

Revealing Structure and Electronic Properties at Organic Interfaces Using TEM

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Abstract

Molecules and atoms at material interfaces have properties that are distinct from those found in the bulk. Distinguishing the interfacial species from the bulk species is the inherent difficulty of interfacial analysis. For organic photovoltaic devices, the interface between the donor and acceptor materials is the location for exciton dissociation. Dissociation is thought to occur *via* a complex route effected by microstructure and the electronic energy levels. The scale of these devices and the soft nature of these materials provide an additional level of difficulty for analysis at these interfaces. The transmission electron microscope (TEM) and the spectroscopic techniques it incorporates can allow the properties of the donor-acceptor interfaces to be revealed. Cross-sectional sample preparation, using modern focused ion beam instruments, has been playing a key role in the progression of interfacial analysis. This powerful instrument combination has the ability to draw conclusions about interface morphology, structure and electronic properties of organic donor-acceptor interfaces at the molecular scale. Recent publications have demonstrated these abilities, and this article aims to summarise some of that work and provide scope for the future.

Introduction

Recent advances in the field of nanoscale electronic engineering have introduced new types of materials suitable for devices. One of the key material classes that are emerging as strong contenders to traditional silicon-based electronics are organics *i.e.* those in which the principal elemental component is carbon. Some typical organic semiconductors include the phthalocyanines, fullerenes and their derivatives *e.g.* PCBM and thiophene polymers *e.g.* poly(3-hexylthiophene)(P3HT).

Organic photovoltaic (OPV) devices have the potential to provide a source of electric power. By using organic semiconductors as the principle photoactive materials, photovoltaics with lightweight and flexible properties could make a competitive alternative to current technology and fill niche applications.[1–5] Organic devices have the added potential to be far cheaper to produce on large scales than comparable inorganic devices.[6–9]

The typical structure for OPV devices consists of thin films of two materials, referred to as the (electron) donor and acceptor.[10] In the highest efficiency devices, these two materials are usually intimately mixed in a thin film as a ‘bulk heterojunction’ architecture but have also been developed as discrete thin films in a ‘bi-layer’ architecture.[11,12] Over the past half-century, it has been identified that the interface between the donor and acceptor materials is a key feature for photovoltaic power generation, and therefore of extreme technological interest.

Consensus surrounds the basic processes that occur within these devices that result in the generation of electrical power. These are outlined in Figure 1 a).[10]

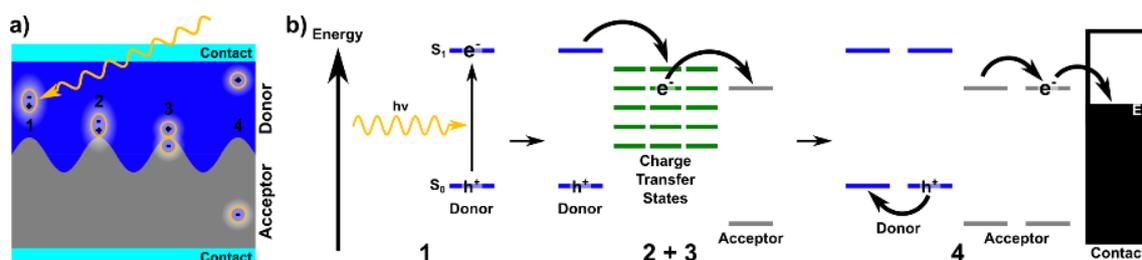


Figure 1 a) Fundamental processes occurring in an organic photovoltaic 1. Photon absorption creating an exciton; 2. Exciton migration within the film; 3. Exciton dissociation into polarons; 4. Polaron migration to contacts. b) Proposed energy level diagram of processes occurring in a). Reprinted and adapted with permission from Brédas et al. Copyright 2009 American Chemical Society, in which the fine electronic structure of the charge transfer state is shown.[13]

The total efficiency of a device is a combination of the proportion of the energy that is transferred through all these processes. Increasing the efficiency of OPV devices has focussed on optimising these individual processes, whether its increasing absorption, dissociating more excitons or reducing the resistance polarons experience.[14,15]

The mechanisms in which photons are absorbed and excitons migrate within the films *via* the Förster and Dexter models are fairly well understood.[10,13,16–18] However, as of yet the mechanism of exciton dissociation has not yet been fully described.[13] From a number of recent publications, it has been proposed that dissociation could occur by the transfer of the excited electron to a ‘charge transfer state’ (CTS), before either relaxation to the ground state (referred to as recombination) or separation into free charges (Figure 1 b).[19–22]

Efficient exciton separation within the CTS, which would lead to more efficient devices, appears to be highly dependent on the microstructure, electronic energy levels and morphology of the donor-acceptor interface. Interfacial characterisation in terms of these aspects is, therefore, vital to guide further development of OPV devices.

Analysing these technologically relevant interfaces is incredibly challenging due to the scale of the thin films produced (typically 10 – 300 nm), the soft nature of the materials used and inherent problems of interfacial analysis. Acquiring data about the aforementioned characteristics can be problematic. Many techniques aim to collect data from bulk samples and infer characteristics of the interface.[23–25] Useful as these techniques are, they do not provide the spatial resolution needed to make claims about the organic interface on the molecular/atomic scale. Gaining an understanding at this scale, for example elucidating specific locations where excitons dissociate/recombine, could drive theoretical and synthetic experimentation to improve device performance.

Transmission electron microscopy (TEM) has the ability to resolve these morphological and structural features which could aid the understanding of interfaces in OPVs. Indeed, high-resolution transmission electron microscopy (HRTEM) has been used extensively in OPV research in recent years.[12,26,27] However accounting for artefacts introduced during specimen preparation and data acquisition in the TEM must be undertaken. In addition to this, there is further potential to probe morphology, crystal and electronic structure of donor-acceptor materials and interfaces, *with* high spatial resolution using HRTEM, high-resolution scanning transmission electron microscopy (HRSTEM) and the associated spectroscopies: energy dispersive X-ray (EDX) spectroscopy, electron energy loss spectroscopy (EELS) and energy filtered TEM (EFTEM), physical explanations of which can be found below. The clear target for this analysis would be the search for and the probing of the fine electronic structure proposed in the CTS.[13] Morphological and electronic characterization on this scale is rapidly developing. This article and the accompanying one by Goode *et al.* identifies some recent work showcasing progress within the field of interfacial characterization using spectroscopy.[28–30]

Imaging Organics in the TEM

Imaging organic materials in the TEM can reveal the microstructure and morphology. However, damage to the material through bond scission (radiolysis), atomic displacement (knock-on damage) and specimen heating can take place.[31–33] Organic materials tend to be composed mainly of low-mass elements and are highly susceptible to these damage mechanisms. This susceptibility can vary enormously depending on the chemical structure, the type of bonding present and molecular orientation with respect to the electron beam. The critical dose for metal-free phthalocyanine, copper phthalocyanine (CuPc) and hexadecachloro copper phthalocyanine (Cl₁₆CuPc) can vary by two orders of magnitude with changes in the chemical structure.[34,35] Although it is difficult to identify a direct relationship between chemical structure and damage susceptibility in organic materials, aromatic and halogenated species appear to be less prone to degradation than aliphatic and non-halogenated analogues.

The energy of the electron beam can also have an effect on the damage inflicted on the sample material. Hayashida *et al.* demonstrated that the critical dose for CuPc increased with increasing accelerating voltage.[36] This suggests that for CuPc, radiolysis is the dominant damage mechanism. It, therefore, follows that higher beam energies should be used for imaging aromatic organic materials. In the same report, however, Hayashida *et al.* also demonstrated a diminishing contrast with increasing incident beam energies. Therefore, a major challenge for TEM characterisation of organic materials is to optimise data collection parameters.[37]

Provided that sample damage can be controlled and accounted for, astonishing data can be collected. Images purporting to resolve the molecular structure of phthalocyanines have been reported since the 1970s.[38,39] Recently, the resolution capabilities of HRSTEM has been exemplified through the work of Haruta and Kurata where the *sub*-molecular structure has been resolved in Cl₁₆CuPc (Figure 2).[40,41]

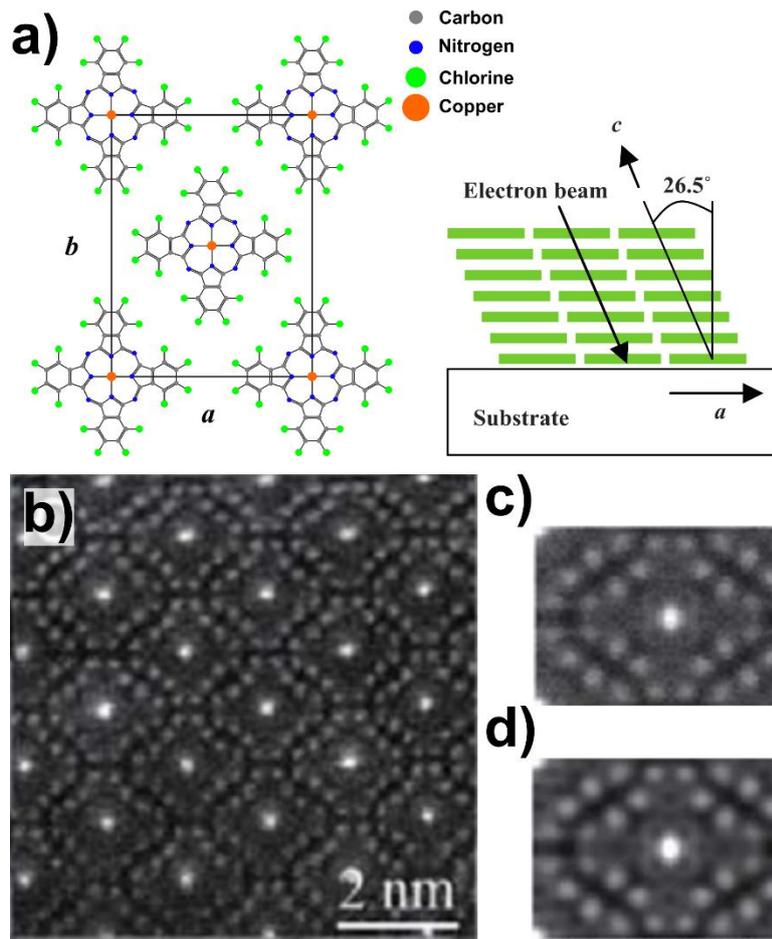


Figure 2 a) Molecular structure and unit cell viewed down the c -axis of $Cl_{16}CuPC$ with a schematic showing the relationship between the incident electron beam and the molecular stack. b) HRSTEM image of a 30 - 40 nm thick $Cl_{16}CuPC$ film. The brightest spots indicate the location of central copper atom stacks. The less intense spots surrounding each of these indicate the location of the 16 chlorine atoms. c) On translational averaging and d) noise filtering, the carbon ring structure of the phthalocyanine becomes visible. Reprinted and adapted with permission from Haruta et al. Copyright 2008 Elsevier and from Haruta and Kurata Copyright 2012 Nature Publishing group.[40,41]

Revealing the Interface

Investigating the organic-organic interface at the atomic/molecular level is challenging. While TEM and scanning transmission electron microscopy (STEM) techniques have the resolution capabilities, when bi-layer film structures are prepared on thin support TEM grids, the beam is transmitted through the specimen, superimposing information from the bulk materials over the interface. Probing the interface between different materials by growing planar heterostructures and examining the stack in top view might simplify the preparation procedure, but makes the analysis/interpretation significantly more difficult as it now becomes almost impossible to distinguish the interfacial species from the relatively large number of bulk species (Figure 3 a).

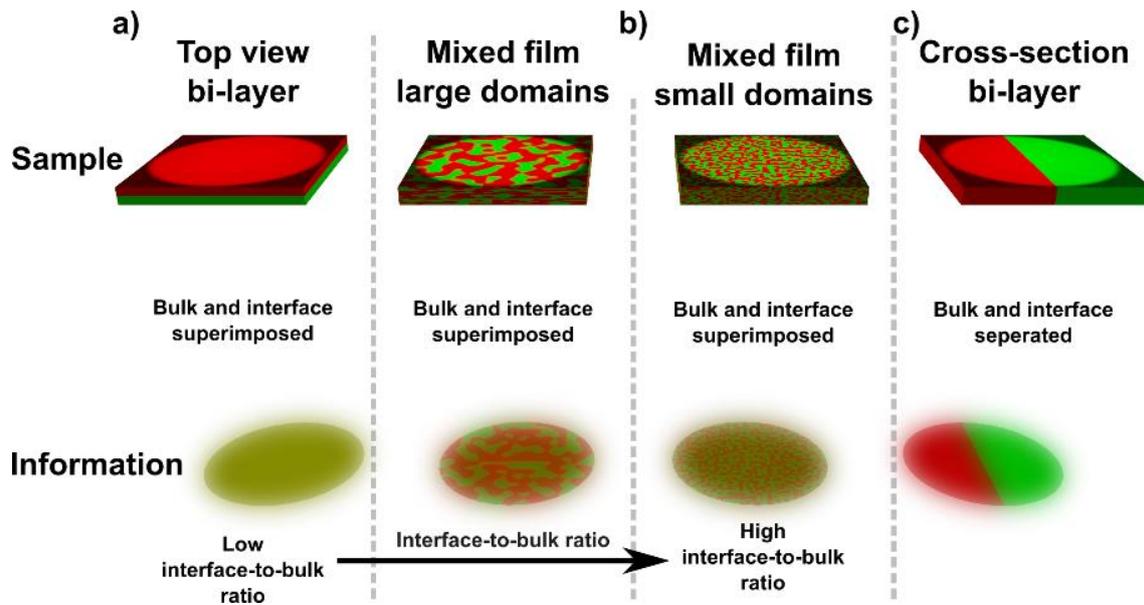


Figure 3 Schematic diagrams describing methods to probe interfaces in TEM samples. a) Top view of bi-layer superimposes bulk and interface. The low interface-to-bulk ratio means that the information from interfacial species is inseparable from that of the bulk. b) The interface-to-bulk ratio can be increased by mixing the two different materials. Preparing films with the smallest domains will result in the highest ratio. c) Cross-sectioning a bi-layer allows the interface to be directly exposed for analysis. The bulk and interfacial species are now separate in the projected information.

Superimposed information can be mitigated by preparing samples in which the ratio of interface-to-bulk species is maximised *i.e.* by intimately mixing the two materials (as used for bulk heterojunction OPV architectures), and deducing the interfacial properties by comparing images or spectra with those of pure materials (Figure 3 b).[11] Pfanmüller *et al.* used a similar approach to analyse P3HT:PCBM bulk-heterojunction films using electron spectroscopic imaging.[42] However, phase separation of materials can occur, increasing the number of bulk species that the incident beam interacts with. Increasing the ratio of interface-to-bulk species is vital for accurate analysis of the interface in mixed films. Provided that phase separation is taken into account, useful information can be gathered, that suggests that this preparation technique can be used to investigate interface species as well as phase separation itself.[42] This approach has the potential to provide a quicker and easier sample preparation procedure, and result in data that would drive further research.

Sample preparation approaches which involve exposing the interface for direct examination in the TEM could provide information about interfaces since superimposed information is avoided. By cross-sectioning planar film architectures such that in the TEM the incident electron beam is parallel to the interface of interest, the bulk material and interface can be analysed and interpreted separately (Figure 3 c). The new challenge now becomes the preparation of the cross-sectional specimen that displays the interface in its native state.

Material cross-sectioning has been traditionally performed using two routes: ultramicrotomy and ion beam milling. Ultramicrotomy involves the sectioning of material, typically embedded in a supporting resin with a microscopic knife and floating on the surface of a liquid bath. This technique is typically used for preparing TEM samples of biological specimens and works best for samples with hardness's that can be matched to that of the resin. However, for organic films grown on hard substrates, *e.g.* silicon, indium doped tin oxide, ultramicrotomy is unsuitable for preparing cross-sectional TEM samples since large scale mechanical damage occurs. The scale of damage observed in

the work of Domanski *et al.* and Nonaka *et al.* is great, revealing the delamination of organic films from contacts and cracking of substrates.[43,44] In addition to this, Jantou *et al.* demonstrated the resolution enhancement when a focused ion beam (FIB) is used to prepare specimens as opposed to ultramicrotomy.[45]

An alternative method to ultramicrotomy uses a beam of accelerated ions which sputters away material from the specimen gradually creating an electron transparent foil. Ion beam milling is generally performed using either a broad beam of argon ions or a focused beam of gallium ions. For materials which are less prone to amorphization, sample preparation using an ion beam can be relatively straightforward. However, for organic materials, significant amorphization is expected. Therefore, for the high-resolution examination of the organic-organic interface, steps must be taken to minimize amorphization during sample preparation. It has been demonstrated in the work by Dürr *et al.* using broad argon ion beam milling in combination with epoxy embedding and Herzing *et al.* and Gilchrist *et al.* using more modern dual beam FIB systems following the *in situ* lift-out procedure, that organic materials can be prepared whilst retaining crystallinity, a sign that significant amorphization has not occurred.[12,27,46] For CuPc/C₆₀ bilayers prepared in this manner, crystallinity is observed extensively (Figure 4 a – d).[12] The TEM damage mechanisms mentioned above are also present in sample preparation using an accelerated ion beam. Since bond scission and atomic displacement would alter the electronic structure found in materials, this damage must be minimized in order to probe electronic structure found at a donor-acceptor interface. In addition to this, specimen heating could also induce a phase change or drive material mixing/segregation.

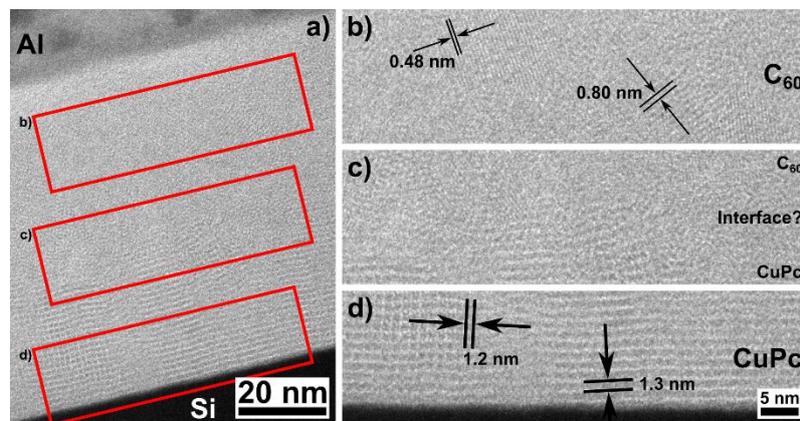


Figure 4 a) Cross-sectional HRTEM image from a CuPc/C₆₀ bi-layer, where lattice fringes in both the CuPc and C₆₀ can be identified. b) In the C₆₀ layer lattice fringes corresponding to the (111) and (200) planes can be observed (0.80 and 0.48 nm respectively). c) The interface between the CuPc and C₆₀ is not clear despite lattice fringes from both materials being observed. d) In the CuPc film lattice fringes from both the (100) and the (001) planes (1.3 and 1.2 nm respectively). In regions where both fringes are observed, the beam is close to parallel to the molecular stack. Scale bar in d) applies to b) and c).

For FIB sample preparation damage reduction methodologies involve decreasing the accelerating voltage, beam current and the angle the beam makes with the thin foil during the final thinning stages.[12,47,48] This can be thought of as reducing the kinetic energy and flux of incident ions perpendicular to the foil. The well-known work by Mayer *et al.* demonstrates the effects of reducing the energy of incident ions using HRTEM imaging.[47] Here, the amorphous material that surrounds a foil (an indicator of the damage) reduces from 22 to 0.5 – 1.5 nm when beam energy is decreased from 30 keV to 2 keV during final thinning stages. Similarly, the work by Prenitzer *et al.* and Ishitani *et al.* clearly describe the improvement of feature milling and ion penetration depth at lower beam

currents and shallower incident angles.[48,49] The success of these methodologies in the context of organic electronics has further been established by Gilchrist *et al.*, using thin film structures composed of CuPc and C₆₀, where structure and morphology have been observed in unprecedented detail using HRTEM (Figure 4).[12]

In addition to these methods, cryo-FIB prepares thin foils at ultra-low temperatures. Similar to the damage reduction that is observed by cooling the foil during TEM imaging, the low temperatures reduce the likelihood that molecular bond breakage occurs, and thus retains the crystal structure for longer when exposed to identical conditions. Cryo-FIB has been employed recently in the work by Marko *et al.* and Edwards *et al.* who examined the effects of controlling the temperature rise of samples containing ice while thinning using a FIB at liquid nitrogen temperatures.[50,51] The cryo-FIB was able to prepare foils of hydrated cells and vitreous ice without devitrification. In addition to these results, the work by Bassim *et al.* used foils of lignite coal and polyacrylamide, prepared using cryo-FIB, in which the fine electronic structure can be retained and examined using X-ray absorption spectroscopy.[52] These results suggest that by using cryo-FIB methods, foils of organic thin films could be prepared in which the electronic structure is retained, and full implementation of the commonly used lift-out technique is starting to be employed under cryo conditions.[53] For the interfaces present in OPVs, sample preparation using a FIB in combination with damage reduction techniques, demonstrate that TEM samples could be prepared for analysis of the electronic structure at interfaces.

Spectroscopic Analysis

The resolution capabilities of TEM and STEM, in combination with carefully dosed imaging and cross-sectioning methods, have allowed structural and morphological information about the organic-organic interface to be obtained. From the work by Gilchrist *et al.* different materials in archetypical photovoltaic devices can be identified using contrast from crystalline regions (phase contrast) within CuPc and C₆₀ in cross-section.[12] On examination of the CuPc film, features observed within the film show a remarkable similarity to those observed in earlier work by Kobayashi *et al.* and Fryer *et al.* on various phthalocyanine films in top view.[31,54–56] This further demonstrates that the cross-sectional methodology described by Gilchrist *et al.* yields TEM foils without significant damage to the crystal structure.[12] Lattice fringes also observed in the C₆₀ film enable the clear distinction between the bulk materials. However, the interface between these materials is still unclear (Figure 4 c). On initial inspection the lack of lattice fringes could be thought of as the interface being comprised of an amorphous interlayer. By using EDX in combination with STEM, the complexity of this interface is revealed; nanoscale morphology extending within the thickness of the foil which is superimposed in the two-dimensional image. The morphology observed at this interface has a similar root mean square roughness to that of individual CuPc films grown under otherwise identical conditions and suggests that diffusion of the molecular species does not occur, creating a chemically sharp, but morphologically rough interface.

In bulk-heterojunction polymer devices, the morphology of the organic films can be extremely complex and have dramatic consequences for device efficiency.[57] Additionally, these types of film are usually less crystalline and make phase contrast, as a mechanism of interface identification, inappropriate. Moench *et al.* investigated the morphology changes occurring in these systems as a function of substrate temperature using STEM EDX.[58] Mixed DCV5T-Me (a sulfur-containing

polymer) and C₆₀ films were grown at room temperature (RT), 80 and 140 °C. At RT, the donor and acceptor materials are highly intermixed and result in devices with intermediate short circuit currents (J_{sc} , indicating lower charge extraction) and efficiencies (Figure 5 a and b). At 80 °C, the active layer forms a more desirable morphology, with carbon islands around 10 nm in size dispersed within a sulfur-rich (DCV5T-Me) network (Figure 5 c and d). A balance between interfacial area and charge extraction is achieved. Device electrical characteristics further support this with increases in J_{sc} and the fill factor, overall leading to a higher efficiency. For substrate temperatures of 140 °C, an undesirable morphology is promoted (Figure 5 e and f). Here, in addition to large film thickness variations, larger scale phase separation is observed further reducing the interfacial area with a loss of percolation pathways also expected. The papers of Gilchrist *et al.* and Moench *et al.*, expertly demonstrate STEM EDX methods for characterising the nanoscale morphology of organic-organic heterostructures.[12,58]

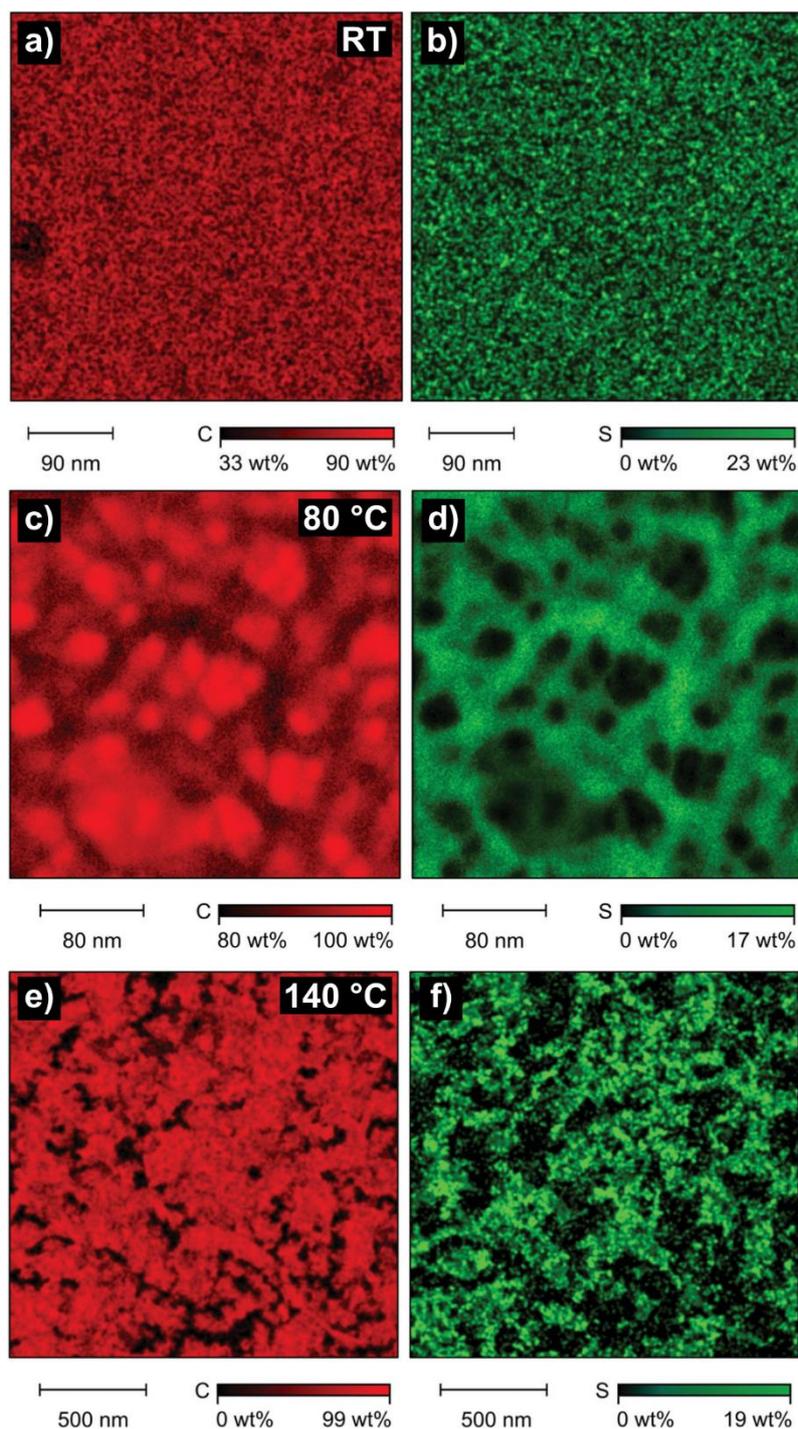


Figure 5 STEM EDX composition maps of carbon and sulfur from DCV5T-Me:C60 films at RT (a and b) 80 °C (c and d) and 140 °C (e and f). Note the scale change at 140 °C. Reprinted and adapted with permission from Moench et al. Copyright 2016 John Wiley and Sons Inc.[58]

One of the major disadvantages of current EDX technology in the TEM is the need for high levels of irradiation to achieve a low error in the quantification results. During collection, therefore, phase separation through sample heating might be occurring in addition to radiolytic damage and atomic displacement. Additionally, the spatial resolution of STEM EDX mapping will be limited by the relatively large interaction volume formed as the beam passes through the specimen. This, therefore, means molecular scale discoveries about organic donor-acceptor interfaces lie beyond the abilities of current STEM EDX methods.

Spectroscopy and imaging methods utilising transmitted, inelastically scattered electrons, on the other hand, yield a far higher spatial resolutions. Electrons can lose energy to the sample, exciting electronic transitions in atoms and molecules in the beam path. The transmitted electrons that have lost part (or even all) of their energy can be separated by a magnetic filter and recorded using a camera. Integrating across the image produced, results in a spectrum showing the distribution of electrons as a function of energy loss. This technique is referred to as electron energy loss spectroscopy (EELS). Additionally, using the same magnetic filter, an image can be produced, which is only formed by electrons that have lost a particular energy range, highlighting spatial regions where particular transitions occurred. This techniques is energy filtered TEM (EFTEM).

Some transitions are characteristic of different materials, and detection can be highly sensitive, for example in the low-loss energy range (typically between 1 – 50 eV energy loss) allowing for lower doses to be used. Provided that spectra can be assigned to a material type, EELS and EFTEM can be used to provide morphological characterisation on the molecular/atomic scale, and is especially useful for the analysis of light elements.

An example of this sensitivity can be seen in the work by Guo *et al.* which shows unique spectra from the materials P3HT, PCBM and PGeBTBT (a germanium containing copolymer) in the valence-loss regions of the EEL spectrum (Figure 6 a).[59] The sensitivity of the material to electron dose is also demonstrated by acquiring spectra from the three materials at increasing electron dose. For all material types an inverse relationship between peak intensity and dose is found (Figure 6 b, c and d). This relationship is attributed to the electronic structure of the material degrading under electron beam irradiation.

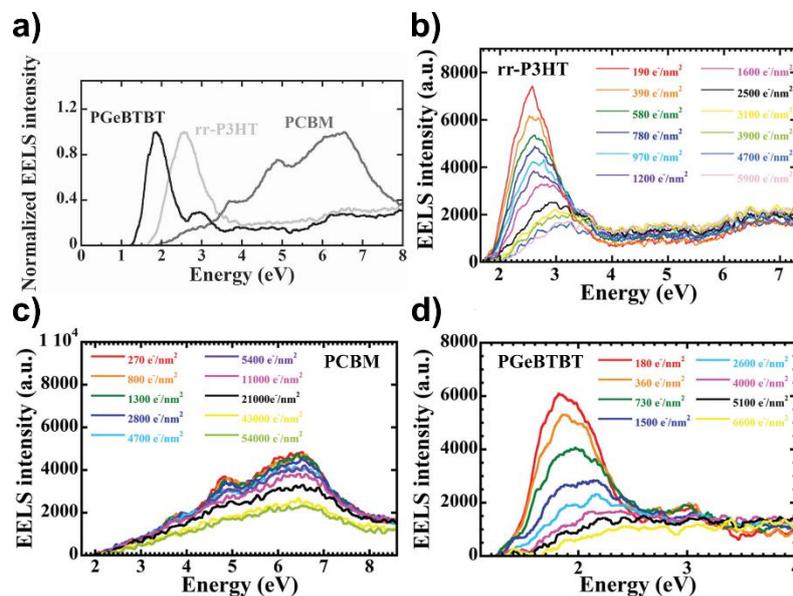


Figure 6 Low-loss EELS of P3HT, PCBM and PGeBTBT, demonstrating unique character of each spectrum (a). Dose-dependent nature of the low-loss EEL signal from P3HT (b), PCBM (c) and PGeBTBT (d). Reprinted and adapted with permission from Guo *et al.* Copyright 2015 John Wiley and Sons Inc.[59]

The group also present the morphological analysis of P3HT:PCBM mixed films showing the scale of phase separation between the two materials using EFTEM imaging (Figure 3). When compared to the STEM EDX data by Moench *et al.* (above) the scale of the phase separation is similar, however,

the EFTEM data has been collected at a fraction of the dose. In this case below the critical dose of P3HT.[58,59]

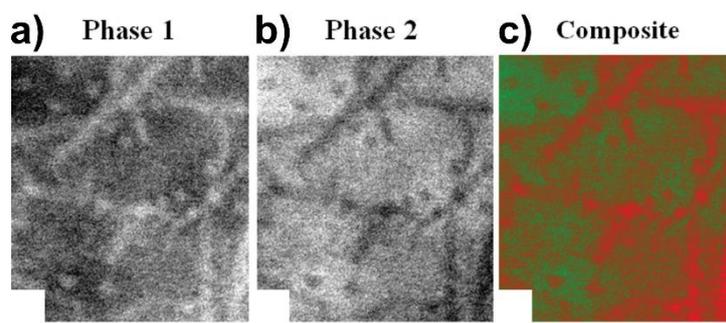


Figure 7 EFTEM imaging of P3HT/PCBM (1:1) mixed film using the low-loss energy region, scale bar represents 100 nm. Following processing using principle component analysis the P3HT rich (a) and PCBM rich (b) regions are identified. A composite image formed from (a) and (b). Reprinted and adapted with permission from Guo *et al.* Copyright 2015 John Wiley and Sons Inc.[59]

For the EFTEM work by Guo *et al.*, the characteristic valence electronic structure from the different species has been used to map distribution. This, however, does not identify the fine electronic structure expected to exist at the donor-acceptor interface. One of the reasons for this is the relatively low energy resolution of these techniques. Higher energy resolutions should enable CTS to be identified and mapped and correlated to morphological or structural features. Energy resolutions of 10 – 20 meV have been reported and applied to probing vibrational states in various materials and even mapping of band-gap excitations at MoS₂/MoSe₂ interfaces. [30,60] The improvement expected in future TEMs equipped with electron energy filters should enable CTS to similarly be mapped to drive device improvement.

Conclusions

The current status of using TEM to probe organic materials and interfaces has been demonstrated in the featured articles. STEM in combination with EDX shows great potential to expose phase distributions between chemically distinct species. The results from Gilchrist *et al.* and Moench *et al.* demonstrate that the nanoscale morphology can be revealed in mixed films and at discrete interfaces.[12,58] Following the results from Guo *et al.*, the use of low-loss transitions in the EEL spectrum has allowed nanoscale morphology to be probed at unprecedented low doses.[59] Cross-sectional FIB preparation of TEM samples has advanced to a point where relatively pristine TEM foils of ideal soft-soft interfaces can be prepared. With the advent of cryo-FIB, damage of the electronic structure of organic materials can be reduced further. With continuing advances made in TEM spectroscopy, higher energy resolution EELS and EFTEM will be key in exposing the mysteries of organic-organic interfaces.

References

- [1] Krebs FC. Fabrication and processing of polymer solar cells: A review of printing and coating techniques. *Sol Energy Mater Sol Cells* 2009;93:394–412. doi:10.1016/j.solmat.2008.10.004.
- [2] Søndergaard RR, Hösel M, Krebs FC. Roll-to-Roll fabrication of large area functional organic materials. *J Polym Sci Part B Polym Phys* 2013;51:16–34. doi:10.1002/polb.23192.

- [3] Pfannmöller M, Kowalsky W, Schröder RR. Visualizing physical, electronic, and optical properties of organic photovoltaic cells. *Energy Environ Sci* 2013;6:2871. doi:10.1039/c3ee41773e.
- [4] Deibel C, Dyakonov V. Polymer–fullerene bulk heterojunction solar cells. *Reports Prog Phys* 2010;73:096401. doi:10.1088/0034-4885/73/9/096401.
- [5] Emmott CJM, Röhr JA, Campoy-Quiles M, Kirchartz T, Urbina A, Ekins-Daukes NJ, et al. Organic photovoltaic greenhouses: a unique application for semi-transparent PV? *Energy Environ Sci* 2015:1317–28. doi:10.1039/C4EE03132F.
- [6] Forrest SR. The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature* 2004;428:911–8. doi:10.1038/nature02498.
- [7] Shaheen SE, Ginley DS, Jabbour GE. Organic-Based Photovoltaics: Toward Low-Cost Power Generation. *MRS Bull* 2005;30:10–9. doi:10.1557/mrs2005.2.
- [8] Brabec CJ, Hauch JA, Schilinsky P, Waldauf C. Production Aspects of Organic Photovoltaics and Their Impact on the Commercialization of Devices. *MRS Bull* 2005;30:50–2. doi:10.1557/mrs2005.10.
- [9] Brédas J-L, Durrant JR. Organic photovoltaics. *Acc Chem Res* 2009;42:1689–90. doi:10.1021/ar900238j.
- [10] Ameri T, Khoram P, Min J, Brabec CJ. Organic ternary solar cells: a review. *Adv Mater* 2013;25:4245–66. doi:10.1002/adma.201300623.
- [11] Heeger AJ. 25th anniversary article: Bulk heterojunction solar cells: understanding the mechanism of operation. *Adv Mater* 2014;26:10–27. doi:10.1002/adma.201304373.
- [12] Gilchrist JB, Basey-Fisher TH, Chang SC, Scheltens F, McComb DW, Heutz S. Uncovering Buried Structure and Interfaces in Molecular Photovoltaics. *Adv Funct Mater* 2014;24:6473–83. doi:10.1002/adfm.201400345.
- [13] Brédas J-L, Norton JE, Cornil J, Coropceanu V. Molecular understanding of organic solar cells: the challenges. *Acc Chem Res* 2009;42:1691–9. doi:10.1021/ar900099h.
- [14] Wong WY, Wang XZ, He Z, Chan KK, Djurišić AB, Cheung KY, et al. Tuning the absorption, charge transport properties, and solar cell efficiency with the number of thienyl rings in platinum-containing poly(aryleneethynylene)s. *J Am Chem Soc* 2007;129:14372–80. doi:10.1021/ja074959z.
- [15] Sullivan P, Jones TS, Ferguson AJ, Heutz S. Structural templating as a route to improved photovoltaic performance in copper phthalocyanine/fullerene (C₆₀) heterojunctions. *Appl Phys Lett* 2007;91:233114. doi:10.1063/1.2821229.
- [16] Feron K, Belcher WJ, Fell CJ, Dastoor PC. Organic solar cells: understanding the role of Förster resonance energy transfer. *Int J Mol Sci* 2012;13:17019–47. doi:10.3390/ijms131217019.
- [17] Sonar P, Fong Lim JP, Chan KL. Organic non-fullerene acceptors for organic photovoltaics. *Energy Environ Sci* 2011;4:1558. doi:10.1039/c0ee00668h.
- [18] Brédas J-L. Applied physics. When electrons leave holes in organic solar cells. *Science* 2014;343:492–3. doi:10.1126/science.1249230.
- [19] Westenhoff S, Howard IA, Hodgkiss JM, Kirov KR, Bronstein HA, Williams CK, et al. Charge recombination in organic photovoltaic devices with high open-circuit voltages. *J Am Chem Soc* 2008;130:13653–8. doi:10.1021/ja803054g.
- [20] Drori T, Sheng CX, Ndobe A, Singh S, Holt J, Vardeny Z V. Below-gap excitation of pi-

- conjugated polymer-fullerene blends: Implications for bulk organic heterojunction solar cells. *Phys Rev Lett* 2008;101:1–4. doi:10.1103/PhysRevLett.101.037401.
- [21] Veldman D, Ipek Ö, Meskers SCJ, Sweelssen J, Koetse MM, Veenstra SC, et al. Compositional and electric field dependence of the dissociation of charge transfer excitons in alternating polyfluorene copolymer/fullerene blends. *J Am Chem Soc* 2008;130:7721–35. doi:10.1021/ja8012598.
- [22] Ohkita H, Cook S, Astuti Y, Duffy W, Tierney S, Zhang W, et al. Charge carrier formation in polythiophene/fullerene blend films studied by transient absorption spectroscopy. *J Am Chem Soc* 2008;130:3030–42. doi:10.1021/ja076568q.
- [23] Ma W, Tumbleston JR, Wang M, Gann E, Huang F, Ade H. Domain Purity, Miscibility, and Molecular Orientation at Donor/Acceptor Interfaces in High Performance Organic Solar Cells: Paths to Further Improvement. *Adv Energy Mater* 2013;3:864–72. doi:10.1002/aenm.201200912.
- [24] Tumbleston JR, Collins BA, Yang L, Stuart AC, Gann E, Ma W, et al. The influence of molecular orientation on organic bulk heterojunction solar cells. *Nat Photonics* 2014;8:385–91. doi:10.1038/nphoton.2014.55.
- [25] Cho SW, DeMasi A, Preston ARH, Smith KE, Piper LFJ, Chauhan K V., et al. Probing the effect of relative molecular orientation on the photovoltaic device performance of an organic bilayer heterojunction using soft x-ray spectroscopies. *Appl Phys Lett* 2012;100:263302. doi:10.1063/1.4731197.
- [26] Oosterhout SD, Wienk MM, van Bavel SS, Thiedmann R, Koster LJA, Gilot J, et al. The effect of three-dimensional morphology on the efficiency of hybrid polymer solar cells. *Nat Mater* 2009;8:818–24. doi:10.1038/nmat2533.
- [27] Herzing AA, Ro HW, Soles CL, Delongchamp DM. Visualization of Phase Evolution in Model Organic Photovoltaic Structures via Energy-Filtered Transmission Electron Microscopy. *ACS Nano* 2013;7:937–44. doi:10.1021/nn402992y.
- [28] Goode AE, Porter AE, Kłosowski MM, Ryan MP, Heutz S, McComb DW. Analytical transmission electron microscopy at organic interfaces. *Curr Opin Solid State Mater Sci* 2016. doi:10.1016/j.cossms.2016.02.005.
- [29] Grogger W, Hofer F, Kothleitner G, Schaffer B. An Introduction to High-resolution EELS in Transmission Electron Microscopy. *Top Catal* 2008;50:200–7. doi:10.1007/s11244-008-9101-4.
- [30] Krivanek OL, Lovejoy TC, Dellby N, Aoki T, Carpenter RW, Rez P, et al. Vibrational spectroscopy in the electron microscope. *Nature* 2014;514:209–12. doi:10.1038/nature13870.
- [31] Fryer JR. Molecular arrays and molecular structure in organic thin films observed by electron microscopy. *J Phys D Appl Phys* 1993;26:B137–44. doi:10.1088/0022-3727/26/8B/022.
- [32] Koshino M, Masunaga YH, Nemoto T, Kurata H, Isoda S. Radiation damage analysis of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) by electron diffraction and electron energy loss spectroscopy. *Micron* 2005;36:271–9. doi:10.1016/j.micron.2004.12.007.
- [33] Egerton RF. Mechanisms of radiation damage in beam-sensitive specimens, for TEM accelerating voltages between 10 and 300 kV. *Microsc Res Tech* 2012;75:1550–6. doi:10.1002/jemt.22099.

- [34] Egerton RF. Control of radiation damage in the TEM. *Ultramicroscopy* 2013;127:100–8. doi:10.1016/j.ultramic.2012.07.006.
- [35] Reimer L. Review of the Radiation Damage Problem of Organic Specimens in Electron Microscopy. In: Siegel BM, Beaman DR, editors. *Phys. Asp. Electron Microsc. and Microbeam Anal.* 1st ed., Wiley; 1975, p. 238–9.
- [36] Hayashida M, Kawasaki T, Kimura Y, Takai Y. Estimation of suitable condition for observing copper–phthalocyanine crystalline film by transmission electron microscopy. *Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms* 2006;248:273–8. doi:10.1016/j.nimb.2006.04.168.
- [37] Williams DB, Carter CB. Part 1: Basics. *Transm. Electron Microsc. A Textb. Mater. Sci.* 2nd ed., New York: Springer US; 2009, p. 86. doi:10.1007/978-0-387-76501-3.
- [38] Murata Y, Fryer JR, Baird T. High resolution image of copper phthalocyanine. *Nature* 1976;263:401–2. doi:10.1038/263401b0.
- [39] Yanagi H, Maeda S, Ueda Y, Michio A. High Resolution Electron Microscopy of Octacyanomethylphthalocyanine-Metal Complexes in Thin Films Hisao. *J Electron Microscop* (Tokyo) 1988;37:177–88.
- [40] Haruta M, Kurata H. Direct observation of crystal defects in an organic molecular crystals of copper hexachlorophthalocyanine by STEM-EELS. *Sci Rep* 2012;2:252. doi:10.1038/srep00252.
- [41] Haruta M, Yoshida K, Kurata H, Isoda S. Atomic resolution ADF-STEM imaging of organic molecular crystal of halogenated copper phthalocyanine. *Ultramicroscopy* 2008;108:545–51. doi:10.1016/j.ultramic.2007.08.011.
- [42] Pfannmöller M, Flügge H, Benner G, Wacker I, Sommer C, Hanselmann M, et al. Visualizing a homogeneous blend in bulk heterojunction polymer solar cells by analytical electron microscopy. *Nano Lett* 2011;11:3099–107. doi:10.1021/nl201078t.
- [43] Domanski AL, Lieberwirth I, Sengupta E, Landfester K, Butt H-J, Berger R, et al. Effect of Morphological Changes on Presence of Trap States in P3HT:PCBM Solar Cells Studied by Cross-Sectional Energy Filtered TEM and Thermally Stimulated Current Measurements. *J Phys Chem C* 2013;117:23495–9. doi:10.1021/jp406014m.
- [44] Nonaka T, Date T, Tomita S, Nagai N, Nishimura M, Murata Y, et al. Phthalocyanines ultrathin alternating layer film on silicon, prepared by molecular beam deposition. *Thin Solid Films* 1994;237:87–90. doi:10.1016/0040-6090(94)90242-9.
- [45] Jantou V, Turmaine M, West GD, Horton MA, McComb DW. Focused ion beam milling and ultramicrotomy of mineralised ivory dentine for analytical transmission electron microscopy. *Micron* 2009;40:495–501. doi:10.1016/j.micron.2008.12.002.
- [46] Dürr AC, Schreiber F, Kelsch M, Dosch H. Optimized preparation of cross-sectional TEM specimens of organic thin films. *Ultramicroscopy* 2003;98:51–5. doi:10.1016/S0304-3991(03)00087-1.
- [47] Mayer J, Giannuzzi LA, Kamino T, Michael J. TEM Sample Preparation and FIB-Induced Damage. *MRS Bull* 2007;32:400–7. doi:10.1557/mrs2007.63.
- [48] Prenitzer BI, Giannuzzi LA, Brown SR, Irwin RB, Shofner TL, Stevie FA. The Correlation between Ion Beam/Material Interactions and Practical FIB Specimen Preparation 2003:216–36. doi:10.1017/S143192760030034.
- [49] Ishitani T, Umemura K, Ohnishi T, Yaguchi T, Kamino T. Improvements in performance of

- focused ion beam cross-sectioning: aspects of ion-sample interaction. *J Electron Microsc (Tokyo)* 2004;53:443–9. doi:10.1093/jmicro/dfh078.
- [50] Marko M, Hsieh C, Moberlychan W, Mannella CA, Frank J. Focused ion beam milling of vitreous water: prospects for an alternative to cryo-ultramicrotomy of frozen-hydrated biological samples. *J Microsc* 2006;222:42–7. doi:10.1111/j.1365-2818.2006.01567.x.
- [51] Edwards HK, Fay MW, Anderson SI, Scotchford CA, Grant DM, Brown PD. An appraisal of ultramicrotomy, FIBSEM and cryogenic FIBSEM techniques for the sectioning of biological cells on titanium substrates for TEM investigation. *J Microsc* 2009;234:16–25. doi:10.1111/j.1365-2818.2009.03152.x.
- [52] Bassim ND, De Gregorio BT, Kilcoyne ALD, Scott K, Chou T, Wirick S, et al. Minimizing damage during FIB sample preparation of soft materials. *J Microsc* 2012;245:288–301. doi:10.1111/j.1365-2818.2011.03570.x.
- [53] Parmenter C, Fay M, Hartfield C, Amador G, Moldovan G. Cryogenic FIB Lift-out as a Preparation Method for Damage-Free Soft Matter TEM Imaging. *Microsc Microanal* 2014;20:1224–5. doi:10.1017/S1431927614007855.
- [54] Kobayashi T, Fujiyoshi Y, Uyeda N. The observation of molecular orientations in crystal defects and the growth mechanism of thin phthalocyanine films. *Acta Crystallogr Sect A* 1982;38:356–62. doi:10.1107/S0567739482000746.
- [55] Kobayashi T, Yase K, Uyeda N. Direct observation of structure change in Ni-phthalocyanine caused by iodine doping. *Acta Crystallogr Sect B Struct Sci* 1984;40:263–71. doi:10.1107/S0108768184002081.
- [56] Fryer JR, Holland F. High Resolution Electron Microscopy of Molecular Crystals. III. Radiation Processes at Room Temperature. *Proc R Soc A Math Phys Eng Sci* 1984;393:353–69. doi:10.1098/rspa.1984.0062.
- [57] Westacott P, Tumbleston JR, Shoaee S, Fearn S, Bannock JH, Gilchrist JB, et al. On the role of intermixed phases in organic photovoltaic blends. *Energy Environ Sci* 2013;6:2756. doi:10.1039/c3ee41821a.
- [58] Moench T, Friederich P, Holzmueller F, Rutkowski B, Benduhn J, Strunk T, et al. Influence of Meso and Nanoscale Structure on the Properties of Highly Efficient Small Molecule Solar Cells. *Adv Energy Mater* 2016;6:n/a – n/a. doi:10.1002/aenm.201501280.
- [59] Guo C, Allen FI, Lee Y, Le TP, Song C, Ciston J, et al. Probing Local Electronic Transitions in Organic Semiconductors through Energy-Loss Spectrum Imaging in the Transmission Electron Microscope. *Adv Funct Mater* 2015;25:6071–6. doi:10.1002/adfm.201502090.
- [60] Tizei LHG, Lin Y-C, Mukai M, Sawada H, Lu A-Y, Li L-J, et al. Exciton Mapping at Subwavelength Scales in Two-Dimensional Materials. *Phys Rev Lett* 2015;114:107601. doi:10.1103/PhysRevLett.114.107601.