

Revealing the Unusual Efficiency Enhancement of Organic Solar Cells with Polymer-Donor-Treated Cathode Contacts

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Electronic Supplementary Information

Abstract The metal oxides with low trap density of states as the electron transport layer are crucial for the high performance of the organic solar cells (OSCs). It is universally acknowledged that modifying n-type metal oxide contacts with polymer donors will harm the carrier extraction on account of the mismatched energy level. However, we find that modifying interlayer consisting of the alcohol amines with some polymer donor additive can unusually enhance the performance of the OSCs. Compared with triethanolamine (TEA) passivated ZnO, TEA:polymer donor treated ZnO shows lower trap density and enhances electron mobility resulting in higher current density in OSC devices. Here, we reveal that the enhanced oxygen-defect passivation ability of TEA with polymer additive is attributed to the enhanced negative electrostatic potential of TEA owing to the hydrogen bond formation between the polymer and the hydroxyl group in TEA. This strategy that enhancing the negative electrostatic potential of the passivators for improving oxygen defect passivation can be extended to other types of organic electronic devices.

Keywords Organic solar cell; Electron transport layer; Trap density; Passivation; Hydrogen bond

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INTRODUCTION

As a consequence of the development of the electron acceptors, organic solar cells (OSCs) have made tremendous progress in the past few years,^[1–13] the power conversion efficiencies (PCEs) of which have exceeded 18% for single-junction devices.^[4,8,14–23] For the typical OSCs, the electron donors and acceptors are sandwiched between two electrodes with their corresponding transport layers which play a vital significance in modulating the work function (WF) of electrodes, promoting the charge extraction and collection process.^[24–27] Consequently, great efforts have been made to modify the interface layer for improving the performance of OSCs.^[24,28–30] Metal oxides which have many advantages such as high transmittance, high conductivity and excellent photostability, have been widely used in organic electronic devices, such as the electron transport layer (ETL) in photovoltaic devices.^[31–35]

However, due to the “Fermi level pinning effect,” severe charge barriers exist at the interface between the metal oxide ETL and organic semiconductors, resulting in inefficient charge transfer and serious carrier accumulation.^[35–37] Oxygen

vacancies, as the main defects on the surface of the metal oxide contacts, forming tremendous trap states which will greatly limit the performance, need to be further modified.^[38–43] The oxygen vacancies as a Lewis acid that contain an empty orbital can result in the formation of net positive charges, which might create favorable conditions for coordination or band formation with some electron-rich functional groups, such as hydroxyl, amino and carbonyl.^[33,44–46] Consequently, many strategies have been put forward to passivate the defect of the surface and tune the work function of the metal oxides for better Ohmic contact, which have achieved brilliant progress.^[47–50] For instance, the n-type fullerene acceptor and the materials with electron-rich groups are also commonly used to modify the ZnO interface in OSCs, as well as perovskite solar cells.^[37,46,51]

One unanticipated finding in this study is that the OSCs with polymer-donor-treated cathode contacts exhibit improved efficiency. We demonstrate that the hydrogen bond formed between the polymer and the hydroxyl group in the triethanolamine (TEA), leads to the improved negative electrostatic potential (ESP) of oxygen atoms of TEA, which contributes to the enhancement of the defect passivation of oxygen vacancies, thus improving the performance of the OSCs. This strategy gives us another perspective that enhancing the negative ESP of the passivators for improving oxygen defect passivation, which may be extended to other types of electronic devices.

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EXPERIMENTAL

The experimental section is detailed in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Photovoltaic Performance

Interface engineering is of great importance for the enhancement efficiency of the OSCs. Among various methods

for modifying the cathode interlayer of OSCs, we found one unanticipated efficiency enhancement in devices with polymer-donor-treated ZnO layer. The OSCs with the inverted structure of indium tin oxide (ITO)/ZnO/modifying layer/active layer/MoO₃/Ag were used in this study. Here, we use TEA with and without several polymer donors, including PM6, PTB7-Th, J61, P3HT, or typical electron acceptors like PC₇₁BM and Y6, to spin-coat on ZnO for the OSC fabrication, the relevant chemical structures, and the schematic diagram were shown in Fig. 1(a). The energy levels of the materials we used in this study are

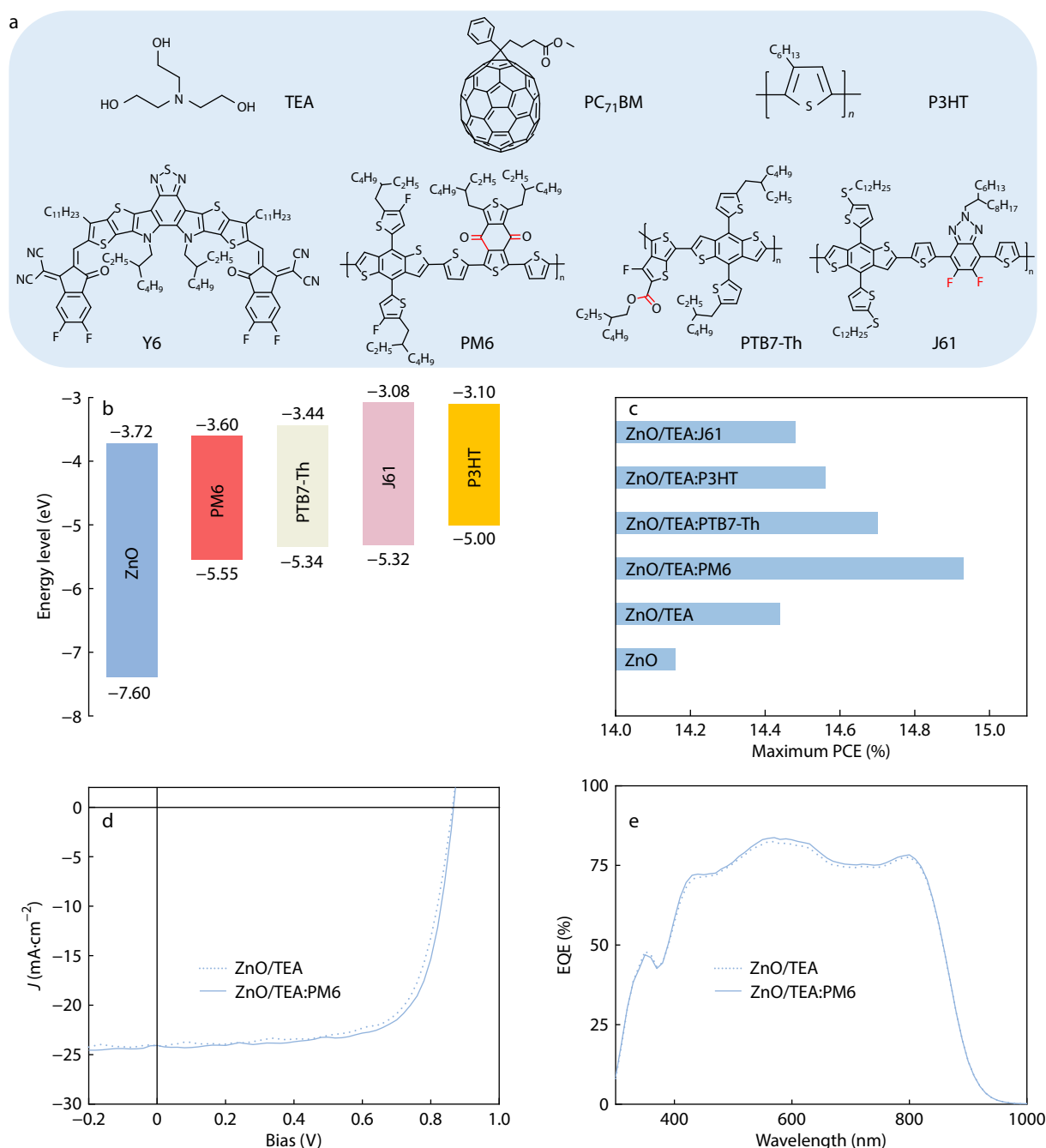


Fig. 1 (a) The chemical structure of the materials used in OSCs devices; (b) The energy level diagram of the polymer donors used in OSCs devices; (c) The maximum PCE of the PM6:Y6-based OSC devices based on ZnO films treated by TEA without and with different p-type polymers; (d) The *J*-*V* curves and (e) the EQE curves of the PM6:Y6 based OSCs with ZnO ETLs treated by TEA and TEA:PM6.

shown in Fig. 1(b).^[52–54] As shown, a charge carrier barrier can be formed if the p-type polymer is used to modify the ZnO films owing to the mismatched energy level. The typical current density-voltage (*J*-*V*) characteristics of devices with the active layer of PTB7-Th: PC₇₁BM are shown in Fig. S1 and Table S1 (in ESI). Compared with TEA-treated ZnO devices, the OSCs based on the ETL consisted of TEA with electron acceptors (Y6 and PC₇₁BM) treated ZnO contact exhibits improved PCE from 7.55% to 8.52% and 8.14%, respectively, which can be attributed to the enhancement of the short current density (*J*_{SC}). It was an expectative result that the cathode contacts modified by electron acceptors improved the device efficiency, which could be attributed to the better energy level alignment and the charge carrier transport improvement. Contrary to expectation, the ZnO films treated by TEA combined with some polymer donors, which was usually regarded to increase the barrier of electron extraction, surprisingly improved the PCEs of the OSC devices to up to 8.65%. To check whether this phenomenon existed in OSCs independent of active layers, we further fabricated the OSCs by using the typical PM6:Y6 blend active layer. The photovoltaic characteristics were measured for devices based on PM6:Y6 active layer and ZnO ETLs treated by TEA with different polymer donors as additives, and the maximum PCEs with TEA and different polymers are shown in Fig. 1(c). As a result, the performance of the OSCs based on the ZnO films with TEA:polymer donor capped was also improved relative to the control devices based on the neat TEA-treated ZnO. The illuminated *J*-*V* curves and photovoltaic parameters are shown in Fig. S2 (in ESI) and Table 1, respectively. The OSC device with TEA treated ZnO films show a *J*_{SC} of 24.71 mA·cm⁻², an open-circuit voltage (*V*_{OC}) of 0.839 V, and a filling factor (FF) of 69.5%, delivering a maximum PCE of 14.44%. The device based on TEA: PM6 capped ZnO shows a *J*_{SC} of 25.13 mA·cm⁻², a *V*_{OC} of 0.842 V, and an FF of 70.5%, delivering a maximum PCE of 14.93%. The *J*-*V* curves and external quantum efficiency (EQE) spectra of OSCs based on TEA or TEA:PM6 treated ZnO, are directly compared in Fig. 1(d) and Fig. 1(e), respectively. Then, we chose PM6 as an example to further investigate the effect of polymer donor additive on the ZnO treatment, owing to the best performance shown in TEA: PM6-treated OSC devices.

Work Function

On the basis of the *J*-*V* results, we consider whether the variation of the work function (WF) of the ETLs leads to the enhancement efficiency of the OSCs. To evaluate the intrinsic electronic property influence of the modifying interlayer on the device performance, the intrinsic electronic properties of TEA treated ZnO film and TEA:PM6 treated ZnO film were studied by ultraviolet electron spectroscopy (UPS) measurement (Fig. 2a). The secondary electron cutoff edge (*E*_{cutoff}) in the high-binding-energy region reflects the WF of the materials. As the previous work illustrated, TEA can modify the WF of the ZnO.^[38] After TEA:PM6 treatment, the WF of ZnO films treated with TEA increases from 3.42 eV to 4.02 eV calculated from the difference between incident photon energy and *E*_{cutoff}, which goes against forming the better Ohmic contact between the active layer and the cathodes. Consequently, the improved performance of the devices should not be attributed to the variation of WF of the ETLs.

Trap Density

Passivating trap of states of the ETLs is another possible reason

Table 1 Photovoltaic parameters of the OSC devices based on PM6:Y6 with the modifying layer consisted of different donors: TEA-capped, TEA-capped, or as-cast ZnO under the illumination of AM 1.5G, 100 mW·cm⁻².

Modifying layer	<i>V</i> _{OC} (V)	<i>J</i> _{SC} (mA·cm ⁻²)	FF (%)	PCE (%)
ZnO	0.841	24.73	68.1	14.16
ZnO/TEA	0.839	24.71	69.5	14.44
ZnO/TEA:PM6	0.842	25.13	70.5	14.93
ZnO/TEA:PTB7-Th	0.841	24.75	70.8	14.70
ZnO/TEA:P3HT	0.842	24.79	69.8	14.56
ZnO/TEA:J61	0.843	25.84	66.5	14.48

which contributes to the improvement of device PCE. We first perform photoluminescence (PL) measurements (Fig. 2b) of the ZnO films with the TEA capping layer and TEA:PM6 capping layer. These ZnO thin films show sharp PL peaks at 381 nm under the excitation at 330 nm. In comparison with the TEA-capping ZnO films, the TEA:PM6 treated ZnO presents 1.2 times stronger PL intensity at 381 nm.^[55,56] There is little difference of PL intensity between untreated ZnO films and neat PM6-treated ZnO films, suggesting that solely PM6 cannot passivate the defect on the surface of ZnO, and only when TEA and PM6 together treat the ZnO films can the enhancing defect passivation be obtained. These results can demonstrate that TEA with a minor amount of PM6 can reduce the electronic defect on the surface of the ZnO thin films, suggesting that PM6 additive can enhance defect passivation of ZnO films.

Furthermore, the total trap density of states of the OSCs can be divided into two parts: the surface trap density of states and the bulk trap density of states. The trap density on the interface between the active layer and contact layer is usually higher than that of the bulks.^[55,57] To further confirm the assistant defect passivation effect of PM6 with TEA on ZnO, we present the evidence within devices by the thermal admittance spectroscopy (TAS) method, respectively. TAS analysis is a well-established and effective technique to quantify characterize both shallow and deep defects of the solar cells.^[58] The trap density of states (tDOS) of PM6:Y6-based devices fabricated with TEA-capped ZnO or TEA: PM6-capped ZnO ETL were extracted from TAS analysis. Fig. 2(c) shows that the device with TEA:PM6-capped has a lower trap density from 4×10^{16} cm⁻³·eV⁻¹ down to 6×10^{15} cm⁻³·eV⁻¹ in the trap region from 0.1 eV to 0.3 eV corresponding shallow energy level defects. These results can fully confirm the effect of PM6 enhancing defect passivation of TEA on ZnO films.

To study the influence of TEA:PM6 treatment on the charge carrier transport properties of the ZnO ETL, the electron mobility, as well as the trap density were measured by space charge limit current method (SCLC).^[59] The electron-only devices were fabricated with a device structure of ITO/TEA-capped ZnO or TEA:PM6-capped ZnO/Al. The electron mobility of TEA-capped ZnO films increases from 6.33×10^{-4} cm²·V⁻¹·s⁻¹ to 7.36×10^{-4} cm²·V⁻¹·s⁻¹ as shown in Fig. 2(d). The total trap density of the TEA-capped ZnO films and TEA:PM6 capped ZnO films are 3.85×10^{16} and 1.57×10^{16} cm⁻³, respectively, which is in agreement with the TAS and PL results and can confirm the increased efficiency attributed to the enhanced trap passivation effect.

Interaction between TEA and Polymer Donor

As discussed above, only combination of PM6 and TEA can

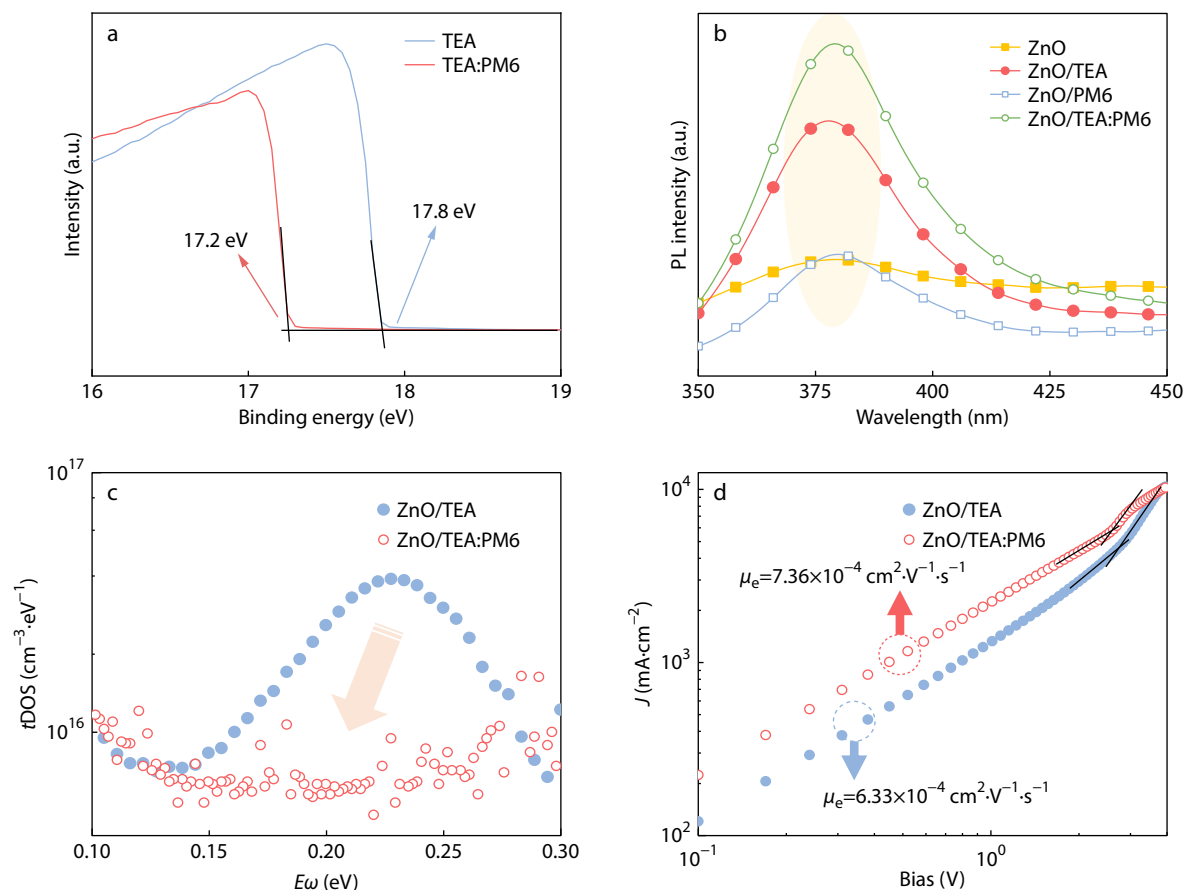


Fig. 2 (a) UPS spectra of the ZnO film treated with TEA and TEA:PM6; (b) PL spectra of the ZnO treated by different materials; (c) TDS results for the PM6:Y6 based devices deposited on TEA-capped ZnO and TEA:PM6 capped ZnO; (d) SCLC measurement for electron-only devices with TEA-capped ZnO and TEA:PM6 capped ZnO.

enhance the performance of OSC devices, which indicates there are some unknown interactions between PM6 and TEA. The organic field-effect transistors (OFETs) were used to estimate the changing electronic properties of the PM6 by adding minor amounts of TEA, which should be noted that the weight ratios of the TEA and polymer are greatly different from the ratios used in OSC devices for the consideration of film formation and conductivity. Fig. S3 (in ESI) shows that with the minor amount of TEA, the hole mobility of PM6 decreases from $8.05 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ to $3.33 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. This result confirmed the interaction between TEA and PM6 existed when blending them, which could adjust the electronic property of the materials.

To further reveal the mechanism of the interaction between PM6 and TEA, ^1H nuclear magnetic resonance (^1H -NMR) was conducted to analyze the monomer of PM6, 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl) benzo[1,2-c:4,5-c'] dithiophene-4,8-dione (BDD), TEA, and TEA-BDD mixture. The ^1H -NMR spectra of TEA-BDD mixture in deuterated chloroform solution show the almost same peaks of BDD, as the ^1H -NMR spectra of neat BDD in deuterated chloroform solution, while the peak at 4.48 ppm (hydrogen on hydroxyl) in TEA shows a slight chemical shift in TEA-BDD solution to 4.62 ppm. This chemical shift indicates that the hydroxyl group in TEA and carbonyl group in the polymer can form the hydrogen bond.^[60] Theoretical simulation was used to verify

this conclusion. The optimized structure of TEA and BDD, calculated by density function theory (DFT) calculation, are shown in Fig. 3(b). The distance between carbonyl group ($\text{C}=\text{O}$) of BDD and the hydroxyl group (OH) of TEA is 1.96 Å which is in the range of hydrogen bond length indicating the formation of hydrogen bond $\text{O}-\text{H} \cdots \text{O}=\text{C}$ in TEA:BDD.^[60] Then, we conducted the molecular ESP maps of TEA and the complex of TEA and BDD, and the average negative ESP of three oxygen atoms of TEA, Table S2 in ESI) has increased from 1.47 eV to 1.61 eV when blending with BDD, which benefit to enhance the ability of TEA passivating oxygen defects. For the devices based on TEA-J61 capped ZnO films, we also find the enhancement of J_{SC} . We have conducted the DFT calculation with the optimized structure of TEA and fluorine-containing building block of J61, demonstrating the fluorine atom can also form the hydrogen bond with TEA, thus improving the average negative ESP of oxygen atoms of TEA from 1.47 eV to 1.63 eV and leading to enhanced defect passivation, which is shown in Fig. S4 (in ESI). The experiments and theoretical calculation illustrate a mechanism that the carbonyl group or the fluorine atoms in polymer donor and the hydroxyl group of TEA can form the hydrogen bond increasing negative ESP of oxygen atoms of TEA then enhancing passivation of oxygen vacancies on ZnO ETL, resulting in improvement of OSCs performance.

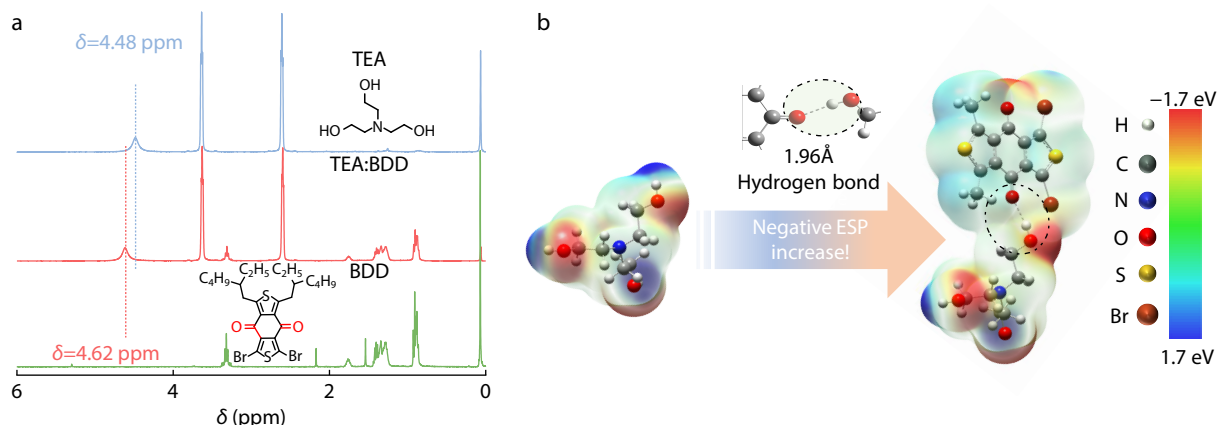


Fig. 3 (a) ^1H -NMR spectra of TEA, BDD, and TEA-BDD mixture; (b) Molecular electrostatic potentials of TEA and TEA-BDD complex by DFT calculation, in which all alkyl side chains of BDD were replaced by methyl groups.

CONCLUSIONS

In summary, we reveal that the polymer donors can enhance the defect passivation owing to the fact that the hydrogen bond between the donor and TEA increases the negative ESP of oxygen atoms of TEA. The TEA:polymer-capped ZnO films exhibit a low trap density and high electron mobility, thus the OSCs devices based on TEA: polymer treated ZnO films showed the superior PCEs to those of the OSC devices based on ZnO or neat TEA-capped ZnO ETLs. The discovery on enhancing the effect of trap passivation *via* increasing the negative ESP of passivators provides another view on improving the performance of the OSCs, which should be extended to other types of organic electronic devices.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2754-9>.

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