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### ARTICLE

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# A ring-locking strategy to enhance the chemical and photochemical stability of A-D-A-type non-fullerene acceptors<sup>†</sup>

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Recently, the power conversion efficiencies (PCEs) of bulk-heterojunction organic solar cells (BHJ-OSCs) based on nonfullerene acceptors (NFAs) have made a very impressive progress. However, few attentions have been paid to the intrinsically chemical and photochemical stability of NFAs, although which are greatly correlated with the resulting device stability. Herein, we describe a new molecular design strategy to enhance the intrinsically chemical and photochemical stability of acceptor-donor-acceptor (A-D-A)-type NFAs by the introduction of ring-locked carbon-carbon double bonds between D-A conjugation, attributed to the removal of hydrogen atoms attached onto the electrophilic double bonds and the formation of intramolecular C-H···O interactions. Based on this strategy, two types of NFAs have been successfully prepared, 2-(1,1-dicyanomethylene)rhodanine-based IDT-CR and IDTT-CR and thiobarbituric acid-based IDT-CT and IDTT-CT. When blended with a wide-bandgap polymer donor (P3HT), the IDTT-CR-based solar cells can exhibit a PCE of 2.86%. Moreover, a much enhanced PCE of 6.13 % was realized by adapting a low-bandgap polymer donor PTB7-Th to pair with IDTT-CT. The fabricated PTB7-Th:IDTT-CT-based OSCs showed very encouraging photostability, the PCE of which can retain over 80% of the initial values after 200 h one sun irradiation in air without UV filter. Such photostability performance has greatly outperformed those from conventional NFAs like ITIC, IT-4F, and IT-M, suggesting the effectiveness of our ringlocking design strategy. Moreover, PTB7-Th:IDTT-CT-based OSCs can also retain ~70% of its initial PCE after heating at 85  $^{\circ}$ C for 100 h. Besides, we also found the inferior device stability for P3HT:IDTT-CR based OSCs is mianly due to the evolution of BHJ film morphology under light illumination.

#### Introduction

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Organic solar cells (OSCs) have attracted great research interests in the past two decades due to their significant advantages of low cost, short energy payback time, light weight, flexible and semitransparent.<sup>1-9</sup> Recently, the development of novel non-fullerene acceptors (NFAs) such as 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)- indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) has successfully broken the long-term domination of fullerene-based acceptors

in OSCs<sup>10</sup>, and has excitingly enabled the power conversion efficiencies (PCEs) of OSCs to exceed 17%<sup>11-17</sup>. Although the PCEs of NFA-based OSCs have potentially met the requirements of commercialization, the corresponding device stability still confronts great challenges.<sup>18-21</sup>

To data, the mainstream design strategy to develop efficient

small molecule NFAs like ITIC, O-IDTBR<sup>22</sup>, 6TBA<sup>23</sup>, Y6<sup>24</sup>, etc. is based on the acceptor-donor-acceptor (A-D-A) structure, in which a strong intramolecular charge transfer (ICT) can be generated to ensure a strong and broad light absorption for effectively harvesting solar energy. Furthermore, such type of NFAs possesses excellent synthetic flexibility to tune their optical/electronic properties as needed by rationally integrating different types of donor and acceptor units. In general, most of A-D-A-type NFAs are synthesized by a typical Knoevenagel condensation between the aldehyde groups in the D units such as indacenodithieno[3,2-b]thiophene (IDTT) derivatives and the active methylene groups in the A units such as 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN), rhodanine (RD), and thiobarbituric acid (TBA).<sup>6</sup> In this manner, the resulting NFAs inevitably contain very electrophilic carbon-carbon double bonds due to the strong push-pull effect, which should be easily attacked by the nucleophiles or photooxidized under light irradiation, as shown in Fig. 1a. This thus would lead to unsatisfied chemical and photochemical stability of NFAs to significantly deteriorate the final device stability.

Typically, the fabrication of OSCs involves a variety of wellknown interface materials containing reactive species, such as the acidic PEDOT and nucleophilic PEIE, and so on. For example, Zhou et al. recently have demonstrated the ITIC derivatives can readily react with the amine species in the PEIE via a typical

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**Fig. 1** (a) The mechanism of A-D-A-type NFAs attacked by the nucleophiles or photooxidized under light irradiation. (b) The structures of IDT-R, IDTT-R, IDTT-T, IDT-CR, IDTT-CR, IDT-CT and IDTT-CT.

nucleophilic addition reaction (i. e. Michael addition), making the resulting device performance extremely poor.<sup>25</sup> Besides PEIE, inorganic charge transporting materials such as zinc oxide (ZnO) also contains a large amount of amine species such as ethanolamine (EA), which are adopted to stabilize the nanoparticles in solutions, however, EA has been also shown to react with ITIC derivatives.<sup>26</sup> Furthermore, they also reported that OH<sup>-</sup> anion as a nucleophile could destroy the C=C bond in ITIC.<sup>27</sup> As a result, it is essential to improve the chemical stability of NFAs in the presence of nucleophilic reagent from the molecular design strategy, which however has been received less attention.

OSCs also face photostability challenges caused by the photodegradation of active layers. Particularly, the active electrophilic double bonds in A-D-A-type NFAs are more chemically vulnerable than the stable aromatic units under illumination.<sup>28, 29</sup> Significant research efforts recently have been devoted to studying the photochemical stability of NFAs. For example, ZnO is well-known as the efficient photocatalyst, which can lead to the degradation of organic dyes under light illumination.<sup>30</sup> When the surface defects of ZnO adsorbed oxygen and water molecules, ITIC and IT-4F will be decomposed at the active layer/ZnO interface under UV illumination.<sup>28, 31</sup> Kim et al. recently investigated the degradation process of structurally similar NFAs, planar O-IDTBR and nonplanar O-IDFBR, and found that the planar configuration can be more resistant to the  $\ensuremath{\text{photodegradation.}}^{32}$  Li et al. reported that the NFAs can possess better anti-photooxidation ability when having deeper lowest unoccupied molecular orbital levels (LUMOs) than the electron affinity of oxygen.<sup>33</sup> Moreover, Brabec et al. revealed that the photostability of ITIC derivatives is strongly dependent on the end-groups and side-chains of the NFAs<sup>34</sup> viend Eucher showed that the ITIC-2F and ITIC-TR<sup>11</sup> based<sup>1/1</sup>OSCs<sup>99</sup>cdA potentially have a device lifetime approaching 10 years under irradiation by white light without UV light, despite affording lower PCEs than those reported elsewhere<sup>35-37</sup>. Nonetheless, new design strategies toward intrinsically photostable NFAs are still lack.

Herein, based on conventional A-D-A type NFAs, IDT-R, IDTT-R, IDT-T<sup>38</sup> and IDTT-T<sup>39, 40</sup>, we have synthesized a series of novel NFAs, IDT-CR, IDTT-CR, IDT-CT and IDTT-CT (Fig. 1b), by using a cyclohexene  $\pi$ -conjugated bridge linked with electronwithdrawing end-groups. Indacenodithiophene (IDT) and IDTT are used as the electron-donating cores, while 2-(1,1dicyanomethylene)rhodanine (RCN) and TBA as the electronwithdrawing end-groups. Accordingly, the resulting NFAs exhibited significantly improved chemical stability against nucleophilic reagent and photochemical stability in comparison to the control NFAs without ring-locked bridge, thereby making the fabricated OSCs with much enhanced stability than those from other high-performance conventional NFAs like ITIC.

#### **Results and discussion**

#### Synthesis and Structural Characterization

The synthetic route of ring-locked NFAs is shown in Scheme 1, and the synthetic details are provides in the ESI.<sup>†</sup> First, 3bromocyclohex-2-enone (1) was synthesized from cyclohexene-1,3-dione as reported.41 Then, a typical basecatalyzed Knoevenagel condensation was carried out, which, however, did not afford the desired cyclohexene-locked acceptors, BrCR and CICT (Scheme 1). After carefully optimizing the reaction conditions, we found a TiCl<sub>4</sub>-promoted condensation can successfully afford the products, according to the literature report in which TiCl<sub>4</sub> was shown to coordinate the ketone species to promote the condensation.<sup>42</sup> Strangely, for the reaction between 1 and TBA dye, the bromine substitution on the resulting product was replaced by chlorine atom, the structure of which can be confirmed by high resolution mass spectrum (HRMS, ESI<sup>†</sup>) and signal-crystal structure (Fig. 3b). This thus suggests an unusual halogen exchange reaction, to which we still have no rational explanation at this stage. Furthermore, it is worth noting that the attempt of synthesizing the INCN-based acceptors unfortunately failed. Finally, the desired ring-locked NFAs, i.e. IDT-CR, IDTT-CR, IDT-CT, and IDTT-CT, were successfully synthesized via a typical Still coupling in high yields over 80%, by using the IDT-tin and IDTT-tin to react with the BrCR and CICT acceptors, respectively. On the other hand, control NFAs without any ring-locked bridges were also prepared for comparison based on the piperidine-catalyzed Knoevenagel condensation reaction as shown in the ESI.<sup>†</sup> All the new NFAs have good solubility, and their structures were fully characterized by nuclear magnetic resonance (NMR) and mass spectrometry, and the detailed data are provided in experimental section (ESI<sup>†</sup>).

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Interestingly, BrCR is found to have two different configurations, *E*-BrCR and *Z*-BrCR, due to the rotation of RCN end-group that can make the formation of two types of noncovalent C–H···O interactions with the neighboring vinylic groups (*E*-configuration) and methylene groups (*Z*-configuration) in the cyclohexene-locked bridge, respectively (Scheme 1). Such interactions enable the corresponding NMR signals with a clear downshift as shown in Fig. 2. For example, the signal of vinylic protons can downshift from 6.6 ppm in the *Z*-configuration to 8.3 ppm in the *E*-configuration. Thus, based on the integration data, the molar ratio between *E*- and *Z*-configurations is 0.64:0.36, which can be still remained in its

subsequent products, i.e. IDT-CR and IDTT-CR (Fig. 2). Furthermore, Pure *E*-BrCR and *Z*-BrCR isomers were successfully separated and their structures were confirmed by the NMR spectra in Fig. S24-S27. We then tried to use them to synthesize IDTT-CR acceptors with single conformation, which, however, failed possibly due to the dynamic change of the noncovalent interactions under reaction conditions (Fig. S37-S38). On the contrary, it is worth noting that due to the symmetric structure of TBA end-group, its resulting products, i.e. CICT, IDT-CT and IDTT-CT, all do not have any isomers, while the <sup>1</sup>H NMR spectra (ESI†) strongly indicate the existence of the noncovalent C–H···O interactions.

Fig. 3 The single crystal X-ray crystallography of (a) Z-BrCR and (b) CICT. For clarity, most of the hydrogen atoms are omitted, and the hydrogen atoms are marked in white, carbon atoms in blue, nitrogen atoms in magenta, oxygen atoms in red, sulfur atoms in yellow, bromine atoms in green, and chlorine atoms in purple.

#### Single Crystal X-Ray Crystallography

Single crystals of BrCR and CICT were successfully obtained by a slow evaporation of the co-solvent system to refine their ground-state geometric structures based on the X-ray crystallography. For BrCR, it is a pity that only Z-configuration crystal was obtained and its structure (Orthorhombic, Pnma space group, Table S1<sup>†</sup>, CCDC2014380) is shown in Fig. 3a, from which it is easily seen that there is a C-H···O bonding existed between the carbonyl group in the RCN unit and the methylene group (C6) in the cyclohexene bridge, with a distance of 2.29 Å and a C6–H···O angle of 123°. Furthermore, a weak C2–H···S bonding can be also observed with a distance of 2.27 Å and an angle of 108°. The crystal structure (Triclinic, P-1 space group, Table S2<sup>†</sup>, CCDC2014381) of CICT is shown in Fig. 3b, in which the two carbonyl groups in the TBA unit form two types of C-H···O bonding with the connecting cyclohexene-based bridge, with a distance of 2.13 Å and 2.29 Å, respectively, and an angle of 125° and 107°, respectively. These noncovalent interactions could be able to act as the conformational locks to planarize and rigidify the  $\pi$ -conjugated molecular backbones of resulting NFAs, which has been well shown to improve charge carrier transport.43 More importantly, based on these results and combined with the above <sup>1</sup>H NMR results, the chemical reactivity of resulting NFAs are expected to be reduced to improve their chemical/photochemical stability, attributed to the removal of hydrogen atoms attached onto the electrophilic double bonds in the D-A conjugation and the formation of intramolecular interactions, which will be discussed later.

#### **Photophysical and Electrochemical Properties**

The UV-Vis absorption spectra of seven NFAs in chloroform solutions  $(10^{-5} \text{ M})$  and as thin films are shown in Fig. 4, and the corresponding data are summarized in Table 1. In solutions, the absorption bands of the ring-locked NFAs are found to not only show a red-shift about 20 nm but also an increased bandbroadening (~120 nm vs ~80 nm for full width at half maxima, FWHM) when comparing with the corresponding control NFAs without ring-locked bridge. This could be attributed to enhanced intramolecular charge transfer (ICT) in the ringlocked NFAs due to the enlarged conjugation length and planarized molecular backbone. Moreover, by changing the central core from IDT to IDTT or the end-groups from RCN to TBA, the absorption maxima  $(\lambda_{\text{max}}s)$  of resulting NFAs all show a clear red-shift with increased molar extinction coefficients Page 4 of 9

( $\varepsilon_{max}$ s), and IDTT-CT thus exhibits the largest  $\lambda_{maxe} o f_r 641_{nm}$ ring-locked bridge into the NFAs also leads to decreased  $\varepsilon_{max}$ s, possibly due to the decease of effective chromophore concentration.

Relative to their solution ones, the film absorption spectra of NFAs without ring-locked bridge all exhibit a red-shift of ~10 nm however with an increased short-wavelength shoulder somewhat indicating that the occurring peak, of intermolecular interactions in their films. On the contrary, the ring-locked NFAs show a negligible red-shift by comparing the film spectra to the solution ones. The optical bandgaps ( $E_{g,opt}$ s) of IDT-R, IDTT-R, and IDTT-T are estimated from the film absorption edge as 1.96 eV, 1.84 eV, and 1.82 eV, respectively, while those of IDT-CR, IDTT-CR, IDT-CT, and IDTT-CT films as 1.78 eV, 1.74 eV, 1.63 eV and 1.63 eV, respectively. The decreased bandgap for the ring-locked NFAs could suggest a potential of improving light-harvesting when used for OSCs.

The electrochemical (EC) properties of these NFAs were investigated by cyclic voltammetry (CV) (Fig. S1<sup>†</sup>). As shown, both IDT-R and IDTT-R exhibit irreversible oxidation and reduction processes, while others all exhibit a quasi-reversible oxidation process. Then, the highest occupied molecular orbital (HOMO) and LUMO energy levels are calculated according to the equation of  $E_{HOMO/LUMO} = -(E_{ox/red,onest} + 4.8) eV$ , which are shown to be effectively affected by tuning the central cores, the  $\pi$ -bridge, and the end-groups, as listed in Table 1. Overall, the HOMO energy levels range from -5.25 eV to -5.44 eV, and the LUMO energy levels range from -3.38 eV to -3.67 eV. Due to enhanced electron-donating ability, the use of IDTT as the central core will lead to increased HOMO energy levels compared to those from IDT, while the use of TBA as end-groups will decrease the LUMO energy levels compared to those from RCN, due to enhanced electron-withdrawing ability. Their electrochemical energy bandgaps ( $E_{g,ec}s_{j}$  Table 1) were also calculated according to the equation of  $E_{g,ec} = E_{LUMO}$  - $E_{HOMO}$ , which are consistent with the above  $E_{g,opt}$ s. The EC characterization of NFAs was also carried out by differential pulse voltammetry (DPV) to compare their CV data as shown in Fig. S1c<sup>†</sup> and Table S3<sup>†</sup>. Based on these results, we can conclude that the introduction of ring-locked bridge is likely to elevate the HOMO/LUMO energy levels.



Fig. 4 Normalized UV-Vis absorption spectra in chloroform solutions and as thin films.

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E<sub>g,ec</sub> (eV) 1.91 1.83 1.87 1.90 1.87 1.78

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Table 1. Optical and electrochemical data of NFAs.												
	NFAs	$\varepsilon_{max}^{a}$ (10 <sup>5</sup> M <sup>-1</sup> cm <sup>-1</sup> )	λ <sub>sol</sub> b (nm)	FWHM <sub>sol</sub> c (nm)	λ <sub>fil</sub> b (nm)	FWHM <sub>fil</sub> c (nm)	E <sub>g,opt</sub> <sup>d</sup> (eV)	<sub>Номо</sub> е (eV)	E <sub>LUMO</sub> e (eV)			
	IDT-R	1.19	576	77	583	97	1.96	-5.44	-3.53			
	IDTT-R	1.43	590	82	598	116	1.84	-5.32	-3.49			
	IDTT-T	1.48	620	77	625	103	1.82	-5.51	-3.64			
	IDT-CR	0.95	598	119	590	151	1.78	-5.34	-3.44			
	IDTT-CR	1.21	610	119	602	154	1.74	-5.25	-3.38			
	IDT-CT	1.02	639	116	655	144	1.63	-5.39	-3.67			
	IDTT-CT	1.34	641	126	653	155	1.63	-5.28	-3.65			

<u>IDTT-CT</u> 1.34 641 126 653 155 1.63 -5.28 -3.65 1.68 <sup>a</sup>Molar extinction coefficients measured in 10<sup>-5</sup> M chloroform solutions. <sup>b</sup>The maximum absorption wavelength of NFAs. <sup>c</sup>Full width at half maxima of absorption bands. <sup>d</sup>Calculated from the film absorption edge ( $\lambda_{edge}$ ) according to the equation of  $E_{g,opt} = 1240/\lambda_{edge}$ . <sup>e</sup>Measured by cyclic voltammograms of NFAs in dichloromethane/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> solution. The HOMO and LUMO energy levels are calculated according to the equation of  $E_{HOMO/LUMO} = -(E_{ox/red} + 4.80)$  eV. <sup>f</sup>Calculated according to the equation of  $E_{g,ec} = E_{LUMO} - E_{HOMO}$ .



**Fig. 5** (a) The illustration of nucleophilic addition reaction of ITIC with EA. Normalized UV–Vis absorption spectra of NFAs, (b) ITIC, (c) IDTT-T, (d) IDTT-CT, (e) IDTT-R and f) IDTT-CR, before and after adding EA in THF:H<sub>2</sub>O mixtures (96:4, V/V). The concentration of NFAs is controlled at  $10^{-5}$  M, while that of EA is  $10^{-3}$  M (b, c, d) and 0.15 M (e, f), respectively.

**Chemical Stability against Nucleophilic Reagent** 

As discussed in the introduction, the A-D-A-type NFAs synthesized by a typical Knoevenagel condensation generally contain very electrophilic carbon-carbon double bonds that can be easily attacked by the nucleophiles such as amine derivatives in the many interface materials for OSCs. Fig. 5a and S2a† illustrate a typical Michael addition underwent between ITIC and EA, and the afforded products were well confirmed by HRMS (Fig. S2b<sup>†</sup>). Initially, EA attacks the  $\beta$ carbon of ITIC and destroys the conjugated structure (Fig. 5a). Then, the terminal acceptor moieties are lost (Fig. S2a<sup>†</sup>). Fig. 5b shows the absorption spectra before and after adding EA (10<sup>-3</sup> M) into the ITIC solution, in which a clear intensity decrease can be found for the ICT-induced absorption band due to the interruption of D-A conjugation. Similarly, the addition of EA into IDTT-T solution also induces a substantial absorption change (Fig. 5c). Nonetheless, the corresponding ring-locked NFAs excitingly show a much enhanced chemical stability against EA as we expected initially. As shown in Fig. 5d, only a 12% decrease of absorption intensity was induced after adding EA into IDTT-CT, and after keeping the mixed solution for 40 min, it was still remained 45% of its initial value. In addition, RCN-based NFAs show an enhanced intrinsically chemical stability against EA, even without ringlocked bridge. We attribute this to the decreased electronwithdrawing ability of RCN-based end-groups that makes the double bond less electrophilic than that in the INCN and TBA based NFAs. However, when increasing the EA concentration from 10<sup>-3</sup> M to 0.15 M and simultaneously extend the reaction time, there is a significant difference still observed for RCNbased NFAs; for IDT-R and IDTT-R (Fig. S3f<sup>†</sup> and 5e), the ICTinduced absorption band showed a decrease of ~25% after 1.5 h, which almost disappeared after 19 h, while for IDT-CR and

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IDTT-CR, over 85% was still remained after 19 h (Fig. S3g<sup>†</sup> and 5f).

#### Photostability

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Photodegradation is one of long-standing challenges for organic photovoltaic materials. We then tested the photostability of NFAs in THF solutions under continuous one sun irradiation (100 mW/cm<sup>2</sup>) by monitoring the change of their absorption. As displayed in Fig. 6a, after 10 min illumination, the UV–Vis absorption intensity of ITIC was reduced by over 50%. To identify whether UV light has a more pronounced effect, the absorption change of ITIC under light with UV filter (transmission spectrum shown in Fig. S4†) was also monitored. However, a negligible impact on enhancing

the photostability was observed as shown in Fig. 6b, indicating UV-light irradiation is not the DMajor<sup>103</sup> Caston<sup>99</sup> for photodegradation of ITIC-type NFAs. Encouragingly, both ringlocked IDTT-CR and IDTT-CT (Fig. 6d and f) demonstrated better photostability in comparison to their analogues without ring-locked bridges (Fig. 6c and e) and ITIC. As shown, after 10 min irradiation, IDTT-T was photodegraded almost completely, while the absorption intensity of IDTT-CT can still remain 90% of its initial value. These results thus strongly illustrate that the ring-locking strategy can significantly enhance the intrinsic photostability of NFAs.



**Fig. 6** Normalized UV–Vis absorption spectra of (a) ITIC, (b) ITIC with UV filter, (c) IDTT-R, (d) IDTT-CR, (e) IDTT-T, and (f) IDTT-CT in THF solutions in air under different irradiation time (100 mW/cm<sup>2</sup>). The concentration of NFAs is controlled at 10<sup>-5</sup> M.



**Fig. 7** (a) Chemical structures of polymer donors P3HT and PTB7-Th. (b) Energy levels of polymer donors and seven acceptors. J-V characteristics of (c) the P3HT:NFAs-based devices and (d) the PTB7-Th:NFAs-based devices.

#### Photovoltaic Performance and Film Morphology

Single-junction inverted OSCs with a device structure of ITO/ZnO/polymer donor:NFAs/MoO<sub>3</sub>/Ag were fabricated to investigate the photovoltaic performance of these ring-locked NFAs and the device fabrication details are provided in ESI<sup>+</sup>. For comparison, the devices of IDT-R, IDTT-R and IDTT-T were also fabricated at the same conditions. Two well-known polymer donors, P3HT and PTB7-Th (Fig. 7a), were used in this work. The energy level alignment of polymer donors and NFAs is shown in Fig. 7b, in which it can be easily seen that all NFAs seem to have compatible energy levels with P3HT donor. Moreover, the LUMO levels of RCN-based NFAs are not compatible to that of PTB7-Th, which are detrimental to the exciton separation. We also employed another widely-used polymer donor, i.e. PBDB-T, to blend with these ring-locked acceptors, but the resulting performance was even worse than that from PTB7-Th (Table S4<sup>†</sup>).

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 Table 2 The optimal photovoltaic parameters<sup>a</sup> of solar cells based on the six acceptors under the irradiation (AMel.5GJe100he mW/cm<sup>2</sup>).

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Donor:acceptor	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm²)	FF (%)	PCE (%)
P3HT:IDT-R	0.73 ± 0.02	3.73 ± 0.32	51.25 ± 0.75	1.29 ± 0.28 (1.57)
P3HT:IDTT-R	0.78 ± 0.02	0.83 ± 0.28	48.18 ± 0.82	0.17 ± 0.26 (0.43)
P3HT:IDT-CR	$0.66 \pm 0.01$	2.62 ± 0.35	49.26 ± 0.74	0.67 ± 0.32 (0.99)
P3HT:IDTT-CR	0.82 ± 0.03	5.61 ± 0.38	55.06 ± 0.94	2.52 ± 0.34 (2.86 )
PTB7-Th:IDTT-T	$0.98 \pm 0.01$	$13.71 \pm 0.31$	62.39 ± 0.61	8.41 ± 0.31 (8.72)
PTB7-Th:IDT-CT	$0.93 \pm 0.01$	11.19 ± 0.26	42.32 ± 0.68	4.40 ± 0.22 (4.62)
PTB7-Th:IDTT-CT	$0.93 \pm 0.01$	12.58 ± 0.27	50.45 ± 0.55	5.89 ± 0.24 (6.13)

<sup>a</sup>Data obtained from the average of 15 individual devices, and the best PCEs are shown in brackets.

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Fig. 7c displays the current density-voltage (J-V) curves of the champion devices of RCN-based NFAs with P3HT as the polymer donor, and the corresponding device parameters are summarized in Table 2. To date, rhodanine-based NFAs has shown a particular compatibility with P3HT donor with an impressive PCE of 7% realized for binary OSCs yet.<sup>6</sup> However here, all the device performance is not very satisfied compared to the state-of-the-art P3HT-based OSCs reported so far, possibly due to that their unfavorable absorption properties (Fig. S5<sup>†</sup>) that lead to very low short-circuit currents ( $J_{sc}s$ ). Overall, the P3HT:IDTT-CR based devices show the highest PCE of 2.86% among them with an open-circuit voltage ( $V_{\rm OC}$ ) of 0.85 V, a  $J_{SC}$  of 5.99 mA /cm<sup>2</sup> and a fill factor (FF) of 56%. Nonetheless, we could not claim that our proposed ring-locked strategy could be able to improve the device efficiency given the fact IDT-CR-based devices even exhibit a lower PCE (0.99%) than that of IDT-R-based ones (1.57%). On the other hand, TBA-based NFAs, IDT-CT and IDTT-CT were also used to blend with the P3HT donor. However, the fabricated devices even performed worse than RCN-based ones, although the TBAbased NFAs exhibit a red-shifted absorption and decreased LUMO levels. Fortunately, when using PTB7-Th as the polymer donor for the TBA-based NFAs, the resulting device efficiency can be significantly improved due to their enhanced compatibility, and the IDT-CT and IDTT-CT -based devices can produce PCEs of 4.62% and 6.13%, respectively, as shown in Fig. 7d and Table 2. As shown, ring-locked IDTT-CT delivered a decreased device performance compared to the IDTT-T analogue with a best PCE of 8.72%. Nonetheless, IDTT-CTbased devices exhibited much enhanced device stability as discussed later. The external guantum efficiency (EQE) spectra (Fig. S6<sup>†</sup>) of P3HT:IDTT-CR and PTB7-Th:IDTT-CT -based devices were also measured under the AM 1.5G solar spectrum (100 mW/cm<sup>2</sup>). For the P3HT:IDTT-CR-based device, the  $J_{sc}$ calculated by the integration of the EQE spectrum is 4.80  $mA/cm^2$ , which does not agree well with the experimental  $J_{sc}$ . The device deterioration is the main reason and will be discussed later. The calculated  $J_{SC}$  (12.17 mA/cm<sup>2</sup>) for PTB7-Th/IDTT-CT-based device was similar to that measured by J-V measurements (5.3% mismatch).



**Fig. 8** The device performance variation under continuous irradiation: (a) P3HT:IDTT-CR device, (b) PTB7-Th:IDTT-CT and (c) PTB7-Th:IDTT-T device in a glovebox with dry nitrogen atmosphere under one sun irradiation (100 mW/cm<sup>2</sup>); PTB7-Th:IDTT-CT devices in air under one sun irradiation (100 mW/cm<sup>2</sup>) (d) with UV filter and (e) without UV filter; (f) PTB7-Th:IDTT-CT devices at 85 °C in a glovebox with dry nitrogen atmosphere.

To check whether the enhanced chemical/photochemical stabilities of our designed ring-locked NFAs would help to improve the device stability, we first studied the device performance variations of P3HT:IDTT-CR, PTB7-Th:IDTT-T and PTB7-Th:IDTT-CT blends under simulated AM 1.5G solar spectrum irradiation in the glove box with dry nitrogen atmosphere, and the corresponding degradation curves of

different photovoltaic parameters are shown in Fig. 8a-c, respectively. The P3HT:IDTT-CR-based devices display dramatic burn-in degradation in the first 5 h, although IDTT-CR has higher chemical/photochemical stabilities than IDTT-CT. After continuously irradiating for 200 h, the PCE of P3HT:IDTT-CR blend exhibited a serious decrease up to ~50%, while only 14% was observed for that of PTB7-Th:IDTT-CT blend. Encouragingly, the photostability of PTB7-Th:IDTT-CT device was found to be much better than that of PTB7-Th:IDTT-T device which only remained 57% of initial PCE under similar test conditions. This result thus directly confirms the advantages of our ring-locked strategy in enhancing the intrinsic stabilities of NFAs.

Beyond that, the photostability of PTB7-Th:IDTT-CT devices in air under one sun irradiation with or without UV filter were further evaluated (Fig. 8d and 8e), both of which can encouragingly show a comparable stability as that treated in dry nitrogen atmosphere, and retain over 80% of the original PCEs. These results thus strongly suggest the negative effects of oxygen and UV-light in degrading the device performance can be alleviated effectively by taking advantage of our proposed ring-locked strategy. By sharp contrast, the device performance of traditional state-of-the-art NFAs such as ITIC, ITIC-4F, and IT-M experienced a more severe decay under similar test conditions, and less than 40% of their original PCEs were retained only after 100 h under one sun exposure in dry nitrogen atmosphere (Fig. S7<sup>†</sup>). Since the device stability of OSCs is also affected by heat, we further checked the thermostability of PTB7-Th:IDTT based devices heated at 85 ℃ in dry nitrogen atmosphere. As shown in Fig. 8f, ~70% of initial PCE can be retained after heating for 100 h.





As discussed above, IDTT-CR exhibits a better chemical and photochemical stabilities than IDTT-CT, however the P3HT:IDTT-CR devices reversely showed a worse device stability. To reveal the reason for the distinct device stability between P3HT:IDTT-CR and PTB7-Th:IDTT-CT, We thus characterized the evolution of blend film morphologies after light irradiation via AFM. As displayed in Fig. 19,118/P3HP3DFP CR blend film show great change in terms of surface roughness with the root mean square roughness (Rq) from 4.27 nm to 8.10 nm after 24 h light irradiation, while a negligible change is observed for the PTB7-Th:IDTT-CT blend film. Consequently, the morphology change should be responsible for the significantly decreased performance for the P3HT:IDTT-CR blend. The above results further indicate the light-induced performance degradation of OSCs is a complicated process, which is related to not only the intrinsic photochemical stability of materials but also the physical film morphology.

#### Conclusions

In summary, we designed and synthesized four ring-locked NFAs, IDT-CR, IDTT-CR, IDT-CT and IDTT-CT by adapting cyclohexene as  $\pi$ -conjugated bridge. Compared with the control NFAs without ring-locked bridge, the ring-locked NFAs have demonstrated significantly enhanced chemical stability against nucleophilic reagents such as primary amine derivatives as well as improved photochemical stability against strong light irradiation, attributed the removal of  $\beta$ -hydrogen atoms in the electrophilic double bonds and the formation of intramolecular C–H···O interactions to stabilize the γ-hydrogen atoms. Meanwhile, the introduction of cyclohexene-based bridge can slightly enlarge the conjugation of acceptors, leading to red-shifted UV-Vis absorption spectra with decreased optical bandgaps. When blended with a widebandgap polymer donor (P3HT), the IDTT-CR-based solar cells exhibited a PCE of 2.86%. Adapting a low-bandgap polymer PTB7-Th to blend with IDTT-CT, the optimized devices showed a PCE of 6.13 %. Although the PCEs are not as high as those of state-of-the-art NFA-based OSCs, these two blends demonstrated a much enhanced device stability. In particular, the PTB7-Th:IDTT-CT-based OSCs can retain over 80% of its initial PCE in air after one sun irradiation without UV filter for 200 h, while ~70% after heating at 85  $^\circ$ C for 100 h. These results thus strongly suggest the use of ring-locked πconjugated bridge is an effective strategy for improving NFAs chemical/photochemical stability and provides a good molecular insight for designing stable NFAs. Moreover the relatively inferior device stability for P3HT:IDTT-CR-based devices further highlights the importance of maintaining stable morphology on the device stability.

#### Conflicts of interest

There are no conflicts to declare.

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