Trannulenes: a new class of photoactive materials for organic photovoltaic devices†

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We report the first large-scale preparation of fluorinated trannulene $C_{60}F_{15}[C(COOMe)_3]_3$ (**TMCMT**) and its application as a photoactive material in organic solar cells. Two types of photovoltaic devices were fabricated: bulk heterojunction cells comprising blends of **TMCMT** with a polyfluorene polymer and bilayer cells based on a planar heterojunction of **TMCMT** with a perylene diimide. Photoluminescence quenching studies suggested that a photoinduced electron transfer occurs from polyfluorene and perylenediimide to **TMCMT**, therefore it behaves as photoinduced electron acceptor. Both types of solar cells comprising **TMCMT** as photoactive material showed clear photovoltaic effects. This proves for the first time the feasibility of the previously anticipated idea of using trannulenes as light-harvesting materials in photovoltaic devices.

Introduction

Trannulenes are a recently discovered type of organic aromatic compound that possess all-*trans*-annulene rings ("trannulene" rings in short) in their molecular frameworks.[1] Conventional annulenes, in particular 18-annulene, comprise alternating bonds in *cis* and *trans* configurations that allow their rings to be flat with all p-orbitals lying perpendicular and overlapping above and below the ring plane as in classical benzene-type aromatics. In contrast, all orbitals in trannulenes lie and overlap parallel to one plane, this phenomenon being called "in-plane" aromaticity.[1]

Though the first ideas about "in-plane" aromaticity were formulated by Schleyer *et al.* as early as 1979,[2] the first experimental evidence of the existence of trannulenes was finally obtained by Taylor *et al.* in 2001 in a study of the derivatization of the fluorinated fullerene $C_{60}F_{18}$.[3] Following this discovery, two other types of fullerene derivatives comprising trannulene rings in their molecular frameworks were reported in 2005.[4,5]

The appearance of the trannulene ring in the fullerene cage dramatically changes its electronic properties and in particular results in a significant increase of the visible absorption in comparison with fullerenes. Intensive absorption bands appear in the ranges 300–500 and 550–730 nm with extinction coefficients as high as $10\,000$–$25\,000$ M^{-1} cm^{-1}. Therefore, the trannulenes show a remarkable green colour in solution and solid

state that makes them unprecedented examples of inherently green fullerene derivatives without need for any chromophore substitution (*i.e.* phthalocyanine residues).

Since trannulenes are strongly light-absorbing fullerene derivatives, they have been considered as promising materials for organic light-conversion devices, in particular, for organic solar cells and photodetectors. Organic solar cells have been extensively studied during the last decade, resulting in a gradual improvement of their power conversion efficiencies from ∼1% at first up to relatively high values of 5–6% achieved in 2008 and 2009.[6–11] Some of the most significant breakthroughs in the field emerged from a systematic study of the active layer morphology effects on the device performance.[12] In addition to the rapid improvement of power conversion efficiencies of organic solar cells, significant progress was achieved in designing devices with appreciable long-term stability.[13,14] A great number of recent publications are related to the design of novel low band gap conjugated polymers used as electron donor materials in photovoltaic devices.[15,16] In contrast, only a few papers have reported on the design of novel electron acceptor fullerene derivatives with improved properties.[17–21] Up to now, there have been just three known examples of fullerene derivatives that yielded somewhat higher power conversion efficiencies than conventional material PCBM.[21–23] To get beyond this level, an innovative approach needs to be applied in the design of novel fullerene-based materials for organic photovoltaics. In particular, the light-harvesting ability of the fullerene component has to be improved significantly to achieve higher short-circuit current densities.

The trannulenes reported here can be considered as an unconventional type of acceptor material for organic photovoltaic devices. The photophysical properties of trannulenes and related donor–acceptor assemblies were studied in great detail.[24] It has been proven that the trannulenes participate as photoinduced electron-acceptors, withdrawing electrons from appropriate donor molecules under excitation by light. Such

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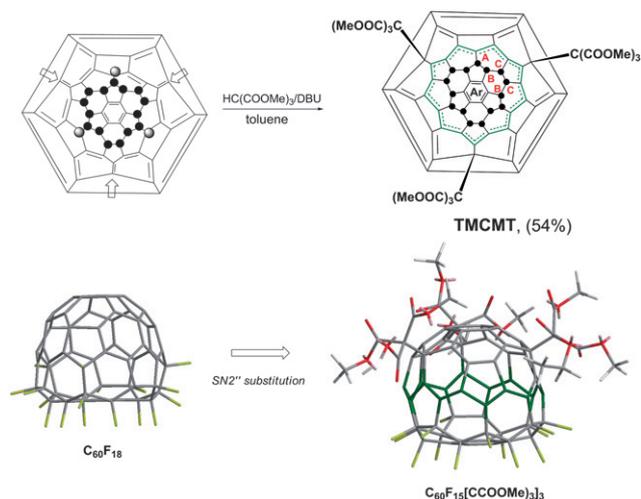
photoinduced charge separation between electron donor and acceptor materials is the main mechanism of charge carrier generation in organic photovoltaic devices. However, no experimental evidence has yet been obtained with respect to the applicability of trannulenes as materials for organic photovoltaic devices. Here we prove for the first time that trannulenes can in principle be used as materials in photovoltaic devices that generate photocurrent under illumination by simulated solar light.

Results and discussion

The investigation of the properties of trannulenes derived from $C_{60}F_{18}$ was strongly limited by the availability of this precursor fluorinated fullerene. All known trannulenes have been synthesized in quantities less than 10 mg, with the exception of one or two compounds that were obtained on the 20–30 mg scale. Recently we developed improved procedures for the preparation and isolation of $C_{60}F_{18}$ that make this compound available on a gram scale.[25,26] This allowed us to start from 0.7 g of $C_{60}F_{18}$ in the reaction with tris(methoxycarbonyl)methane and 1,8-dia-zabicyclo[5.4.0]undec-7-ene and obtain 560 mg of emerald-green trannulene **TMCMT** (Scheme 1, 54% yield).

The preparation and purification procedure is very facile (carried out in 6 h) and the yield of trannulene **TMCMT** is high compared to the previous best yields of 25–35% for trannulenes,[27] making this exotic fullerene-based material available in quantities sufficient for thorough investigation of its physical properties and its use in optoelectronic devices. At the same time, we succeeded in investigating the chemical transformations of **TMCMT** and related trannulenes.[28]

The composition and molecular structure of **TMCMT** was proven by ^1H, ^{19}F and ^{13}C NMR spectra (Fig. 1). The ^1H NMR spectrum consists of a single resonance at 4.06 ppm due to the protons of the methoxycarbonyl groups. Two signals at 135.1 and 142.6 ppm with relative integral intensities of 1:4 were observed in the ^{19}F NMR spectrum. However, there are three types of symmetrically non-equivalent fluorine atoms in the trannulene structure that are expected to give three resonances
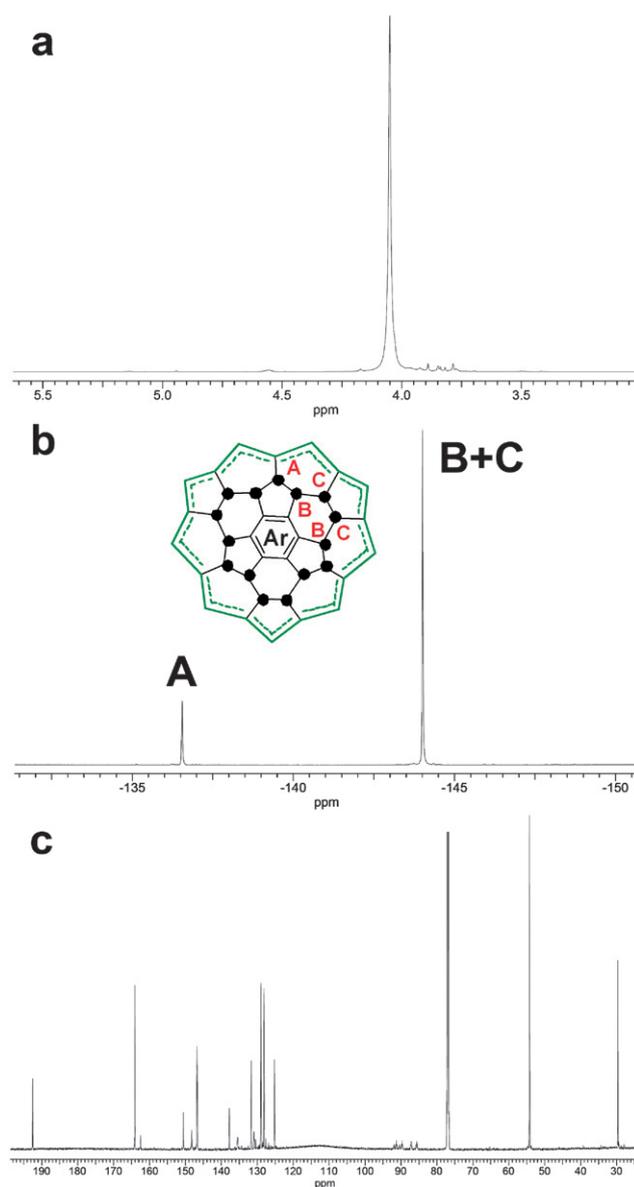

Fig. 1 The (a) ^1H NMR, (b) ^{19}F NMR and (c) ^1H-decoupled ^{13}C NMR spectra of **TMCMT**.

with integral intensities of 1:2:2. Two out of three signals in the ^{19}F NMR spectra of known trannulenes always have very close chemical shifts and overlap in some cases, as we observed for **TMCMT**.[9] The ^{13}C NMR spectrum of **TMCMT** was very similar to that reported in literature for another trannulene derived from $C_{60}F_{18}$.[9] Thus, the obtained NMR data confirmed that **TMCMT** has the trannulene structure shown in Scheme 1.

Fullerenes and their derivatives are known as strong electron acceptors that quench the fluorescence of many organic donor molecules *via* photoinduced electron transfer. The trannulene **TMCMT** is a specific fullerene derivative that has 15 electron-withdrawing fluorine atoms attached to the carbon cage that make it even more electronegative. Therefore, the first reduction potential of **TMCMT** lies at −0.08 V *vs.* saturated calomel electrode (SCE). This is *approx.* 0.5 V more positive than the first reduction potential of C_{60} (about −0.60 V *vs.* SCE). This

Scheme 1 Synthesis of **TMCMT**.

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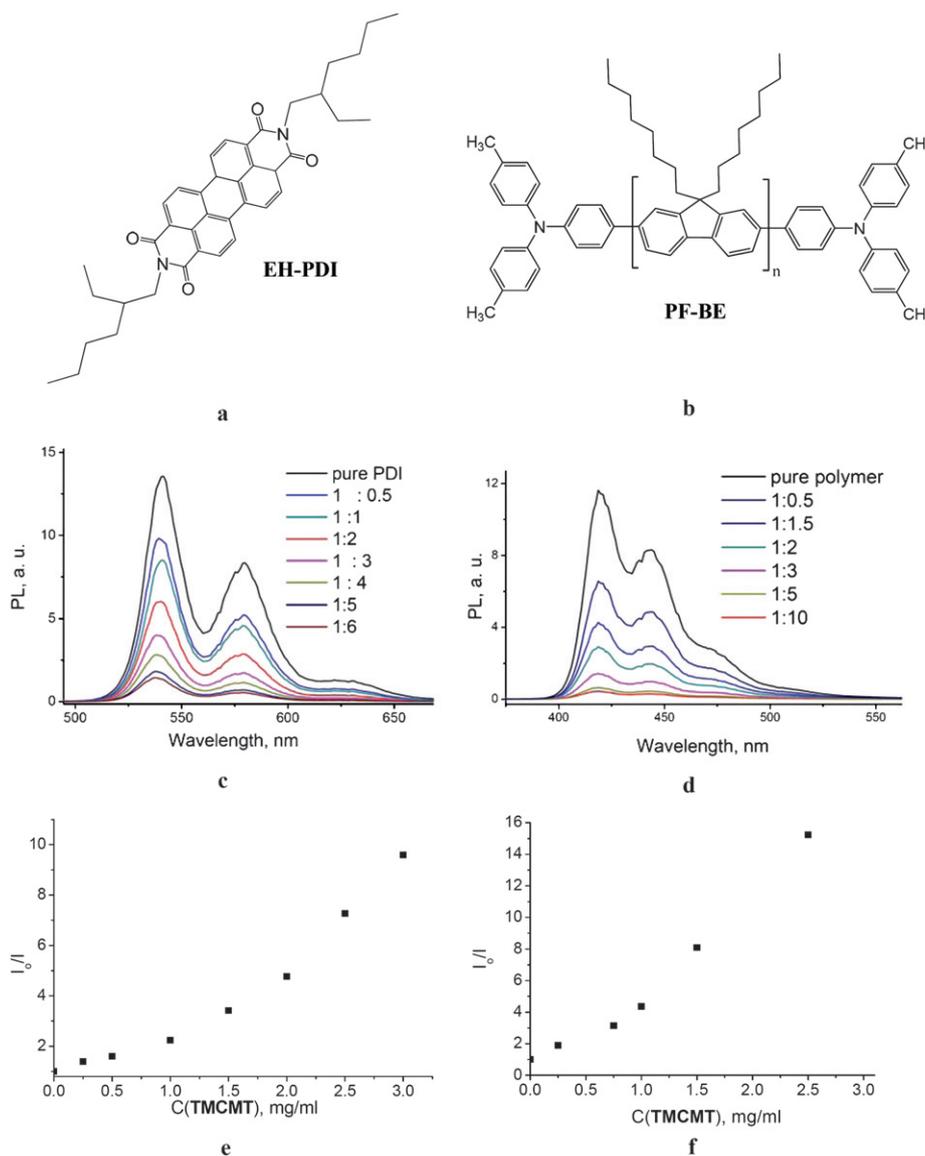*J. Mater. Chem.*, 2009, **19**, 7738–7744 | 7739

Fig. 2 The molecular structures of (a) **EH-PDI** and (b) **PF-BE**. The change in the PL intensity of (c) **EH-PDI** and (d) **PF-BE** with addition of **TMCMT** and (e, f) the corresponding Stern–Volmer plots illustrating the quenching behavior.

electrochemical data suggest that **TMCMT** is a much more powerful electron acceptor than pristine fullerene. Indeed, the LUMO level of **TMCMT** should lie at *ca.* −4.8 to −5.1 eV, very close to the HOMO levels of zinc phthalocyanine (ZnPc, −5.3 eV)[29] and poly(3-hexylthiophene) (P3HT, −5.1 eV),[30] two of the most widely used electron donor materials for small molecular and polymer solar cells, respectively. The proximity of the acceptor LUMO and the donor HOMO energy levels might result in a ground-state charge separation; the resulting salts are usually not light-sensitive and cannot be applied as photoactive materials in photovoltaic cells. Such considerations suggest that conventional donor materials such as ZnPc and P3HT do not fit well for the combination with **TMCMT** as electron acceptor in photovoltaic devices. Some other donor molecules with lower donor capability (with higher ionization potentials or deeper-lying HOMO energy levels) have to be found for this purpose. For instance, some substituted small molecular

perylene bisimides (such as **MPDI** or **EH-PDI**, E(HOMO) = −5.8 eV)[31] and polyfluorene polymers (such as **PF-BE**, E(HOMO) = −5.5 eV)[32] can serve as readily available electron donor compounds, satisfying the aforementioned electronic requirements for their use in composites with **TMCMT**.

To check for the existence of a photoinduced charge separation between **TMCMT** and the perylene bisimide **EH-PDI** or polyfluorene **PF-BE**, we carried out photoluminescence (PL) quenching experiments in solution, finding that the trannulene was able to quench quite efficiently the PL of both donor compounds. The decrease in the PL intensity with addition of **TMCMT** is a manifestation of the quenching of the excited donor species (**EH-PDI*** and **PF-BE***) *via* either an energy or an electron transfer to the acceptor **TMCMT**.[33]

For diffusion-limited quenching, the PL intensity (I) of **EH-PDI** or **PF-BE** should linearly depend on the concentration of the quencher, which is **TMCMT** in our case. This follows from
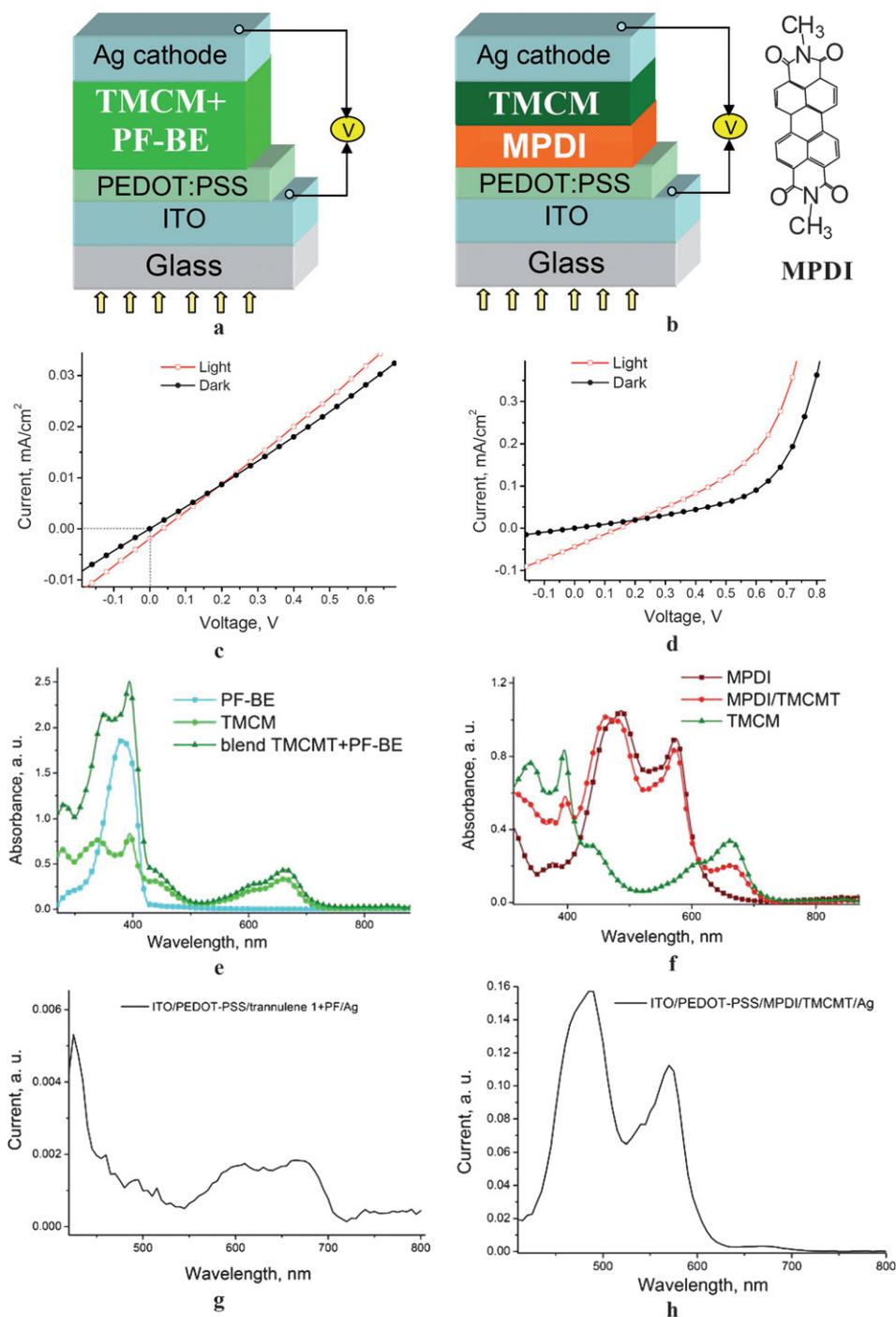
Fig. 3 The layout of (a) the bulk heterojunction and (b) bilayer cells with (c, d) the corresponding *I–V* curves. (e, f) The absorption spectra of thin films comprising pristine materials and their combinations. The photocurrent response spectra of (g) the bulk heterojunction and (h) bilayer photovoltaic cells.

the Stern–Volmer equitation $I_0/I = 1 + K_{sv}[\text{TCTM}]$, where I_0 is the initial PL intensity measured before addition of **TMCMT**.

However, quenching of the emission of both **PF-BE** and **EH-PDI** by trannulene shows a superlinear behavior in the Stern–Volmer plots (Fig. 2e,f). Superlinear quenching effects observed here might be a consequence of the reabsorption of the emission coming from the **PF-BE** or **EH-PDI** by trannulene **TMCMT**, which was introduced in successively increased

amounts into the system. **TMCMT** has rather intense absorption bands at 350–500 and at 550–720 nm that overlap significantly with the emission bands of **PF-BE** and **EH-PDI**, providing the necessary condition for reabsorption (see Fig. S3†).

The observed PL quenching of **EH-PDI** and **PF-BE** by **TMCMT** can be related to electron transfer or to energy transfer in these systems.[33] We could assume that the PL quenching is at least in part a result of a photoinduced charge separation

between the **EH-PDI** or **PF-BE** and **TMCMT**, similar to other numerous known composites of fullerene derivatives with electron donor species.

Photovoltaic cells with a double-layer planar heterojunction and a single-layer bulk heterojunction architecture were fabricated using **TMCMT** as the electron-accepting material (Fig. 3a,b)). Silver was used as a cathode material in all cases since its work function (-4.7 eV) fits well to the LUMO level energy of **TMCMT** (*ca.* -5.0 eV). At the same time, silver is known to have low reactivity towards fluorine-containing materials. In contrast, aluminium, which is known as a conventional cathode material, has too low a work function (-4.08) and might react with the fluorine-loaded organic layer at the interface, bringing about undesired side effects.

Additionally, some single-layer and single-component ITO/PEDOT-PSS/**MPDI**/Ag and ITO/PEDOT-PSS/**PF-BE**/Ag devices were fabricated as reference cells. However, these showed no observable photovoltaic behavior. Both the bilayer and the bulk heterojunction photovoltaic cells comprising **TMCMT** showed clear photovoltaic effects, as seen in the *I–V* curves depicted in Fig. 3c,d. The bulk heterojunction cells yielded short circuit current densities (I_{SC}) of ~1.6×10^{-3} mA/cm², open-circuit voltages (V_{OC}) of 40 mV, fill factors (FF) of 23% and solar simulator power conversion efficiencies (η) below 10^{-4}%. The bilayer cells demonstrated much better output characteristics: I_{SC} = 0.05 mA/cm², V_{OC} = 160 mV, FF = 31% and η = 2.5×10^{-3}%.

We emphasize that **MPDI** and **PF-BE** are just model donor compounds that we selected here to prove the feasibility of an application of trannulenes as light-harvesting materials in photovoltaic devices; better-suited materials could be found in the future to optimize trannulene-based solar cells. The performance of the selected materials **MPDI** and **PF-BE** is limited partially by their relatively high HOMO level energies that differ from the LUMO level energy of **TMCMT** by only 0.5–0.8 eV (see Figs. S1 and S2†). As approximately 0.3 eV is lost due to a barrier at the active layer–electrode interfaces,[30] the maximal open circuit voltages (V_{OC}) for the solar cells comprising **PF-BE/TMCMT** and **MPDI/TMCMT** are estimated to be around 0.2 V and 0.5 V, respectively.

Another severe limitation comes from the ITO/PEDOT:PSS anode work function, which is reported to be -5.2 eV.[34] This value is 0.3 and 0.6 eV higher than the HOMO levels of the selected donors **PF-BE** and **MPDI** (**EH-PDI**), respectively. The large energy barrier for the extraction of holes from the active layer to the anode might decrease the open circuit voltage of the devices (see Figs. S1 and S2†). However, due to electronic effects at the interface, even a conventional formulation of PEDOT:PSS has a good contact to polymer materials with HOMO level energies down to at least -5.7 eV.[30] The open-circuit voltages measured for **PF-BE/TMCMT** and **MPDI/TMCMT** are significantly lower than the respective values of 0.2 V and 0.5 V potentially achievable for these systems with balanced electrode work functions. Therefore, we assume that the V_{OC} of trannulene-based devices is still partially limited by the energy barrier at the anode–active layer interface. Further studies should account for this effect and result in the design of some better-suited anode and hole-transporting materials.

The photocurrent response spectra for photovoltaic devices comprising **TMCMT** are shown in Fig. 3g,h, and can be compared with the absorption spectra of the pristine components and their composites (Fig. 3e,f). The **MPDI** features dominate strongly over the **TMCMT** bands in the active layer absorption spectrum. The contributions of these counterparts become even more unbalanced in the photocurrent response spectrum, where the **TMCMT** band at 600–700 nm forms just a shoulder to the major **MPDI** band at 450–580 nm. Most probably, **MPDI** acts as a photoactive chromophore more efficiently than **TMCMT**. This explains the low intensity of the trannulene band in the photocurrent response spectrum.

In the case of the **PF-BE/TMCMT** bulk heterojunction cells, the polymer **PF-BE** has no absorption above 450 nm, and therefore the trannulene **TMCMT** is mostly responsible for the light harvesting in the visible range. The photocurrent response spectrum reveals a characteristic trannulene band at 500–700 nm, proving unambiguously that this material indeed generates a photocurrent in polymer bulk heterojunction devices.

Conclusion

We have proved the feasibility of the previously suggested idea to use trannulenes as light-harvesting components in organic solar cells.[1] Trannulene **TMCMT** was synthesized, characterized and applied as a photoactive material in organic bilayer and bulk heterojunction solar cells. It was shown that the trannulene serves as a truly photoactive component, since it harvests light and allows the generation of free charge carriers. Though the performances of the first fabricated photovoltaic devices with trannulenes were relatively low, further substantial improvements might be achieved as a result of careful optimization of these systems. Firstly, chemical modification of the trannulene structure could potentially allow one to attain better electronic, charge transport and optical properties in these materials. Alternatively, one might be able to apply new electron donor counterparts (instead of **PF-BE** and **MPDI**) possessing electronic properties that better match those of the trannulenes, and providing better hole transport.

In is also notable that trannulenes show good environmental stability: they do not react with moisture in the air and solvents, and do not undergo oxidation in air even at elevated temperatures.[3,9] Moreover, monoanions of trannulenes are greatly stabilized by the electron-withdrawing action of the fifteen fluorine atoms attached to the carbon cage. Therefore, a combination of trannulenes with equally stable electron donor materials might yield in the future fully air-stable organic photovoltaic cells that will require minimal or even no protective encapsulation.

Experimental section

Materials and instrumentation

All reagents and solvents were purchased from Acros Organics or Aldrich and used as received. Polymer **PF-BE** was purchased from ADS company.

The absorption spectra were recorded with a Varian 3G UV-VIS spectrophotometer. Photoluminescence spectra were measured with a MUT GmbH Tristan light fiber spectrometer using monochromated light (375 nm) from a 900 W Xe lamp as excitation. The photocurrent spectra were measured with a SRS

830 lock-in amplifier using monochromated light from a 75 W Xe lamp as excitation. *I–V* characteristics were recorded from devices with active area size of *ca.* 0.1 cm^2 using a Keithley 236 sourcemeter, and illumination was provided by a KHS Steuernagel solar simulator calibrated to correspond to 100 mW/cm^2 at AM1.5.

Synthesis of TMCMT

Fluorinated fullerene $C_{60}F_{18}$ (700 mg, 0.66 mmol) was dissolved in 400 ml of dried toluene (distilled over metallic sodium) and then 387 mg (2 mmol) of tris(methoxycarbonyl)methane was added in one portion. The resulting solution and the whole reaction setup was degassed and then filled with argon. Afterwards, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 100 mg, 0.65 mmol) solution in 50 ml of dry toluene was added dropwise over 15–30 min to the rapidly stirred reaction mixture. After addition of DBU, the reaction mixture was stirred for an additional 30 min and then poured on to the top of a silica gel column (Acros organics, 40–60 μ, 60 Å). Elution with a mixture of 97:3 v/v toluene/ethyl acetate yielded **TMCMT** as a dark green solution. This solution was concentrated *in vacuo* (rotary evaporator), and the residue was washed with hexane and dried in air. **TMCMT** (560 mg) was obtained as a dark green solid with 54% yield.

^{1}H NMR (CDCl$_3$, 600 MHz), δ = 4.06 (s, 27H) ppm. ^{19}F NMR (CDCl$_3$, 282 MHz), δ = −137.14 (s, 3F), −144.58 (s, 12F) ppm. ^{13}C NMR (CDCl$_3$, 200 MHz), δ = 29.68 (*C*(COOMe)$_3$), 54.3 (OMe), 70.99 (cage sp^3 C), 85.69 (*C*F), 87.23 (*C*F), 89.72 (*C*F), 90.39 (*C*F), 91.3 (*C*F), 91.99 (*C*F), 125.26, 128.19, 129, 130.96, 131.71, 135.45, 135.58, 137.84, 146.8, 146.94, 148.3, 150.62, 162.54, 164.13 ppm. ESI-MS: calculated for $C_{81}H_{27}F_{15}O_{18}$ *m/z* = 1572.10; observed for [**TCTM**]$^-$ *m/z* = 1572.14. FTIR spectrum (KBr pellet) υ = 465 (vw), 540 (vw), 562 (w), 584 (w), 658 (w), 671 (w), 688 (w), 732 (w), 764 (vw), 814 (m), 861 (vw), 935 (w), 946 (w), 968 (w), 1008 (w), 1026 (m), 1034 (m), 1056 (m), 1078 (vs), 1119 (vs), 1147 (s), 1168 (m), 1184 (m), 1244 (s), 1281 (vs), 1363 (vw), 1400 (w), 1437 (m), 1459 (m), 1630 (w), 1748 (vs), 2957 (w) cm^{-1}.

Photovoltaic cells

To make a bilayer cell, a 40 nm thick film of a perylene bisimide **MPDI**, which is insoluble in organic solvents, was vacuum-evaporated on ITO slides coated with PEDOT-PSS. Trannulene **TMCMT** was afterwards spin-coated on the top of the **MPDI** films at 6000 rpm from a solution in dichloromethane, to avoid damaging the donor layer. Finally, a 100 nm thick silver cathode was evaporated *in vacuo* on to the active layer to finalize the device. For the bulk heterojunction cell, a blend of **PF-BE/TMCMT** (1:1 w/w; 30 mg/ml in chloroform) was spin-coated at 1500 rpm on ITO slides coated with PEDOT-PSS, and then the Ag cathode was deposited *in vacuo*.

Acknowledgements

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