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OPINION

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Reconsidering figures of merit for performance and stability of perovskite photovoltaics†

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The development of hybrid organic–inorganic halide perovskite solar cells (PSCs) that combine high performance and operational stability is vital for implementing this technology. Recently, reversible improvement and degradation of PSC efficiency have been reported under illumination–darkness cycling. Quantifying the performance and stability of cells exhibiting significant diurnal performance variations is challenging. We report the outdoor stability measurements of two types of devices showing either reversible photo-degradation or reversible efficiency improvement under sunlight. Instead of the initial (or stabilized) efficiency and T_{80} as the figures of merit for the performance and stability of such devices, we propose using the value of the energy output generated during the first day of exposure and the time needed to reach its 20% drop, respectively. The latter accounts for both the long-term irreversible degradation and the reversible diurnal efficiency variation and does not depend on the type of process prevailing in a given perovskite cell.

Broader context

The quality of solar cells is commonly quantified by their power conversion efficiency (PCE) and by their lifetime, defined as the time when the PCE drops to 80% of its initial value. Metal-halide perovskites are semiconductors exhibiting physical properties highly beneficial for the photovoltaic conversion of solar energy. Perovskite solar cells (PSCs) have already reached PCEs above 22%. Particular interest is in the realization of tandem PSC/silicon cells. Tandem devices with PCEs over 30% could be realized with a low additional cost to current silicon technology. However, the poor operational stability of PSCs has been the main limiting factor. Moreover, unlike conventional photovoltaic devices, PSCs often exhibit reversible degradation processes, leading to significant PCE variation during a day–night cycle. This makes quantifying the performance and stability challenging: if the PCE drops during the day but recovers during the night (or *vice versa*), what is the cell's lifetime? How can the performances of different device architectures, with various diurnal dynamics, be compared? We propose using the energy output generated during the first day of operation and the time needed to reach its 20% drop as the figures of merit for the performance and stability of such devices, respectively.

The commercialization of hybrid organic–inorganic halide perovskite solar cells (PSCs) requires the development of devices combining high Power Conversion Efficiency (PCE) and extended operational stability. The latter has been the Achilles heel of PSCs. Moreover, testing protocols for assessing the PCE[1,2] and operational lifetime[3,4] of PSCs need to be developed.

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The cell lifetime is defined as the time when the PCE drops to 80% of its initial value (T_{80}).[5] The most widely used method for studying PSC stability is to monitor the PCE under continuous simulated sunlight illumination. Under real operational conditions, however, solar cells are exposed to alternating periods of illumination and darkness (diurnal cycling).

Recently, complete recovery during the dark period following the photoinduced degradation of state-of-the-art PSCs (PCE ~ 20%) was reported.[6,7] On the other hand, the opposite, so-called fatigue-like behavior, was observed in tests comprising multiple 12 hour cycles of darkness and illumination: PCE degradation during dark periods (to ≤50%) and complete or partial recovery under subsequent PSC illumination by simulated sunlight.[8,9] In our view, this reversible PCE evolution is related to the well-known light soaking effect.[10–12]

Thus, there is no doubt that testing under continuous illumination does not adequately reflect the long-term performance of PSCs under the diurnal cycles experienced in real-world applications. Reasonable stability assessment protocols should include light/dark cycles resembling the day/night phases of outdoor photovoltaic operation.[7] Herein, based on the experimental results, we suggest that the figures of merit for the device performance and stability should be reconsidered.

Degradation experiments were performed with glass/ITO/SnO_2/$Cs_{0.05}((CH_3NH_3)_{0.15}(CH(NH_2)_2)_{0.85})_{0.95}PbI_{2.55}Br_{0.45}$/Spiro-OMeTAD/Au cells (type I) and glass/ITO/TiO_2/$CH_3NH_3PbI_3$/Spiro-OMeTAD/Au mini-modules (type II). For the stability assessment, the cells were exposed to continuous illumination by simulated sunlight indoors (ISOS-L-1 protocol[5]) and natural outdoor sunlight in Sede Boqer (the Negev Desert, Israel) with performance testing under simulated sunlight three times a day (ISOS-O-1 protocol[5]). The initial PCE values were ~15% and ~10% for the devices of type I and type II, respectively. Details of device preparation and characterization and the initial device performance are presented in the ESI.†

Analysis of the PCE changes of the type I cells under continuous illumination by simulated sunlight indoors (see Fig. S1 in the ESI†) suggests T_{80} ~ 1 h. This parameter will be referred to as T_{80}^{cont}.

Fig. 1a depicts the PCE evolution for these devices over two weeks of outdoor exposure. During the first 11 days, the cell efficiency degraded under illumination but substantially recovered during the nights. As a result, the "morning" PCE values were higher than the "evening" values. The effect of the night periods led to much slower long-term degradation dynamics (as compared with the continuous illumination experiment). Obviously, T_{80}^{cont} is a misleading parameter since under real operational conditions the cell PCE would cross the 80% mark multiple times, as shown in Fig. 1a. This demonstrates the significance of light–dark cycling in stability measurements.

Nighttime recovery typically does not lead to 100% restoration of the initial efficiency, due to two superimposed factors: the presence of irreversible degradation mechanisms and/or a recovery process requiring time longer than one night. Furthermore, a number of degradation processes can occur simultaneously, and different mechanisms may dominate at different

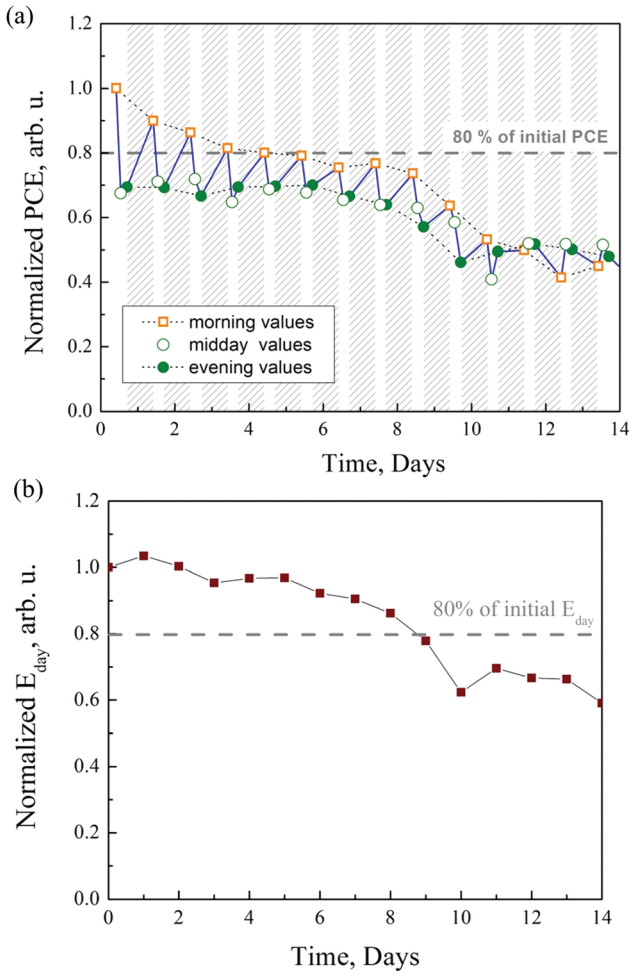

Fig. 1 (a) PCE evolution of the glass/ITO/SnO_2/$Cs_{0.05}((CH_3NH_3)_{0.15}(CH(NH_2)_2)_{0.85})_{0.95}PbI_{2.55}Br_{0.45}$/Spiro-OMeTAD/Au cell (type I) during two weeks of outdoor exposure to natural sunlight. (b) Evolution of the daily energy output, E_{day}, generated by this cell, normalized by its value on the first day. For simplicity, we used a constant P_{in} = 1 Sun for the E_{day} calculation. All lines are guides for the eye.

degradation stages defining the dynamics of PCE change during a day. For example, for the curve shown in Fig. 1a, the "morning" and "evening" PCE values become much closer to each other after a certain aging time and even invert during days 12–14. In other words, the cell demonstrates fatigue-like behavior at the later degradation stages, similar to type II devices (see below). The underlying reversible and irreversible degradation mechanisms are beyond the scope of this contribution and will be discussed elsewhere.

If light–dark cycling is to be used for stability measurements, we suggest that a new set of figures of merit should be used to describe the performance, stability and their interplay in PSCs. Intuitively, the cell lifetime can be estimated using the evolution of the maximum PCE values measured every day, T_{80}^{max} (*i.e.*, morning values in the case shown in Fig. 1a, up to day 10). Contrary to T_{80}^{cont} ~ 1 h, which ignores the recovery processes, T_{80}^{max} (~4 d) accounts for irreversible losses and/or incomplete recovery during one night. However, it does not account for the

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dynamics of the diurnal degradation, and therefore, it can lead to a misleading conclusion in terms of the total energy generated by the cell during its lifetime:[13–15]

$$E_{T_{80}^{\max}} = \int_0^{T_{80}^{\max}} \mathrm{PCE}(t) \times P_{\mathrm{in}}(t) \times \mathrm{d}t, \quad (1)$$

where P_{in} is the incoming sunlight power (for simplicity, P_{in} = 1 Sun = 100 mW cm^{-2}).

It is worth noting that the $E_{T_{80}^{\max}}$ calculated using only the maximal diurnal PCE values (the dashed upper curve in Fig. 1a) during $T_{80}^{\max}$ = 4 d gave an almost 20% overestimation as compared to that calculated using the measured diurnal dynamics of the PCE during these first four days of exposure (see Fig. S2 and related discussion in the ESI†).

Fig. 1b depicts the evolution of the daily energy output generated by the type 1 cell, E_{day}:

$$E_{\mathrm{day}} = \int_0^{t_{\mathrm{day}}} \mathrm{PCE}(t) \times P_{\mathrm{in}}(t) \times \mathrm{d}t, \quad (2)$$

where t_{day} is the illumination time during one day.

Now, we can estimate $T_{80}' \approx 9$ d as the time when E_{day} drops to 80% of its value on the first day of exposure. We suggest that this T_{80}' is a reliable figure of merit for PCE stability, taking into account both the reversible and irreversible degradation of the cell performance.

Accordingly, the total energy generated by the cell during its lifetime can be properly calculated as:

$$E_{T_{80}'} = \int_0^{T_{80}'} \mathrm{PCE}(t) \times P_{\mathrm{in}}(t) \times \mathrm{d}t. \quad (3)$$

This value may serve as the figure of merit for the interplay between the cell performance and its stability whose overall improvement is the ultimate purpose of any photovoltaic technology. A similar parameter has already been employed for other photovoltaic technologies.[14] An important advantage of our approach is that it does not depend on a certain type of PCE change during the day/night (light/dark) cycle. In particular, the type II modules demonstrated fatigue-like behavior: a pronounced performance enhancement during the day followed by "degradation at night" (Fig. 2a). In both device types, we observed (a) the superposition of reversible and irreversible degradation mechanisms, and (b) a dramatic difference compared to the results from the continuous illumination experiment. The use of T_{80}' and $E_{T_{80}'}$ (Fig. 1b and 2b) as figures of merit for the cell lifetime and performance is appropriate for both cell types, and allows the comparison of the overall performance of different cells and devices.

Finally, we discuss the reliability of the initial PCE as a representation of PSC performance. As a rule, PCE is measured after the short preconditioning time needed for the stabilization of cell parameters.[16] An appropriate preconditioning time should be chosen for each cell separately depending on its transient characteristics and it might take hours in some cases.[2] Christians *et al.*[17] showed that the improvement of PCE under illumination might take even hundreds of hours

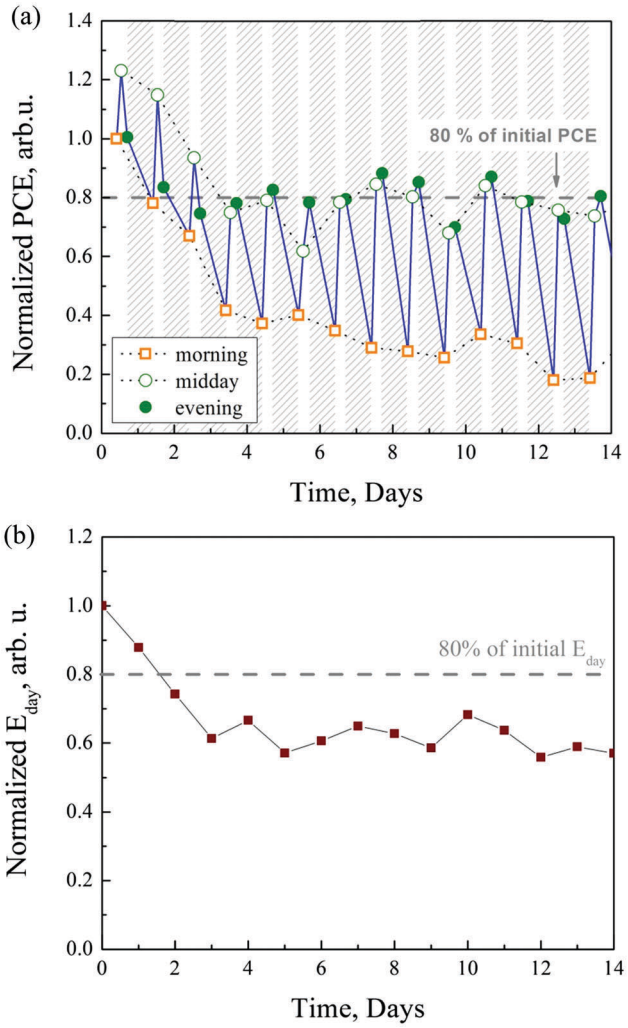

Fig. 2 (a) PCE evolution of type II mini-modules (glass/ITO/TiO_2/$MAPbI_3$/Spiro-OMeTAD/Au) during their outdoor sunlight exposure. (b) Evolution of the daily energy output generated by this cell. For simplicity, we used a constant P_{in} = 1 Sun for the E_{day} calculation. All lines are guides for the eye.

(see Fig. S18 in ref. 17). The choice of the preconditioning time might determine the reported efficiency value and mask the real picture in terms of energy production. Obviously, such a protocol is not suited for determining the cell performance in stability assessing experiments, especially for solar cells with reversible degradation, where pre-measurement conditioning can superimpose on continuing degradation. Furthermore, this value is not representative of the actual cell performance under operational conditions, where long preconditioning is impractical. Instead, we suggest that the energy output (E_{day}) during the first day of exposure (which automatically accounts for the naturally occurring preconditioning history) can serve as a universal figure of merit for the initial cell performance.

In our work, we use the ISOS-O-1 protocol[5] for outdoor aging. This allows the degradation effect to be separated from the non-trivial variations of the PSC's PCE throughout the day,[18] reflecting the effects of the diurnal variations in ambient temperature and the intensity and spectrum of natural sunlight.[19]

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At a further stage of the research, degradation experiments with both sample aging (preferably biased at the maximum power point[4]) and *I–V* curve measurements under outdoor sunlight (ISOS-O-2 protocol[5]) can be performed. In this case, the above variations should be taken into account in the calculations of E_{day}, T_{80}' and $E_{T_{80}'}$.

Inspired by our outdoor experiments, we strongly recommend including light/dark cycles[4,7] in indoor stability testing to mimic the diurnal cycling. In this case, E_{day} should be understood as the energy generated by the cell during one cycle. Unlike outdoor assessment, such an indoor procedure might be implemented in most of the laboratories characterizing solar cell lifetimes, as they simply require intermittent measurements that are otherwise similar to stability characterization under constant illumination. Exact protocols for such experiments (*e.g.*, duration of the light and dark periods, frequency of PCE measurements, *etc.*) will have to be determined. Though our approach is time consuming, it provides universal parameters for cell comparison, independent of device architecture and degradation types.

In summary, by analyzing the evolution of the outdoor performance of two PSC types with opposite diurnal dynamics, we demonstrated that PSC degradation under real operational conditions involves a number of reversible and irreversible processes. These findings demonstrate the significance of including light/dark cycling as part of the stability testing of PSCs.

The diurnal dynamics of the cell PV parameters suggest that a new set of figures of merit should be defined for the performance, stability and their interplay in PSCs. The PSC's daily energy output, E_{day}, should be used as a figure of merit for its performance, rather than the PCE value measured at a given time. As a figure of merit for PCS stability, we propose the time needed to reach a 20% drop in E_{day} (T_{80}'). This T_{80}' accounts for both the PCE's long-term irreversible degradation and its reversible diurnal variations, and does not depend on the type of process prevailing in a given cell. This approach provides universal parameters for cell comparison, independent of device architecture and degradation types, in terms of their performance (E_{day}), stability (T_{80}') and the interplay between them $\left(E_{T_{80}'}\right)$.

Author contributions

M. V. K., I. V.-F. and E. A. K. conceived the idea. M. V. K., I. V.-F., F. B., M. L.-C. and E. A. K. designed the experiments. Y. G. and F. D. G. fabricated the devices of type I and conducted their initial characterization. T. M., G. U., J. P. A. B. and T. A. fabricated the devices of type II and conducted their initial characterization. B. R. P., G. S., V. T., M. M. and H.-G. R. conducted indoor degradation experiments. M. V. K. and K. M. A. conducted outdoor degradation experiments. M. V. K. and E. A. K. wrote the first draft. All coauthors participated in the exchange and analyses of the results as well as in the editing the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References

1 N. G. Park, M. Grätzel, T. Miyasaka, K. Zhu and K. Emery, Towards stable and commercially available perovskite solar cells, *Nat. Energy*, 2016, **1**, 16152.
2 R. B. Dunbar, B. C. Duck, T. Moriarty, K. F. Anderson, N. W. Duffy, C. J. Fell, J. Kim, A. Ho-Baillie, D. Vak, T. Duong, Y. Wu, K. Weber, A. Pascoe, Y.-B. Cheng, Q. Lin, P. L. Burn, R. Bhattacharjee, H. Wang and G. J. Wilson, How reliable are efficiency measurements of perovskite solar cells? The first inter-comparison, between two accredited and eight non-accredited laboratories, *J. Mater. Chem. A*, 2017, **5**, 22542–22558.
3 D. Wang, M. Wright, N. K. Elumalai and A. Uddin, Stability of perovskite solar cells, *Sol. Energy Mater. Sol. Cells*, 2016, **147**, 255–275.
4 K. Domanski, E. A. Alharbi, A. Hagfeldt, M. Grätzel and W. Tress, Systematic investigation of the impact of operation conditions on the degradation behaviour of perovskite solar cells, *Nat. Energy*, 2018, **3**, 61.
5 M. O. Reese, S. A. Gevorgyan, M. Jørgensen, E. Bundgaard, S. R. Kurtz, D. S. Ginley, D. C. Olson, M. T. Lloyd, P. Morvillo, E. A. Katz, A. Elschner, O. Haillant, T. R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K. R. Kirov, G. Trimmel, T. Rath, O. Inganäs, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. Laird, C. McGuiness, S. (Jimmy) Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D. M. DeLongchamp, R. Rösch, H. Hoppe, N. Espinosa, A. Urbina, G. Yaman-Uzunoglu, J.-B. Bonekamp, A. J. J. M. van Breemen, C. Girotto, E. Voroshazi and F. C. Krebs, Consensus stability testing protocols for organic photovoltaic materials and devices, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 1253–1267.
6 E. H. Anaraki, A. Kermanpur, L. Steier, K. Domanski, T. Matsui, W. Tress, M. Saliba, A. Abate, M. Grätzel, A. Hagfeldt and J.-P. Correa-Baena, Highly efficient and stable planar perovskite solar cells by solution-processed tin oxide, *Energy Environ. Sci.*, 2016, **9**, 3128–3134.
7 K. Domanski, B. Roose, T. Matsui, M. Saliba, S.-H. Turren-Cruz, J.-P. Correa-Baena, C. R. Carmona, G. Richardson, J. M. Foster, F. De Angelis, J. M. Ball, A. Petrozza, N. Mine, M. K. Nazeeruddin, W. Tress, M. Grätzel, U. Steiner, A. Hagfeldt and A. Abate, Migration of cations induces reversible performance losses over day/night cycling in perovskite solar cells, *Energy Environ. Sci.*, 2017, **10**, 604–613.
8 F. Huang, L. Jiang, A. R. Pascoe, Y. Yan, U. Bach, L. Spiccia and Y.-B. Cheng, Fatigue behavior of planar $CH_3NH_3PbI_3$ perovskite solar cells revealed by light on/off diurnal cycling, *Nano Energy*, 2016, **27**, 509–514.

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9 F. Liu, Q. Dong, M. K. Wong, A. B. Djurišic, A. Ng, Z. Ren, Q. Shen, C. Surya, W. K. Chan, J. Wang, A. M. C. Ng, C. Liao, H. Li, K. Shih, C. Wei, H. Su and J. Dai, Is excess PbI_2 beneficial for perovskite solar cell performance, *Adv. Energy Mater.*, 2016, **6**, 1502206.

10 C. Zhao, B. Chen, X. Qiao, L. Luan, K. Lu and B. Hu, Revealing underlying processes involved in light soaking effects and hysteresis phenomena in perovskite solar cells, *Adv. Energy Mater.*, 2015, **5**, 1500279.

11 S. Lv, S. Pang, Y. Zhou, N. P. Padture, H. Hu, L. Wang, X. Zhou, H. Zhu, L. Zhang, C. Huang and G. Cui, One-step, solution-processed formamidinium lead trihalide ($FAPbI_{(3-x)}Cl_x$) for mesoscopic perovskite–polymer solar cells, *Phys. Chem. Chem. Phys.*, 2014, **16**, 19206–19211.

12 P. Docampo, J. M. Ball, M. Darwich, G. E. Eperon and H. J. Snaith, Efficient organometal trihalide perovskite planar-heterojunction solar cells on flexible polymer substrates, *Nat. Commun.*, 2013, **4**, 2761.

13 V. Turkovic, S. Engmann, N. Tsierkezos, H. Hoppe, U. Ritter and G. Gobsch, Long-Term Stabilization of Organic Solar Cells Using Hindered Phenols as Additives, *ACS Appl. Mater. Interfaces*, 2014, **6**, 18525.

14 R. Roesch, T. Faber, E. von Hauff, T. M. Brown, M. Lira-Cantu and H. Hoppe, Procedures and Practices for Evaluating Thin-Film Solar Cell Stability, *Adv. Energy Mater.*, 2015, **5**, 1501407.

15 Q. Burlingame, B. Song, L. Ciammaruchi, G. Zanotti, J. Hankett, Z. Chen, E. A. Katz and S. R. Forrest, Reliability of Small Molecule Organic Photovoltaics with Electron-Filtering Compound Buffer Layers, *Adv. Energy Mater.*, 2016, **6**, 1601094.

16 E. L. Unger, E. T. Hoke, C. D. Bailie, W. H. Nguyen, A. R. Bowring, T. Heumüller, M. G. Christoforo and M. D. McGehee, Hysteresis and transient behavior in current–voltage measurements of hybrid-perovskite absorber solar cells, *Energy Environ. Sci.*, 2014, **7**, 3690–3698.

17 J. A. Christians, P. Schulz, J. S. Tinkham, T. H. Schloemer, S. P. Harvey, B. J. T. de Villers, A. Sellinger, J. J. Berry and J. M. Luther, Tailored interfaces of unencapsulated perovskite solar cells for >1000 hour operational stability, *Nat. Energy*, 2018, **3**, 68.

18 Y. Reyna, M. Salado, S. Kazim, A. Pérez-Tomas, S. Ahmad and M. Lira-Cantu, Performance and Stability of Mixed $FAPbI_{3(0.85)}MAPbBr_{3(0.15)}$ Halide Perovskite Solar Cells Under Outdoor Conditions and the Effect of Low Light Irradiation, *Nano Energy*, 2016, **30**, 570–579.

19 Q. Burlingame, L. Ciammaruchi, G. Zanotti, E. A. Katz and S. R. Forrest, Outdoor Operation of Small-Molecule Organic Photovoltaics, *Org. Electron.*, 2017, **41**, 274–279.