since chain orientation and packing on surfaces treated with organic moieties is different from the bulk³³ (the surface of TFT was treated with HMDS as described in Experimental) charge mobility along the substrate surface is expected to be different from that perpendicular to the substrate.

Applications in planar heterojunction PV cells

To investigate the performance of TPAPV in OPV cells, planar heterojunction cells were fabricated using fullerene C₆₀ (Nano-C) as the electron-acceptor. As mentioned above, we chose to fabricate planar heterojunction architectures since cells performance reflects more clearly materials characteristics. The device structure is ITO (140 nm)/TPAPV/C₆₀/BCP (10 nm)/Ag (120 nm), where ITO is Indium Tin Oxide and BCP represents a thermally evaporated thin layer of bathocopruine (Aldrich) as buffer layer. The thicknesses of TPAPV and C₆₀ were varied to assess the cell performance dependence on the respective active layer thickness. The TPAPV layer was firstly varied from 3 to 18 nm, while keeping the C_{60} layer at 50 nm, then the fullerene C₆₀ layer was varied for the best performing TPAPV thickness. The topography of the TPAPV layer in the devices, investigated by AFM, showed a relatively flat surface with a Rrms of ca. 0.31 nm (Figure S3 in Supplementary Info).

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Table 2 shows the devices performance and Figure 6 shows the *J-V* curves measured for the cells.

Table 2. Device characteristics under simulated AM1.5G solar illumination with an intensity of 100 mW/cm².

Donor/acceptor	J _{SC}	Voc	FF	PCE
	(mA/cm ²)	(V)	(%)	(%)
TPAPV (3 nm)/C ₆₀ (50 nm)	2.88	0.92	47.7	1.21
TPAPV (6 nm)/C ₆₀ (50 nm)	2.89	0.92	47.8	1.23
TPAPV (12 nm)/C ₆₀ (50 nm)	2.80	0.92	46.9	1.17
TPAPV (18 nm)/C ₆₀ (50 nm)	2.64	0.95	43.4	1.05
TPAPV (6 nm)/C ₆₀ (40 nm)	2.88	0.91	46.5	1.18
TPAPV (6 nm)/C ₆₀ (30 nm)	2.70	0.93	46.5	1.12



Figure 6. Current density–voltage (J–V) curves measured for planar heterojunction cells fabricated with TPAPV/C₆₀(50 nm).

The most efficient structures correspond to cells with TPAPV (6 nm)/ C_{60} (50 nm) active layers. The obtained V_{OC} values (0.91-0.95 V) are among the highest found for small-molecule organic PV cells (highly efficient small-molecule cells exibiting PCE of 8.26 % demonstrated V_{OC} values of 0.94 V³⁴) and are higher than those found for bulk-heterojunction cells using either triphenylamine-based polymers (a wide variety of TPAbased donor polymers reported by T. Yasuda provided BHJ cells with $V_{\rm OC}$ values ranging from 0.62 to 0.93 V³⁵) or triphenyl-based small molecules as the electron donor (a series of small molecules containing TPA moieties as end-groups provided BHJ cells with $V_{\rm OC}$ values of 0.58-0.80 V³⁶). However, J_{SC} and FF values are relatively low, therefore accounting for the observed relatively low cells performance. On the one hand, a limited exciton diffusion length for TPAPV is seen, as the optimum J_{SC} is obtained for a TPAPV thickness of 6 nm. On the other hand, based on the J-V curves obtained under dark conditions (Figure S2, Supplementary Info), which show low shunt resistance, we suggest that the observed moderate FF values may be related with unfavorable morphologic characteristics of the thermally evaporated TPAPV layer (e.g. rough crystals) which create physical shunts for the charges in the active layer. Further optimization of the cell performance may be accomplished by better tailoring TPAPV layer characteristics (e.g. by solvent annealing) or through the application of BHJ cells, since the fluorescence quenching

studies performed for TPAPV: $PC_{61}BM$ blends showed encouraging results.

Conclusions

A new small molecule containing an all-trans *p*phenylenevinylene core end-capped with triphenylamine groups (TPAPV) was synthesised through a Suzuki coupling reaction with a good yield (73 %). Time-resolved fluorescence studies performed on TPAPV:PC₆₁BM blend films demonstrated strong fluorescence quenching of excitons photogenerated in TPAPV (decrease in one order of magnitude of first excited state lifetime) and therefore suggest that TPAPV may find applications in heterojunction PV cells with PC₆₁BM as the acceptor component. Planar heterojunction PV cells fabricated using TPAPV and fullerene C₆₀ showed V_{oc} values of 0.91-0.95 V which are among the highest for smallmolecule organic cells.

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Fluorescence quenching studies enabled to preview potential applications of a new small molecule as electron-donor in organic solar cells. Results of planar heterojunction cells are also shown.

