ORGANIC SOLAR CELLS

Unfavourable interactions enable stability

Use of polymer and small-molecule semiconductors with relatively poor miscibility helps the long-term stability of the morphology and photovoltaic performance of bulk heterojunction films used in organic solar cells.

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Organic solar cells (OSCs) have the potential to provide inexpensive green energy using materials that can be deposited from solution, which could enable cheap and large-scale manufacturing of solar cells similar to newspaper printing. The most efficient type of OSC active layer is typically a blend made from two components, one semiconducting polymer (that transports the holes) and one semiconducting small molecule (that transports the electrons), which intimately mix in a so-called bulk heterojunction structure with small regions of pure polymer and pure small molecules and extensive regions where the two components mix for easy separation of charges[1]. Optimization of the bulk heterojunction structure through material and process engineering has resulted in OSCs with power conversion efficiency suitable for commercial use, yet lack of stability has remained a significant drawback[2]. An intrinsic source of degradation is the large-scale separation of the polymer and small molecules over time, which tend to demix into pure phases like oil and water. Chemical intuition based on the paradigm of 'like dissolves like' suggests that similar materials with favourable interactions are most likely to remain mixed. Counterintuitively, Masoud Ghasemi and co-workers suggest in their recent *Nature Materials* Article[3] that the key to stable OSCs is not to use miscible components, but rather to use components that interact so unfavourably that they effectively freeze in place in a well-mixed blend (Fig. 1).

Finding a polymer–small-molecule pair that has a bulk heterojunction structure as its thermodynamic minimum — meaning that over time the blend will inch toward this well-mixed morphology — while achieving high power conversion efficiency has proven difficult[4]. In all of the highest-performance combinations of polymers and small molecules tested by the authors, the enthalpic component of the Flory–Huggins parameter (χ_{H}) — a value inversely related to the miscibility, or favourability of interaction, between the two materials — is too high to
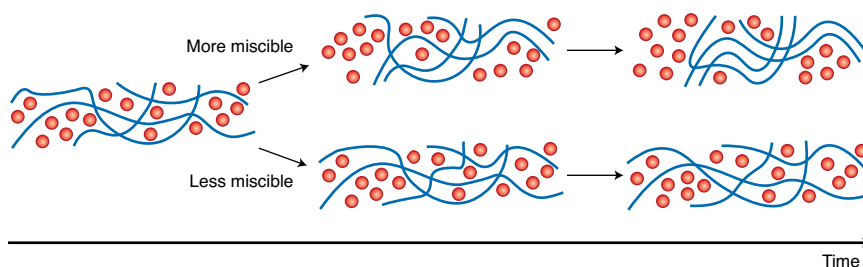
Fig. 1 | Evolution of bulk heterojunction morphology. High-performing solar cells require bulk heterojunctions with large mixed regions where the donor (polymer, blue) and acceptor (small molecule, red) materials are in close proximity. More miscible materials (top) are subjected to a reduced thermodynamic force driving them away from a mixed configuration, yet they are not completely stable and tend to phase-separate over time. Less miscible materials (bottom) experience a higher thermodynamic driving force towards phase separation, yet lack of diffusion hampers redistribution thus kinetically stabilizing the initial morphology.

make a bulk heterojunction that is thermodynamically stable.

Ghasemi and co-workers suggest stabilizing the bulk heterojunction blends kinetically by making the interactions between the polymer and small molecules as unfavourable as possible to stop interdiffusion. The authors tested a range of high-performance polymer–small-molecule blends, finding that the activation energy of diffusion increased nearly linearly with $\chi_{H}T$ (where T is the temperature of the active layer). As a result, the lower the thermodynamic stability of a bulk heterojunction blend (higher χ_{H}), the higher its kinetic stability (low diffusivity). They also fabricated OSCs based on these blends and measured how the photovoltaic performance changed over time. Strikingly, many polymer–small-molecule blends with low diffusivity were found to maintain their electronic performance, while all high-miscibility blends degraded over time.

The researchers estimated the diffusive properties of the small molecules through the polymer matrix by depositing a polymer layer on a small-molecule film, then measured how many of the small molecules penetrated the polymer over time using secondary ion mass spectroscopy (SIMS). These data were also used to estimate χ_{H} for

every polymer–small-molecule blend. Although effective, these diffusivity measurements are difficult and time consuming in practice, as every polymer–small-molecule blend must be tested for its particular diffusive properties. Additionally, SIMS measurements require specialized equipment and cannot measure diffusivity in polymer–small-molecule blends when the small molecule does not have a distinct elemental marker (such as inclusion of fluorine with a non-fluorinated polymer). As such, a simpler method to predict diffusivity in a polymer–small-molecule blend is necessary. To this end, the researchers demonstrated that the glass-transition temperature (T_{g}) of the small molecules and the elastic modulus of the polymers are metrics that are both simple to measure and strongly correlate with the diffusivity of the small molecule through the polymer. As a result, clear relationships between OSC stability, diffusion, χ_{H}, T_{g} and elastic modulus can be put forth: OSCs are more stable when small-molecule diffusivity is low; diffusivity of the small molecule decreases with increased (more unfavourable) χ_{H}; χ_{H} increases with increasing elastic modulus of the polymer and T_{g} of the small molecule. Thus, high-modulus polymers

and high-T_g small molecules are the most promising candidates for stable OSCs. Underscoring this point, the OSC made with the highest-modulus polymer and the highest-T_g small molecule in the test library showed entirely stable OSC performance over time.

Relying on kinetics, rather than thermodynamics, thus proves the most promising strategy for high performing and stable OSCs. The emphasis on kinetically trapping morphologies after processing puts greater emphasis on the importance of OSC processing and post-processing, rather than merely relying on the miscibility of its components. A kinetically stable morphology must have its processing and post-processing conditions finely tuned to ensure stability[5,6] while also optimizing maximum photovoltaic performance[7,8]. Choosing the right processing approach may thus ultimately prove as important for stable high-performance OSCs as the choice of the organic semiconductors themselves.

The increase in stability with increasing T_g and elastic modulus also suggests that polymer–small-molecule blends may not be suitable for solar cells demanding high flexibility or even stretchability. In particular, devices envisioned for integration with skin or clothing typically require low elastic modulus[9]. Polymers with high elastic moduli are thus largely unsuitable for such devices; similarly, high-T_g small molecules have been shown to lead to a high elastic modulus of the OSC blend[10]. More work may be done to determine if polymers with low enough modulus may still counteract the embrittling effects of high-T_g small molecules while maintaining OSC stability, yet the findings by Ghasemi and colleagues cast doubts on the possibility of using polymer–small-molecule blends to realize stretchable and highly flexible OSCs that are also morphologically stable. Blends in which both organic semiconductors are polymers, which typically have lower diffusivity than small molecules, may represent the only path forward in the development of stable OSCs with high mechanical deformability[11].

There also remain questions about how ternary blends may affect the stability of OSCs. Many of the highest-performance OSCs include more than one polymer blended with a small molecule[12]. It remains unclear whether both polymers must contribute to stabilizing the blend or whether only one polymer with high modulus is necessary to stabilize the devices. In the latter case, a possible strategy to stabilize OSCs might be the use of a high-modulus polymer additive solely as a stabilizing component.

The strong correlation between OSC stability and diffusion is not inevitable, but it has been conjectured before; the merit of the work by Ghasemi and co-workers is to correlate OSC stability with metrics one degree removed from diffusion — elastic modulus and T_g — which is both surprising and far more useful in rational design. Through these two simple metrics — elastic modulus and T_g — a significant number of polymers and small-molecule acceptors can be effectively eliminated as candidates for stable OSCs. This simple pre-screening tool brings a future with low-cost green energy one step closer. ❐

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