

**Neat C60:C70 buckminsterfullerene mixtures enhance
polymer solar cell performance**

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Neat C₆₀:C₇₀ buckminsterfullerene mixtures enhance polymer solar cell performance

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Abstract

We demonstrate that bulk-heterojunction blends based on neat, unsubstituted buckminsterfullerenes (C_{60} , C_{70}) and a thiophene-quinoxaline copolymer (TQ1) can be readily processed from solution. Atomic force and transmission electron microscopy as well as photoluminescence spectroscopy reveal that thin films with a fine-grained nanostructure can be spin-coated, which display a good photovoltaic performance. Replacement of substituted fullerenes with C_{60} or C_{70} only results in a small drop in open-circuit voltage from 0.9 V to about 0.8 V. Thus, a power conversion efficiency of up to 2.9 % can be maintained if C_{70} is used as the acceptor material. Further improvement in photovoltaic performance to 3.6 % is achieved, accompanied by a high internal quantum efficiency of 75 %, if a 1:1 C_{60} : C_{70} mixture is used as the acceptor material, due to its improved solubility in *ortho*-dichlorobenzene.

1. Introduction

Polymer solar cells are hailed for their potential to become a cheap renewable energy technology. Particularly attractive is high-throughput coating of device components such as the active layer from solution onto a flexible substrate, which promises to be particularly cost-effective. The bulk-heterojunction, which comprises an intimate blend of electron donor and acceptor materials, is the most widely studied type of organic semiconductor architecture.¹ The highest power conversion efficiencies are routinely achieved with electron-donating conjugated polymers that are blended with one of various fullerene acceptors. The most successful fullerene derivatives such as the commonly used phenyl- C_x -butyric acid methyl esters (PC_xBM ; $x = 61$ or 71) carry solubilising moieties, which considerably ease processing from solution.

However, a major disadvantage with the use of these fullerene derivatives is the increased materials cost,² which is associated with the additional synthesis steps that are needed to attach exohedral substituents to the fullerene cage. As a result, PC₆₁BM and PC₇₁BM are considerably more expensive than the neat, unsubstituted buckminsterfullerenes C₆₀ and C₇₀ (Table 1). Since the electron acceptor fraction comprises 50-80 wt% of a typical bulk-heterojunction, it is desirable to exchange substituted fullerenes with neat buckminsterfullerenes, which would significantly reduce the cost of the semiconductor material. The use of C₆₀:C₇₀ mixtures would be particularly cost-effective since a mixture with a typical ratio of about 4:1 is the immediate product that is obtained from fullerene synthesis,^{3,4} which could be used without the need for separation.

The use of unsubstituted fullerenes is complicated by their relatively poor solubility in organic solvents as compared to substituted fullerene derivatives, which has been highlighted as early as 1995 in the seminal work by Yu *et al.*¹ For instance, at ambient conditions up to 107 g L⁻¹ of PC₆₁BM and 203 g L⁻¹ of PC₇₁BM can be dissolved in *ortho*-dichlorobenzene (*o*DCB),⁵ which is a common processing solvent for polymer solar cell blends. In contrast, only about 21 g L⁻¹ of the 'spherical' C₆₀ and 24 g L⁻¹ of the more polarisable C₇₀ are soluble at 20 °C.^{6,7} Both, C₆₀ and C₇₀ display atypical solubility behaviour with a maximum solubility of about 27 g L⁻¹ at 37 °C and 38 g L⁻¹ at 55 °C, respectively (Fig. 1). Strikingly, the solubility of C₆₀:C₇₀ fullerene mixtures is somewhat higher than for the neat components, which has been explained with the formation of solid solutions.⁷ Thus, in principle, an adequate amount of polymer:buckminsterfullerene blend material can be dissolved in *o*DCB in order to facilitate, *e.g.*, spin-coating, which is the preferred processing method for lab-scale devices. However, during film formation the poor solubility of unsubstituted fullerenes has the tendency to induce rapid crystallisation of the acceptor as well as detrimental coarsening of the blend nanostructure. As a result, early studies have struggled to achieve a good

photovoltaic performance with solution-processed polymer:C₆₀ bulk-heterojunction blends,^{1,8} which has diverted attention from neat buckminsterfullerene as an electron acceptor material in bulk-heterojunction devices.

Instead, bilayer architectures that comprise a solution-processed donor polymer layer and an evaporated C₆₀ layer have been studied more extensively.⁹⁻¹³ Geiser *et al.* have recently reported that thermal annealing of bilayer devices comprising a poly(3-hexylthiophene) (P3HT) and a C₆₀ layer can yield a power conversion efficiency *PCE* ~ 2.6 % due to partial diffusion of the donor and acceptor material.¹⁴

In spite of the difficulties associated with processing of unsubstituted fullerenes, several studies have succeeded in solution-processing of polymer:buckminsterfullerene bulk-heterojunction thin films with a homogeneous nanostructure. For instance, P3HT:C₆₀ bulk-heterojunction devices have been demonstrated to yield a promising *PCE* of about 2 to 2.5 % provided that suitable solvent mixtures are used¹⁵ or post-deposition thermal or vapour annealing is employed.¹⁴⁻¹⁷ Another intriguing work has explored the use of all-polythiophene diblock copolymers as a compatibiliser, where C₆₀ was crafted to the side chain of one of the alkylthiophene blocks, leading to a *PCE* ~ 2.6 %.¹⁸ However, the most promising result was recently achieved by Lin *et al.* who have reported solution-processed small molecule donor:C₇₀ photovoltaic devices with an impressive *PCE* as high as 5.9 %.¹⁹ Despite this recent progress, the use of buckminsterfullerene mixtures has not been explored, even though their superior solubility in organic solvents can be expected to aid nanostructure formation in bulk-heterojunction blends.

Thus, here we compare the use of neat buckminsterfullerenes and C₆₀:C₇₀ mixtures in polymer solar cell blends. As the donor material we selected the copolymer poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl] (TQ1), which is an attractive choice due to its particular ease of synthesis,²⁰ good photo-stability,²¹ high glass transition

temperature,²² and good photovoltaic performance with a *PCE* of up to 6-7 %.^{20,23} We find that a homogeneous nanostructure can be achieved with the neat buckminsterfullerenes as well as C₆₀:C₇₀ mixtures as the acceptor material, and that the highest efficiency is obtained for solar cells based on the mixtures.

2. Results and discussion

In a first set of experiments we studied the optical properties of solutions of 2 g L⁻¹ C₆₀, C₇₀ and a 1:1 C₆₀:C₇₀ mixture in *o*DCB. Whereas C₆₀ solutions appear purple, solutions containing C₇₀ feature a distinct burgundy colour due to the stronger absorption of C₇₀ between 400 to 600 nm (Fig. 2a). UV-vis spectra of solutions with different C₆₀:C₇₀ ratios show an isosbestic point at 362 nm, indicating that the UV-vis spectra of mixtures are linear superpositions of the spectra of the neat components (Fig. 2b).

To examine the solubility of C₆₀, C₇₀ and a 1:1 C₆₀:C₇₀ mixture in *o*DCB we prepared saturated solutions by adding an excess of fullerene material to *o*DCB followed by incubation at 37 °C and continuous stirring. Then, saturated solutions were thoroughly centrifuged and the supernatant was extracted. The amount of fullerene material dissolved in the supernatant was determined by weighing the solid content that remained after evaporation of *o*DCB. We noted that the C₆₀:C₇₀ mixture dissolved considerably more rapidly than the neat buckminsterfullerenes, for which a longer incubation time of two days was necessary in order to ensure that the solubility limit had been reached. Based on a comparison of three saturated solutions of each material we found a similar solubility of 27 ± 2 g L⁻¹ and 26 ± 4 g L⁻¹ for neat C₆₀ and C₇₀, respectively, which is in good agreement with previously reported values (*cf.* Fig. 1).^{6,7} In contrast, for the 1:1 C₆₀:C₇₀ mixture we deduced a slightly higher solubility of 33 ± 1 g L⁻¹ at 37 °C (note that Ref. 7 reports a solubility of about 40 g L⁻¹ at 50 °C for 1:1

C₆₀:C₇₀ in *o*DCB). For all subsequent experiments we first carefully dissolved the fullerene material in *o*DCB by heating at 37 °C for two days. Then, TQ1 solutions were added to obtain complete blend solutions with a ratio of 1:1 TQ1:fullerene material by weight. We chose to work with a 1:1 blend ratio, which is different to the optimal 1:3 stoichiometry of TQ1:PC₇₁BM blends^{20, 24} but allows a higher TQ1 concentration and hence solution viscosity in case of TQ1:C₆₀:C₇₀ blends. Moreover, in order to further limit phase separation during film formation we synthesised a high molecular-weight grade of TQ1 with a number-average molecular weight $M_n \sim 76 \text{ kg mol}^{-1}$ and a polydispersity index $PDI \sim 2.6$ (see Experimental section for details on synthesis), which gave rise to relatively viscous solutions.

We used atomic force microscopy (AFM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) to examine the nanostructure of spin-coated thin films (see Fig. 3a for 2:1:1 TQ1:C₆₀:C₇₀ and ESI, Fig. S1† and S2†, for 1:1 TQ1:C₆₀ and 1:1 TQ1:C₇₀). Tapping mode AFM images suggest a homogeneous surface texture with a root mean square (RMS) roughness of only 0.5 nm. The resolution limit of AFM is given by the diameter of the tip, which was 30 nm. In corresponding TEM bright field images no distinct, phase-separated domains can be resolved and SAED patterns only reveal an amorphous halo, indicating that no fullerene crystals have formed (note that TQ1 does not feature a crystalline phase²⁴).

Photoluminescence (PL) spectroscopy was performed in order to gain better insight into the proximity of donor and acceptor molecules in the investigated bulk-heterojunctions (Fig. 3b and ESI, Fig. S1† and Fig. S2†). We calculated the PL quenching ratio Φ according to:

$$\Phi = \int \text{PL}_{TQ1}(\lambda) d\lambda / \int \text{PL}_{TQ1:fullerene}(\lambda) d\lambda \quad (1)$$

where $PL_{TQ1}(\lambda)$ and $PL_{TQ1:fullerene}(\lambda)$ describe the PL spectrum of neat TQ1 and the TQ1:fullerene blend, respectively. Our measurements revealed that in TQ1:C₆₀:C₇₀ films the polymer emission is strongly quenched as evidenced by a large PL quenching ratio $\Phi \sim 125$, which indicates good charge transfer from TQ1 to the acceptor material. Thus, we conclude that TQ1:C₆₀:C₇₀ blends are finely mixed, in agreement with the homogeneous nanostructure inferred from AFM and TEM. Whereas for TQ1:C₇₀ we observed a similar value $\Phi \sim 128$, for TQ1:C₆₀ we found a slightly lower $\Phi \sim 37$, indicating a slightly coarser blend nanostructure.

To examine the photovoltaic performance of the here studied TQ1:buckminsterfullerene blends, devices were fabricated with a standard configuration of glass/ITO/PEDOT:PSS/active layer/LiF/Al. The thickness of the active layers was chosen to coincide with the first interference maximum around 110 nm (*cf.* transfer matrix modelling below). Reference 1:1 TQ1:PC₆₁BM devices yielded a high $V_{oc} \sim 0.91$ V and a maximum power point $MPP \sim 3.5$ mW cm⁻² under AM 1.5G illumination with an intensity of 100 mW cm⁻², *i.e.* a $PCE \sim 3.5$ % (Table 2), which is comparable to results obtained previously for the same processing conditions.²⁵ TQ1:C₆₀ and TQ1:C₇₀ devices displayed a slightly lower $MPP \sim 2.5 \pm 0.1$ mW cm⁻² and $MPP \sim 2.9 \pm 0.12$ mW cm⁻². Intriguingly, the use of buckminsterfullerenes only slightly reduced the open-circuit voltage by $\Delta V_{oc} \sim 0.1$ -0.15 V, which is a similar decrease as reported for P3HT devices upon exchange of PC₆₁BM with C₆₀.¹⁵ Our previous square-wave voltammetry measurements revealed that PC₆₁BM and C₆₀ have similar lowest unoccupied molecular orbital (LUMO) levels of -4.3 eV.²⁶ Hence, the slight difference in V_{oc} may be attributed to the increased tendency of buckminsterfullerenes to aggregate. Strikingly, the use of C₆₀:C₇₀ mixtures as the acceptor material considerably enhanced the photovoltaic performance with a $MPP \sim 3.6 \pm 0.1$ mW cm⁻² if an equal mixture of C₆₀ and C₇₀ was used, *i.e.* 2:1:1 TQ1:C₆₀:C₇₀ (Fig. 4a and Table 2). For these devices the $V_{oc} \sim 0.78$ V is situated in between values obtained for TQ1:C₆₀ and TQ1:C₇₀. However, we

observe an increase in fill factor FF to 0.54 ± 0.01 and in short-circuit current density J_{sc} to $8.4 \pm 0.1 \text{ mA cm}^{-2}$, which is accompanied by an increase in external quantum efficiency EQE to more than 40% at the peak absorption around 580 nm (Fig. 4b). Moreover, we prepared a set of devices based on a buckminsterfullerene ratio of 4:1 $C_{60}:C_{70}$, which is typically obtained from fullerene synthesis.^{3,4} For 5:4:1 TQ1: C_{60} : C_{70} devices we found a $MPP \sim 2.6 \pm 0.2 \text{ mW cm}^{-2}$, which is comparable to TQ1: C_{60} devices with $MPP \sim 2.5 \pm 0.1 \text{ mW cm}^{-2}$, indicating that the synthesised buckminsterfullerene mixture can be used as the acceptor material in polymer solar cells without loss in performance.

In a final set of experiments we used transfer matrix modelling to estimate the maximum J_{max} that can be extracted from 2:1:1 TQ1: C_{60} : C_{70} devices as a function of active layer thickness (Fig. 5). We used the transfer matrix model described in Ref. 27, for which we determined the refractive index and extinction coefficient of a 2:1:1 TQ1: C_{60} : C_{70} thin film by modelling variable-angle spectroscopic ellipsometry spectra (ESI, Fig. S3†). We could confirm that the first interference maximum is located at a thickness of 110 nm. We compared these calculations with the experimentally measured J_{sc} of a series of devices that varied in their active layer thickness, controlled by choosing different spin-coating speeds and by varying the initial solution concentration (ESI, Fig. S4†). Independent of the active layer thickness, the internal quantum efficiency $IQE = J_{sc}/J_{max}$ had a high value of about 75%, which highlights the potential of buckminsterfullerene mixtures as the acceptor material in polymer solar cells.

3. Conclusions

We have shown that neat buckminsterfullerenes can be processed from *o*DCB and that the solubility increases if fullerene mixtures are used. Thin films of bulk-heterojunction blends comprising buckminsterfullerenes and the non-crystalline donor polymer TQ1 feature

a fine-grained nanostructure, which gives rise to a promising photovoltaic performance that is maximised if fullerene mixtures are used as the donor material. As a result, we demonstrate a record efficiency for polymer solar cells based on non-substituted fullerenes with a maximum power point of up to $3.6 \pm 0.1 \text{ mW cm}^{-2}$ and an internal quantum efficiency of 75 %.

Certainly, the use of unsubstituted fullerene mixtures as the acceptor material is an attractive approach also in combination with other donor polymers. Moreover, we anticipate that –similar to PC₆₁BM:PC₇₁BM:TQ1 ternary blends²⁸ – bulk-heterojunctions based on C₆₀:C₇₀ mixtures display improved thermal stability.

4. Experimental Section

Materials

C₆₀ and C₇₀ (purity 99%) were purchased from Solenne BV. TQ1 (number-average molecular weight of $M_n \sim 76 \text{ kg mol}^{-1}$; polydispersity index $PDI \sim 2.6$) was prepared according to the following procedure: In a 250 mL 2-necked round-bottom flask equipped with a condenser 5,8-dibromo-6,7-difluoro-2,3-bis(3-(octyloxy)phenyl) quinoxaline (11.5 g, 16.5 mol) and 2,5-bis(trimethylstannanyl)thiophene (6.765 g, 16.5 mmol) were dissolved in 115 mL dry and degassed toluene. The solution was stirred and heated to 90 °C under nitrogen atmosphere. Pd₂(dba)₃ (302 g, 2 mol%) and P(*o*-Tol)₃ (402 mg, 8 mol %) were dissolved in 2 mL dry degassed toluene and injected into the monomer solution. During the reaction, the mixture turned from red via purple to blue accompanied by a strong increase in viscosity. After 1 hour of total reaction time, the reaction product was cooled down. Then, the polymer was reverse precipitated with ethanol (1:2 v/v ratio) and collected via gravity filtration. The polymer was re-dissolved in 200 mL toluene at 60 °C under nitrogen and vigorously stirred with 200 mL of an aqueous 10% sodium diethyldithiocarbamate solution for 1 hour. After cooling, the organic

layer was washed 4 times with 200 mL deionised water and subsequently reverse precipitated with methanol (1:1 v/v ratio) and collected via gravity filtration. The reverse precipitation was repeated with acetone (1:3 v/v ratio) and finally with ethanol (1:2 v/v ratio), which resulted in small, dark blue polymer fibres. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm), 7.85 (b, 4H, ArH), 7.34 (b, 2H, ArH), 7.22 (b, 2H, ArH), 7.11 (b, 2H, ArH), 6.85 (b, 2H, ArH), 3.71 (b, 4H, O-CH₂), 1.52 (b, 4H, CH₂), 1.36-1.0 (b, 20H, CH₂), 0.88 (b, 6H, CH₃). The molecular weight was determined by size exclusion chromatography (SEC) with an Agilent PL-GPC220 instrument calibrated relative to polystyrene.

UV-vis absorption spectroscopy

Measurements were performed with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrophotometer on 0.1 wt% fullerene solutions in *ortho*-dichlorobenzene (*o*DCB).

Photoluminescence (PL) spectroscopy

PL spectra of thin films were recorded using an Oriel liquid light guide and a Shamrock SR 303i spectrograph coupled to a Newton EMCCD silicon detector. The films were excited using a blue PMM-208G-VT laser pump (4 mW cm⁻²) with a wavelength of 405 nm.

Atomic force microscopy (AFM)

Measurements were done with NTEGRA Probe NanoLaboratory (NT-MDT, Zelenograd, Russia) in tapping mode and in air using a NT-MDT golden silicon cantilever with a tip diameter of 30 nm.

Transmission electron microscopy (TEM)

Samples were prepared by floating off spin-coated films in water, followed by collection with TEM copper mesh grids. TEM images were recorded with a G² T20 Tecnai instrument operated at an acceleration voltage of 200 kV.

Photovoltaic Devices

Photovoltaic devices were fabricated on ITO-patterned glass substrates coated with PEDOT:PSS (Heraeus, Clevis P VP Al 4083, annealed at 120 °C for 15 min after spin-coating, thickness ~40 nm). The active layers were spin-coated from *o*DCB-solutions, which were heated at 80 °C for ~2h prior to deposition. In addition, fullerene-solutions were heated at 37 °C for two days before TQ1 was added. A LiF layer (thickness ~ 6 Å) and aluminium (thickness ~ 90 nm) top electrodes were deposited via thermal evaporation under vacuum (below 4×10^{-6} mbar). *J-V* curves were recorded with a Keithley 2400 Source Meter under AM 1.5G illumination with an intensity of 100 mW cm⁻² from a solar simulator (Model SS50A, Photo Emission Tech., Inc.). The light source used was a 180 watt xenon arc lamp solar simulator (Photo Emission Tech.); the intensity was calibrated using a standard silicon photodiode calibrated at the Energy Research Centre of the Netherlands (ECN). The active layer thickness was measured with a Dektak 150 surface profiler (estimated error ± 7 nm).

External quantum efficiency (EQE)

EQE spectra of characterised devices were recorded with a home-built setup using a Newport Merlin lock-in amplifier. Devices were illuminated with chopped monochromatic light through the transparent ITO.

Variable Angle Spectroscopic Ellipsometry (VASE)

Ellipsometric measurements for determination of the optical constants of 2:1:1 TQ1:C₆₀:C₇₀ were performed with an RC2 ellipsometer from J.A. Woollam Co., Inc. (USA). The CompleteEASE software package from J.A. Woollam Co., Inc. (USA) was used for modelling the optical constants using b-splines. A 225 nm thick 2:1:1 TQ1:C₆₀:C₇₀ film was spin coated on a Si substrate with ~1 nm native oxide according to the same preparation protocol used for photovoltaic devices. The modelled extinction coefficient was used to validate the model by comparing the calculated absorption coefficient with a transmission spectrum of a 2:1:1 TQ1:C₆₀:C₇₀ film on glass.

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Figures

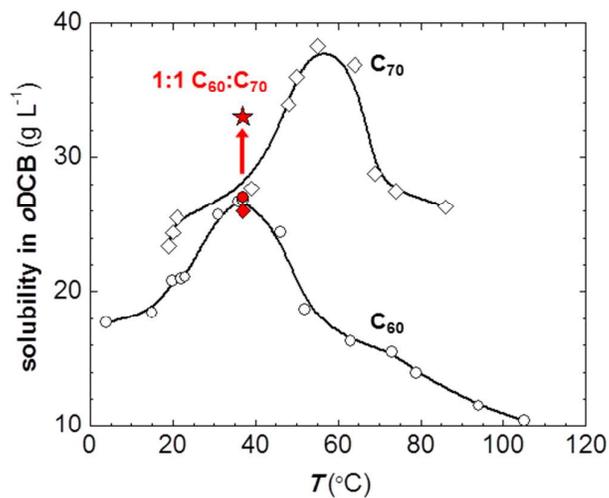


Fig. 1 Solubility of C₆₀ (circles), C₇₀ (diamonds) and a 1:1 C₆₀:C₇₀ mixture (star) in oDCB as a function of temperature; data reproduced from Refs. 6, 7 (open symbols) and measured in this study (filled symbols).

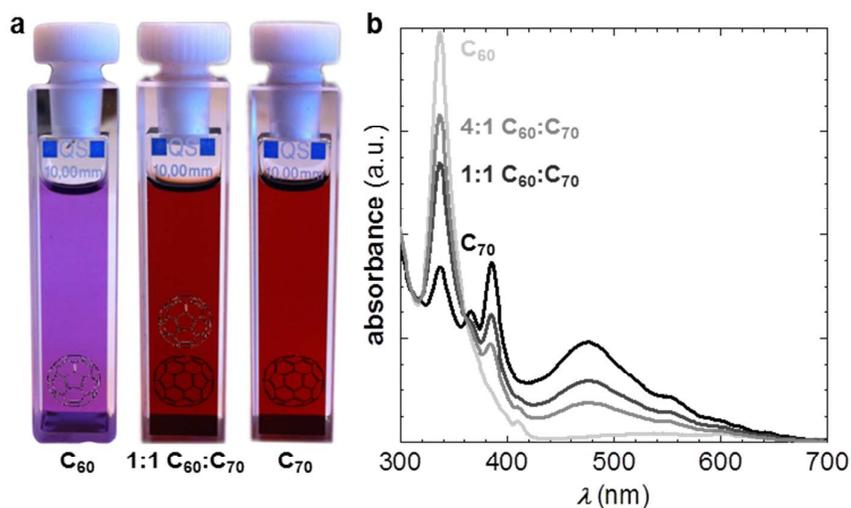


Fig. 2 (a) Solutions of ~ 2 g L⁻¹ C₆₀, C₇₀ and a 1:1 C₆₀:C₇₀ mixture in oDCB; insets: chemical structures of the fullerenes; (b) UV-Vis absorbance spectra of 0.01 g L⁻¹ fullerene solutions in oDCB with varying C₇₀ fraction.

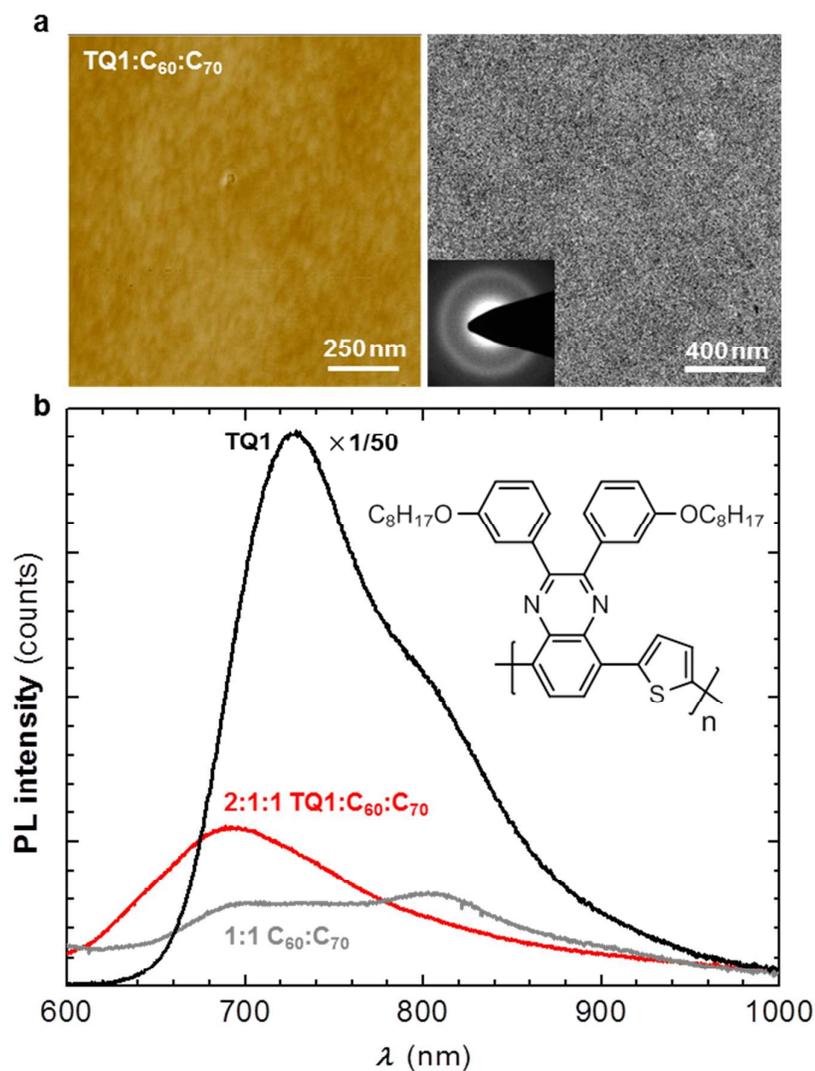


Fig. 3 (a) AFM height image and TEM bright field image of a 2:1:1 TQ1:C₆₀:C₇₀ film; inset: selective area electron diffraction (SAED) pattern; (b) Photoluminescence (PL) spectra of a neat TQ1 film (black, signal reduced 50 times), 1:1 C₆₀:C₇₀ (grey) and 2:1:1 TQ1:C₆₀:C₇₀ (red). Inset: chemical structure of TQ1.

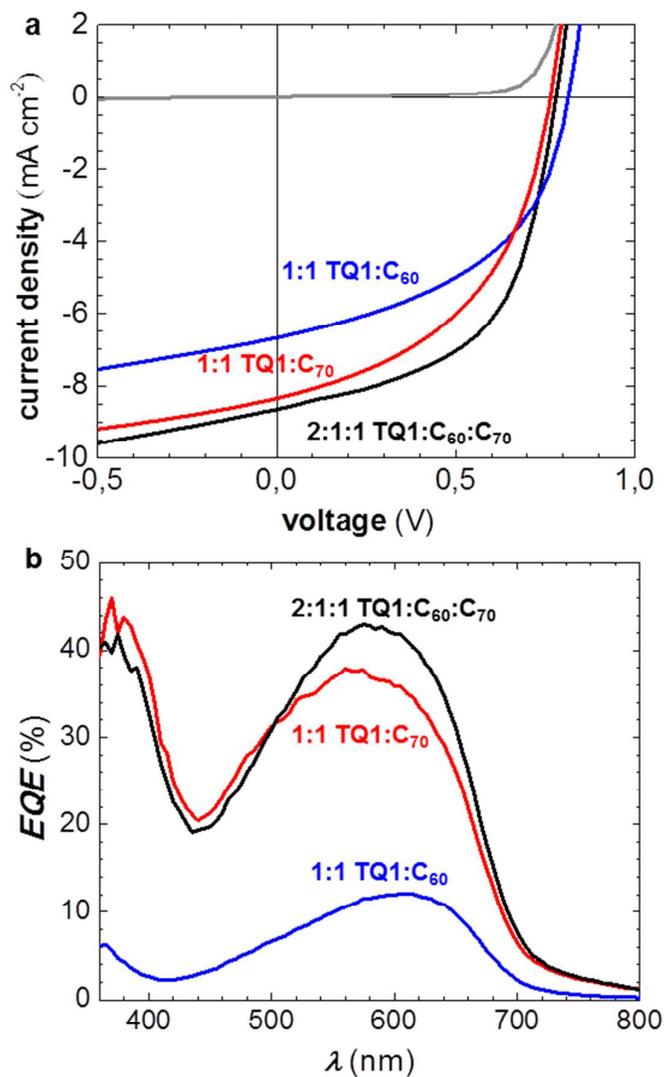


Fig. 4 (a) Representative current-voltage characteristics and (b) corresponding EQE spectra of optimised TQ1:C₆₀ (blue), TQ1:C₇₀ (red) and 2:1:1 TQ1:C₆₀:C₇₀ devices (black); for active layer thicknesses see Table 2.

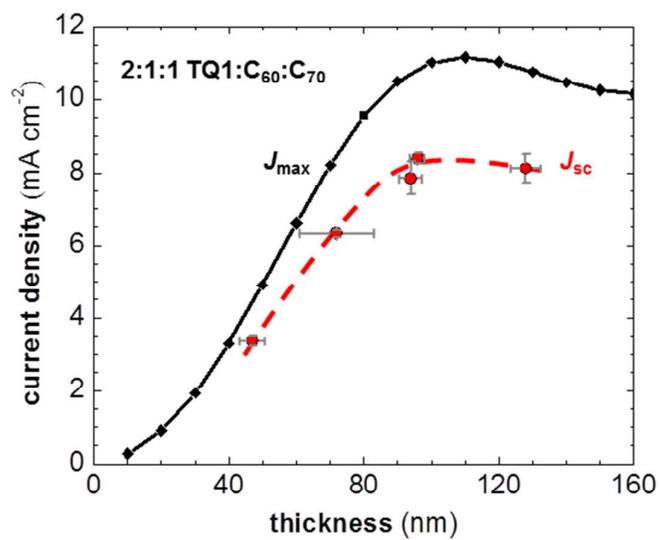


Fig. 5 Maximum calculated J_{\max} according to transfer matrix modelling (assuming a layer thickness of 80 nm for ITO and 40 nm for PEDOT:PSS; black diamonds) and measured J_{sc} of 2:1:1 TQ1:C₆₀:C₇₀ devices (red circles) as a function of active layer thickness. Error bars indicate the standard deviation of J_{sc} for four devices on the same substrate.

Table 1. Current cost of various fullerenes if 1 g of material is purchased [source Solenne BV].

Fullerene	cost (€ g^{-1})
C ₆₀	15
C ₇₀	150
PC ₆₁ BM	150
PC ₇₁ BM	780

Table 2. Performance of optimised solar cells (average of 3-4 devices on the same substrate; best performance in brackets): thickness of the active layer, short-circuit current density J_{sc} , open-circuit voltage V_{oc} , fill factor FF and maximum power point MPP .

Blend	thickness (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF (-)	MPP (mW cm ⁻²)
1:1 TQ1:PC ₆₁ BM	95 ± 5	7.5 ± 0.1	910 ± 3	0.48 ± 0.01	3.4 ± 0.1 (3.5)
1:1 TQ1:C ₆₀	97 ± 6	6.6 ± 0.2	810 ± 10	0.48 ± 0.01	2.5 ± 0.1 (2.6)
5:4:1 TQ1:C ₆₀ :C ₇₀	131 ± 2	7.2 ± 0.2	770 ± 20	0.46 ± 0.03	2.6 ± 0.2 (2.8)
2:1:1 TQ1:C ₆₀ :C ₇₀	96 ± 2	8.4 ± 0.1	780 ± 4	0.54 ± 0.01	3.6 ± 0.1 (3.7)
1:1 TQ1:C ₇₀	120 ± 2	8.2 ± 0.2	760 ± 3	0.45 ± 0.03	2.9 ± 0.2 (3.1)

Table of contents entry

Blends based on unsubstituted buckminsterfullerenes (C_{60} , C_{70}) and a thiophene-quinoxaline copolymer (TQ1) can be readily processed from solution. Solar cell efficiencies of up to 3.6 % were achieved with a 1:1 C_{60} : C_{70} mixture as the acceptor material, accompanied by a high internal quantum efficiency of 75 %, due to the improved solubility in ortho-dichlorobenzene compared to either of the neat fullerenes.

Keywords: buckminsterfullerene, mixture, fullerene, polymer solar cell, photovoltaics

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Neat C_{60} : C_{70} buckminsterfullerene mixtures enhance polymer solar cell performance