Black phosphorus quantum dots for boosting light harvesting in organic photovoltaics

Shenghua Liu [a], Shenghuang Lin [a], Peng You [a], Charles Surya [b], Shu Ping Lau [a], Feng Yan [a]

Abstract: *Although organic photovoltaics (OPVs) have been investigated for more than 2 decades, the power conversion efficiencies of OPVs are much lower than those of inorganic or perovskite solar cells. One effective approach to improve the efficiency of OPVs is to introduce additives to enhance light harvesting as well as charge transportation in the devices. Here, black phosphorus quantum dots (BPQDs) are introduced in OPVs as an additive for the first time. By adding BPQDs with the weight percentage of only 0.055 % relative to polymer donors in the OPVs, the device efficiencies can be dramatically improved for more than 10%. It is worth noting that the weight percentage is much lower than those of any other additives used in OPVs before, which is mainly due to the 2-dimentional nature as well as the strong broadband light absorption and scattering of the BPQDs. This work paves a way for using 2-dimentional quantum dots in OPVs as a cost-effective approach to enhance device efficiencies.*

Quantum dots (QDs) with size-dependent band structures have demonstrated numerous applications in optoelectronic devices, including photodetectors, light-emitting diodes and solar cells[1-5] Black phosphorus QDs (BPQDs) have attracted much attention recently because of their 2 dimensional (2D) character, unique optical properties and high carrier mobilities[6-8]. Thanks to their broadband light absorption, BPQDs have been used as biological fluorescence agents in HeLa cell imaging[9]. Due to their excellent near-infrared (NIR) photothermal effect as well as high biocompatibility, they have been successfully used in cancer photothermal therapy[6]. In addition, they have been utilized in ultrafast laser for their remarkable nonlinear optical characteristics[10]. Another fascinating property of BPQDs is the high absorption coefficient in a broad wavelength region[6,11,12], making them promising for photovoltaic applications, which, however, has not been reported until now.

In the past two decades, rapid progress on the power conversion efficiencies (PCEs) of organic photovoltaics (OPVs) has been witnessed [13-15]. Due to relatively low carrier mobilities of organic semiconductors, the organic active layers in OPVs normally have thin thicknesses (~100 nm) to ensure efficient carrier transportation, which leads to relatively poor solar light absorption of OPVs in comparison with inorganic counterparts[16,17]. To overcome this drawback, one approach is to introduce additives such as plasmonic nanoparticles[18,19], high mobility nanotubes[20] and other conjugated polymers[21] in OPVs to enhance light absorption as well as carrier transportation in the devices. In comparison with organic semiconductors, some 2-D materials, such as black phosphorus (BP) and MoS_2, have shown much higher light absorption coefficient at the same thickness[12, 22, 23]. Theoretical calculations demonstrate that one or two -layer BP films can absorb ~10% light in visible region, which have the thicknesses of only around 1 nm[12]. Therefore, the incorporation of BP in OPVs can enhance the light absorption of the devices with little influence on the active layer thickness. In a ternary OPV, the band energy levels of an additive are critical to device performance and a cascaded band structure is needed in the active layer to enable efficient separation of electrons and holes[21]. Because the band structure of BPQDs can be conveniently tuned by changing their size and thickness to meet the above requirement, we consider that BPQDs would be an ideal additive for OPVs.

In this paper, we report for the first time the application of BPQDs in OPVs to boost light harvesting. We synthesized BPQDs with various sizes and incorporated them into the active layers of two representative OPVs based on polythieno[3,4-b]-thiophene:benzodithiophene:[6,6]-phenylC_{71}-butyric acid methyl ester (PTB7:PC_{71}BM) or poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b; 4,5-b0]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl]:PC_{71}BM (PBDTTT-EFT:PC_{71}BM)[24,25]. Significant enhancement up to 10% was observed in the PCEs of the OPVs prepared at optimum conditions, mainly due to the enhanced light harvesting of the devices. It is notable that the optimum weight percentage of BPQDs relative to the organic donor (PTB7 or PBDTTT-EFT) in the devices is only about 0.055%, which is much lower than the amount of any other additives used in OPVs before. The astonishing effect can be attributed to the strong light absorption and scattering as well as the 2D nature of the BPQDs. This work paves a way for using novel 2D QDs in OPVs in the future.

BPQDs were prepared by probe sonication with BP crystals in N-methyl-2-pyrrolidone (NMP) solution, which is a convenient technique used to exfoliate many 2D layered materials[26-28]. Three different sizes of BPQDs with the same concentration in NMP were synthesized by controlling the centrifugation rates of the precursor. Figure 1a shows the Raman spectra of bulk BP and BPQDs. For BPQDs, three featured peaks can be observed, representing one out-of-plane phonon mode (A^1_g) located at 361.5 cm^{-1} and two in-plane modes, B_{2g} and A^2_g, located at 438.5 and 466.1 cm^{-1}, respectively. For bulk BP, the three prominent peaks are presented at 360.5, 437.2 and 464.7 cm^{-1}. So the A^1_g, B_{2g} and A^2_g modes of the BPQDs are red-shifted by approximate 1, 1.3 and 1.4 cm^{-1}, respectively, being consistent with the values reported before[6, 29]. Figure 1b shows the TEM image of a class

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of well distributed BPQDs (Diameter: ~4.5 nm) with rather uniform sizes. The BPQD concentration in NMP was determined to be ~0.55 mg/ml by inductively coupled plasma with atomic emission spectroscopy (ICP-AES, 7000DV, PerkinElmer). Figure 1c-e show the TEM images of BPQDs with average sizes of 3, 4.5 and 6 nm, respectively. The structural features of the BPQDs can be found in high-resolution TEM (HRTEM) images in the insets. The lattice fringe of 0.18-0.19 nm can be assigned to the (121) plane of the BP crystal[30]. As shown in Figure 1f-h, over 160 samples were measured to get the diameter distribution of BPQDs in each group and the corresponding average diameters of BPQDs are 3.00±0.82 nm, 4.50±0.88nm and 6.00±0.97nm, respectively. According to the statistical AFM analysis of 100 BPQDs, the corresponding thicknesses of the BPQDs are mainly distributed at 1.9±0.9 nm, 2.4±1.3 nm, and 2.8±1.1 nm, as shown in Figure 1i-k.

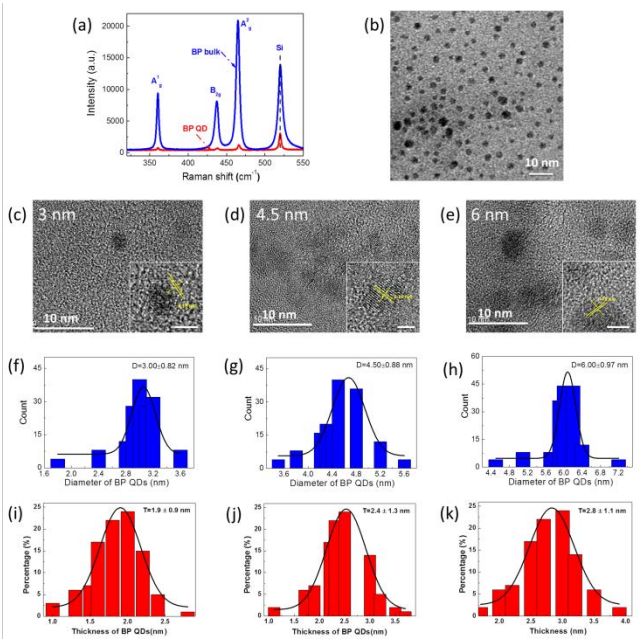

Figure 1. (a) Raman spectra of bulk BP (bule line) and BPQDs (red line). (b) TEM image of BPQDs with average diameter of 4.50±0.88 nm. TEM images of individual BPQDs with different sizes of (c) 3.00±0.82 nm (d) 4.50±0.88 nm (e) 6.00±0.97 nm, Inset: high resolution TEM images of the corresponding BPQDs, Scale bar = 2 nm. (f)-(h) Statistical analysis of the lateral sizes of 160 BPQDs measured from the corresponding TEM images and (i)-(k) the corresponding thickness distribution of the BPQDs measured from AFM images.

Ultraviolet (UV)–visible absorption spectra of BPQDs with different sizes (D=3, 4.5, 6 nm) in NMP solvent were characterized. As shown in Figure 2a, the BPQDs can absorb light in the wavelength region from UV to ~750nm, which covers the absorption region of the OPVs to be studied. With the decrease of the BPQD size, the light absorption curve shifts to a shorter wavelength region due to the increase of the average bandgap of the QDs induced by quantum confinement. We find that the control sample of BP flakes (size: ~60 nm) shows a flatter absorption spectrum because of the smaller bandgap (See supporting information, Figure S1).

The photoluminescence (PL) spectra of BPQDs with various sizes are shown in Figure 2b. A typical broad PL peak located at ~600 nm can be observed for each sample due to the broad distribution of BPQD sizes. For the three samples, the PL intensity increases with the increase of size, which is consistent with the effect of particle size on PL spectra reported before[31]. According to the PL peak position, we can estimate the average bandgap of BPQDs to be 2.0 eV. Assuming the band levels of BPQDs expended for the same magnitude due to quantum confinement, we can estimate the onset of the valence band and the bottom level of the conduction band of the BPQDs to be at 5.32 eV and 3.32 eV[27], respectively.

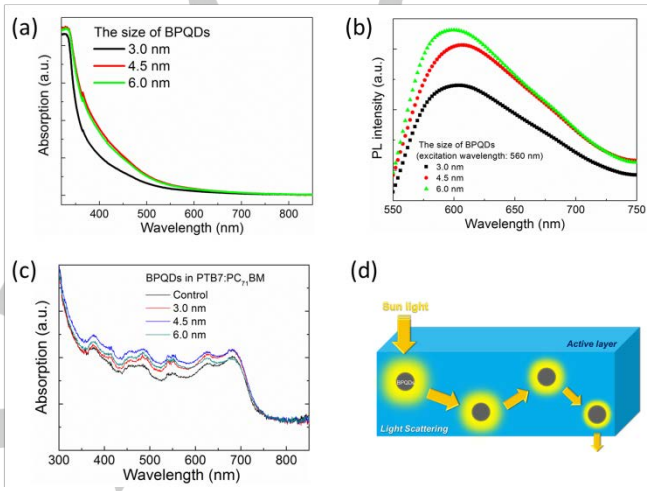

Figure 2. (a) UV-visible absorption and (b) PL spectra of different sizes of BPQDs in NMP solutions. All samples have the same concentration of BPQDs in the solutions. (c) UV-visible absorption of PTB7:$PC_{71}BM$ layer with the introduction of BPQDs of different sizes. The addition amounts for all samples are 1 vol.%. (d) Schematic diagram of light absorption and scattering by BPQDs in an organic layer.

OPVs with the device structure shown in Figure 3a were fabricated by solution process on indium tin oxide (ITO) glass substrates[19]. First, we fabricated OPVs based on PTB7:$PC_{71}BM$ with the addition of BPQDs (average size: D=4.5 nm) for different concentrations. Control devices without BPQDs were also prepared under the same preparation conditions. Figure 3b shows the energy diagram of the device with BPQDs. All energy levels of PTB7:$PC_{71}BM$ were chosen from literature[21]. Cascaded band structure can be formed in the ternary device, which is favorable for efficient carrier separation and can prohibit carrier recombination in the devices[21].

Figure 3c shows the current density-voltage (J-V) characteristics of the OPVs added with BPQDs of different concentrations. The additions of 0.5, 1.0, 3.0 vol.% of BPQD solution in the precursors of the OPVs correspond to the weight percentages of only 0.0275, 0.055 and 0.165% for BPQDs relative to PTB7 in the devices, respectively. Detailed photovoltaic parameters, including open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), PCE and PCE enhancement, were summarized in Tables S1 in the supplementary information. The OPVs with 1.0 vol.% addition of BPQD solution show the highest average PCE of 8.6%, which is relatively increased for 11.7% in

comparison with control devices. The increased PCE is mainly due to the improved J_{sc} by the BPQDs while the V_{oc} and FFs of the devices have little improvements. Control experiments of adding 0.5 - 3 vol.% pure NMP solvent exhibit obvious decreases of average PCEs (See supporting information, Figure S2 and Table S1), indicating that the above performance enhancement is not due to the addition of NMP solvent. External quantum efficiencies (EQEs) of the OPVs were subsequently measured to better illuminate the performance enhancement of the devices. As shown in Figure 3d, EQE shows the maximum value when the addition concentration of BPQDs is 1 vol.%. For 3 vol.% addition level, the decreased EQE is presumably due to the negative effect of NMP and the aggregation of BPQDs that can induce carrier recombination in the active layer. It is interesting to note that the optimum addition level of BPQDs is only about 0.055% relative to the weight of PTB7, which is much lower than the weight percentages of any other additives used in OPVs before.[21] In addition, we find that the optimum addition level is also 1 vol. % for 3nm and 6nm BPQDs (See supporting information, Figure S2 and Table S2 and S3).

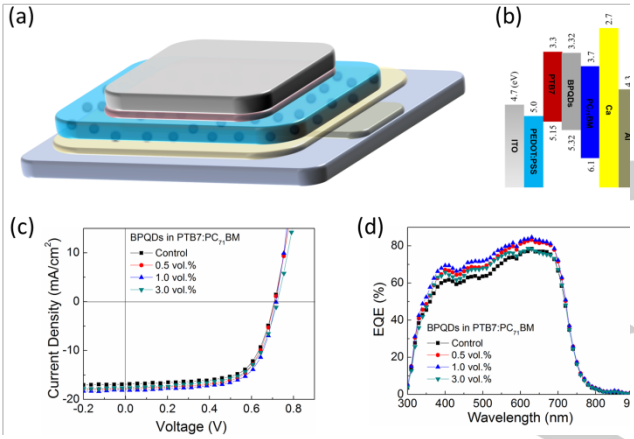

Figure 3. (a) Device architecture of the OPVs with the incorporation of BPQDs in bulk heterojunction active layer. (b) Band structure of the BPQD-based OPVs. (c) Current density-voltage (J-V) and (d) EQE characteristics of the best control device and the devices with various addition levels (0.5, 1.0, 3.0 vol.%) of BPQDs (size: 4.5 nm).

Next, we investigated the size effect of BPQDs on OPV performance. Figure 4a shows the J-V curves of the OPVs with BPQDs blended in the active layers prepared at the same condition. V_{oc} and FF of all the devices are very similar, while J_{sc} and PCE of the devices are obviously improved in comparison with the control device. The devices incorporated with 4.5 nm BPQDs exhibit the highest improvement of PCE and the relative enhancement is about 8.3%. All of the photovoltaic parameters of the devices are summarized in Table S4 in the supplementary information. Figure 4b shows the EQEs of the devices, which are consistent with the enhanced J_{sc} of the devices. The EQEs of the devices are dramatically improved by the BPQDs in the whole absorption region and the highest EQE value is observed when 4.5 nm BPQDs were introduced.

To shed light on the improvement of J_{sc} of the devices, we characterized UV-visible absorption spectrum of PTB7:$PC_{71}BM$ films with the addition of BPQDs with different sizes, as shown in Figure 2c. The thicknesses of the films were kept to be identical (~80 nm). Significant improvement of the light absorption of the active layer induced by the added BPQDs can be observed in the whole wavelength range between 300-800 nm, which can be attributed to broadband light absorption as well as light scattering induced by the BPQDs in the active layers. The incorporation of 4.5 nm BPQDs results in the most remarkable increase of light absorption, which is consistent with the maximum enhancement of J_{sc} and EQE of the devices prepared at the same condition. Besides light absorption, light scattering induced by BPQDs in OPVs (Figure 2d) can enhance light harvesting as well, which has also been observed in OPVs with the incorporation of other nanoparticles[19, 32]. Since the diameter of the BPQDs *D* is much smaller than the light wavelength *λ*, Rayleigh scattering induced by BPQDs occurs in the devices. According to Rayleigh approximation[33], the scattering cross section of a BPQD is proportional to $D^6\lambda^{-4}$. So BPQDs with bigger sizes can lead to stronger light scattering. However, the number of BPQDs in the active layer decreases with the increase of particle size. Therefore, the highest light absorption induced by 4.5 nm BPQDs is the compromise of all of the factors.

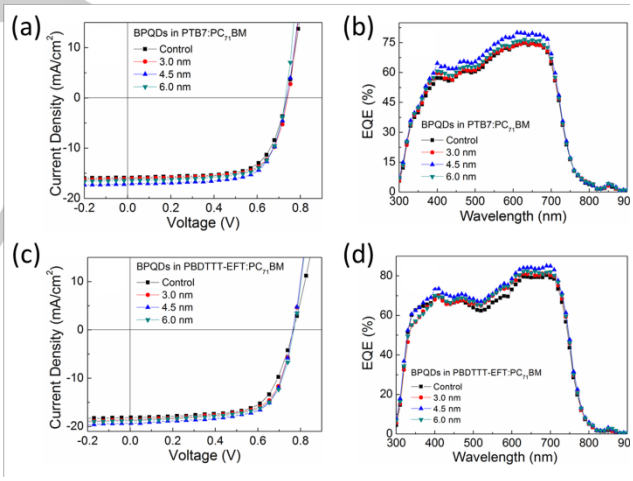

Figure 4. (a) J-V and (b) EQE curves of the best control device and the OPVs based on PTB7:$PC_{71}BM$ added with 1 vol.% BPQDs with various sizes (3, 4.5, 6 nm). (c) J-V and (d) EQE plots of the best control device and the OPVs based on PBDTTT-EFT:$PC_{71}BM$ with the addition of 1 vol.% BPQDs with various sizes(size: 3, 4.5, 6 nm).

To test the general effect of BPQDs in OPVs, another type of devices based on PBDTTT-EFT:$PC_{71}BM$ were fabricated with the addition of three different BPQDs under the same preparation conditions[25]. Figure 4c and 4d show the J-V and EQE curves of the OPVs added with different size BPQDs in active layers, respectively. Detailed photovoltaic parameters of the devices including average V_{oc}, J_{sc}, FF, PCE and PCE enhancement are summarized in Table S5 in the supplementary information. It is notable that, with only 1 vol.% addition in the active layers, the

average PCEs of devices doped with BPQDs of the sizes of 3, 4.5, 6 nm are 9.69%, 9.95%, and 9.85%, respectively, demonstrating the maximum relative PCE enhancement of 10.7% in comparison with control devices. The PCE enhancement is mainly attributed to the increase of J_{sc}, which is similar to the case of PTB7:$PC_{71}BM$ -based OPVs. Similarly, BPQDs can induce obvious improvement of EQEs in the whole absorption region of the devices due to the enhancement of light harvesting.

To characterize the influence of BPQDs on carrier transport in the active layers of OPVs, hole-only devices with the device structure of ITO/PEDOT:PSS/blend layer/Au and electron-only devices with the structure of ITO/ZnO/blend layer/Al were prepared. Electron and hole currents versus bias voltages were measured in the devices with the addition of different size BPQDs. The electron and hole mobilities were extracted by fitting the curves with the formula for space charge limited currents (SCLCs)[21, 34]. We find that the average electron and hole mobilities exhibit little changes in comparison with the control devices without BPQDs (See supporting information, Figure S3). Therefore, the addition of BPQDs has little effect on carrier transportation in organic active layers, presumably due to the fact that small BPQDs cannot form continuous conduction paths in the organic layers.

We also added BP flakes with two different average sizes of ~60 nm and ~150 nm in OPVs based on PBDTTT-EFT:$PC_{71}BM$ (See supporting information, Figure S4 and Table S6). The addition of 60 nm BP flakes has little influence on the device performance while 150 nm flakes can slightly decrease the PCEs of the devices. The PL spectrum of the 60 nm BP flakes shows the PL peak at the wavelength of ~810 nm (See supporting information, Figure S5), corresponding to the bandgap of 1.53 eV. So the onset of the valence band and the bottom level of the conduction band for the BP flakes are estimated to be 5.10 eV and 3.57 eV, respectively. Since the HOMO level of PBDTTT-EFT is 5.24 eV, the addition of BP flakes cannot form a cascaded band structure in the active layer, which is not favorable for charge separation in the device. In addition, we find that the BP flakes do not improve carrier mobilities in the devices (See supporting information, Figure S6). Therefore, it is reasonable to find that the BP flakes cannot improve the PCEs of the OPVs. These results further confirm that the size of the BPQDs is critical to the device performance when they are incorporated in OPVs.

In summary, we introduced solution prepared BPQDs into OPVs to boost the light harvesting of the devices for the first time. Dramatic improvement of PCEs was obtained when BPQDs were added in active layers with the weight percentage of only 0.055%, which is mainly attributed to the strong light absorption and scattering of the BPQDs in a broad wavelength region. In comparison with any other additives used in OPVs, BPQDs have a much lower addition level that can substantially improve device efficiencies for more than 10% (See supporting information, Table S7). Therefore, this is a cost-effective technology for improving the efficiencies of OPVs. This work opens a window for integrating various novel 2D materials in solution processed new generation photovoltaic devices.

Acknowledgements

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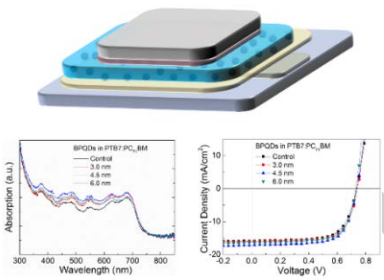
Layout 1:

COMMUNICATION

The power conversion efficiencies of organic photovoltaics are dramatically improved by introducing black phosphorus quantum dots (BPQDs) for only 0.055 % in weight relative to donor polymers due to the boosted light harvesting of the devices. The fascinating effect was attributed to the strong light absorption as well as the 2-dimensional character of the BPQDs. A pronounced size effect of BPQDs on the performance enhancement is observed.



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