Using fluorinated and crosslinkable fullerene derivatives to improve the stability of perovskite solar cells

Lingbo Jia[1], Lixiu Zhang[2], Liming Ding[2, †], and Shangfeng Yang[1, †]

[1]Hefei National Laboratory for Physical Sciences at Microscale, Key Laboratory of Materials for Energy Conversion (CAS), Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

[2]Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China

Organic–inorganic hybrid perovskite solar cell (PSC) is a third-generation photovoltaic technology[1, 2], and the certified power conversion efficiency (PCE) has reached 25.5% (https://www.nrel.gov/pv/cell-efficiency.html), which can rival solar cells based on crystalline-Si and other inorganic semiconductors. The intrinsic instability of perovskite materials could impede PSC commercialization[3]. To date, a variety of strategies such as composition engineering, additive engineering, interface engineering and encapsulation technique are employed to improve the long-term stability of PSCs[4–9]. In particular, fullerene materials with high electron mobility, high electron affinity, small reorganization energy and adjustable energy level have been widely utilized as interfacial layers or additives in PSCs for efficiency and stability improvement[10]. Among them, fluorinated and crosslinkable fullerene derivatives can improve the stability of PSCs effectively. The fluorinated fullerene derivatives could improve the moisture stability because of the hydrophobicity of fluorine atom. The crosslinked fullerene derivatives can protect the electron-transport layers (ETLs) against solvent erosion during perovskite solution deposition, and the as-formed organic networks can improve mechanical stability of PSCs.

Humidity can deteriorate the performance of PSCs. In-situ encapsulation over perovskite film by using fluorine-substituted fullerene derivatives acquired excellent device stability against humidity destruction. In 2016, Jen *et al.* reported a fluoroalkyl-substituted fullerene derivative (DF-C_{60}, Fig. 1) and used it as an additive to make inverted fullerene/$CH_3NH_3PbI_3$ bulk-heterojunction (BHJ) PSCs[11]. DF-C_{60} passivated the defects of perovskite surface and facilitated charge transfer, yielding a PCE of 18.11%. The unencapsulated device demonstrated high ambient stability, after being stored under 60 ± 5% relative humidity (RH) for one month, the device kept >83% of its initial PCE. DF-C_{60} was further incorporated into $CH_3NH_3Pb_{0.5}Sn_{0.5}I_3$ to make graded heterojunction (GHJ) PSCs[12]. The GHJ device offered an improved PCE (15.61%) with reduced photovoltage deficit. Additionally, the perfluoroalkyl chains in DF-C_{60} can effectively retard moisture penetration into Pb–Sn perovskites and also suppress Sn^{2+} oxidation. In 2017, novel fluorinated isoxazolino[60]fullerene

(IS-1 and IS-2, Fig. 1) and pyrazolino[60]fullerene derivatives (PI-1 and PI-2, Fig. 1) were synthesized by Martín *et al.*, and they were used to construct ETL-free PSCs[13]. The suitable LUMO energy levels contribute to the increased open-circuit voltage (V_{oc}) and the higher PCE of $CH_3NH_3PbI_3$:IS2 device, while fullerene helped to improve the photostability of the device. Two fluorinated $PC_{61}BM$ derivatives (3F-$PC_{61}BM$ and 5F-$PC_{61}BM$, Fig. 1) were used as n-type additives to make $CH_3NH_3PbI_3$ BHJ PSCs[14]. The incorporation of 0.1 wt% 3F-$PC_{61}BM$ can fill pinholes and passivate the defects to form a flat and dense BHJ perovskite film, suppressing moisture permeation under ambient condition. As a result, the device kept ~80% of its initial PCE after 550 h storage in N_2, whereas the control device decayed to 80% after 240 h storage. More recently, Yang *et al.* developed a double-site defect passivation strategy by using a perfluoroalkyl- and pyridine-functionalized fullerene derivative (C_{60}-PyF15, Fig. 1), which was added into $CH_3NH_3PbI_3$ layer to make inverted fullerene/perovskite BHJ PSCs[15]. The device gave a PCE of 20.10%, and there was coordination between pyridine moiety and Pb^{2+} and also hydrogen bonding between fluorine atom and $CH_3NH_3^+$. The improved hydrophobicity and suppressed ion migration endowed the device much better ambient and thermal stabilities. The device can retain 85% and 81% of its initial PCE after exposing for 1400 and 660 h under ambient condition (25 ± 5 °C, ~35% RH) and under heating at 85 °C in N_2 without encapsulation, respectively.

Several fluoroalkyl-substituted fullerene derivatives were combined with other fullerene materials to make a moisture-resistant mixed-fullerene interfacial layer for PSCs. In 2016, Jen *et al.* combined N-methyl-2-(2-perfluorooctylphenyl)-3,4-fullero-pyrrolidine (F-C_{60}, Fig. 1) with bis-adduct of N-methyl-2-(2,3,4-tris(2-(2-methoxyethoxy)ethoxy)phenyl)-3,4-fulleropyrrolidium iodide (bis-C_{60}) to form a robust and efficient cathode interlayer atop of $PC_{61}BM$ in $CH_3NH_3PbCl_{3-x}I_x$ PSCs[16]. Benefitting from the hydrophobicity of F-C_{60}, the device demonstrated a remarkable stability, retaining ~80% of its original PCE after exposing to an ambient condition (20% RH) for two weeks without encapsulation, whereas the control device with bis-C_{60} cathode interlayer decayed to zero under the same condition. Recently, Deng *et al.* reported two $PC_{61}BM$ analogues, [6, 6]-phenyl-C_{61}-butyric acid 1H, 1H-trifluoro-1-ethyl ester (3F-$PC_{61}BM$) and [6, 6]-phenyl-C_{61}-butyric acid 1H, 1H-tridecafluoro-1-heptyl ester (C_6F_{13}-$PC_{61}BM$, Fig. 1)[17], which were used to make hybrid ETLs with $PC_{61}BM$
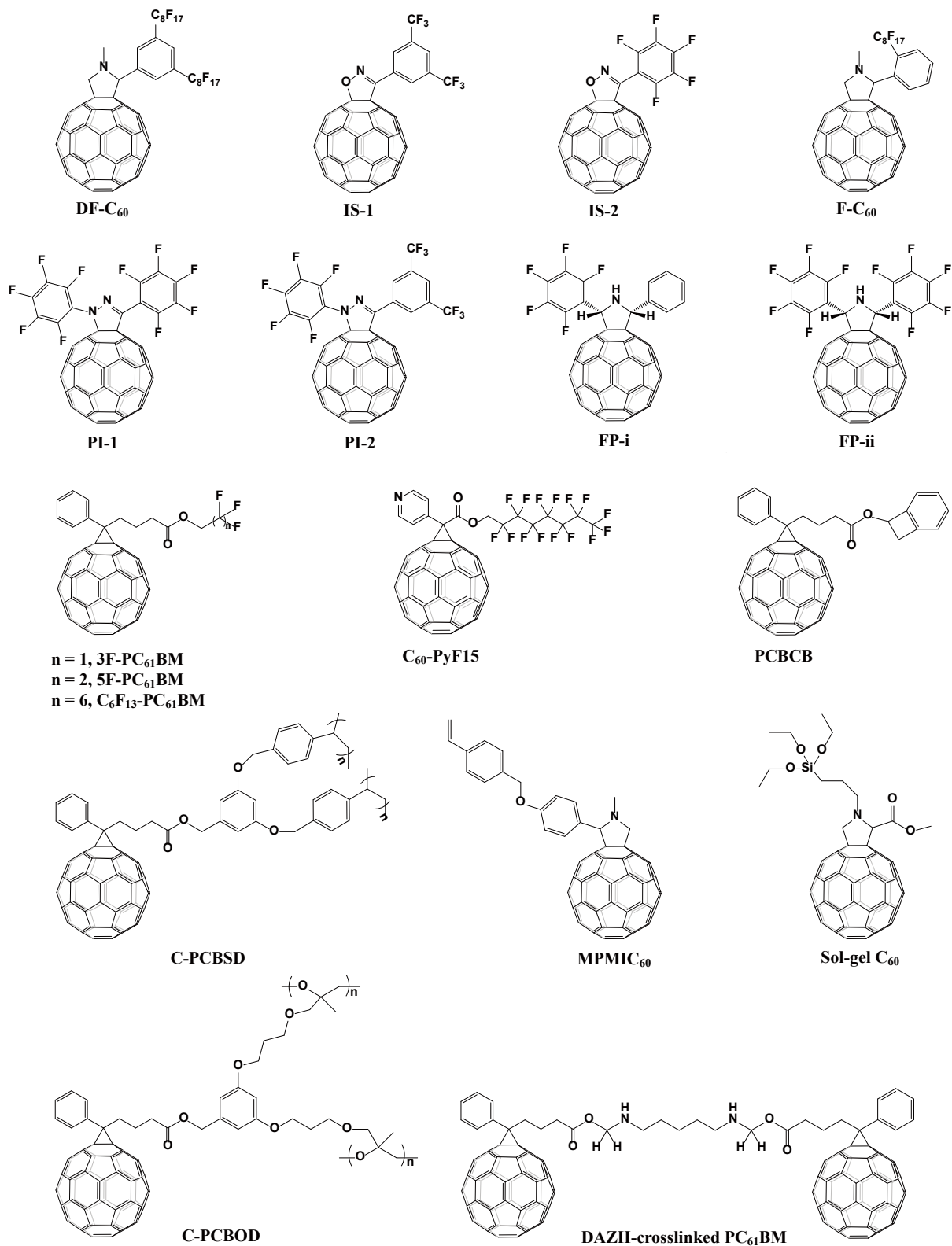

Correspondence to: L M Ding, ding@nanoctr.cn; S F Yang,
    sfyang@ustc.edu.cn

Fig. 1. Molecular structures of fluorinated and crosslinkable fullerene derivatives.

in inverted $CH_3NH_3PbI_3$- and $(FA_{0.83}MA_{0.17})_{0.95}Cs_{0.05}Pb(I_{0.9}Br_{0.1})_3$-based PSCs, delivering PCEs of 18.37% and 19% for 1 wt% 3F-$PC_{61}BM$-containing device, respectively. The upward-oriented fluorocarbon chains formed a thin moisture-resistant layer. The 1 wt% C_6F_{13}-$PC_{61}BM$-containing $CH_3NH_3PbI_3$ PSCs showed a much better ambient stability, keeping over 80% PCE after 33 days storage under 40%–60% RH in air. In 2020,

Feng *et al.* synthesized 2-(perfluorophenyl)-5-phenyl-C_{60}-fulleropyrrolidine (FP-i) and 2,5-bis-(perfluorophenyl)-C_{60}-fulleropyrrolidine (FP-ii, Fig. 1), which were introduced as ETLs in $CH_3NH_3PbCl_{3-x}I_x$ PSCs[18]. The hydrogen bonds between the organic cation of perovskite and F atom within FP-i and FP-ii, as well as the enhanced hydrophobicity led to good passivation and humidity stability, keeping 70%–85% of

its initial PCE after 70 h in ambient air.

Though fullerene-based ETLs demonstrate fascinating electron transport/extraction capability and excellent electronic contact with perovskite films, the partial erosion of fullerene films by the solvents (e.g. N, N-dimethylformamide, dimethyl sulfoxide) used for processing perovskite film may yield defective film with shunting paths. Multilayer spin-coating deposition sometimes results in poor device performance. Furthermore, mechanical stress is the primary reason for mechanical failure of PSCs[19]. Introducing crosslinkable fullerene derivatives is a sound solution to these issues.

In 2016, Snaith *et al.* developed two crosslinkable fullerene derivatives called sol-gel C_{60} and PCBCB (Fig. 1) to form robust fullerene films during $CH_3NH_3PbI_{3-x}Cl_x$ preparation[20]. Sol-gel C_{60} was crosslinked *via* hydrolysis-condensation reaction, and crosslinked PCBCB ETL was achieved by annealing at 200 °C *via* ring-opening reaction of benzocyclobutene moiety. Both solvent-resistant fullerene ETLs resulted in reduced shunting paths and improved hole-blocking properties. Another novel thermally crosslinkable styrene-functionalized fullerene derivative $MPMIC_{60}$ (Fig. 1) was synthesized by Dauskardt *et al.* to replace fragile $PC_{61}BM$ and C_{60} ETL in both n–i–p and p–i–n $CH_3NH_3PbI_3$ PSCs[19]. A solvent-resistant film formed by $MPMIC_{60}$ exhibited 10-fold and 14-fold enhancement in fracture resistance over $PC_{61}BM$ and C_{60}, respectively. The device gave higher V_{oc} and short-circuit current density (J_{sc}) than $PC_{61}BM$ device. Later on, Hsu *et al.* introduced a crosslinkable [6,6]-phenyl-C_{61}-butyric styryl dendron ester (C-PCBSD, Fig. 1) into $CH_3NH_3PbI_xCl_{3-x}$ *via* anti-solvent method to enhance the crystallization of perovskite films and passivate the defects, as well as improving electron extraction[21]. Crosslinked network of C-PCBSD could prevent the fullerene layer being washed away by subsequent solution processing, and protect the active layer against moisture. The devices can maintain 84.6% of its initial PCE after 180 h storage in ambient (40 ± 5% RH). In 2017, Petrozza *et al.* used in-situ crosslinked C-PCBSD in n–i–p $CH_3NH_3PbI_3$ PSCs[22], and C-PCBSD can form a robust and solvent-resistant thin film atop of TiO_2 to improve the quality of upper perovskite films, promoting charge extraction. The device exhibited an enhanced PCE close to 19% with a V_{oc} above 1.1 V. In 2018, Liao *et al.* further developed a composite ETL combining C-PCBSD with π-conjugated graphdiyne (GD), which was sandwiched between TiO_2 and perovskite films in n–i–p $CH_3NH_3PbI_3$ PSCs[23]. The GD introduced into C-PCBSD formed a face-on stacked film through a strong π–π stacking interaction. Besides, the thermally annealed C-PCBSD:GD film provided a robust and adhesive network with excellent solvent resistance to overcome interfacial erosion, which contributed to efficient charge extraction of ETL, improved crystallinity of perovskite films, leading to a PCE of 20.19% and improved stability (retaining 80% PCE after 500 h storage under ambient condition with 25%–30% RH). More recently, Marder *et al.* mixed PCBCB with a poly(methacrylate) derivative (CL) to form an ETL for p–i–n $Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.9}Br_{0.1})_3$ PSCs, which can be thermally insolubilized[24]. The device with PCBCB:CL ETL demonstrated improved PCE (18.5%) and remarkable thermal stability, keeping 92% of its stabilized power output after 3000 h storage in N_2 at 85 °C.

Another crosslinked fullerene derivative [6, 6]-phenyl-C_{61}-butyric oxetane dendron ester (C-PCBOD, Fig. 1) *via* photo-curing was developed to modify TiO_2 surface in n–i–p PSCs[25]. C-PCBOD was safe in the following deposition of $CH_3NH_3PbI_3$ precursor solution. It could passivate the trap-states of TiO_2 and facilitate the charge transfer, yielding PCEs of 15.9% and 18.3% for devices based on compact TiO_2 and mesoporous TiO_2 ETL, respectively. To overcome the brittleness of perovskite films, which limits the application in flexible PSCs, in 2019, Liao *et al.* introduced C-PCBOD as a plasticizer into $CH_3NH_3PbI_3$ films to form an organic network to passivate the grain boundaries as well as the trap states within perovskite layer[26]. The rigid and flexible devices offered PCEs of 20.4% and 18.1%, respectively. Under a stretching of Δ10.0 nm/μm, the C-PCBOD-containing device retained 62% of its initial PCE, while the control device kept 42%. The robust fullerene network could prevent device decomposition in air, retaining 72% of the initial value after 960 h storage in air (25 ± 5% RH). $PC_{61}BM$ crosslinked by 1,6-diazidohexane (DAZH, Fig. 1) *via* a UV light curing was reported[27]. The crosslinked $PC_{61}BM$ layer demonstrated improved solvent-resistance, and the $FA_{0.66}MA_{0.34}PbI_{2.85}Br_{0.15}$ device gave a PCE of 18.4% for small-area and 14.9% for modules, respectively.

To check the details about above-mentioned fullerene derivatives, their application, device performance parameters, and stability, you may find Table S1 in the Supporting Information. By applying fluorinated and crosslinkable fullerene derivatives, scientists successfully improved the efficiency and stability of PSCs. More innovative fullerene materials containing fluorine and crosslinkable moieties are desired.

Acknowledgments

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/1674-4926/42/12/120201.

References

[1] Zheng X, Hou Y, Bao C, et al. Managing grains and interfaces via ligand anchoring enables 22.3%-efficiency inverted perovskite solar cells. Nat Energy, 2020, 5, 131

[2] Fang Z, Zeng Q, Zuo C, et al. Perovskite-based tandem solar cells. Sci Bull, 2021, 6, 621

[3] Cheng Y, Ding L. Pushing commercialization of perovskite solar cells by improving their intrinsic stability. Energy Environ Sci, 2021, 14, 3233

[4] Chu L, Ding L. Self-assembled monolayers in perovskite solar cells. J Semicond, 2021, 42, 090201

[5] Shang Y, Fang Z, Hu W, et al. Efficient and photostable CsPbI₂Br solar cells realized by adding PMMA. J Semicond, 2021, 42, 050501

[6] Cheng M, Zuo C, Wu Y, et al. Charge-transport layer engineering in perovskite solar cells. Sci Bull, 2020, 65, 1237

[7] Cheng Y, Yang Q D, Ding L. Encapsulation for perovskite solar cells. Sci Bull, 2021, 66, 100

[8] Wang R, Mujahid M, Duan Y, et al. A review of perovskites solar

cell stability. Adv Funct Mater, 2019, 29, 1808843

[9] Li X, Zhang F, He H, et al. On-device lead sequestration for perovskite solar cells. Nature, 2020, 578, 555

[10] Jia L, Chen M, Yang S. Functionalization of fullerene materials toward applications in perovskite solar cells. Mater Chem Front, 2020, 4, 2256

[11] Liu X, Lin F, Chueh C C, et al. Fluoroalkyl-substituted fullerene/perovskite heterojunction for efficient and ambient stable perovskite solar cells. Nano Energy, 2016, 30, 417

[12] Rajagopal A, Liang P W, Chueh C C, et al. Defect passivation via a graded fullerene heterojunction in low-bandgap Pb-Sn binary perovskite photovoltaics. ACS Energy Lett, 2017, 2, 2531

[13] Sandoval-Torrientes R, Pascual J, Garcia-Benito I, et al. Modified fullerenes for efficient electron transport layer-free perovskite/fullerene blend-based solar cells. ChemSusChem, 2017, 10, 2023

[14] Chang C Y, Wang C P, Raja R, et al. High-efficiency bulk heterojunction perovskite solar cell fabricated by one-step solution process using single solvent: synthesis and characterization of material and film formation mechanism. J Mater Chem A, 2018, 6, 4179

[15] Jia L, Huang F, Ding H, et al. Double-site defect passivation of perovskite film via fullerene additive engineering toward highly efficient and stable bulk heterojunction solar cells. Nano Today, 2021, 39, 101164

[16] Zhu Z, Chueh C C, Lin F, et al. Enhanced ambient stability of efficient perovskite solar cells by employing a modified fullerene cathode interlayer. Adv Sci, 2016, 3, 1600027

[17] Xing Z, Li S H, Xie F F, et al. Mixed fullerene electron transport layers with fluorocarbon chains assembling on the surface: a moisture-resistant coverage for perovskite solar cells. ACS Appl Mater Interfaces, 2020, 12, 35081

[18] Yuan Q, Han D, Yi S, et al. Fluorinated fulleropyrrolidine as universal electron transport material for organic-inorganic and all-inorganic perovskite solar cells. Org Electron, 2020, 77, 105492

[19] Watson B L, Rolston N, Bush K A, et al. Cross-linkable, solvent-resistant fullerene contacts for robust and efficient perovskite solar cells with increased J_{sc} and V_{oc}. ACS Appl Mater Interfaces, 2016, 8, 25896

[20] Wojciechowski K, Ramirez I, Gorisse T, et al. Cross-linkable fullerene derivatives for solution-processed n–i–p perovskite solar cells. ACS Energy Lett, 2016, 1, 648

[21] Li M, Chao Y H, Kang T, et al. Enhanced crystallization and stability of perovskites by a cross-linkable fullerene for high-performance solar cells. J Mater Chem A, 2016, 4, 15088

[22] Tao C, Van Der Velden J, Cabau L, et al. Fully solution-processed n–i–p-like perovskite solar cells with planar junction: how the charge extracting layer determines the open-circuit voltage. Adv Mater, 2017, 29, 1604493

[23] Li M, Wang Z K, Kang T, et al. Graphdiyne-modified cross-linkable fullerene as an efficient electron-transporting layer in organometal halide perovskite solar cells. Nano Energy, 2018, 43, 47

[24] Tremblay M H, Schutt K, Pulvirenti F, et al. Benzocyclobutene polymer as an additive for a benzocyclobutene-fullerene: application in stable p–i–n perovskite solar cells. J Mater Chem A, 2021, 9, 9347

[25] Kang T, Tsai C M, Jiang Y H, et al. Interfacial engineering with cross-linkable fullerene derivatives for high-performance perovskite solar cells. ACS Appl Mater Interfaces, 2017, 9, 38530

[26] Li M, Yang Y G, Wang Z K, et al. Perovskite grains embraced in a soft fullerene network make highly efficient flexible solar cells with superior mechanical stability. Adv Mater, 2019, 31, 1901519

[27] Qiu W, Bastos J P, Dasgupta S, et al. Highly efficient perovskite solar cells with crosslinked PCBM interlayers. J Mater Chem A, 2017, 5, 2466

Lingbo Jia got her BS from Soochow University in 2017. Now she is a PhD student at University of Science and Technology of China under the supervision of Prof. Shangfeng Yang. Her research focuses on the synthesis of novel fullerene derivatives and their applications in perovskite solar cells.

Lixiu Zhang got her BS from Soochow University in 2019. Now she is a PhD student at University of Chinese Academy of Sciences under the supervision of Prof. Liming Ding. Her research focuses on perovskite solar cells.

Liming Ding got his PhD from University of Science and Technology of China (was a joint student at Changchun Institute of Applied Chemistry, CAS). He started his research on OSCs and PLEDs in Olle Inganäs Lab in 1998. Later on, he worked at National Center for Polymer Research, Wright-Patterson Air Force Base and Argonne National Lab (USA). He joined Konarka as a Senior Scientist in 2008. In 2010, he joined National Center for Nanoscience and Technology as a full professor. His research focuses on innovative materials and devices. He is RSC Fellow, the nominator for Xplorer Prize, and the Associate Editors for Science Bulletin and Journal of Semiconductors.

Shangfeng Yang got his PhD from Hong Kong University of Science and Technology in 2003. He then joined Leibniz Institute for Solid State and Materials Research, Dresden, Germany as an Alexander von Humboldt Fellow and a Guest Scientist. In Dec 2007, he joined University of Science and Technology of China as a full professor. His research interests include the synthesis of fullerene-based nanocarbons toward applications in energy devices. He is a RSC Fellow.