

## Review



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# Excitons and the lifetime of organic semiconductor devices

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While excitons are responsible for the many beneficial optical properties of organic semiconductors, their non-radiative recombination within the material can result in material degradation due to the dumping of energy onto localized molecular bonds. This presents a challenge in developing strategies to exploit the benefits of excitons without negatively impacting the device operational stability. Here, we will briefly review the fundamental mechanisms leading to excitonic energy-driven device ageing in two example devices: blue emitting electrophosphorescent organic light emitting devices (PHOLEDs) and organic photovoltaic (OPV) cells. We describe strategies used to minimize or even eliminate this fundamental device degradation pathway.

## 1. Introduction

The optical properties of organic semiconductor materials are primarily determined by excitons, or molecular excited states that are mobile within the solid in which they are generated. The excitonic nature of organics is a result of the weak, *electrostatic* van der Waals cohesive forces that bind the material into the solid state. This is in marked contrast to inorganic semiconductors that are *chemically* bound by strong covalent and/or ionic forces, whereby electrons are shared by all the ions forming the crystal lattice. Hence, in one case (organics), the excitons are tightly bound into small Frenkel-like states, whereas in the other case (inorganics) they are very loosely bound Wannier–Mott states that are often unstable at room temperature. The primary electronic differences between these two classes of materials are summarized in [table 1](#).

While excitons are responsible for the many beneficial optical properties of organics, they also are responsible for the mechanisms leading to their degradation over time. The fundamental role that excitons play in the

**Table 1.** Comparison of properties of organic and inorganic semiconductors.

property	inorganics	organics
bonding	covalent/ionic	van der Waals
charge transport	band transport	polaron hopping
charge mobility	approximately 1000 cm <sup>2</sup> /V s	less than 1 cm <sup>2</sup> /V s
conduction levels	bands	frontier orbitals
peak absorption	10 <sup>3</sup> –10 <sup>4</sup> cm <sup>−1</sup>	10 <sup>5</sup> –10 <sup>6</sup> cm <sup>−1</sup>
exciton species	Wannier–Mott	Frenkel
exciton-binding energy	10–100 meV	100–1000 meV
exciton radius	approximately 100 Å	approximately 10 Å

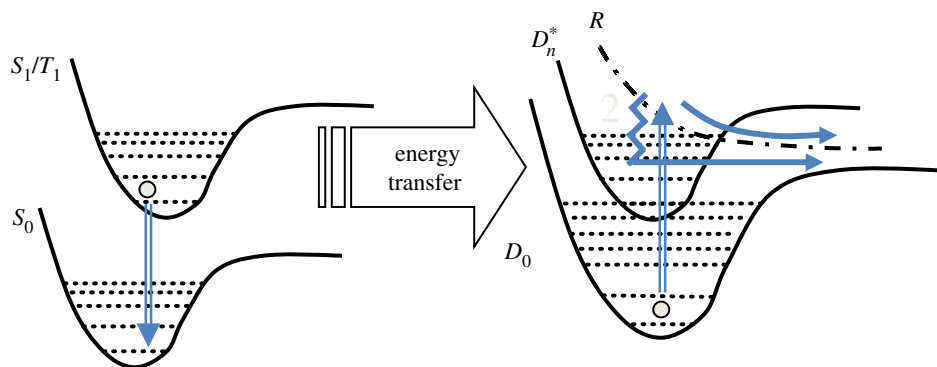
failure of both blue electrophosphorescent organic light emitting devices (PHOLEDs) and organic photovoltaics (OPVs) have been unambiguously identified in recent studies. Here, we briefly review those studies and illustrate means whereby high device performance as well as long operational lifetimes can be simultaneously achieved by careful exciton management within the active regions of organic devices.

## 2. Operating lifetime of blue PHOLEDs

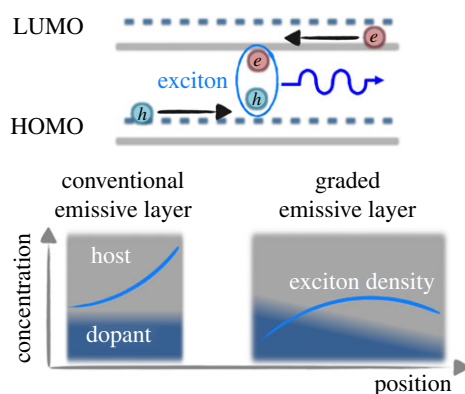
Since their first demonstration in 2001 [1], blue PHOLEDs have been found to have very short operational lifetimes—only a few tens of hours compared with hundreds of thousands to millions of hours for red and green emitting analogues [2]. This finding has been universally observed and is independent of the choice of phosphor or conductive host molecules, suggesting that the cause is of fundamental rather than purely extrinsic origin. This led to a study by Giebink *et al.* [3] that showed that the long-term deterioration of luminance was due to an energy-driven Auger-like process shown in figure 1, whereby an electrically generated triplet exciton on the phosphor encounters a charge (polaron) on a nearby host molecule [4]. The collision results in the de-excitation of the exciton, momentarily promoting the polaron to a very high energy in excess of 7 eV in blue OLEDs where it has a significant probability of engaging in a dissociative reaction with the molecule (most likely the host, in the case studied by Giebink *et al.*). The molecular product of this reaction creates a defect state within the energy gaps of the dopant and host. Subsequent triplets that are generated on a phosphor in the vicinity of the defect can readily transfer to the mid-energy gap state and subsequently non-radiatively recombine prior to emission.

While this pathway has a low probability for success in any given triplet-polaron encounter, the density of excitations in a PHOLED is sufficiently high when operated at brightnesses required in displays and lighting appliances (i.e. approx. 100–3000 cd m<sup>2</sup>) to result in rapid degradation in emission efficiency. Indeed, Giebink *et al.* estimated that 5 in 10<sup>8</sup> such exciton–polaron collisions results in formation of a non-radiative defect in the longest lived blue PHOLEDs, which is sufficient to cause significant reduction in luminance in a matter of hours. As the probability for molecular dissociation is an exponential function of energy, the lower exciton energies available in red and green emitters results in a dramatically reduced probability for molecular decomposition, and hence greatly increased lifetimes. Further, the very long lifetime of the triplet state in phosphorescent OLEDs (500 ns–10 µs) makes this destructive event far more likely to occur than in fluorescent emitters that rely on short lived (1–10 ns) and quantum mechanically allowed singlet exciton emission.

There are several means for reducing the effects of exciton-induced degradation in PHOLEDs. These include (i) reducing the exciton lifetime via the design of molecular species with improved metal–ligand charge transfer or through modification of structure and morphology of the device



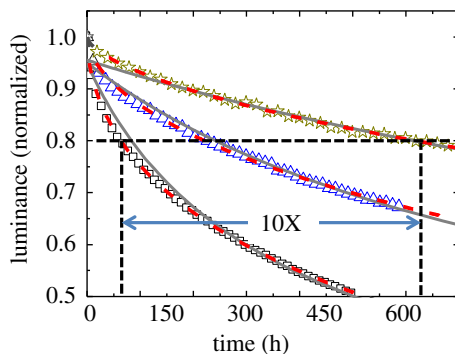
**Figure 1.** Auger process showing exciton–polaron annihilation resulting in dissociation (state  $R$ ) of the host molecule. Here,  $S_0$  is the excitonic ground state,  $S_1/T_1$  is the first singlet/triplet excited state, respectively,  $D_0$  is the polaronic ground state and  $D_n^*$  is a higher excited state that induces transfer of energy to the molecule, and hence excitation into  $R$ . Similar exciton–exciton annihilation processes might also be active. (Adapted from [1].) (Online version in colour.)



**Figure 2.** Illustration of scheme for increasing blue PHOLED operational lifetime by reducing exciton–polaron annihilation interactions. Top: energy diagram of the host and dopant molecules used in a demonstration resulting in a  $10\times$  improvement in PHOLED lifetime. Here, the dopant,  $\text{Ir}(\text{dmp})_3$  conducts holes in its highest occupied molecular orbital (HOMO) and the host, mCBP, conducts electrons in its lowest unoccupied MO (LUMO). In a conventional blue emitting PHOLED (bottom, left), the dopant and host concentrations are uniformly distributed across the EML, resulting in a high concentration of triplet excitons and electron–polarons near the cathode. By grading the dopant (bottom, right), the high energy triplet excitons are more evenly distributed across the EML, resulting in a decrease in exciton–polaron encounters, and hence decreased dissociative reactions as in figure 1. (Online version in colour.)

emitting region [5], (ii) reducing the exciton and polaron densities in the PHOLED emission layer [6] (EML), or (iii) decreasing the probability for localization of energy on a bond on the host molecule through rapid exciton thermalization. Whichever approach is taken, practical schemes require that the overall high performance (e.g. quantum efficiency, colour coordinates and efficacy) of the PHOLED be maintained. In our recent work, we have engineered a structure that reduces the exciton density (solution (ii)) while maintaining and even improving the blue PHOLED performance compared with that achieved by a conventional device [6]. This proof-of-concept suggests that while excitons result in both the high luminance efficiency and the degradation pathway in PHOLEDs, they can nevertheless be managed to result in practical high-performance devices with acceptable operational lifetimes.

The method used to decrease exciton density, and hence the probability for exciton–polaron annihilation, is schematically illustrated in figure 2 [6]. In conventional PHOLEDs, the exciton population is typically generated at either the cathode or the anode side of the EML, as the



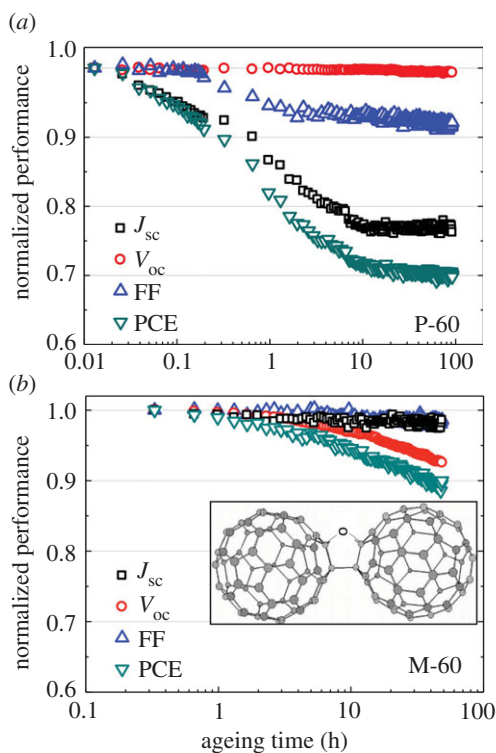
**Figure 3.** Operational lifetime of blue PHOLEDs normalized to an initial luminance of  $1000 \text{ cd m}^{-2}$ , or approximately 10 times normal display brightness. Conventional (squares), graded EML (triangles) and stacked, graded EML PHOLED (stars) are shown with the horizontal line corresponding to the T80 point: i.e. the time that the luminance has decayed to 80% of its initial value. (Adapted from [6].) (Online version in colour.)

conductive host has either higher electron or hole mobility. This leads to charge pile-up nearest to the point of injection of the lowest mobility carrier. It is in this pile-up zone where most excitons are formed. In our demonstration, we combined an electron conducting host molecule, 4,4'-bis(3-methylcarbazol-9-yl)-2,2'-biphenyl (mCBP), and blue dopant iridium (III) tris[3-(2,6-dimethylphenyl)-7-methylimidazo[1,2-f] phenanthridine] ( $\text{Ir}(\text{dmp})_3$ ). This phosphor emits a cyan colour with CIE coordinates [0.15, 0.29]. Importantly,  $\text{Ir}(\text{dmp})_3$  has a high hole mobility. By grading the dopant concentration from 8% at the cathode side to 18% at the anode side of the EML, the hole mobility in the film is therefore increased from cathode to anode, while the electron mobility decreases along this same direction, effectively spreading the carriers more uniformly throughout the layer. This, in turn results in a nearly uniform generation of excitons via electron-hole recombination across the EML, thereby lowering the local density of excitons and polarons without sacrificing either quantum efficiency or increasing voltage. Indeed, the quantum efficiency, particularly at high current densities, is found to be higher than in conventional, uniformly doped PHOLEDs since parasitic effects such as triplet-polaron and triplet-triplet annihilation [7,8] are also reduced at the lower exciton density.

As shown in figure 3, the operational lifetime of the graded EML PHOLED is approximately three times longer than its uniformly doped analogue. Further widening of the effective EML thickness by stacking two graded EML blue emitting PHOLEDs results in a 10-fold increase in operational lifetime, reaching  $\text{LT}_{80}$  after 616 h starting with a luminance of  $1000 \text{ cd m}^{-2}$  (stars, figure 3). (Here,  $\text{LT}_{80}$  is the time it takes for the luminance to decay to 80% of its initial value.) While this extrapolates to over 20 000 h from a starting luminance of  $100 \text{ cd m}^{-2}$  and is comparable to lifetimes of similarly 'light blue' fluorescent chromophores, it nevertheless falls short of the stringent requirements for displays that allow only approximately 5% reduction in brightness from a given pixel during the display operational history [2]. Nevertheless, this result provides a clear demonstration that reducing the long-lived triplet population can effectively extend operational lifetime and that energetically driven molecular decomposition is indeed much more active in blue than in analogous red or green emitting devices. Furthermore, it provides a strategy for maintaining very high device performance as well as a long operational lifetime—while both properties depend on the presence of excitons, excited state management can be used to simultaneously achieve both benefits without compromise.

### 3. Operating lifetime of organic photovoltaics

As exciton-polaron-induced dissociative reactions have been identified as a fundamental failure mechanism in PHOLEDs, it is reasonable to expect that similar processes might also be active in



**Figure 4.** Performance over time for (a) planar and (b) mixed SubPc/C<sub>60</sub> OPVs. Here,  $J_{sc}$  is the short circuit current,  $V_{oc}$  is open circuit voltage, FF is fill factor and PCE is power conversion efficiency. Inset: potential decay product during burn-in [4,12]. (Online version in colour.)

the degradation of OPVs. Indeed, this has been found to be the case with an important difference: in OPVs, the exciton alone appears to drive molecular decomposition without involving a polaron due to the unique chemical nature of fullerenes employed as acceptors in most high-efficiency devices. The rate of loss in power conversion efficiency, which can be particularly rapid during the early use (or ‘burn-in’) period of operation [9,10], can be fit to a model that is dependent solely on the exciton density, in spite of the fact that the polaron density in efficient solar cells can even exceed that in PHOLEDs under normal operating conditions [11].

This burn-in degradation for the case of an archetype subphthalocyanine chloride (SubPc)/C<sub>60</sub> planar heterojunction cell shown in figure 4a exhibits a rapid decrease in PCE during the first 10 h of operation, after which the degradation saturates to approximately 70% of its initial value. It is also seen in figure 4 that almost all the degradation in PCE is due to a decrease in short circuit current density, which corresponds to a decrease in cell responsivity over time.

Models and experiments [11,13] have unambiguously attributed the OPV ageing process to the formation of defects in the active region due to exciton-induced molecular decomposition, analogous to the mechanism of Giebink *et al.* for PHOLEDs discussed above [3]. In fullerene-based OPVs, however, the exciton itself promotes the formation of higher order oligomers [12] of C<sub>60</sub> (e.g. C<sub>120</sub>, C<sub>180</sub>, etc.) that have a reduced exciton lifetime, or quench excitons that otherwise would diffuse to the donor–acceptor junction of the OPV and subsequently be dissociated into free charge that is collected at the contacts. The oligomers, including the compound C<sub>120</sub>O is shown in the inset, figure 4. Given the high order of symmetry of C<sub>60</sub> molecules, the intermolecular reaction sites are readily available to induce these chemical changes when sufficient energy is supplied. However, oligomerization is far less likely when C<sub>60</sub> is replaced by the lower symmetry C<sub>70</sub> molecules as there are fewer sites that can be positioned adjacent to each other to allow for

such reactions to occur. Indeed, it is observed that OPVs based on C<sub>70</sub> show a reduced tendency for burn-in loss [11], contrary to the case of C<sub>60</sub> in figure 4a.

A simple method to reduce oligomerization and other energy-driven molecular degradation pathways is to develop architectures that increase the exciton dissociation rate (and hence the probability of defect formation during its lifetime) without also reducing cell performance. In fact, bulk [14] and mixed heterojunction [15] cells have precisely this property: by placing a donor–acceptor interface very near to the point of exciton generation, the exciton almost immediately dissociates after light absorption, leaving it less time to engage in dissociative molecular reactions. Indeed, for this same reason, such blended cells also have higher efficiencies—excitons immediately dissociate into charge carriers prior to recombination. The charge carriers thus generated are free to travel along contiguous domains of either the donor (in the case of holes) or acceptor (for electrons) molecules until they are collected at the appropriate device contacts. In a bulk heterojunction cell, the domains are typically formed by casting from solution, where partially miscible donor and acceptor molecular species phase segregate into a highly interconnected network of nanometre-sized domains [14,16]. In the case of small molecules, similar nanocrystalline domains form by co-deposition of appropriately matched donor and acceptor molecules [17]. For these structures to provide both high efficiency and long operational lifetime, the width of a domain must be considerably shorter than an exciton diffusion length, thus effectively shutting down the non-radiative recombination process.

An example of the effectiveness of this strategy is shown in figure 4b, where we plot the lifetime performance of a mixed heterojunction SubPc/C<sub>60</sub> OPV that is otherwise identical to the planar structure in figure 4a. It is apparent that the burn-in decay has been considerably reduced, and possibly eliminated in the mixed junction cell. The remaining degradation is due to a longer term, extrinsic mechanism. However, recent work in our laboratory shows that long extrapolated lifetimes (more than 10 years) can be obtained in mixed heterojunction cells while maintaining very high efficiencies and stabilities even at elevated temperatures.

## 4. The long-lived future of organic electronic devices

It is apparent that with careful exciton management, organic electronic devices can be both efficient and long-lived. The key to achieving this fortuitous combination is to design structures that harvest the exciton before it has the opportunity to dump its considerable energy onto localized bonds on the constituent molecules. There are numerous approaches to achieving this balance. Reducing the exciton lifetime or density, and preventing bimolecular recombination processes that can promote the excitations to very high energies are demonstrated routes to long-lived devices.

While reducing the effectiveness of energy-driven processes that lead to molecular decomposition, there are several other factors that must be addressed to achieve long lifetime and high performance. It is clear that the molecular species used in the devices must be robust, stable and relatively immune from decomposition or morphological changes. For example, post-deposition crystallization can lead to electrical shorts or physical damage to the active device region. And underlying all of these processes is the importance of using highly pure starting materials. Indeed, there is no case where an electronic device, either organic or inorganic, has performed better, or lived longer, using impure versus highly purified source materials. This uncompromising demand for high purity is particularly difficult to achieve in organic materials where possibly solution processing of large molecules of undefined molecular weights is often the norm.

Hence, it is the combination of appropriate molecular engineering and materials combinations, achievement of very high-purity materials and precise deposition methods, control of film morphology and use of advantageous device architectures that form the basis of the many essential criteria that must be met to capture both high performance and long-term operation in a single device. Success with such approaches suggests that organic devices have the potential to achieve operational lifetimes perhaps as long as conventional inorganic semiconductor devices



when used under the appropriate operational conditions (e.g. temperature, environment, etc.). While we have a very long way to go before demonstrating such extended operational lifetimes in organic devices, there do not appear to be fundamental limitations to stability that clearly distinguish these two broad but very different classes of electronic materials.

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