Dual-function interface engineering for efficient perovskite solar cells

Yigang Luan1,2 | Fuhui Wang1,2 | Jing Zhuang1,2 | Tao Lin1 | Yuanzhi Wei1,2 | Ningli Chen1,2 | Yanyan Zhang3 | Fuyi Wang2,3 | Ping Yu2,3 | Lanqun Mao2,3 | Huibiao Liu1,2 | Jizheng Wang1,2

1Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China
2University of Chinese Academy of Sciences, Beijing, China
3Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Analytical Chemistry for Living Biosystems, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

Correspondence
Huibiao Liu and Jizheng Wang, Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, 100190, China.
Email: liuhb@iccas.ac.cn (L. H.) and jizheng@iccas.ac.cn (J. W.)

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Abstract
Interface engineering has been proven a powerful tool to improve performances of the perovskite solar cells (PSCs). Herein, highly π-conjugated graphdiyne (GDY) is employed as an interface linker between the perovskite film and the hole transport layer (HTL). It is found that GDY can significantly suppress the formation of metallic Pb (a detrimental defect), and reduces carrier recombination. The linker can also form π-π stacking interaction with the HTL, and facilitates transport and collection of photogenerated holes. The perovskite/GDY/HTL combination leads to large improvement in both power conversion efficiency (from 19.94% to 22.17%) and device stability. In addition, the GDY is also applied to the 3D/2D PSCs, and an outstanding PCE of 23.42% is achieved.

KEYWORDS
interface engineering, interface linker, passivation, perovskite solar cells, π-π interaction

1 | INTRODUCTION

Due to their low cost and high power conversion efficiencies, lead halide perovskite solar cells (PSCs) have become promising technology for future clean energy harvesting.1-6 Currently, the most popular PSCs are planar ones, in which the active perovskite film is sandwiched between an electron transport layer (ETL) and hole transport layer (HTL). In the standard architecture of the planar PSCs (ITO/ETL/perovskite/HTL/Au), the most widely used HTL (ETL) is Spiro-OMeTAD (SnO2).7 In such PSCs, there exist plenty of defects on the surface of the perovskite film, which can cause serious carrier recombination and thus results in energy loss.8-10
The defects can also induce severe perovskite/Spiro-OMeTAD interface instability, and hence leads to rapid device degradation during storage or under operation.\textsuperscript{11,12} A series of different materials, including PbI\textsubscript{2}, alkylammonium halogen salts, wide-bandgap inorganic oxides and lewis acid/bases, have been introduced to passivate the surface defects of the perovskite film.\textsuperscript{13-21} For example, Wu et al. have used a multiple ligand molecule to suppress the formation of surface Pb\textsuperscript{0} by promoting the back-oxidation of Pb\textsuperscript{0} to Pb\textsuperscript{2+}.\textsuperscript{13} These studies simply focused on the perovskite/passivator interaction, and ignored the passivator/HTL interaction. Actually, the passivator should also function as a strong interface linker and well interacts with the HTL in order to efficiently transfer photo holes from the perovskite film to the HTL. It is crucial to explore powerful interface linkers to upgrade the PSCs (cathode/ETL/perovskite/linker/HTL/anode).

In this study, we employed graphdiyne (GDY), a 2D planar carbon allotrope (formed by connecting two adjacent benzene rings (sp\textsuperscript{2}) with a diacetylenic linkage (sp) in the graphyne structure\textsuperscript{22-30}), as interface linker for the perovskite ((FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3-y}Cl\textsubscript{y})\textsubscript{x}) and the HTL (Spiro-OMeTAD). We found that the GDY can efficiently reduce defects by suppressing the formation of metallic Pb on the surface of the perovskite film, and meanwhile form strong \pi-\pi interaction with Spiro-OMeTAD. As a result, the PCE increased from 19.94\% to 22.17\%, and the device humidity, thermal and air stabilities were all greatly enhanced. Furthermore, we employed GDY to treat the surface of 3D/2D perovskite film, and a superior PCE of 23.42\% was obtained.

2 | RESULTS AND DISCUSSION

2.1 | GDY/perovskite and GDY/HTL interactions

In this study, GDY was deposited on the perovskite film ((FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3-y}Cl\textsubscript{y})\textsubscript{x}) as interface linker between the perovskite film and HTL (Spiro-OMeTAD). X-ray photoelectron spectroscopy (XPS) was used to study the film composition. As indicated in Figure 1A,
the perovskite films with GDY surface modification have shown increased C signal compared to the control perovskite film. Figure S1 shows the XPS result of GDY, which clearly represents the GDY characteristic peaks of 284.8 (C 1 second), 399.8 (N 1 second), 532.5 eV (O 1 second), and the four C 1 second sub-peaks located at 284.5 (C≡C), 285.0 (C=C), 286.4 (C—O), and 288.7 eV (C=O). The increased C content in the modified film is an indication that GDY is present on the perovskite film. Figure S3 shows the transmission electron microscopy (TEM) image of GDY, revealing its multilayer nanosheets structure. The scanning electron microscopy (SEM) images of the perovskite films with/without the GDY are given in Figure S4. It is seen that the GDY spread well on the surface of perovskite film. Atomic force microscopy (AFM) results revealed that the surface roughness in the region of 10 × 10 µm slightly increases from 25.7 to 28.2 nm after the GDY modification (Figure S5). In addition, we conducted time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements (Figure S6), which also prove the GDY presence on the perovskite surface. Figure 1B shows the Pb 4f core-level spectra of the GDY modified film and the control film, the two main peaks located on 138.6 and 143.5 eV are appointed to lead iodide, and the two weak peaks at 136.9 and 141.7 eV are associated to metallic Pb. It can be seen that as more and more GDY is added to the surface of perovskite, the metallic Pb peaks become weaker and weaker, and finally disappeared. This indicates that GDY is able to suppress the formation of metallic Pb. Due to the sp hybridized structure, out-of-plane p\(_{x/y}\) \(\pi/\pi^*\) and in-plane p\(_{xy}\) \(\pi/\pi^*\) are present in GDY, both can lead to strong interactions between GDY and metal ions, including Pb\(^{2+}\) and PbI\(_2\). In addition, the Pb 4f in the XPS red-shifts in the binding energy when GDY and PbI\(_2\) are mixed. It is speculated that GDY provides electrons to Pb atom through coordination interaction, resulting in the increase of electron cloud density around Pb atom (Figure S7). Hence, it should be the GDY-Pb\(^{2+}\) interaction (GDY donates electrons to Pb\(^{2+}\)) that inhibits the reduction of Pb\(^{2+}\) to metallic Pb, leading to the observed suppression of metallic Pb formation. The UV-vis spectra of the perovskite films are given in Figure S8, it is seen that GDY does not influence light absorption of the modified perovskite film.

To investigate the interaction between GDY and the hole transporter Spiro-OMeTAD, 5 mg GDY and 2 mg Spiro-OMeTAD were mixed in chlorobenzene, then centrifuged and washed with chlorobenzene for three times to remove excess Spiro-OMeTAD. After vacuum drying at 60°C for 10 hours, brown powders (GDY-S) were obtained. The Raman spectra collected from GDY and GDY-S powders are shown in Figure 1C. The GDY shows its three distinct peaks: D band at around 1398.8 cm\(^{-1}\), G band at around 1582.9 cm\(^{-1}\), and the vibration in the acetylenic linkages at around 2185.8 cm\(^{-1}\). For the GDY-S, the G band shifts from 1582.9 to 1596.1 cm\(^{-1}\), indicating that interaction occurs between GDY and Spiro-OMeTAD. In the meantime, the D/G peak intensity ratio is decreased from 0.84 to 0.81. This red shift of the G band and the drop of the D/G ratio indicate that there are \(\pi/\pi\) interaction between GDY and Spiro-OMeTAD. In the device fabrication, Spiro-OMeTAD was spin-coated onto the GDY-modified perovskite surface and acts as HTL, we thereby are interested in knowing how such \(\pi/\pi\) interaction affects the Fermi level and the HOMO position of the Spiro-OMeTAD film when Spiro-OMeTAD is put on top perovskite/GDY. From the ultraviolet photoelectron spectroscopy (UPS) study shown in Figure 1D and Figure S9, it is found that the Fermi level is moved up by 0.11 eV (from −3.82 to −3.71 eV). This provides an electric field, which drives holes from perovskite to the Spiro-OMeTAD. The HOMO position of the perovskite/GDY/Spiro-OMeTAD is lower than that of perovskite/Spiro-OMeTAD by 0.21 eV. The lower HOMO here means less energy loss, which would increase the photovoltage.

### 2.2 Performances of the PSCs

The device structure (glass/ITO/SnO\(_2\)/perovskite/GDY/Spiro-OMeTAD/Au) of planar PSCs is shown in Figure 2A, and a cross-sectional SEM image is provided in Figure S10. The PSCs without GDY were also fabricated for comparison as control device. The device performance depends on GDY amount added on perovskite as shown in Figure S11 and Table S1, which indicates that the optimum content of GDY is 0.05 mg mL\(^{-1}\). The J-V curves of the best control and GDY devices are shown in Figure 2B. Control device shows a PCE of 19.94% (\(J_{sc}: 23.28\) mA cm\(^{-2}\), \(V_{oc}: 1.135\) V, FF: 75.45%) under reverse scan, whereas the GDY device has a much higher PCE of 22.17% (\(J_{sc}: 24.67\) mA cm\(^{-2}\), \(V_{oc}: 1.162\) V, FF: 77.31%). The statistical parameters of the control and GDY devices are shown in Figure S12 (25 devices for each case), which indicates good reproducibility of the results, confirming that the GDY treatment can indeed greatly improve the device performance. It is seen that the average \(J_{sc}\), \(V_{oc}\), FF, and PCE of the control devices are 23.21 mA cm\(^{-2}\), 1.135 V, 74.13% and 19.52%, respectively, while, for the GDY devices are 23.96 mA cm\(^{-2}\), 1.158 V, 77.35 and 21.47%, respectively. Meanwhile, the hysteresis of typical GDY device is also reduced compared with control device as shown in Figure S13. The improvement can be ascribed to the GDY-induced defect passivation and the GDY-enhanced hole transfer at the perovskite/Spiro-OMeTAD interface. Figure 2C shows external quantum efficiency (EQE) spectra and integrated \(J_{sc}\) of the control...
and GDY devices. The integrated $J_{sc}$ calculated from EQE curve for the control device and the GDY device is 22.96 and 23.55 mA cm$^{-2}$, respectively, in line with the $J-V$ results. Figure 2D shows the steady output efficiency of the devices at maximum power point (MPP). It shows that the PCEs of the control and GDY devices stabilize at ~19.03 and 21.20%, respectively.

2.3 Charge transfer dynamics

The space-charge limit current (SCLC) measurement was adopted to confirm the passivation effect brought by GDY (with device structure of glass/ITO/SnO$_2$/perovskite/PCBM/Ag). Figure S14 show the dark $I-V$ curves of control and GDY modified devices, respectively. The calculated electron trap density of the GDY modified film is $\sim$9.85 $\times$ 10$^{15}$ cm$^{-3}$, while the control film is $\sim$1.70 $\times$ 10$^{16}$ cm$^{-3}$. This demonstrates that GDY indeed plays a significant role in reducing defects. Such defects reduction can effectively lower carrier recombination and facilitate carrier transport. The steady photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were used to explore the effect of GDY on hole transfer at the perovskite/Spiro-OMeTAD interface (Figure 3A,B). As shown in Figure 3A, the PL intensity of perovskite/GDY/Spiro-OMeTAD is lower than that of perovskite/Spiro-OMeTAD, implying the enhanced hole transfer from perovskite to Spiro-OMeTAD. As shown in Figure 3B, the average carrier lifetime ($\tau_{ave}$) of the glass/perovskite/Spiro-OMeTAD is $\sim$113 ns, whereas that of the glass/perovskite/GDY/Spiro-OMeTAD is $\sim$58 ns (Table S2). The significantly reduced $\tau_{ave}$ strongly indicates that GDY can effectively speed up hole transfer at the perovskite/HTL interface, hence greatly suppress carrier recombination. Consequently, the device performance is largely improved.

We tested $J_{sc}$ and $V_{oc}$ at various light intensities. Figure S15 shows $J_{sc}$ as a function of incident light intensity, and linear correlations were observed for both devices. The control device gives a slope of 0.96, and the GDY device gives a slope of 0.98. Both slopes are close to 1, indicating negligible bimolecular recombination in the two PSCs. Figure 3C shows $V_{oc}$ vs incident light intensity. It can be found the control device has a slope of 1.92 $k_B T/q$, and the GDY device has a lower slope of 1.53 $k_B T/q$ (where $k_B$ is the Boltzmann constant, $T$ is temperature, and $q$ is the elementary charge.). It is known that the slope deviation from $k_B T/q$ indicates the presence of defect-assisted Shockley-Read-Hall recombination in the PSCs. Hence, these results further confirmed that the...
monomolecular Shockley-Read-Hall recombination has been largely suppressed in the perovskite layer by the GDY modification.

Figure 3D displays the impedance spectroscopy (IS) spectra of the devices measured at $-0.6$ V in dark. The inset shows the equivalent circuit, where $R_{tr}/C_1$ represents the hole transfer process at the perovskite/HTL ($R_{tr}$ is hole transfer resistance and $C_1$ is interfacial capacitance); $R_{rec}/C_2$ represents the recombination process associated with perovskite ($R_{rec}$ is recombination resistance and $C_2$ is chemical capacitance). The fitting shows that $R_{rec}$ of the control and GDY devices are $2.2$ and $3.1$ k$\Omega$, respectively. In IS, larger $R_{rec}$ means less carrier recombination. The larger $R_{rec}$ of the GDY device should be originated from the GDY-induced defect passivation. Meanwhile, the GDY device has a smaller $R_{tr}$ ($39$ vs $47$ $\Omega$), which should come from the GDY-enhanced hole transfer at the perovskite/HTL interface.

2.4 Stability

Besides PCE, the humidity, air and thermal stabilities of the perovskite materials and devices are very important factors for their practical applications. Figure 4A displays the X-ray diffraction (XRD) patterns of the control and GDY modified films under an 85% relative humidity (RH), and Figure 4B shows the XRD patterns under thermal treatment at 120°C. The peak located at 12.7° (14.1°) is signal from PbI$_2$ (001) (perovskite [110]). As shown in Figure 4A and Figure S16, during the humidity aging test the PbI$_2$ peak becomes stronger and stronger for both films, meaning both perovskite films are decomposing along with time. However, the decomposition is much slower for the GDY modified film. This is also observed in the thermal aging test (Figure 4B and Figure S18). Figure 4C shows the perovskite degradation index (the ratio of the peak intensity of PbI$_2$ to perovskite): the higher the index, the larger the decomposition. It can be seen that after 5 hours humidity aging test, the index for the control and GDY devices are 1.92 and 1.23, respectively. The suppressed decomposition was also evidenced by the light absorption tests shown in Figure S17 (the GDY modified film shows slower reduction in absorption intensity). This enhanced humidity stability is due to the hydrophobic nature of GDY. After 2 hours thermal aging test, the index is only 1.09 for the GDY modified films whereas 1.53 for the control device. The enhanced thermal stability can
be attributed to the good thermal stability of GDY itself and its capability of reducing metallic Pb defects.14,54,55

Figure 4D gives the device humidity aging tests under a range of RH from 25 to 85% in air (25°C). It is observed that the GDY device exhibits much higher humidity stability. Under 85% RH, the control device remains only 65% of its initial PCE after 166 hours aging, while the GDY device still holds 82% of its initial PCE. The thermal stability tests at 60°C are provided in Figure 4E. It shows that after 400 hours, the control device remains only 75% of its initial PCE, whereas GDY device still maintains 90% of its initial PCE. Finally, the air stability tests at room temperature are given in Figure 4F (the devices were stored in dark ambient environment without any encapsulations). It is found that although both devices exhibit good air stability in the 45-day test, the GDY device performs relatively better. The enhanced stabilities are obviously brought in by GDY, which produces a robust perovskite/linker/HTL key part for the device.

2.5 3D/2D Cells

Encouraged by the high performance of the GDY modified PSCs, we have also applied the GDY to 3D/2D perovskite surface to fabricate PSCs with a structure of glass/ITO/SnO2/(3D/2D) perovskite/GDY/Spiro-OMeTAD/Au (Figure S19). In a previous work, we reported self-crystallized 2D perovskite grown on top of 3D perovskite film \(((\text{FAPbI}_3)_{1-x} \text{MAPbBr}_3 \text{Cl}_y)_{x}\) using a solution of p-methoxyphenethylammonium iodide (CH3O-PEAI) in isopropanol (IPA), followed by an annealing treatment at 100°C for 10 minutes.21 Besides, the treatment of CH3O-PEAI also passivates the perovskite defects. The typical J-V curves of the 3D/2D device (glass/ITO/SnO2/(3D/2D) perovskite/Spiro-OMeTAD/Au) and 3D/2D/GDY device are shown in Figure 5A and Figure S21 (the device parameters with different GDY’s amounts are given in Table S3.). It can be seen that the optimal GDY concentration is 0.05 mg mL\(^{-1}\). Both the \(J_{sc}\) and FF are increased compared with the control device (3D/2D device), which is due to the GDY-enhanced hole transfer at 3D/2D perovskite/HTL interface. The J-V curves of best devices are shown in Figure 5B. The best 3D/2D/GDY device shows a PCE of 23.42%, a \(V_{oc}\) of 1.194 V, a \(J_{sc}\) of 24.43 mA cm\(^{-2}\) and a FF as high as 80.29%. The best 3D/2D/GDY device shows a steady output efficiency of 22.67%, While that of for the control device is 21.49% (Figure 5C). The PCEs distribution is given in Figure 5D, showing good reproducibility.

FIGURE 4 XRD patterns of the perovskite films in the aging test: (A) under 85% RH, and (B) at 120°C. (C) Peak intensity ratio of PbI\(_2\) phase (001) to perovskite phase (110). (D) Device humidity stability test under 25% to 85% RH at 25°C. (E) Device thermal stability test at 60°C for 400 hours. (F) Device air stability test.
In summary, we applied GDY as interface linker for efficient PSCs (glass/ITO/SnO₂/perovskite/GDY/Spiro-OMeTAD/Au). GDY can interact with the Pb²⁺ and hence prevent Pb²⁺ from being reduced to metallic Pb. This suppresses carrier recombination and perovskite decomposition. Meanwhile, GDY is also capable of forming π-π interaction with the HTL (Spiro-OMeTAD). This significantly enhances hole transfer from the perovskite to the HTL and hence is beneficial for photo hole collection. The two effects collectively lead to a great PCE improvement (from 19.94 to 22.17%) and largely enhanced the device stabilities. In the 400 hours thermal aging test at 60°C, the GDY device can keep 90% of its initial PCE, while the percentage for the control device is only 75%. In addition, the GDY was also applied to the 3D/2D PSCs, and an outstanding PCE of 23.42% was obtained, together with a FF as high as 80.29%. The success of GDY here indicates that such acetylenic-containing carbon semiconductors could be promising interface linkers for future optoelectronics.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

ORCID
Jizheng Wang https://orcid.org/0000-0003-0477-4145

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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