A Simple n-Dopant Derived from Diquat Boosts the Efficiency of Organic Solar Cells to 18.3%

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TOC GRAPHIC

Abstract

Molecular doping has recently been shown to improve the operating characteristics of organic photovoltaics (OPVs). Here, we prepare neutral Diquat (DQ) and use it as n-dopant to improve the performance of state-of-the-art OPVs. Adding DQ in ternary bulk-heterojunction (BHJ) cells based of PM6:Y6:PC₇₁BM is found to consistently increase their power conversion efficiency (PCE) from 16.7 to 17.4%. Analyses of materials and devices reveal that DQ acts as *n*-type dopant and morphology modifier for the BHJ leading to observable changes in its surface topography. The resulting *n*-doped BHJs exhibit higher optical absorption coefficients, balanced ambipolar transport, longer carrier lifetimes and suppressed bimolecular recombination, which are ultimately responsible for the increased PCE. Finally, the use of DQ was successfully extended to OPVs based on PM6:BTP-eC9:PC₇₁BM for which a maximum uncertified PCE of 18.3% was achieved. Our study highlights DQ as a promising dopant for application in next generation organic solar cells.

Main text

Organic photovoltaics (OPVs) represent a promising emerging technology for renewable energy generation.¹ The recent development of the nonfullerene acceptor Y6²⁻³ (full chemical names of all materials can be found in **Experimental Section**) and its derivatives have helped boosting the power conversion efficiency (PCE) of OPVs to over 18%⁴⁻⁸. However, further improvement in materials,⁹ processing methodologies and microstructural engineering of both the photoactive layers and cell architecture,¹⁰ are needed to attain ultimate performance that has recently been predicted to surpass 20% for single-junction OPVs¹¹.

Molecular doping has been exploited as a promising and highly versatile strategy to improve the performance of organic semiconductor devices including organic field-effect transistors (OFETs)¹²⁻¹⁵ and organic light-emitting diodes (OLEDs)¹⁶ by tuning the electronic properties of the host organic semiconductor(s). More recently, the introduction of molecular dopants directly into bulk-heterojunction (BHJ) OPVs has also proven effective in enhancing the performance of state-of-the-art cells¹⁷⁻³². Specifically, tiny amount of doping was found to enhance the short-circuit current (J_{sc}) and fill factor (FF) (see the summary of relevant literature in **Table S1**) of highly efficient OPVs by improving the carrier photogeneration efficiency and suppressing bimolecular recombination while simultaneously affecting the morphology of the BHJ. To this end, *p*-type dopants have been the most studied systems with their *n*-type counterparts receiving significantly less attention.¹⁷⁻²¹ A notable example is benzyl viologen (BV), which has recently been used to *n*-dope a range of BHJs ultimately resulting to OPV cells with a maximum PCE of 17.1%.¹⁷

Motivated by the work on BV-doped OPVs, we prepared the strong electron accepting molecule diquat (DQ) by the chemical reduction of diquat dibromide (DQ²⁺:2Br⁻) and studied its application as an *n*-type dopant in state-of-the-art OPVs. DQ²⁺:2Br⁻ and related 2,2'-bipyridinium species are well-known herbicides, which have also been extensively investigated as redox mediators in biological and photocatalytic systems³³. Despite this interest, reports of

the use of the fully reduced DQ species as a reducing agent are very rare.^[35] This likely relates to the poor stability and high reactivity of the DQ in ambient atmosphere, a common issue with electron rich organic reductants (n-type dopants).³⁴ Nevertheless, given the ready availability of the DQ^{2+} precursor, we speculated that we might be able to readily isolate the neutral DQ by exploiting its solubility difference with the charged precursor.

The applicability of DQ as an electronic dopant was tested in a ternary BHJ system composed of PM6:Y6:PC₇₁BM. A remarkable PCE of 17.4% is achieved upon DQ (0.01 wt%) addition directly into the BHJ as compared to 16.7% measured for non-doped/pristine (control) OPV cells. Analyses of materials and devices shows that the enhanced performance relates to the interactions between DQ and the host semiconductors that lead to changes in the BHJ morphology and (opto)electronic properties. Importantly, the use of DQ was successfully extended to the binary system PM6:IT-4F and the ternary system PM6:BTP-eC9:PC₇₁BM where equally impressive enhancement in PCE (uncertified) from 13.0 to 14.3% and 17.4 to 18.3%, respectively, were recorded. The work highlights the broader use of n-doping as an effective strategy towards improving the OPV performance.

The preparation of DQ (**Figure 1a**) was inspired by the work of Lee *et al.*,³⁴ and relies on the fact that both DQ^{2+} and the radical cation resulting from its one electron reduction ($\text{DQ}^{\bullet+}$) are charged species soluble in water, whereas the doubly reduced neutral DQ is water insoluble and organic solvent soluble. Therefore, the addition of a chemical reducing agent (NaBH_4) to a biphasic mixture of DQ^{2+} in water and toluene results in the *in situ* reduction of DQ^{2+} , initially to a red coloured radical cation ($\text{DQ}^{\bullet+}$), followed by a second reduction to a yellow solution of DQ. Since DQ preferentially dissolves in the toluene layer it can be separated via physical extraction. For the purpose of this study, the toluene was replaced with chloroform (CF) or chlorobenzene (CB) and the solution was stored inside a nitrogen glovebox, where it remained stable for several weeks. To perform the doping process, the required amount of DQ solution

in CF was added into the targeted CF solution of the BHJ components according to published procedures.¹⁷

Figure 1. (a) Schematic illustration of the steps used for DQ synthesis from diquat dibromide ($\text{DQ}^{2+} \cdot 2\text{Br}^-$) and the corresponding two-electron redox reactions. (b) Energy level diagram of various materials considered. (c) Relative EPR spectra of PM6:Y6:PC₇₁BM films without and with DQ (0.01 wt%). (d) Absorption coefficient of PM6:Y6:PC₇₁BM blend films without and with DQ (0.01 wt%). (e) Surface energies of the various films measured via the contact angle technique.

DQ may also be formed electrochemically by reducing the air stable DQ^{2+} .³⁵ This method provides a convenient way to measure the orbital energies of DQ via cyclic voltammetry (CV) (**Figure S1**). Evidently, DQ undergoes two reversible, one-electron oxidations with half-wave potentials at -1.27 eV and -0.85 eV versus ferrocene. These values are converted into highest occupied molecular orbital (HOMO) energies in **Table S2** and **Figure 1b**, to allow for easier comparison to those of the organic semiconductors employed. The shallow HOMO levels of both DQ (-3.53 eV) and $\text{DQ}^{•+}$ (-3.95 eV) suggests that Diquat is a promising n-type dopant for a wide range of organic semiconductors. In the context of this study, the HOMO of both DQ

and DQ^{*+} are shallower than the lowest unoccupied molecular orbital (LUMO) of the electron acceptors studied including Y6 (-4.10 eV)³⁶, PC₇₁BM (3.91 eV)³⁷, IT-4F (-4.14 eV)³⁸, and BTP-eC9 (-4.05 eV)⁴ (for chemical structures see **Figure S2**). Thus, we expect efficient n-type doping due to electron transfer from the HOMO of DQ to the LUMO of these acceptors. We have also evaluated the energy levels for all organic semiconductors via Density Functional Theory (DFT) calculations (**Figures S2** and **Table S2**). The calculated HOMO for DQ in the gas phase is at -3.74 eV, whereas if the effects of the chloroform solvent are taken into account³⁹, the DFT HOMO energy becomes -3.61 eV, in good agreement with the experimentally determined value of -3.53 eV. Moreover, the calculated HOMO of DQ^{*+} is 0.63 eV below that for DQ, which is consistent with the measured value of 0.42 eV.

To acquire more direct evidence of the aforementioned doping process we employed electron paramagnetic resonance (EPR) measurements. This allows measurement of the charge transfer-induced free electrons (polarons) within the host organic semiconductor. As shown in **Figure S3**, neat Y6 and PC₇₁BM films exhibit a negligible EPR signal at 100 K while its intensity increases significantly upon doping with DQ (0.01 wt%), suggesting a successful electron transfer from DQ to Y6 and PC₇₁BM. Evidence of free electron formation was also observed in the ternary blend PM6:Y6:PC₇₁BM doped with DQ (**Figure 1c**), further supporting the n-type dopant character of DQ for these host semiconductors.

The effect of n-type doping was further studied by Kelvin Probe (KP) measurements (**Figure S4** & **Table S3**). Addition of small amounts of DQ (0.01 wt%) shifts the work function (WF) of Y6 and PC₇₁BM films up by 0.13 and 0.10 eV, respectively, indicating effective n-doping of both materials. This is also the case for the ternary PM6:Y6:PC₇₁BM BHJ for which the WF is found to shift from -4.58 to -4.47 eV upon doping with DQ (0.01 wt%). The KP measurements provide direct evidence of the n-type dopant character of DQ for both Y6 and PC₇₁BM in excellent agreement with the EPR results.

It has recently been shown that in addition to electronic doping, the strong interactions between the dopant molecules and the host semiconductor(s) could also lead to noticeable changes in the microstructure and optical properties of the resulting layers.^{17, 24} To explore whether similar changes occur with DQ, we performed UV-Vis absorbance spectroscopy measurements on the various host semiconductors. Indeed, films of Y6 and PC₇₁BM doped with DQ exhibit clear and consistently higher absorption coefficients than the pristine layers in agreement with previous findings (**Figure S5**)^{21-22, 24-25} The absorption coefficient of the ternary PM6:Y6:PC₇₁BM BHJ layer doped with DQ (0.01 wt%) also increases (**Figure 1d**), highlighting the generic effect of DQ doping on these semiconducting blends. Although the origin of the latter effect remains elusive, we hypothesize that DQ acts as nucleating agent that is able to affect (improve) the crystallization process of the BHJ during solidification. Direct modification of the morphology of organic polymers during solidification using nucleating agents is a known phenomenon in organic materials such as high-density polyethylene and it has been exploited to improve its physical properties including optical, mechanical, water transmission rate etc.⁴⁰ In the case of DQ-BHJ system, the aforementioned electron transfer process (**Figure 1b**) leads to strong electrostatic interaction between the dopant and the host components and acts as a nucleating agent. Details of the observed structural changes will be discussed later.

The similarity in the impact of DQ on the different host semiconductors suggests good miscibility.²⁰ To verify this hypothesis, we performed contact-angle measurements (**Figure S6**) on solid layers of the DQ as well as on all organic semiconductors studied. The surface energies of these materials were also calculated using the Owens, Wendt, Rabel and Kaelble (OWRK) method and summarised in **Table S4** and **Figure 1e**. The DQ, PM6, Y6, and PC₇₁BM solid films exhibit surface energies of 26.9, 13.2, 31.0, and 36.1 mN m⁻¹, respectively. Because of its moderate surface energy, DQ is expected to disperse/diffuse uniformly across both the donor and acceptor phases within the BHJ. Such distribution of dopants across the donor/acceptor

heterojunction has been shown to yield BHJs with improved internal morphology, reduced charge recombination, and improved charge generation.^{20, 23, 32, 41} The surface energy of PM6:Y6:PC₇₁BM decreases from 20.9 to 17.9 mN m⁻¹ after DQ doping (0.01 wt%), indicating that the surface morphology of the BHJ has changed slightly after doping.⁴² However, the change is very small and close to the experimental error of the measurements. Another possible explanation for the observed change is the alteration of the surface texture and will be discussed next.

To investigate the role of DQ on the microstructure of the BHJ, pristine (w/o) and DQ-doped (DQ) layers comprised of PM6:Y6:PC₇₁BM were analysed by Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS). The (010) peaks representing the π - π stacking are located at 1.71 Å⁻¹ for PM6, 1.81 Å⁻¹ for Y6, and 1.30 Å⁻¹ for PC₇₁BM (**Figure S7**). 2D diffraction patterns and line-cut profiles (**Figure 2a-b**) suggest that DQ (0.01 wt%) does not induce notable changes on the molecular orientation and crystal structure of the different components, in agreement with previous reports on ultralow concentration doping of various BHJ systems^{17, 20, 25}. The GIWAXS patterns obtained for the pristine and DQ-doped BHJs show a strong diffraction peak, in the out-of-plane direction, located at 1.75 Å⁻¹, which is associated to the π - π stacking of molecules oriented perpendicular to the substrate, while a lamellar stacking peak at 0.29 Å⁻¹ is visible in the in-plane direction. These observations suggest that the BHJ exhibits a predominantly face-on molecular packing, without significant (or measurable) changes in peak position, orientation and intensity related to the presence of DQ. The coherence length, derived from the width of x-ray-diffraction π - π stacking peaks using the Scherrer equation, was also calculated to be ≈ 31.5 Å for both pristine and DQ-doped BHJs. From the GIWAXS data it is evident that the DQ-doped (0.01 wt%) BHJ exhibits similar microstructural characteristics to the undoped BHJ, indicating that the observed differences in surface topography are not due to drastic changes in the packing motif of the materials.

The effect of DQ doping on the surface morphology of the PM6:Y6:PC₇₁BM BHJs was also investigated using atomic force microscopy (AFM) measurements (**Figure 2c-d**). Although the root-mean-square (RMS) of the surface roughness of the BHJ layers remains similar for both undoped and DQ-doped layers (1.11 nm vs. 1.03 nm), the latter is characterized by the presence of distinct nanofiber-like features ≈ 35 nm in length (clearly visible in the phase image in **Figure 2d**). No such features are visible in the undoped BHJ (**Figure 2c**). Previously, similar surface characteristics have been shown to benefit the exciton dissociation and charge transport within the BHJ, ultimately leading to higher J_{SC} .⁴³⁻⁴⁴ More evidence of the morphological differences come from the height histograms extracted from the AFM images (**Figure 2e**). The DQ-doped layer exhibits narrower height distribution as compared to pristine BHJ, which indicates a smoother and better-defined surface texture as a result of the nanofiber-like features. To elucidate the origin of these nanofiber-like structures, we also performed AFM analysis on the neat donor and acceptor layers without and with DQ (0.01 wt%) (**Figure S8**). For all three materials studied, the presence of DQ appears to reduce the surface roughness and consistently yielding smoother layers. This generic effect is better illustrated in the corresponding height histograms in **Figure S8** where large shifts towards small height values are consistently observed upon doping. As a result, the ensuing solid layers are smoother and denser since they contain fewer voids. Moreover, the absence of any material segregation supports our earlier hypothesis that DQ molecules disperses uniformly, at least in the doping concentration(s) investigated, within the host semiconductor(s) while simultaneously making the solid layers smoother.

Complementary information to AFM analysis were obtained via transmission electron microscopy (TEM) measurements (**Figure S9**). When compared to the undoped (w/o) BHJ, layers containing a low concentration of DQ (0.01 wt%) exhibit domain-like features ≈ 50 nm in size. Increasing the DQ content to 0.1 wt% leads to a noticeable increase in the domain size to 100-200 nm. The AFM and TEM results provide direct evidence of the role of DQ as an

effective morphology modifier. The altered morphology is believed to be one of the key reasons for the improved charge transport observed (**Figure 3c-d**, **Figure S11** and **Figure S16c-e**), which under optimal doping conditions also enhances the OPV performance.

Figure 2. (a) Two-dimensional GIWAXS patterns of PM6:Y6:PC₇₁BM without and with DQ (0.01 wt%). (b) The corresponding in-plane and out-of-plane line cuts of the GIWAXS patterns. AFM height images of PM6:Y6:PC₇₁BM layers (c) without and (d) with DQ (0.01 wt%), and corresponding phase images (bottom). (e) Surface height histograms of BHJ films without and with DQ obtained by AFM.

To evaluate the impact of DQ doping on the operating characteristics of the OPV, we fabricated solar cells based on the standard architecture comprised of ITO/PEDOT:PSS/BHJ:DQ/PFN-Br/Ag (inset in **Figure 3a**). The weight ratio of DQ was first optimized (**Figure S10** and **Table S5**) and representative curves of the ensuing cells are presented in **Figure 3a**, while a summary of the key device parameters is given in **Table 1**. Evidently, the undoped (pristine) OPVs exhibit a maximum PCE of 16.7% with a J_{SC} of 25.64 mA cm⁻², an open-circuit voltage (V_{OC}) of 0.860 V, and an FF of 75.7%, which is comparable to the published results for PM6:Y6:PC₇₁BM cells based on the standard architecture employed⁴⁵⁻⁴⁷. Remarkably, OPVs doped with DQ exhibit an improved PCE of 17.4%, primarily due to a higher J_{SC} (26.48 mA cm⁻²) and a slightly increased FF (76.1%). To understand the origin of

this improvement in the DQ-doped cells, the external quantum efficiency (EQE) of the devices was measured and analysed (**Figure 3b**). For all cells, the integrated current density (J_{cal}) values deduced from the EQE spectra match well with the values obtained from the J - V curves measured under simulated solar illumination within $\pm 3\%$. To this end, we note that for DQ-doped OPVs, the EQE increases by 3.6% due to the higher photoresponse in the spectra ranges 395-475 nm and 580-935 nm. This observation is in agreement with a higher absorption coefficient of the DQ-doped BHJ shown in **Figure 1d**, which ultimately leads to a $\approx 3.3\%$ increase in J_{SC} . As can be seen in **Figure S10b**, the cell's EQE continuous to increase with increasing DQ concentration up to 0.1 wt% resulting in higher J_{SC} (**Table S5**).

Table 1. Summary of operating parameters of OPVs based on three different BHJ systems without (w/o) and with the DQ dopant (DQ), measured under simulated solar illumination of AM 1.5G (100 mW cm^{-2}).

BHJ System	Dopant	V_{OC} [V]	J_{SC} [mA cm^{-2}]	J_{cal} [mA cm^{-2}] ^a	FF [%]	PCE [%] ^b
PM6:Y6: PC ₇₁ BM	w/o	0.860	25.64	24.89	75.7	16.7 (16.2 $\pm$ 0.2)
	DQ ^c	0.862	26.48	26.03	76.1	17.4 (17.0 $\pm$ 0.2)
PM6:IT-4F	w/o	0.856	20.34	19.85	74.9	13.0 (12.8 $\pm$ 0.1)
	DQ ^d	0.862	21.98	21.44	75.7	14.3 (14.0 $\pm$ 0.2)
PM6:BTP-eC9:PC ₇₁ BM	w/o	0.855	26.21	26.03	77.7	17.4 (17.1 $\pm$ 0.2)
	DQ ^e	0.856	26.93	26.89	79.4	18.3 (18.0 $\pm$ 0.2)

^aData from EQE measurement; ^bAverage uncertified PCE of 20 devices; ^cThe amount of DQ is 0.01 wt%. ^dThe amount of DQ is 0.02 wt%; ^eThe amount of DQ is 0.01 wt%.

To further study the origin of the higher J_{SC} and FF measured upon n-doping with DQ, we measured the hole and electron mobilities using the space-charge limited current (SCLC) technique (**Figure 3c-d** and **Table S6**). A key observation here is that both electron and hole currents increase upon doping with DQ. In the case of hole-only devices such enhancement indicates an increase mobility since hole concentration is expected to remain the same, if not lower. Indeed, analysis of the data indicates that the average hole (μ_{h}) and electron (μ_{e}) mobility of the DQ-doped layers increase as compared to undoped (pristine) layers. Increasing the DQ

concentration further (0.1 wt%, **Figure S11a**) is found to detrimental for μ_h to $2.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while μ_e keeps increasing ($6.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This is in line with previous observations and is attributed to the synergetic effects of morphology improvements and electronic doping.^{17,}
²² To verify the SCLC results, we used photo-induced charge-carrier extraction in a linearly increasing voltage (photo-CELIV) technique to measure the carrier mobility (μ) in pristine and *n*-doped layers using:²⁶

$$\mu = 2d^2 / (3At_{max}^2(1 + 0.36\Delta j/j_0)) \quad (1)$$

Here, d is the active layer thickness, A is the voltage rise speed of the applied voltage pulse, t_{max} is the time to reach the extraction current maximum, Δj and j_0 is a shifting and initial current step, respectively. **Figure S11b** displays the derived results for both layers. Evidently, the mobility of the faster charge carrier in DQ-doped devices is approximately 159% higher than the value derived for the undoped cells, in good agreement with the SCLC measurements. Besides, SCLC analysis reveal a well-balanced μ_h/μ_e ratio within BHJ upon DQ-doping (0.94) as compared to undoped cells (1.26). Thus, we conclude that the observed changes in the charge transport characteristics of the BHJ are primarily responsible for the higher J_{sc} (26.48 mA cm^{-2} vs. 25.64 mA cm^{-2}) and slightly enhanced FF (76.1% vs. 75.7%) for DQ-doped OPV.⁴⁸ When the concentration of DQ increases to 0.1 wt%, the μ_h/μ_e ratio decreases to 0.28 and the FF reduces to 69.2%. The latter result highlights the importance of doping optimization in boosting the cell's PCE.

Figure 3. (a) J - V characteristics of the PM6:Y6:PC₇₁BM BHJ cells before and after DQ doping (0.01 wt%). The inset figure in (a) is the schematic of the cell architecture used in this work. (b) EQE of the studied OPV cells where $\Delta\text{EQE} = \text{EQE}_{(\text{DQ})} - \text{EQE}_{(\text{w/o})}$. (c) SCLC of hole-only devices and (d) electron-only devices without and with DQ. (e) Bimolecular recombination rate constant (k_{rec}) of OPVs without and with DQ (0.01 wt%).

The carrier mobility analysis provided unambiguous evidence that DQ-doping affects the charge transport within the BHJ. To investigate whether the latter also affects the charge-carrier recombination dynamics within the cells, we performed light intensity transient photovoltage (TPV) and charge-extraction (CE) measurements (**Figure S11c-d**). A charge carrier lifetime (τ) of 3.8 μs is obtained in DQ-doped cells at 200 mW cm^{-2} , which is significantly longer than in pristine cells (2.3 μs), indicating a lower carrier recombination rate in DQ-doped BHJs. Moreover, the carrier density of DQ-doped devices is higher than that of undoped cells at various light intensities. This increased carrier density (n) is consistent with the EPR and Kelvin probe measurements in **Figure 1b-c**. To verify this hypothesis we calculated the bimolecular recombination rate constants (k_{rec}) from the carrier lifetime and charge carrier densities using:⁴⁹

$$k_{\text{rec}} = 1/[(\lambda+1)n\tau] \quad (2)$$

where λ is the recombination order. Evidently, k_{rec} for the DQ-doped cell is lower than that of the pristine cell at all given light densities (**Figure 3e**). Thus, on the basis of the extensive body

of experimental evidence presented so far it becomes clear that DQ doping has a synergistic effect on modifying the optical, electronic and morphological properties of the BHJ, which are ultimately responsible for the reduced bimolecular recombination and the improved cell performance.

Figure 4. (a) J - V characteristics of the PM6:BTP-eC9:PC₇₁BM BHJ cells before and after DQ doping (0.01 wt%). The inset figure in (a) shows the histogram and Gaussian fit of PCEs of the OPV without (black) and with DQ (red). (b) EQE (solid line) and J_{cal} (dashed line) of the OPV cells. (c) A summary of reported PCE values for molecularly doped BHJ OPVs.¹⁷⁻³²

Lastly, we explored the applicability of the DQ-doping strategy to two additional state-of-the-art acceptors namely IT-4F and BTP-eC9 (**Figure 1b**). The acceptor molecules were blended with the PM6 donor polymer to form the binary (PM6:IT-4F)⁵⁰ and ternary (PM6:BTP-eC9:PC₇₁BM)⁷ BHJs (**Figure S12-13** and **Table S7-8**). As summarized in **Table 1**, the introduction of DQ directly into the BHJs is found to consistently enhance the cells' overall PCE when compared to undoped devices. Remarkably, DQ-doped OPVs based on PM6:BTP-eC9:PC₇₁BM yield an impressive maximum uncertified PCE of 18.3%, as a consequence of the increased J_{SC} and improved FF (**Figure 4a** and **Table 1**). This is the highest PCE value reported to date for molecularly-doped BHJ OPVs (**Figure 4c** and **Table S1**).¹⁷⁻³² The enhanced PCE is attributed to the higher values of FF and J_{SC} (**Table 1**), and the increased EQE (**Figure 4b**), in agreement with the observations for PM6:Y6:PC₇₁BM-based cells (**Figure 3a-b**). The statistical distribution of the uncertified PCE values obtained from 20 devices are shown as

insert in **Figure 4a**, while the corresponding J - V curves and performance parameters are presented in **Figure S14** and summarized **Table S9**, respectively. These data demonstrate the reproducibility and reliability of the performance enhancement upon n -doping the BHJs with DQ.

In order to elucidate the origin of the enhanced performance in DQ-doped (0.01 wt%) PM6:BTP-eC9:PC₇₁BM cells, we analysed the pristine and n -doped BHJ layers using AFM (**Figure S15**). Although both films exhibit visible nanofiber-like topographies, these features are more pronounced in the DQ-doped layer. This difference is clearer in the height histogram of **Figure S15g** where a narrowing in the distribution and a shift towards smaller heights, are observed. These results indicate the presence of a smoother BHJ upon DQ-doping in excellent agreement with the findings for PM6:Y6:PC₇₁BM (**Figure 2e**). Furthermore, EPR analysis of the PM6:BTP-eC9:PC₇₁BM BHJs (**Figure S16a**) confirms the n -doping character of DQ in agreement with theoretical predictions based on the materials' energetics (**Figure 1b**). Similar to the PM6:Y6:PC₇₁BM system (**Figure 3**), PM6:BTP-eC9:PC₇₁BM layers containing optimal amounts of DQ exhibit higher absorption coefficient (**Figure S16b**), increased μ_h & μ_e (**Figure S16c-e**), longer carrier lifetimes (**Figure S16f**), higher charge densities (**Figure S16g**), and lower bimolecular recombination rates when deployed in OPVs (**Figure S16h**).

Lastly, we studied the impact of DQ doping on the thermal and operational stability of PM6:BTP-eC9:PC₇₁BM OPV cells. As shown in **Figure S17a**, doped devices exhibit better thermal stability than pristine cells under continuous thermal stressing at 100 °C in a N₂ glove box. Furthermore, maximum power point tracking (MPPT) measurements performed at room temperature, show that the DQ-doped cells are more stable than the pristine OPV. The severe degradation in PCE observed under MPPT conditions is an interesting phenomenon and is most likely attributed to light-induced effects within the active layer.⁵¹ Although preliminary, the thermal and operational stability results show that DQ can improve not only the PCE but also the lifetime of these OPVs.

In conclusion, we reported a convenient method to isolate DQ and investigated its use as n-type dopant for BHJs in high-efficiency OPVs. The shallow HOMO of DQ (-3.53 eV) and DQ^{*+} (-3.95 eV) were shown to generate free polarons and reduce the work function of the host BHJ, while the relatively low surface energy of DQ suggests it is miscible with both the donor and acceptor phases, although further focused work is needed to verify this hypothesis. We demonstrated that the interaction between DQ and the host semiconductor(s) underpins several important observations, including: (i) Increased absorption coefficient of the BHJs, (ii) modified microstructure/morphology, (iii) increased and balanced hole/electron mobilities, (iv) longer carrier lifetimes, (v) increased charge carrier densities, (vi) reduced bimolecular recombination losses. The unique combination of all these attributes led to a consistent enhancement of the PCE in several BHJ systems culminating to the maximum uncertified PCE value of 18.3% obtained for OPVs based on the *n*-doped ternary system PM6:BTP-eC9:PC₇₁BM:DQ(0.01 wt%). Our work highlights DQ as promising dopant for boosting the performance and operational stability of best-in-class OPVs.

ASSOCIATED CONTENT

Supporting Information Available: Fabrication and characterization details of OPVs, methodology for DFT calculations, CV measurements, AFM measurements, TEM measurements, SCLC measurements, contact angle and surface energy characteristics, EPR measurement, GIWAXS measurement, light intensity characterization of OPVs.

Notes

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Supporting Information

A Simple n -Dopant Derived from Diquat Boosts the Efficiency of Organic Solar Cells to 18.3%

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Experimental details

Full chemical names of materials: PM6: Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)], Y6: 2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2,"30":4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile), PC₇₁BM: [6,6]-phenyl-C71-butyric acid methyl ester, and PFN-Br: Poly[9,9-bis(3'-(N,N-dimethyl)-N-ethylammonium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]dibromide.

Dopant solution preparation: To a solution of 1,1'-ethylene-2,2'-bipyridinium dibromide (Diquat Dibromide, 130 mg) from Sigma Aldrich in deionised water (10 ml) was added toluene (12 mL) dropwise in ambient conditions. Sodium borohydride (95 mg, 2.5 mmol) powder was added into the bilayer system and the mixture left to stand. The colourless aqueous layer immediately becomes deep red with the generation of hydrogen gas. After 8 h, the aqueous layer became colourless while the top toluene layer was yellow. The toluene layer was separated and the solvent was removed under vacuum chamber of glove box. The resulting residue was weighed and dissolved in chloroform (CF) or chlorobenzene (CB) in a dry nitrogen glove box (≈ 10 ppm O₂).

Solar Cell Fabrication: PM6, Y6, PC₇₁BM, IT-4F, and BTP-eC9 were purchased from Solarmer Materials Inc. Indium tin oxide (ITO) coated glass substrates (Kintec Company, 10 Ω sq.⁻¹) were cleaned by sequential ultrasonication in dilute Extran 300 detergent solution, deionized water, acetone, and isopropyl alcohol for 10 min each. The substrates were then subjected to a UV-ozone treatment step for 10 min. Next, a thin layer (≈ 40 nm) of PEDOT:PSS was spin-coated onto the UV-treated substrates and then dried on a heating plate at 150 °C for

10 min. The samples were then transferred into a dry nitrogen glove box (≈ 10 ppm O_2). The PM6:Y6:PC₇₁BM (D:A = 1:1:0.2, 15 mg mL⁻¹ in total) was dissolved in CF with chloronaphthalene (CN) (0.5%, v/v). PM6:IT-4F (ratio 1:1, 20 mg mL⁻¹ in CB and added 0.5 vol% DIO). PM6:BTP-eC9:PC₇₁BM (ratio 1:1:0.2, 17 mg mL⁻¹ in CF and added 0.5 vol% DIO). For the doping process, the DQ in CF or CB with certain concentrations (0, 0.01, 0.05, 0.1 mg mL⁻¹) was added directly into BHJ solution, and then the blend solution was stirred over 30 minutes at room temperature. The active solutions were then spun onto PEDOT:PSS layer. A layer of 5 nm of PFN-Br (0.5 mg mL⁻¹ in methanol) was spun from on top of the BHJ layer. Finally, the samples were placed in a thermal evaporator and 100 nm of silver was then thermally evaporated at 5×10^{-6} mbar through a 0.1 cm² pixel area shadow mask.

Device Characterization: UV-vis spectra were recorded on a Cary 5000 instrument in single beam mode in 1 cm quartz cuvettes. *J-V* measurements of solar cells were performed in an N₂ filled glove box using a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5G, with a KG-5 silicon reference cell certified by Newport. EQE was characterized using an EQE system (PV measurement Inc.). Measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of incident photons on the sample was calculated for each wavelength by using a silicon photodiode calibrated by The National Institute of Standards and Technology (NIST). A Bruker AFM was used to image the surface of the various layers in tapping mode.

Cell Stability Measurements: The thermal stability of OPV cells was assessed using intermittent *J-V* measurements performed whilst the device being maintained at constant temperature of 100 °C inside a nitrogen-filled glove box (≈ 10 ppm O_2). The operational stability of the cells was also assessed using maximum power point tracking (MPPT) measurements performed using a perturb and observe algorithm. The MPPT measurements were performed inside a

Lakeshore CRX-4K cryogenic probe station and while the device was illuminated with white light (Thorlabs, MCWHL5).

Cyclic voltammetry measurements: CV measurements were conducted in a saturated solution of anhydrous diquat dibromide in degassed dimethyl formamide with tetrabutylammonium hexafluorophosphate (0.1 M), using a Pt working electrode, a Pt mesh counter electrode, and an Ag/AgCl reference electrode, with the ferrocene redox couple acting as internal reference.

SCLC measurement: The carrier mobilities of the PM6:Y6:PC₇₁BM were determined by fitting the dark current to the space-charge-limited current (SCLC) model. The device structures were glass/ITO/PEDOT:PSS/BHJ/MoO₃/Ag (Hole-only devices) and glass/ITO/ZnO/BHJ/PFN-Br/Ag (Electron-only devices). The electric-field dependent SCLC mobility was estimated

using Equation: $J(V) = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \exp\left(0.89\beta \sqrt{\frac{V-V_{bi}}{L}}\right) \frac{(V-V_{bi})^2}{L^3}$, where μ_0 is zero-field mobility,

L is the film thickness, J is the dark current density, V is the voltage, ϵ_0 is vacuum permittivity, ϵ_r is dielectric constant, and β is field activation factor.

GIWAXS measurements: GIWAXS measurements were performed at the BL11 NCD-SWEET beamline at ALBA Synchrotron Radiation Facility (Spain). The incident X-ray beam energy was 12.4 eV, while incidence angle (α_i) was set between 0.1-0.12°. The scattering patterns were recorded using a Rayonix® LX255-HS area detector, which consists of a pixel array of 1920 × 5760 pixels (H × V) with a pixel size of 44 × 44 μm². Data are expressed as a function of the scattering vector (q), which was calibrated using Cr₂O₃ as standard sample, at a sample to detector distance of 200.5 mm. 2D GIWAXS patterns were corrected as a function of the components of the scattering vector with a Matlab® script designed for this purpose (Aurora Nogales, Edgar Gutiérrez, (2019), 2D Representation of a Wide Angle X Ray Scattering pattern as a function of Q vector components).

TEM measurement: TEM measurements were performed using a FEI Titan 80-300 TEM equipped with an electron monochromator and a Gatan Imaging Filter (GIF) Quantum 966. For

preparing the TEM samples, the active solutions were spun onto PEDOT:PSS layer and then floated in a water bath. The BHJ films were scooped and transfer to a TEM grid and dried inside a vacuum chamber.

EPR measurement: All EPR spectra were recorded using X-band continuous wave Bruker EMX PLUS spectrometer (BrukerBioSpin, Rheinstetten, Germany) equipped with standard resonator for high sensitivity continuous-wave electron paramagnetic resonance and operating at (9.384688) GHz. The low temperature (100 K) spectra were measured using a liquid helium setup with 25 dB microwave attenuation with 5 GHz modulation amplitude and 100 kHz modulation frequency.

Density Functional Theory (DFT) calculation: The HOMO and LUMO were obtained with the DFT code NWChem¹, the B3LYP exchange-correlation (xc) functional²⁻³ and the DZVP orbital basis⁴. Structures were rendered with VESTA.⁵

Light-Intensity Dependence Measurements: Light-intensity dependence measurements were performed with PAIOS instrumentation (Fluxim) (steady-state and transient modes). Transient photo-voltage (TPV) measurements monitor the photovoltage decay upon a small optical perturbation during various constant light-intensity biases and at open-circuit bias condition. Variable light-intensity biases lead to a range of measured V_{OC} values that were used for the analysis. During the measurements a small optical perturbation ($<3\%$ of the V_{OC} , so that $\Delta V_{OC} \ll V_{OC}$) is applied. The photovoltage decay kinetics of all devices follow a mono-exponential decay: $\delta V = A \exp(-t/\tau)$, where t is the time and τ is the charge carrier lifetime. The “charge extraction” (CE) technique was used to measure the charge carrier density n under open-circuit voltage condition. The device is illuminated and kept in open-circuit mode. After light turn-off, the voltage is switched to zero or taken to short-circuit condition to extract the charges. To obtain the number of extracted charges, the current is integrated. The carrier lifetimes follow a power law relationship with charge density: $\tau = \tau_0 n^{-\lambda}$. The bimolecular recombination constant

k_{rec} were then inferred from the carrier lifetimes and densities according to $k_{\text{rec}} = 1/(\lambda+1)/n\tau^2$, where λ is the recombination order. Photo-CELIV measurements (ramp rate 200 V ms⁻¹, delay time: 0 s, offset voltage: 0 V, light-pulse length: 100 μ s) were also performed using PAIOS for different light intensities. The light intensity is given in the maximum power of the LED source (100% $\approx$ 200 mW cm⁻²).

Table S1. Summary of performance parameters (J_{sc} , FF, and PCE) of OPVs with different n-type and p-type dopants incorporated in the BHJ.

Type	Dopant	Dopant Amount	Active layer	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	Reference
N-type	Diquat (DQ)	0.01 wt%	PM6:BTP-eC9	26.9	79.4	18.3	This work
	w/o	/	:PC ₇₁ BM	26.2	75.7	17.4	
	Benzyl Viologen	0.004 wt%	PM6:Y6:PC ₇₁ BM	26.3	77.0	17.1	6
	w/o	/		25.7	75.0	16.3	
	Benzyl Viologen	0.04 wt%	PM6:BTP-CO-4Cl	25.76	76.5	16.77	7
	w/o	/		25.24	73.2	15.63	
	N-DMBI	0.01mg/mL	PTB7-Th:FOIC	23.08	65.8	11.21	8
	w/o	/		21.68	62.7	10.14	
	TBAI	0.04 wt %	PBDB-T:N2200	12.45	65.3	7.00	9
	w/o	/		11.54	58.4	5.81	
	N-DMBI	0.3 wt %	PCE-10:N2200	10.4	52.3	4.4	10
	w/o	/		9.4	46.5	3.5	
	BCF	0.01 wt%	PM6:Y6	25.96	73.47	16.0	11
	w/o	/		25.48	72.34	15.4	
P-type	BCF	0.001mg/mL	PTB7-Th:FOIC	22.77	65.5	10.94	8
	w/o	/		21.68	62.7	10.14	
	BCF	0.1 wt %	PBDB-T:ITIC	15.90	66.8	10.03	12
	w/o	/		15.41	64.5	9.52	
	BCF	0.05 wt%	PCE10:PC ₇₁ BM	17.50	68.6	9.6	13
	w/o	/		16.56	67.7	8.9	
	BCF	Solvent vapor doping	PCE10:PC ₇₁ BM	17.29	65.6	9.4	14
	w/o	/		16.38	69.0	8.6	
	F4-TCNQ	0.02 mg/ml	FATZ:IT-M	18.19	70.41	12.22	15
	w/o	/		17.80	68.69	11.89	
	F4-TCNQ	0.1 wt %	PBDB-T:ITIC:PC ₇₁ BM	16.12	70.0	10.08	16
	w/o	/		15.10	67.0	8.86	
	F4-TCNQ	0.01 wt %		17.39	61.8	8.6	17

w/o	/	PBDTTT-EFT:PC ₇₁ BM	17.11	55.2	7.6	
F4-TCNQ	0.4 wt%	PCDTBT:PC ₇₁ BM	14.0	63.0	7.94	18
w/o	/		11.0	67.0	6.41	
F4-TCNQ	0.5 wt%	P3HT:PC ₆₀ BM	9.89	68.0	4.02	19
w/o	/		8.96	63.0	3.45	
F4-TCNQ	5x10 ⁻⁶ mol%	P3HT:PC ₆₀ BM	9.83	72.0	4.06	20
w/o	/		9.42	70.0	3.68	
F4-TCNQ	0.5 wt%	PCPDTBT:PC ₆₀ BM	10.31	56.0	3.62	21
w/o	/		9.42	55.4	3.28

Figure S1. Cyclic voltammetry curve for DQ (calibrated by Fc/Fc⁺ redox couple).

Table S2. LUMO and HOMO of various materials evaluated by CV measurement and DFT calculations.

Material	CV ^a		DFT	
	LUMO [eV]	HOMO [eV]	LUMO [eV]	HOMO [eV]
DQ	/	-3.53	-0.91	-3.74
DQ ⁺	/	-3.95	/	-4.24
PM6	-3.64	-5.45	-2.91	-5.25
Y6	-4.10	-5.65	-3.91	-5.92
PC ₇₁ BM	-3.91	-5.87	-3.55	-6.05
IT-4F	-4.14	-5.66	-3.84	-5.90
BTP-eC9	-4.05	-5.64	-3.89	-5.87

^aThe Data of PM6, Y6, PC₇₁BM, IT-4F, BTP-eC9 are from the previous literatures.²²⁻²⁶

Figure S2. (a)-(f) Molecular structure of DQ, PM6, Y6, PC₇₁BM, IT-4F, and BTP-eC9 investigated in this study, and their HOMO and LUMO calculated via DFT. (C: gray, H: white, S: yellow, O: red, N: blue, F: light green spheres).

Figure S3. Relative EPR spectra of (a) Y6 and (b) PC₇₁BM without and with DQ (0.01 wt%).

Figure S4. Work function of (a) Y6, (b) PC₇₁BM, and (c) PM6:Y6:PC₇₁BM without and with DQ (0.01 wt%) obtained from Kelvin Probe at 200 different positions.

Table S3. Statistical work function on various materials films obtained from Kelvin Probe.

Solid surface		Work function [eV]
Y6	w/o	-4.617±0.004
	DQ ^a	-4.490±0.003
PC ₇₁ BM	w/o	-4.519±0.004
	DQ	-4.418±0.005
PM6:Y6:PC ₇₁ BM	w/o	-4.575±0.005
	DQ	-4.467±0.006

^aThe amount of DQ is 0.01 wt%.

Figure S5. Absorption coefficient of (a) PM6, (b) Y6, and (c) PC₇₁BM blend films without and with DQ (0.01 wt%).

Figure S6. Photographs of water (top row) and formamide (bottom row) droplets in contact with the various surfaces. ^aThe amount of DQ is 0.01 wt%.

Table S4. Contact angles and surface energy various materials.

Solid surface	Water contact angle ^a	Formamide contact angle	Surface energy [mN m ⁻¹] ^b
DQ	77.5±1.5°	74.5±1.1°	26.9±1.8
PM6	110.7±0.4°	95.4±0.4°	13.2±1.4
Y6	96.5±0.3°	71.1±0.4°	31.0±1.3
PC ₇₁ BM	100.8±0.5°	63.7±0.4°	36.1±1.4
BHJ (w/o)	103.3±0.4°	83.5±0.4°	20.9±1.2
BHJ (DQ) ^c	108.1±0.5°	89.0±0.4°	17.9±1.1

^aAverage angle of 5 films.

^bSurface energy was converted based on OWRK method.

^cThe amount of DQ is 0.01 wt%.

Figure S7. Two-dimensional GIWAXS patterns of (a) PM6, (b) Y6, and (c) PC₇₁BM films. (d)-(f) The corresponding in-plane and out-of-plane line cuts of the GIWAXS patterns.

Figure S8. AFM analysis of individual materials namely the polymer donor PM6 and the acceptor molecules Y6 and PC₇₁BM. (a-c) Topography images, phase images and height histograms for PM6 layers without and with DQ. (d-f) Topography images, phase images and height histograms for Y6 layers without and with DQ. (g-i) Topography images, phase images and height histograms for PC₇₁BM layers without and with DQ. ^aThe amount of DQ is 0.01 wt%.

Figure S9. TEM images of PM6:Y6:PC₇₁BM BHJ: (a) without DQ, (b) with 0.01 wt% DQ, and (c) with 0.1 wt% DQ.

Figure S10. (a) J - V curves and (b) EQE curves of OPVs based on PM6:Y6:PC₇₁BM doped with different concentration of DQ.

Table S5. Photovoltaic parameters of PM6:Y6:PC₇₁BM devices with different weight ratios of Diquat (DQ) dopant under illumination of AM 1.5G (100 mW cm⁻²).

Concentration [wt%]	Concentration [mol%]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	J_{cal} [mA cm ⁻²]	FF [%]	PCE [%] ^a
w/o	w/o	0.860	25.64	24.89	75.7	16.7 (16.2±0.4)
0.005	1.4	0.859	26.16	/	76.4	17.2 (16.7±0.3)
0.01	2.9	0.862	26.48	26.03	76.1	17.4 (17.0±0.2)
0.05	14.3	0.861	26.70	/	72.4	16.6 (16.2±0.3)
0.1	28.68	0.855	26.81	26.38	69.2	15.9 (15.5±0.2)

^aAverage PCE of 20 devices.

Table S6. Summary of hole (μ_h) and electron (μ_e) mobilities of PM6:Y6:PC₇₁BM without and with DQ obtained from SCLC model, and the charge carrier mobility (μ) obtained from photo-CELIV measurements.

Type	μ_h [$\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹]	μ_e [$\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹]	μ_h/μ_e	μ [$\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹]
w/o	4.4 (4.0±0.3)	3.5 (3.1±0.2)	1.26	3.7 (3.2±0.4)
0.01 wt% DQ	6.3 (6.2±0.2)	6.7 (6.2±0.3)	0.94	5.8 (5.1±0.5)
0.1 wt% DQ	2.0 (1.7±0.2)	6.9 (6.5±0.2)	0.28	/

Figure S11. (a) SCLC of hole-only and electron-only devices with 0.1 wt% DQ (b) Photo-CELIV of OPV based PM6:Y6:PC₇₁BM without and with DQ (0.01 wt% DQ). Light intensity dependence of (c) charge carrier lifetime, and (d) carrier density measured for the same cells.

Figure S12. (a) J - V curves of OPV cells based on PM6:IT-4F doped with different concentration of DQ. (b) EQE (solid line) and J_{cal} (dashed line) of the OPV cells.

Table S7. Photovoltaic parameters of PM6:IT-4F devices with different concentration of DQ under illumination of AM 1.5G (100 mW cm⁻²).

Concentration [wt %]	Concentration [mol %]	V_{OC} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%] ^a
w/o	w/o	0.856	20.34	74.9	13.0 (12.8±0.1)
0.004	1.1	0.855	21.42	70.6	12.9 (12.5±0.3)
0.02	5.7	0.862	21.98	75.7	14.3 (14.0±0.2)
0.04	11.4	0.860	21.94	73.1	13.8 (13.6±0.2)
0.2	57.2	0.846	22.46	63.9	12.1 (11.8±0.2)

^aAverage PCE of 20 devices.

Figure S13. *J-V* curves of OPVs based on PM6:BTP-eC9:PC₇₁BM doped with different concentration of DQ.

Table S8. Photovoltaic parameters of PM6:BTP-eC9:PC₇₁BM devices with different concentration ratios of DQ under illumination of AM 1.5G (100 mW cm⁻²).

Concentration [wt %]	Concentration [mol %]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%] ^a
w/o	w/o	0.855	26.21	77.7	17.4 (17.1±0.2)
0.005	0.7	0.855	26.67	79.1	18.0 (17.7±0.2)
0.01	1.4	0.856	26.93	79.4	18.3 (18.0±0.2)
0.02	2.7	0.856	27.17	76.2	17.7 (17.4±0.3)

^aAverage PCE of 20 devices.

Figure S14. *J-V* curves of 20 devices based on PM6:BTP-eC9:PC₇₁BM doped with 0.01 wt% of DQ.

Table S9. Summary of operating parameters of 20 OPV cells based on PM6:BTP-eC9:PC₇₁BM doped with 0.01 wt% of DQ, measured under illumination of AM 1.5G (100 mW/cm²).

Number	V _{OC} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]
1	0.856	26.93	79.4	18.3
2	0.857	26.99	77.5	17.9
3	0.857	26.86	77.2	17.8
4	0.860	26.90	77.9	18.0
5	0.858	27.10	77.2	18.0
6	0.855	26.68	79.7	18.2
7	0.857	26.97	77.5	17.9
8	0.855	26.83	79.0	18.1
9	0.855	26.80	79.8	18.3
10	0.856	26.77	78.9	18.1
11	0.854	27.09	78.6	18.2
12	0.850	26.72	78.3	17.8
13	0.855	26.86	78.4	18.0
14	0.851	26.58	79.7	18.0
15	0.853	26.69	78.9	18.0
16	0.855	26.89	77.8	17.9
17	0.852	26.81	77.7	17.7
18	0.855	26.69	78.9	18.0
19	0.856	26.66	78.9	18.0
20	0.854	26.94	78.4	18.0

Figure S15. (a) AFM topography image of PM6:BTP-eC9:PC₇₁BM without dopant. (b) A higher resolution image of the highlighted region in (a) and the corresponding line scans (c). (d-f) Lower and higher magnification AFM images and corresponding line scans for PM6:BTP-eC9:PC₇₁BM layer with 0.01% DQ. (g) Height histograms extracted from the pristine and DQ-doped AFM images in (a) and (d).

Figure S16. (a) Relative EPR spectra of PM6:BTP-eC9:PC₇₁BM films without and with DQ. (b) Absorption coefficient of PM6:Y6:PC₇₁BM blend films without and with DQ. J-V of (c) hole-only devices and (d) electron-only devices without and with DQ. (e) Photo-CELIV of OPV based PM6:BTP-eC9:PC₇₁BM without and with DQ. (f) Light intensity dependence of charge carrier lifetime and (g) carrier density calculated from the same OPV cells. (h) Bimolecular recombination rate constant (k_{rec}) of OPVs without and with DQ. The amount of DQ used is 0.01 wt%.

Figure S17. Evolution of PCE of PM6:BTP-eC9:PC₇₁BM-based BHJ OPVs without and with DQ (0.01 wt%): (a) PCE vs. time for OPV cell maintained at 100 °C, and (b) under maximum power point tracking (MPPT) testing.

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