Bulk-Heterojunction with Long-Range Ordering: C_{60} Single Crystal with Incorporated Conjugated Polymer Networks

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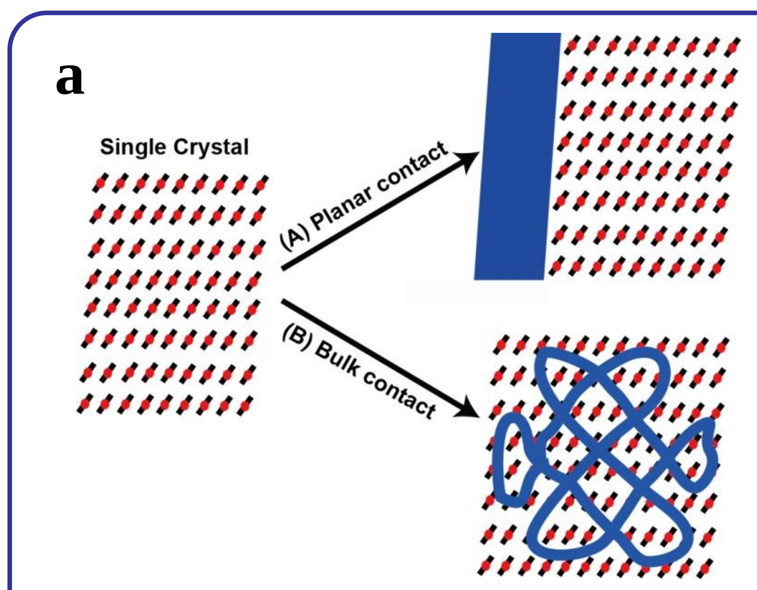
Abstract:

Single-crystal organic semiconductors are ideal active materials for organic optoelectronic devices by virtue of their outstanding charge mobility. It is necessary to interface these single crystals with other foreign materials to achieve varied optoelectronic functions. However, it is challenging to fabricate three-dimensional interfaces inside single crystals so as to form a “bulk-heterojunction” structure because single crystals are typically homogeneous,. In this work, C_{60} single crystals are prepared grown in a organogel of Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenvinylene] (MEH-PPV), a typical conjugated polymer. Instead of pure crystals, C_{60} crystals containing MEH-PPV nanofibers are obtained. Essentially, nanofiber networks of MEH-PPV gel are incorporated into growing C_{60} crystals and penetrate through the crystals, resulting in a crystal/gel-network interpenetrating composites. The single-crystallinity of the crystalline component is demonstrated by X-ray diffraction and electron diffraction analysis. Moreover, distinct charge-transfer inside the composites is indicated by the photoluminescence quenching. As such, through gel incorporation, we obtain a bulk-heterojunction of C_{60} single crystal and MEH-PPV nanofiber network, which has potential to be high performance optoelectronic materials.



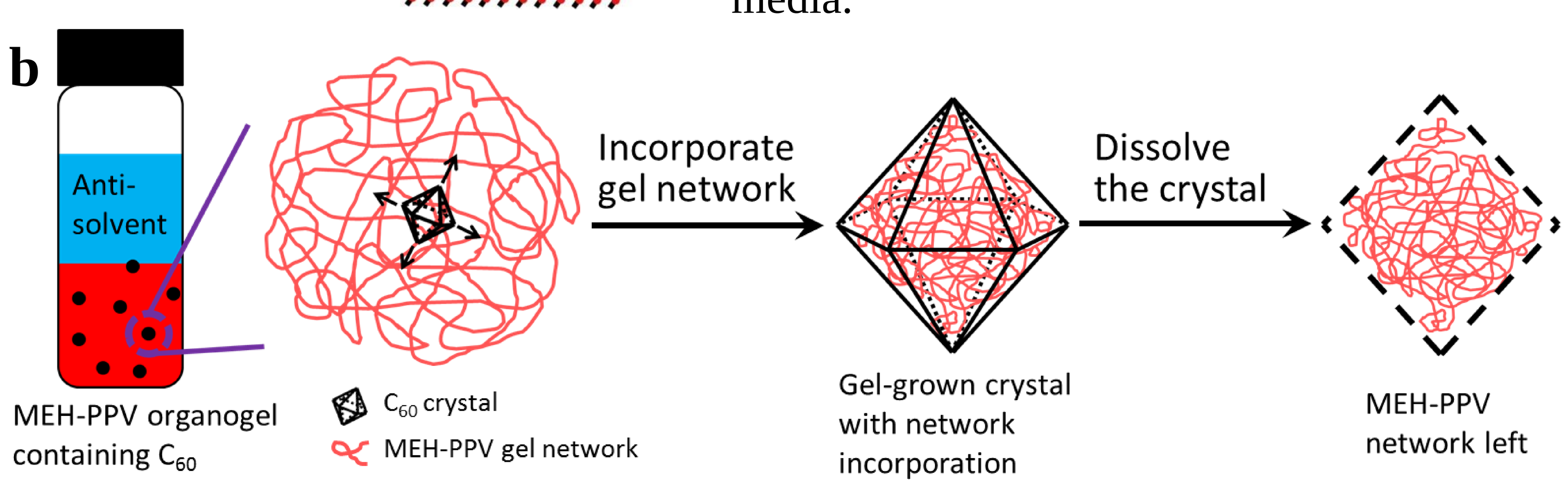
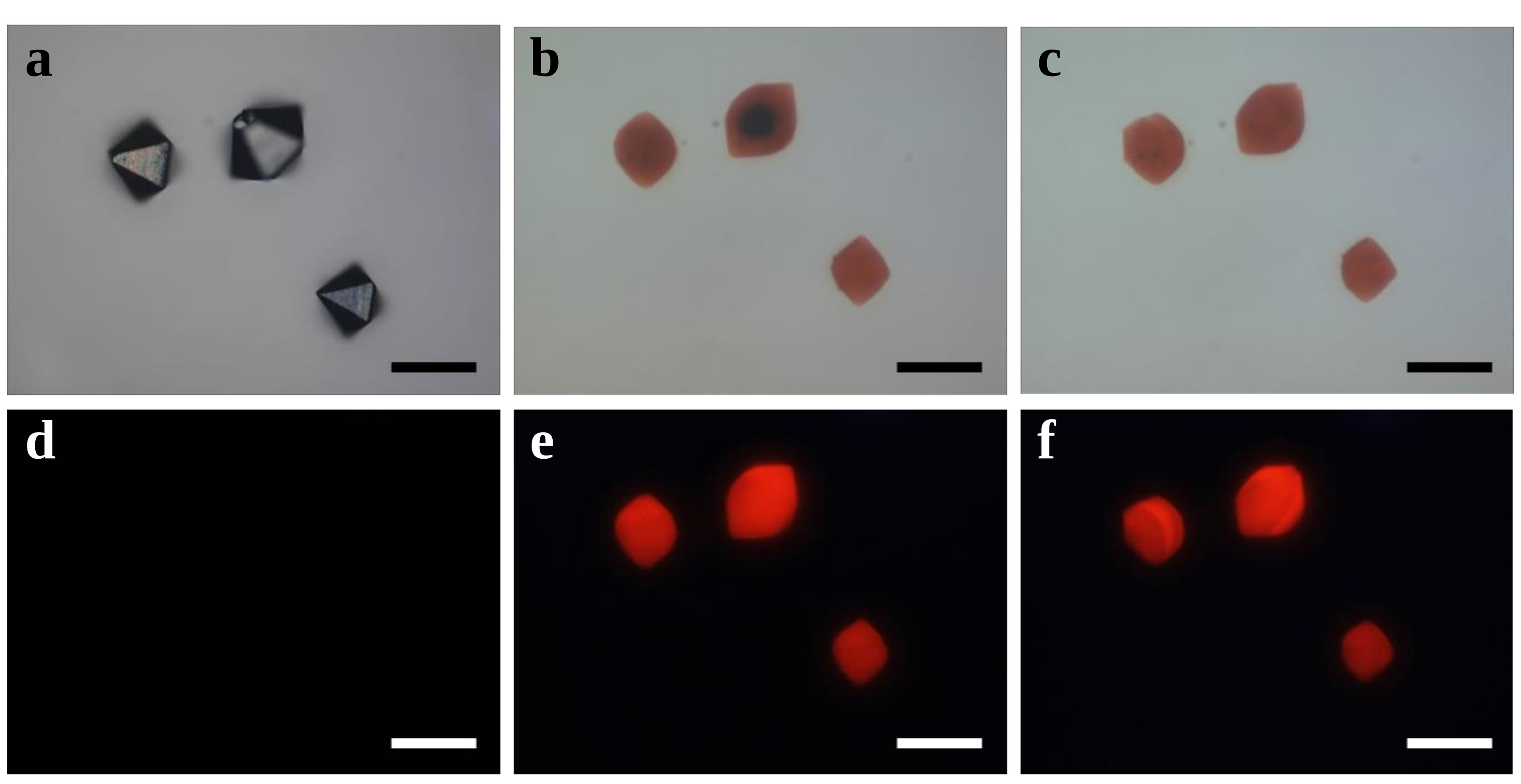


Fig. 1 (a) A schematic representation of two ways to interface organic single crystals with foreign materials. Route A: Planar contact is made from the outer surfaces of a single crystal. Route B: Bulk contact is constructed inside a single crystal as foreign materials are incorporated into the crystal. **(b)** A schematic representation of a crystal growing in gel media.



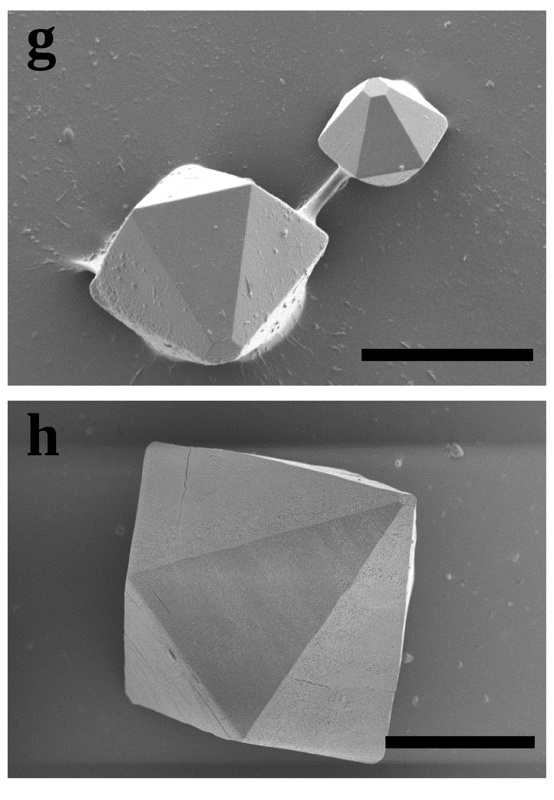
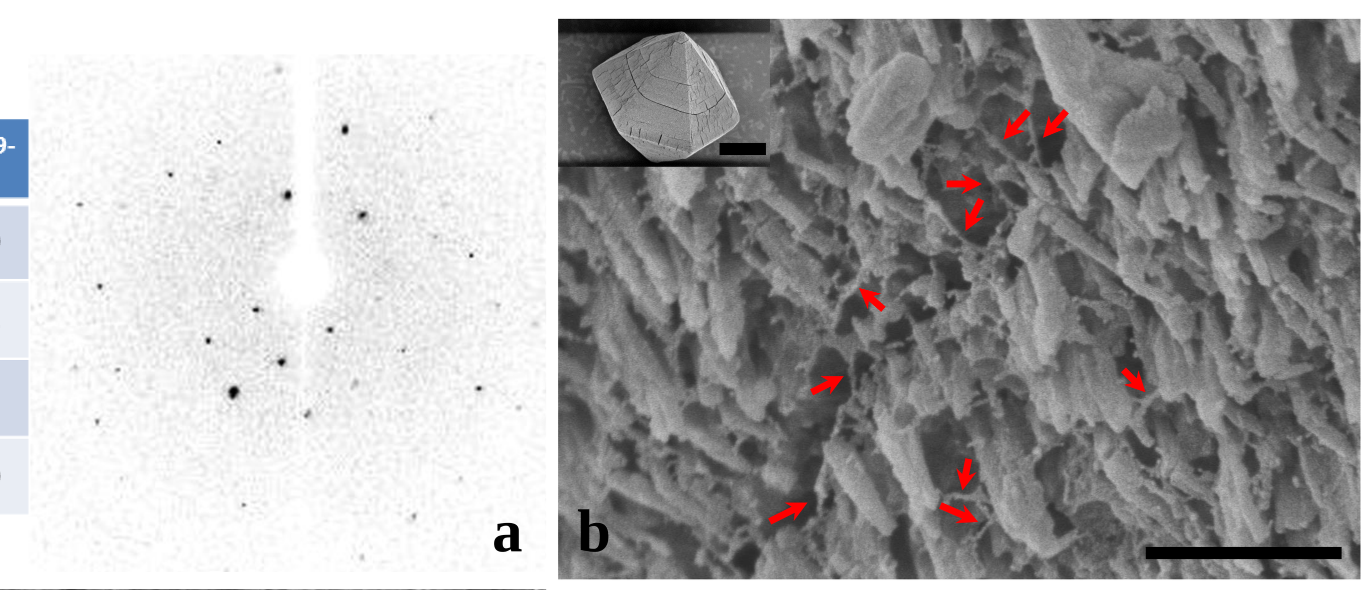


Fig. 2 (a-c) Optical microscope images of C_{60} crystals grown from MEH-PPV organogel before (a), during (b) and after (c) dissolving the crystals. Shape-resembled red MEH-PPV residues are left. **(d-f)** Fluorescence microscope images of the same area in a-c, respectively, with the same exposure time (10s). The photoluminescence of MEH-PPV is quenched in the as-grown C60 crystals. **(g)** A SEM image of crystals with dried MEH-PPV gel coated on the surface. (h) A SEM image of the as-grown crystal after dissolving all the polymer attached to the surface in THF. Tiny cracks are found at the surface, which may caused by the exchange of solvent molecules. Scale bar: (a-g) 200μm, (h) 50μm

	Crystals	PDF#49-2128
a,b	10.13	10.10
c	10.72	10.72
α,β	90.0	90.0
γ	120.0	120.0



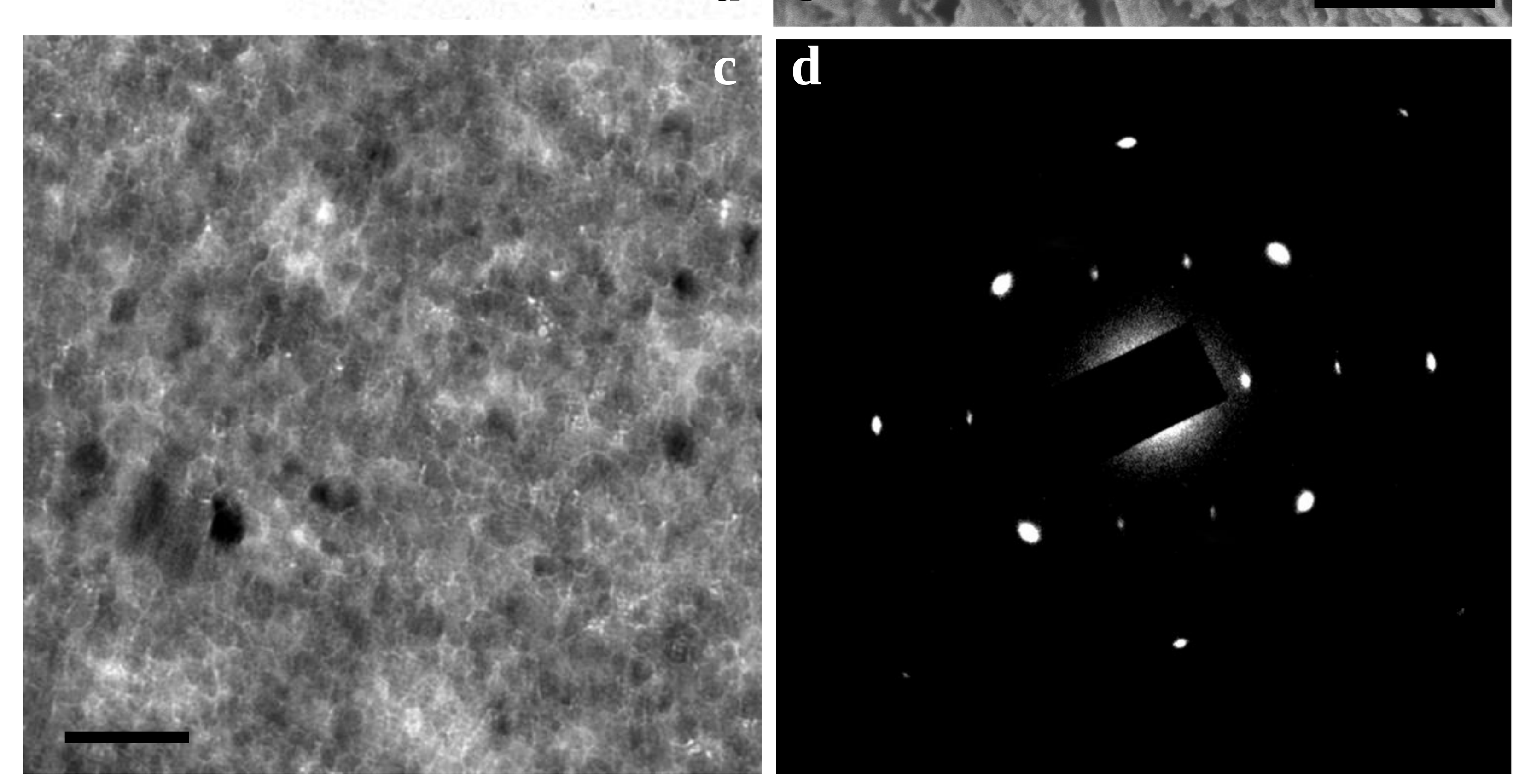


Fig. 3 (a) Single-crystal XRD analysis and pattern of the composite crystals. The measured lattice parameters match well with the PDF card of $C_{60}\cdot 2CCl_4$ and single set of X-ray diffraction spots are found. **(b)** SEM images of an etched crystal, showing MEH-PPV fibers (red arrows) on the etched surface (inset: image of the whole etched crystal). **(c)** TEM image of a piece of 100nm-thick slice of composite crystals cut by ultrathin section. **(d)** A SAED pattern (region of ~2μm in diameter) of composite crystals after vacuum and thermal anneal to remove internal CCl_4 molecules. Scale bar: (b) 500nm, inset: 50μm, (c) 200nm.

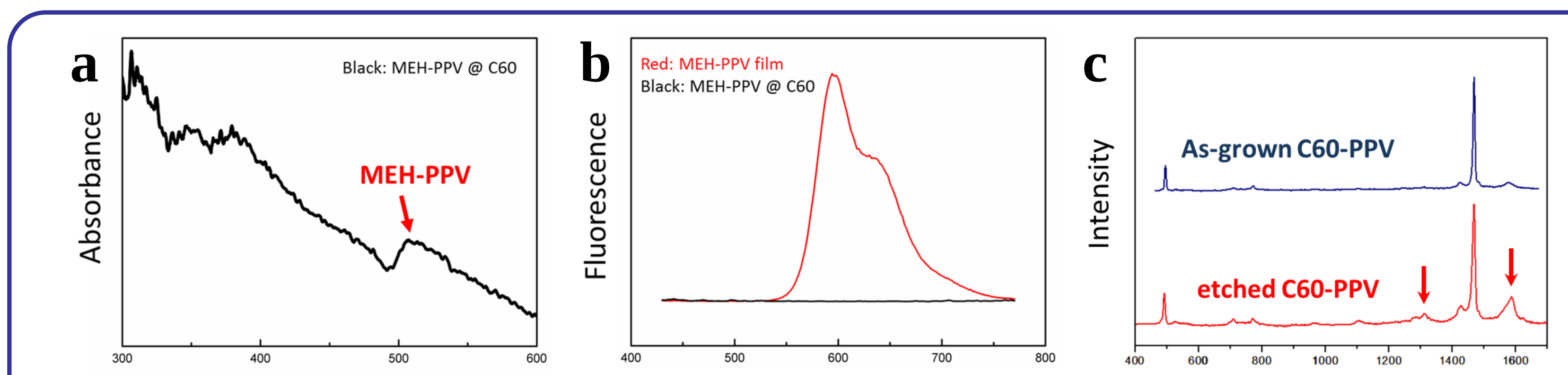


Fig. 4 (a) UV/Vis diffuse reflectance spectra of the gel-grown crystals. The red arrow highlights the absorbance peak of MEH-PPV. (b) Fluorescence spectra of MEH-PPV film (red) and powders of the composite crystals (black). Distinct photoluminescence quenching is shown, revealing the charge-transfer phenomenon of the composite single crystals. (c) Raman spectra of the as-grown crystals (blue) and etched crystals with MEH-PPV enriched on surface (red). The red arrows point out the peaks of MEH-PPV (around 1300 cm^{-1} and 1580 cm^{-1}).

Conclusions

In summery, we have prepared C_{60} single crystals in MEH-PPV organogel. The nanofiber networks of MEH-PPV penetrate through the fullerene single crystals without destroy the long range order of the crystal host. Moreover, charge-transfer between these two typical organic semiconductors reveals the formation of bulk-heterojunction. As such, the gel incorporation method provides an novel and facile strategy to construct bulk-heterojunction inside organic semiconductor single crystals, which may become ideal active materials for organic optoelectronic devices.

Acknowledgement

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References

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