Quasi-3D Simultaneous Topographical, Optical, Chemical and Electrical Mapping of Organic Solar Cells at the Nanoscale

Naresh Kumar1, Alina Zoladek-Lemanczyk1, Anne A. Y. Guilbert2, S. M. Tuladhar2, T. Kirchartz2,3,4 B. C. Schroeder3, Iain McCulloch5, Jenny Nelson2, Debdulal Roy1,∗ and Fernando A. Castro1 ∗

Keywords: Solar cell, polymer blend, photocurrent, Tip-enhanced optical spectroscopy, PC-AFM

Novel optoelectronic devices use advanced nanomaterials systems, such as multi-component organic or hybrid semiconductors, where nanoscale morphology can crucially affect performance1,2,3. However, currently there are few analytical techniques that can directly correlate morphology with optoelectronic properties or chemical composition at nanometre length-scales presenting a major obstacle to device optimisation4. Herein, we demonstrate a unique approach that allows simultaneous quasi-3D topographical, optical, chemical and electrical mapping of organic optoelectronic devices with an optical and photocurrent lateral resolution of 15 – 20 nm by combining tip-enhanced optical spectroscopy (TEOS) with photoconductive atomic force microscopy (PC-AFM) into a single measurement. We show that the rich information obtained from these multi-parameter measurements, directly correlating nanoscale local composition with topography and optoelectronic properties, can be used to infer the 3D composition distribution in the blend, successfully describe the relationship between nanostructure and performance in bulk heterojunction organic photovoltaic (OPV) devices, and identify routes to performance improvement.

Recent years have seen a steep rise in efficiency of organic solar cells, due in part to the growing appreciation of the importance of film nanomorphology in determining device performance5. An OPV device consists of two electrodes sandwiching an active layer, typically a blend of a polymer acting as electron donor (D) and a fullerene derivative acting as electron acceptor (A). In contrast to inorganic solar cells, light absorption generates bound excitons in OPV devices that need to be dissociated into free charge carriers at a D-A heterojunction for photocurrent generation. Furthermore, short exciton diffusion lengths in organic semiconductors mean that the domain structure within the D-A blend films needs to be optimised to generate charges efficiently whilst maintaining well-connected pathways within each material type for efficient charge collection4. Therefore, D-A blends with coarse phase-separated morphologies (> 100 nm) typically yield low device efficiency due to poor charge generation6,7 whilst blends with very intimate phase mixing yield worsened device performance due to poor charge collection or rapid recombination8. Various studies have

1National Physical Laboratory, Teddington, Middlesex, U.K. TW11 0LW, 2Department of Physics, Imperial College London, London, U.K. SW7 2AZ, 3IEK-5 Photovoltaik, Forschungszentrum Juelich 52425, Germany, 4Faculty of Engineering and CENIDE, University of Duisburg-Essen,9 Carl-Benz-Strasse 199, 47057 Duisburg, Germany, 5Department of Chemistry, Imperial College London, London, U.K. SW7 2AZ
Corresponding authors: fernando.castro@npl.co.uk;debdulal.roy@npl.co.uk
demonstrated that local microstructure, and hence the device performance, is a function of material choice\(^9\), D-A blend ratio\(^10\) and process route\(^11\). For instance, fullerene-rich blends often result in devices with the highest photocurrent\(^12\). Whilst surface imaging techniques such as AFM have been used to correlate the performance of solar cells with the apparent size of the observed domains\(^13,14\), the rationale to relate domain size to device performance is neither consistent nor well understood. Part of the uncertainty results from the phase-separated domains being often impure in composition; in fact, several reports indicate that pure domains may be rare in polymer-fullerene blends\(^9, 15, 16\). Additionally, it is known that the polymer:fullerene ratio may vary laterally within blend films leading to mesoscale variations in photocurrent generation/collection, complicating the relationship between average blend ratio and device performance\(^17\). Therefore, understanding the interplay of local morphology, chemical composition, and photocurrent generation in OPVs demands simultaneous multi-parameter measurements with nanoscale resolution.

In recent years, PC-AFM has been used to probe the optoelectronic properties of operating organic solar cells, providing correlation between topography and photovoltaic performance with typical lateral resolution of 20 - 50 nm\(^18, 19, 20\). However, this technique cannot provide direct information about chemical composition. On the other hand, TEOS is a powerful technique that allows simultaneous mapping of the chemical composition (via Raman and photoluminescence (PL) signals) and topography of a surface at the nanoscale\(^21\). In addition to investigating OPV polymer-blends\(^22\), TEOS has been used to probe nanoscale chemical composition in a wide range of research areas such as catalysis, semiconductors, biology, single-wall carbon nanotubes, graphene and single molecule detection\(^23\). In TEOS, placing a sharp metal or metal-coated tip at the centre of a laser focus results in localised surface plasmon (LSP) resonance at the tip-apex, which enhances and confines the electromagnetic field \((E)\) to an area similar to the size of the tip-apex (called near-field) with a decay length \(< 10 \text{ nm}\)\(^24, 25\). The probe depths for Raman and PL maps are determined by the near-field electric field dependence of Raman \((\propto E^4)\) and PL \((\propto E^2)\)\(^26\) signal intensities and for a near-field penetration of 10 nm are estimated to be \(\approx 2.5 \text{ nm}\) and \(\approx 5 \text{ nm}\), respectively. The lateral resolution is similar for both tip-enhanced Raman and PL maps, typically being \(< 25 \text{ nm}\), which is about ten times better than the diffraction-limited lateral resolution (200 – 300 nm) of a confocal microscope\(^23\).
Herein, we propose the use of combined tip enhanced Raman and PL data analysis as a unique capability to probe chemical and structural information laterally and vertically with similar (nanoscale) resolution. By combining this capability with PC-AFM, we present the first direct simultaneous mapping of morphology, chemical composition and photoelectrical properties of an operating organic solar cell device with nanoscale resolution. A schematic diagram of the experimental set-up and the solar cell device used in this work is shown in Fig. 1 (see Supplementary Figure S1 for further details of the optical set-up). A Ag-coated AFM tip placed in the laser focus and in contact with the solar cell device active layer surface performs the dual function of a plasmonic probe for TEOS measurements and a cathode for PC-AFM measurements. To demonstrate the capability of this new method we choose to investigate blends of Poly[(2,1,3-benzo thia diazole-4,7-diyl)alt-(4,9-dihydro-4,4,9,9-tetraoctylbenzo\[1′′,2′′:4,5;4′′,5′′:4′,5′][bis silolo[3,2-b:3′,2′-b′][dithiophene-2,7-diyl]] (C8SiIDT-BT) and 1′,4′-Dihydro-naphtho[2′,3′:1,2][5,6]fullerene-C_{60} (ICMA) (Fig. 2a). Similar indacenodithiophene (IDT) polymer-based solar cells have shown > 7% efficiency\(^{27}\). We selected ICMA as the acceptor molecule due to its ability to form large apparent domains\(^{28}\) in the polymer blend and yet deliver a useful photocurrent\(^{5}\) of ≈ 2.8 mA/cm\(^2\) (see Supplementary Table S1 and Figure S2). Topographical domains of 50 - 250 nm can be clearly seen in the AFM topography image of C8SiIDT-BT:ICMA(1:1) blend film shown in Fig. 2b. The non-uniform character of these C8SiIDT-BT (hereafter referred to as
“polymer”) blends with ICMA (hereafter referred to as “fullerene”), in contrast to [6,6]-phenyl-C60 butyric acid methyl ester (PC60BM) (see Supplementary Figure S3), enables us to probe multiple compositions in a single device and hence directly correlate local fullerene content with photocurrent generation efficiency. The optical spectrum of the C8SiIDT-BT:ICMA blend (Fig. 2c) consists of three spectrally well-separated bands, representing Raman peaks from the polymer molecules and photoluminescence (PL) peaks from both polymer and fullerene molecules (see Fig. 2 caption for details). Sensitivity of the optical signal detection was maximised prior to conducting combined TEOS and PC-AFM measurements by measuring plasmonic enhancement of the Ag-coated tip on pristine C8SiIDT-BT and ICMA films (see Supplementary Note 1). Only the Ag-coated AFM tips exhibiting high plasmonic enhancement were utilised for the combined TEOS and PC-AFM mapping.

Figure 2 | C8SiIDT-BT:ICMA blend. a, Molecular structures of C8SiIDT-BT and ICMA molecules. b, AFM topography image of C8SiIDT-BT:ICMA blend. c, Confocal optical spectrum from the blend. Integration time: 1 s. The Raman and PL bands from C8SiIDT-BT and ICMA are highlighted. Green region contains Raman peaks from the polymer at 864 cm\(^{-1}\), 1279 cm\(^{-1}\), 1356 cm\(^{-1}\), 1382 cm\(^{-1}\) and 1545 cm\(^{-1}\), blue region contains the broad photoluminescence (PL) peak from polymer at 3800 cm\(^{-1}\) (667 nm, 1.86 eV) and the purple region contains PL peak from fullerene at 5400 cm\(^{-1}\) (746 nm, 1.66 eV). The Raman peak of ICMA at 1467 cm\(^{-1}\) is too weak to be observed in the optical spectrum.

High-resolution maps of topography, fullerene PL, polymer Raman, polymer PL and photocurrent around a single island on the C8SiIDT-BT:ICMA photoactive layer are presented in Fig. 3a-3e, respectively. The lateral resolution of the PL and photocurrent maps is estimated to be between 15 – 20 nm as indicated by Gaussian fitting of line profiles in Fig. 3g and 3h, respectively. Here, the polymer Raman signal is used to map the distribution of polymer content on the blend.
surface, since the intensity of Raman peaks is proportional to the number of chromophores. The intensity of polymer PL and fullerene PL depends on the local composition as well as the local degree of mixing of the two components (due to exciton quenching near the D-A interface). Therefore, the comparison of Raman and PL signal intensities allows us to probe the degree of mixing independent of the relative local polymer content.\textsuperscript{29, 30}

Figure 3| Combined TEOS & photocurrent mapping of C8SiIDT-BT:ICMA solar cell device. Maps of a, topography, b, polymer PL (3800 cm\(^{-1}\) (667 nm) peak intensity), c, fullerene PL (5400 cm\(^{-1}\) (746 nm) peak intensity), d, photocurrent, and e, polymer Raman (1382 cm\(^{-1}\) Raman peak intensity), acquired simultaneously around an island in C8SiIDT-BT:ICMA solar cell device. Spectra integration time: 0.5 s. f, Polymer PL and photocurrent intensity profiles averaged over the areas (going from left to right) marked by dashed squares in b and d. g, Intensity profile along the black line marked in c. h, Intensity profile along the black line marked in d. Resolution of the PL and photocurrent maps are calculated from the FWHM of the fitted Gaussian curves to be 19 nm and 15 nm, respectively.

Within the island, the polymer PL is reduced (Fig. 3b) while both fullerene PL (Fig. 3c) and the photocurrent under short circuit conditions (Fig. 3d) increase, relative to the region outside the islands. A higher fullerene PL emission in polymer blends has previously been assigned to the presence of large fullerene aggregates\textsuperscript{29,30}. The polymer Raman map (Fig. 3e) indicates that such fullerene aggregates are not at the surface of our samples. Indeed the polymer Raman intensity is equally uniform both inside and outside the island indicating that the distribution of polymer content near the top surface (within \(\approx 2.5\) nm) is homogeneous. The inverse correlation between polymer PL and photocurrent (Fig. 3f), combined with the increased fullerene PL seems to indicate a decreased relative polymer-to-fullerene composition at the subsurface within the island (below the Raman probing depth). Using the fact that Raman and PL probes different depths within the sample, < 2.5 nm
and < 5 nm respectively, we propose that the fullerene molecules aggregate at the subsurface leading to topographical features and that the top surface consists of a uniform matrix, likely a fine mixture of donor and acceptor molecules. This suggests that the fullerene aggregation is beneficial for efficient charge collection, leading to higher photocurrent in those regions.

It is interesting to observe distributed nanoscale pockets of higher photocurrent inside the islands (Fig. 3d), which implies a finer structure not visible from topography measurements. Similarly, we also notice very small areas with high photocurrent outside the island, which we will refer to as “current hotspots”. Care needs to be taken when interpreting nanoscale variation is (photo)current atomic force microscopy measurements as these can be caused by experimental artefacts and random current fluctuations\(^{20}\) (even in nominally homogeneous samples). We show below that the combination of photocurrent with spectroscopic data is a powerful method to ensure that the variations are real and significant. Fig. 4 shows average photocurrent, polymer PL, polymer Raman and fullerene PL intensity values per pixel as a function of the collection area inside the circle marked in Fig. 3d. The average polymer Raman signal is roughly constant, indicating a uniform average polymer content over these length-scales. However, as the collection area increases, average photocurrent and fullerene PL per pixel strongly increase while the average polymer PL per pixel slightly decreases. In fact, this trend is observed over several hundreds of nanometres of probe area, eventually reaching saturation as the radius approaches 1 \(\mu\)m (see Supplementary Figure S4). At such large length-scales the spatially-resolved device performance begins to resemble that of the macroscopic solar cell.

![Figure 4: Photocurrent and spectroscopic analysis outside the topographic island. a, Average photocurrent, b, average intensity of polymer PL (green circles), fullerene PL (blue triangles), and polymer Raman signals (red squares) per pixel as a function of the collection area inside the circle marked in Fig. 3e, with the radius increasing from 10 - 150 nm in the direction of the arrow. All average data per pixel is normalised by the mean value for the entire collection area for easier comparison of trends.](image)

The area-averaged photocurrent should be constant if the photocurrent generation efficiency were homogeneous at the tens of nanometre scale. This is clearly not the case; the strong dependence of photocurrent on probe area indicates strong local variations in photocurrent generation efficiency in
the blend film. This is supported by the observation of small photocurrent hotspots outside the islands. The increase in fullerene PL with constant polymer Raman intensity indicates a change in local subsurface morphology as the probe area samples a more fullerene-rich domain, similar to that observed inside the “islands” in Fig. 3c. These results indicate that the local composition of the current hotspots is similar to that found inside the islands and that the local current variations are indeed real. This points to a hierarchical 3D nanoscale blend structure containing small areas with optimal morphology and a large area with poor photocurrent generation/collection efficiency. We calculated the average photocurrent inside the good areas (current hotspots or islands) to be 1.5-2.3 times higher than the overall average current, indicating a substantial potential improvement in short circuit current if a more uniformly optimised morphology can be obtained.

Based on the simultaneous TEOS and PC-AFM maps and analysis presented in Fig. 3 and 4, we propose a schematic morphological description of the top 10 nm of the C8SilDT-BT:ICMA active layer (Fig. 5). The cross-sectional scheme shows the distribution of polymer and fullerene molecules at the surface (<2.5 nm) and the sub-surface around an island and two current hotspots (at each side of the island). Whilst composition is uniform along the surface skin, the subsurface region contains localized larger domains rich in fullerene that lead to better charge collection and increased photocurrent. Such detailed insights into the relationship between structural and functional properties of operating solar cell device cannot be obtained from traditional methods (and not even by the individual TEOS or PC-AFM alone). Such simultaneous high-resolution Raman, PL and photocurrent maps were reproducibly obtained on several different C8SilDT-BT:ICMA solar cell devices using different Ag-coated tips in our laboratory.

Figure 5: Proposed composition of C8SilDT-BT:ICMA blend surface. Schematic diagram showing the relative distribution of fullerene and polymer molecules within the top 10 nm thickness around an island of the C8SilDT-BT:ICMA blend surface revealed by combined TEOS and PC-AFM mapping in Fig. 3. TEOS-PC-
AFM probe is also partially shown (not to scale) with an indication of the different probe depths of the near field Raman and PL measurements.

Additionally, for comparison we also carried out simultaneous TEOS and PC-AFM mapping of C8SiIDT-BT:PC60BM solar cell samples that present a more intermixed morphology and found photocurrent, topography and donor-acceptor composition to be fairly homogeneous on the tens of nm length-scale (see Supplementary Note 2).

To conclude, we have demonstrated a novel measurement method that allows simultaneous mapping of local morphology, chemical composition, optical and electrical properties at the nanoscale (< 20 nm lateral resolution). The ability to directly identify the effect of local composition on optoelectrical properties was demonstrated by mapping C8SiIDT-BT:ICMA blend solar cells exhibiting a hierarchical structure with a combination of nanoscale current hotspots and larger islands of high efficiency and optimised blend ratio composition dispersed in a low efficiency blend background. We believe such heterogeneous structure is likely to be present in other blend systems as well. Additionally, the complementary information and depth of resolution of different methods was used to probe 3D information with similar nanoscale resolution in all three dimensions, allowing a better understanding of the distribution of blend composition within 10 nm from the surface and its relationship to the photocurrent generation and collection. Currently, such detailed insights into the interplay of 3D morphology, chemical composition, exciton dynamics and photocurrent generation at the nanoscale inside OPV devices cannot be directly obtained by any other analytical technique. We expect that the rich information that can be obtained from such multi-parameter measurements will play a significant role in guiding the rational design of a range of nanomaterial-based electronic devices.

Methods

**TEOS-PCAFM Probes:** TEOS probes were prepared by first oxidising contact-mode Si AFM tips (Mikromasch, Estonia) to a thickness of 300 nm SiO$_2$ and thermally coating the oxidised AFM tips with Ag to a nominal thickness of 150 nm at a pressure of $10^{-6}$ mbar. A slow deposition rate of 0.05 nm/s was used to achieve a low roughness of the Ag-coating. A thicker Ag coating of 150 nm was used for the probes compared to the typical thickness of 50 – 60 nm that is commonly used for making TEOS probes to ensure that the coating had sufficient conductivity for PC-AFM measurements. Despite the 150 nm coating resulting in tip-apex size of 50 – 70 nm (see inset of Fig. 1), a high plasmonic enhancement (see Supplementary section S3) and excellent lateral resolution (Fig. 3) was obtained in TEOS measurements. Lateral resolution better than the average tip apex if often observed and result from the fact that the coating is often not uniform and local domains on the tip can act as hotspots of high plasmonic activity.

**Solar cell device structures:** Solar cell devices were prepared by first spin-coating filtered PEDOT: PSS (Clevios AI 4083, Germany) aqueous solution onto ITO-coated glass coverslips (Prazisions Glas & Optik
GmbH, Germany) at 3500 RPM for 60 s and annealed in air at 150 °C for 20 minutes. Then, 20 mg/ml solution of C8SiIDT-BT (Synthesised at Imperial College London) & ICMA (Plextronics, Inc., USA) (Weight ratio 1:1) in chlorobenzene was spin-coated on top of the PEDOT: PSS layer at 4000 RPM for 120 s followed by 5000 RPM for 60 s. For the combined TEOS and PC-AFM measurements, the Ag-coated tip acted as the cathode (top electrode) for the solar cell device. However, for the macroscopic characterisation, calcium (=20 nm) and aluminium (=100 nm) were subsequently deposited on top of solar cell blends to act as the top electrode by thermal evaporation at a pressure of ≈10⁻⁶ mbar. Current density–voltage (J–V) characteristics of the devices were measured using Keithley 236 Source Measure Unit. Solar cell performance was measured using a xenon lamp with AM1.5G filters and 100 mW/cm² illumination solar simulator (Oriel Instruments, UK).

**TEOS set-up and measurements:** A home-built TEOS system in transmission mode was used for this work that consisted of an inverted confocal microscope (Nikon, Japan) fitted with an AFM (AIST-NT, The Netherlands) on top. A Raman spectrometer (Horiba Scientific, UK) attached with an electron multiplying charged coupled device (EMCCD) detector (Andor Technology, Ireland) with quantum efficiency > 50% from 400 – 900 nm was used to collect the optical spectra. A radially polarised (ARCoptix, Switzerland) laser beam of wavelength 532 nm was focused onto the sample using a 100× 1.49 NA oil-immersion objective lens (Nikon, Japan). A very low laser power of 10 µW at the sample was used for all measurements. Fine alignment of Ag-coated tip and the laser spot was carried out using an XYZ piezoelectric scanner. All TEOS and PC-AFM measurements were conducted in contact mode AFM inside a nitrogen environment.

**Acknowledgements**

The authors acknowledge funding from the Technology Strategy Board (TSB) SCALLOPS project (UK), the Supersolar Hub and EL grant.

**Author contributions**

NK and DR designed and built the TEOS set-up. NK and AZ implemented PC-AFM and optimised the combined TEOS/PC-AFM setup under direction of DR and FC. NK and AZ collected the data. BS and IM synthesised the polymer. AG, SMT, TK and JN prepared solar-cell blend samples along with complete solar cell devices, and performed macroscopic sample characterisation. NK, AZ, JN, TK and FC analysed the data. FC and NK wrote the manuscript. All authors contributed to the discussion of results and preparation of the manuscript.

**Additional information**

Supplementary information is available in the online version of the paper.

**Competing financial interests**

The authors declare no competing financial interests.
References


S1. Optical set-up for the simultaneous TEOS and PC-AFM measurements

**Figure S1** Optical set-up. A detailed schematic of the optical set-up for conducting combined TEOS and PC-AFM mapping is presented here. A 532 nm laser is radially polarised before focusing onto the solar cell device using 100x 1.49 NA oil immersion objective lens with an inverted confocal microscope. The diffraction-limited Raman spatial resolution of the confocal microscope is 218 nm (calculated using \((0.61\times\lambda)/\text{NA}\), where \(\lambda\) is the wavelength of excitation laser and NA is numerical aperture of the objective lens) Raman scattered light is collected by the same objective lens and sent to the Raman spectrometer via a multimode optical fibre with a pinhole of 25 µm to reject the out of focus light for confocal measurements. All near-field measurements were conducted using contact mode AFM in a nitrogen environment.
S2. C8SiIDT-BT:ICMA and C8SiIDT-BT:PC60BM blends solar cells device performance

Table S1: Device characteristics of C8SiIDT-BT:ICMA and C8SiIDT-BT:PC60BM blend solar cells under 100 mW/cm² AM1.5G illumination.

<table>
<thead>
<tr>
<th>Blends</th>
<th>Si-IDTBT:ICMA (1:3)</th>
<th>Si-IDTBT:ICMA (1:1)</th>
<th>Si-IDTBT:PC61BM (1:1)</th>
<th>Si-IDTBT:PC61BM (1:3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pristine</td>
<td>Annealed</td>
<td>Pristine</td>
<td>Annealed</td>
</tr>
<tr>
<td>Jsc (mA/cm²)</td>
<td>1.19</td>
<td>2.79</td>
<td>6.34</td>
<td>3.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.34</td>
<td>3.16</td>
<td></td>
</tr>
<tr>
<td>Voc (V)</td>
<td>0.72</td>
<td>0.93</td>
<td>0.91</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.82</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>FF</td>
<td>0.41</td>
<td>0.35</td>
<td>0.36</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td>0.33</td>
<td>0.45</td>
</tr>
<tr>
<td>PCE %</td>
<td>0.35</td>
<td>0.91</td>
<td>2.10</td>
<td>3.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.58</td>
<td>0.74</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Device Structure: ITO/PEDOT:PSS/Blend/Ca/Al

Blend concentration:
- Si-IDTBT:ICMA = 20 mg/ml
- Si-IDTBT:PC60BM = 20 mg/ml

Thickness of the active layer: 66 – 70 nm

Area of the solar cells: 0.045 cm²

Annealing: 150 °C for 30 min

Figure S2: Current-density-voltage characteristics of C8SiIDT-BT:ICMA and C8SiIDT-BT:PC60BM blends solar cells under 100 mW/cm² AM1.5G light. a, Effect of increasing fullerene content in the current; b, Effect of thermal annealing (dotted lines).
S3. AFM topography image of C8SiIDT-BT:PC60BM solar cell blend

Figure S3| AFM topography image of C8SiIDT-BT:PC60BM solar cell blend. Compared to the topography of C8SiIDT-BT:ICMA solar cell blend shown in Fig 2b, topography of C8SiIDT-BT:PC60BM solar cell blend shows absence of submicron features or domains indicating a more thorough mixing of polymer and fullerene molecules.

S4. Average photocurrent per pixel as a function of probe area in C8SiIDT-BT:ICMA solar cell

Figure S4| Average photocurrent per pixel as a function of the probe area. a, AFM topography image of a 2 × 2 µm² area of the C8SiIDT-BT:ICMA (1:1 by weight) solar cell. b, photocurrent map in short circuit conditions of the blend area in a, showing large islands of high photocurrent. c, Average photocurrent per pixel as a function of radius of probe area. Probe area was calculated using
a circle starting from the center of the area in a, and truncated when it became large enough to reach the end of the image. All pixels covered (even partially) by the circle were included in the calculation. Note how the photocurrent response becomes apparently homogeneous when the probe area radius approaches 1 µm.

Supplementary Note 1

Plasmonic enhancement of Raman and PL signals from pristine C8SiIDT-BT and ICMA thin films

Enhancement factor (EF) of the near-field signal in a TEOS experiment is a measure of the plasmonic enhancement of electromagnetic field at the tip-apex and is usually calculated as:

\[
EF = \frac{(I_{\text{Tip-in}} - I_{\text{Tip-out}})}{I_{\text{Tip-out}}} / \frac{A_{\text{NF}}}{A_{\text{FF}}},
\]

Figure S5 | Plasmonic enhancement of Raman and PL signals. a, Near-field (Ag-coated tip in contact with the sample) and far-field (Tip away from the sample) optical spectra of pristine C8SiIDT-BT polymer film showing the plasmonic enhancement of polymer PL at the tip-apex. Inset shows near-field and far-field spectra of the Raman peaks of the polymer from the zoomed in area marked by the dotted square. b, Near-field and far-field optical spectra of the pristine ICMA sample.

where \( I_{\text{Tip-in}} \) and \( I_{\text{Tip-out}} \) are the optical signal intensities with the tip in-contact and retracted from the sample, respectively. \( A_{\text{FF}} \) and \( A_{\text{NF}} \) are the areas contributing to the far-field and near-field optical signals, which can be estimated from the far-field and near-field spatial resolutions, respectively.

The far-field spatial confocal resolution is normally theoretically calculated by using the nominal properties of the optical components and laser of the system. For our system we have also
measured the confocal resolution experimentally. By measuring and analyzing a well-known sample of a single wall carbon nanotube we know that the confocal resolution of our system is 230 nm and therefore we would not be able to distinguish smaller features without the use of plasmonic enhancement by a metallic tip. The near-field spatial resolution was measured from the TEOS PL map (Fig. 3b) to be 19 nm. $I_{\text{Tip-in}}$ and $I_{\text{Tip-out}}$ of the Raman and PL peaks were calculated by fitting a set of Lorentzian (for Raman peaks) & Gaussian (for PL peaks) peaks to the spectra. Using eq. (1) the EF of the 3800 cm$^{-1}$ (667 nm) C8SiIDT-BT PL peak, 5400 cm$^{-1}$ (746 nm) ICMA PL peak and 1382 cm$^{-1}$ C8SiIDT-BT Raman peak was calculated to be 263, 202 and 851, respectively.

It should be noted that this near-field enhancement of optical signals originates from the plasmonic enhancement of electromagnetic (EM) field at the sharp Ag-coated tip-apex from a very small region of diameter $\approx$ 19 nm. This plasmonic confinement of the EM field is responsible for the nanoscale spatial resolution obtained in the Raman and PL maps presented in this work.

Reference


**Supplementary Note 2**

**Simultaneous TEOS and PC-AFM mapping of C8SiIDT-BT:PC60BM solar cell**

We carried out simultaneous TEOS and PC-AFM mapping of a C8SiIDT-BT:PC60BM solar cell device using the same experimental set-up shown in Fig. 1 and S1. In contrast to the C8SiIDT-BT:ICMA blend topography that consists of islands ranging from 50 – 250 nm diameter (Fig 2b), AFM topography image of C8SiIDT-BT:PC60BM blend in Fig. S6a shows absence of any sub-micron features indicating a more intimate mixing of the C8SiIDT-BT & PC60BM molecules.

Fig. S6b – S6f show the topography, PC60BM PL, C8SiIDT-BT Raman, C8SiIDT-BT PL and photocurrent maps measured simultaneously from 0.5 $\times$ 1 $\mu$m$^2$ area (marked with dotted rectangle in Fig. S6a) of the C8SiIDT-BT:PC60BM solar cell device. Topography map in Fig. S6b again shows absence of any sub-micron size topographical features. Maps of PC60BM PL, C8SiIDT-BT Raman and C8SiIDT-BT in Fig. S6c – S6e indicate a uniform distribution of polymer and PC60BM molecules in the blend film. Furthermore, a uniform generation of photocurrent from the C8SiIDT-BT:PC60BM blend surface is observed in Fig. S6f, consistent with a C8SiIDT-BT:PC60BM mixed phase.
Figure S6 | Simultaneous TEOS and PC-AFM mapping of C8SiIDT-BT:PC60BM solar cell. a, AFM topography image of C8SiIDT-BT:PC60BM blend surface b, Topography c, PC60BM PL (4693 cm\(^{-1}\) (709 nm) peak intensity) d, C8SiIDT-BT Raman (1382 cm\(^{-1}\) peak intensity) e, C8SiIDT-BT PL (3800 cm\(^{-1}\) (667 nm) peak intensity) f, photocurrent maps from 0.5 × 1 µm\(^2\) area (marked with dotted rectangle in a) of the C8SiIDT-BT:PC60BM solar cell containing 40 × 20 pixels. Topography, Raman, PL and photocurrent signals were measured simultaneously from the solar cell with an integration time of 0.5 s at each pixel.

Thermally annealing of this PCBM sample (150° for 30 minutes) led to a significant reduction in device performance (Table S1). Combined TEOS/PC-AFM measurements showed that after annealing, a relatively pure PCBM rich domain is formed (polymer PL decreases without increase in photocurrent) which leads an overall reduction in photocurrent generation efficiency (lower photocurrent) of the device as shown in Fig. S6. This indicates a difference in the ability to mix between ICMA or PCBM and this IDT polymer.
Figure S7 | Simultaneous TEOS and PC-AFM mapping of annealed C8SiIDT-BT:PC60BM solar cell. a, Topography b, PC60BM PL (4693 cm$^{-1}$ peak intensity) c, C8SiIDT-BT Raman (1382 cm$^{-1}$ peak intensity) d, C8SiIDT-BT PL (3800 cm$^{-1}$ peak intensity) e, photocurrent maps from 2.0 µm × 1.2 µm area of annealed C8SiIDT-BT:PC60BM solar cell made using 50 × 30 pixels. Topography, Raman, PL and photocurrent signals were measured simultaneously from the solar cell with an integration time of 0.5 s at each pixel.