Strong Intermolecular Interactions Induced by High Quadrupole Moments Enable Excellent Photostability of Non-Fullerene Acceptors for Organic Photovoltaics

Joel Luke, Emily J. Yang, Yi-Chun Chin, Yuxuan Che, Lisa Winkler, Darius Whatling, Chiara Labanti, Song Yi Park, and Ji-Seon Kim*

Understanding degradation mechanisms of organic photovoltaics (OPVs) is a critical prerequisite for improving device stability. Herein, the effect of molecular structure on the photostability of non-fullerene acceptors (NFAs) is studied by changing end-group substitution of ITIC derivatives: ITIC, ITIC-2F, and ITIC-DM. Using an assay of in situ spectroscopy techniques and molecular simulations, the photodegradation product of ITIC and the rate of product formation are identified, which correlates excellently to reported device stability, with ITIC-2F being the most stable and ITIC-DM the least. The choice of acceptor is found to affect both the donor polymer (PBDB-T) photostability and the morphological stability of the bulk heterojunction blend. Molecular simulations reveal that NFA end-group substitution strongly modulates the electron distribution within the molecule and thus its quadrupole moment. Compared to unsubstituted-ITIC, end-group fluorination results in a stronger, and demethylation a weaker, molecular quadrupole moment. This influences the intermolecular interactions between NFAs and between the NFA and the polymer, which in turn affects the photostability and morphological stability. This hypothesis is further tested on two other high quadrupole acceptors, Y6 and IEICO-4F, which both show impressive photostability. The strong correlation observed between NFA quadrupole moment and photostability opens a new synthetic direction for photostable organic photovoltaic materials.

1. Introduction

Organic photovoltaics (OPVs) have seen impressive efficiency improvements in the last few years due to the development of non-fullerene acceptors (NFAs), particularly the new Y6 (2,2′-((2Z,2′Z)-(12,13-bis(2-ethylhexyl)-3,9-diundecyl)-12,13-dihydro-1H-thia[3,4-c]thieno[2″,3″:4,5]pyrrolo[3,2-g]thieno[2′,3′:4,5]thieno[2,3-b]indole-2,10-diyl))bis(methanylylidene)-bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)dimalononitrile) family, which has achieved efficiencies of over 18%. However, the poor operational lifetimes of many high performing NFAs limit their use in commercial modules. It is therefore important to understand the degradation mechanisms of these acceptors to enable the synthesis of more stable acceptor materials.

One of the most popular acceptor families is based on ITIC (3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-b]dithiophene), which utilizes a fused conjugated IDTT (indacenodithienothiophene) core with strongly electron-withdrawing INCN (2-(3-oxo-2,3-dihydroinden-1-ylidene)-1,2-b:5,6-b′-dithiophene), which utilizes a fused conjugated ITDT (indacenodithiophene) core with strongly electron-withdrawing INCN (2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile) groups on the periphery, and out of plane 4-hexylphenyl sidechains that are used to limit π-π stacking and reduce self-aggregation in the blend. When compared to fullerenes, ITIC shows better performance due to its strong visible-near IR absorption, leading to a high external quantum efficiency. Understanding degradation mechanisms of organic photovoltaics (OPVs) is a critical prerequisite for improving device stability. Herein, the effect of molecular structure on the photostability of non-fullerene acceptors (NFAs) is studied by changing end-group substitution of ITIC derivatives: ITIC, ITIC-2F, and ITIC-DM. Using an assay of in situ spectroscopy techniques and molecular simulations, the photodegradation product of ITIC and the rate of product formation are identified, which correlates excellently to reported device stability, with ITIC-2F being the most stable and ITIC-DM the least. The choice of acceptor is found to affect both the donor polymer (PBDB-T) photostability and the morphological stability of the bulk heterojunction blend. Molecular simulations reveal that NFA end-group substitution strongly modulates the electron distribution within the molecule and thus its quadrupole moment. Compared to unsubstituted-ITIC, end-group fluorination results in a stronger, and demethylation a weaker, molecular quadrupole moment. This influences the intermolecular interactions between NFAs and between the NFA and the polymer, which in turn affects the photostability and morphological stability. This hypothesis is further tested on two other high quadrupole acceptors, Y6 and IEICO-4F, which both show impressive photostability. The strong correlation observed between NFA quadrupole moment and photostability opens a new synthetic direction for photostable organic photovoltaic materials.

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efficiency between 350 and 750 nm. Since the introduction of ITIC, it has been paired with a myriad of polymers,[4,5] and its structure has been modified in numerous ways, including side-chain engineering,[6] and core or end-group modification.[7–10]

High performances have been achieved with ITIC-based acceptors reaching efficiencies of over 14%.[11] However, despite some ITIC containing bulk heterojunction (BHJ) blends demonstrating good thermal stability,[12] ITIC devices commonly show initial burn-in losses,[13] limiting their operational lifetime and commercial applicability. Previously, we have suggested that this burn-in loss is related to the intrinsic instability of ITIC toward light, with ITIC undergoing a light-induced conformational change that disrupts packing and results in trap formation.[14] Other groups have suggested that cis/trans isomerization of the vinyl group linking the core and end-groups is also an important step in ITIC degradation, allowing for epoxide formation under oxygen,[15] or a triplet mediated electrocyclization followed by a hydride shift resulting in an isomeric photodegradation product that quenches absorption.[16]

Additionally, ITIC has also been shown to be incompatible with certain interlayers such as ZnO and polyethylenimine.[17–20] Morphological instability has similarly been suggested to contribute to burn-in.[21] Other NFAs have also been shown to degrade via conformational change such as IDTBR[22] although when the NFA is more rigid, such as Y6, this degradation pathway is closed off.[23] However, despite Y6 demonstrating good photostability there are additional problems with its morphological stability in BHJ blends.[24]

More promisingly for the ITIC class of acceptors, the stability of fluorinated ITIC-2F has been shown to exceed an extrapolated $T_{90}$ of over 10 000 h, with stability being highly dependent on side-chain and end-group modification, where dimethylation of the end-groups leads to extremely poor stability.[25] The initial morphology is also shown to be highly important for ITIC-2F stability, with burn-in fill factor (FF) losses arising from polymer reorganization and diffusion limited aggregation of the acceptor.[26]

Despite these studies it is still not clear why some ITIC derivatives demonstrate very different burn-in behavior and photostability. Herein, we compare ITIC to two of its derivatives, ITIC-DM and ITIC-2F, in which the former has shown very poor, and the latter very good burn-in stability (molecular structures in Figure 1).[25] ITIC-DM has two inductive methyl substituents attached to each INCN end-group, and ITIC-2F (also known as IT-4F) has two electronegative fluorine atoms substituted on each end-group. ITIC-DM was originally fabricated to raise the lowest occupied molecular orbital (LUMO) level of the acceptor for improved open-circuit voltage ($V_{OC}$).[7] whilst

![Figure 1. Chemical structures of a) ITIC-DM, b) ITIC, and c) ITIC-2F. End-group substituents are highlighted in red; d) absorption spectra of neat films of ITIC-DM, ITIC, and ITIC-2F before and after 7 days of 1 sun white LED illumination; e) in situ Raman spectra of neat acceptor films taken at increasing 514 nm laser bleaching time, f) extracted peak intensities from (e) at 1577, 1456, and 1345 cm$^{-1}$ for all three derivatives.](image-url)
ITIC-2F has a narrower bandgap, and deeper energy levels due to the electronegativity of the fluorine resulting in a lower $V_{OC}$ but high current in OPV blends due to the harvesting of lower energy photons. The photostability of devices of these acceptors with PBDB-T polymer donor (poly[(2,6-(4,8-bis(5-(2-ethylhexyl)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′:5′,6′-c′]dithiophene-4,8-dione))] are reported in the literature, with on overall BHJ blend morphological stability. The authors of this study find that ITIC crystallinity increases during photaging, whilst ITIC-DM shows some chemical instability. However, no detailed degradation mechanisms are given. In this study, we first investigate the role of ITIC acceptor end-group substitution on photostability and its impact on morphological stability in blends with PBDB-T donor polymer. We extend our study to other high performance NFA acceptors such as Y6 and IEICO-4F (2,2′-(22,22′-Z)-((4,4,9,9-tetrakis(4-hexylphenyl))-4,9-dihydro-sindaceno[1,2-b:5,6-b′]-dithiophene-2,7-diyl)bis(4-(2-ethylhexyl)oxy)dithiophene-5,2-diyl)bis(methanlylidene)bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)dimalononitrile). By using an assay of in situ spectroscopy techniques combined with molecular simulations, we identify the photodegradation product and the rate of product formation in ITIC NFAs. Moreover, we demonstrate a strong correlation between NFA molecular quadrupole moment and its photostability, and the impact that has on overall BHJ blend morphological stability.

2. Results and Discussion

2.1. Neat Film Photodegradation

We first study neat films of ITIC, ITIC-DM, and ITIC-2F. They were degraded in an inert atmosphere under white light LED illumination with an intensity of $\sim 100 \text{ W m}^{-2}$ (emission spectrum in Figure S1, Supporting Information). The fresh and 7-day aged absorption spectra of neat films are given in Figure 1b. The fresh ITIC absorption spectrum consists of a main absorption peak at 708 nm. ITIC-DM has a similarly shaped peak slightly blue-shifted (704 nm), whilst the main peak of ITIC-2F is red-shifted by 28 nm compared to ITIC. Upon aging, the main acceptor peak is quenched; ITIC and ITIC-DM show similar amounts of quenching, 38% and 33%, respectively, whilst the ITIC-2F peak intensity is only quenched by 18%. Additionally, there is an increase in absorption between 400 and 500 nm which is assigned to a degradation product with a slightly higher bandgap than the fresh molecule. We have previously suggested that this degradation product is the result of a conformational change, namely INCN end-group rotation. However, more recently this high energy absorption has been assigned to the product of a triplet mediated isomerization, which we will discuss in more detail below. Regardless of the nature of this peak it is indicative of product formation and is most prominent in the aged ITIC-DM spectra, indicating significant degradation product formation in this film.

To highlight the changes in absorption upon ageing, difference spectra between fresh and degraded films are given in Figure S2, Supporting Information. All ITIC derivatives show a loss of optical density (OD) at $\sim 700 \text{ nm}$ indicating molecular photo-bleaching, and an increase of OD at 500 nm due to formation of a higher bandgap degradation product. In terms of intensity loss, ITIC and ITIC-DM show a similar degree of loss in OD, whilst ITIC-2F shows comparatively less. ITIC-DM shows the most blue-shifted product and the highest increase in product absorption with ITIC and ITIC-2F both showing less. With methylation the new optical absorption peak is slightly narrower and higher in energy than ITIC, whilst ITIC-2F shows a red-shift of 38 nm compared to ITIC. This red-shift is similar to the red-shift upon fluorination in the fresh films. This suggests that the energetics of the new species is affected by end-group modifications and can therefore not just result from a simple loss of end-groups. Instead, the changes are likely to result from a conformational, morphological, or isomeric change, which will be discussed in detail later.

To investigate the nature of degradation in more detail accelerated in situ laser degradations were carried out under nitrogen with an excitation of 514 nm which is resonant with the increasing high energy absorption assigned to the degradation product. Baseline Raman spectra at increasing degradation times are shown in Figure 1e. Raman spectroscopy is used as it is sensitive to both the molecular structure and conformation, allowing for detailed characterization of degradation products. Consistent with the changes in absorption it is evident that ITIC-DM shows the largest spectral changes, followed by ITIC, and with ITIC-2F showing only minor changes. With degradation, ITIC and ITIC-DM show an increase in Raman intensity which is ascribed to growing in of the degradation product that absorbs at 500 nm. This absorption is resonant with the 514 nm excitation laser leading to selective enhancement of the Raman intensity of the degradation product. The peak changes observed are the same as those we have previously reported. There is a general increase in most peaks, highlighting the similarity between ITIC and the degradation product. However, the alkene peak at 1550 cm$^{-1}$ doesn’t increase, and instead a new alkene peak at 1577 cm$^{-1}$ grows in. Similarly, a high frequency carbonyl peak also grows in. To demonstrate the relative rates of product formation for the different derivatives the peak intensities of the new alkene at 1577 cm$^{-1}$, and thiophene peaks at 1456 and 1345 cm$^{-1}$ are extracted and shown in Figure 1e. Depending on the derivative, all the peaks increase at a similar rate, this rate being fastest for ITIC-DM, and much slower for ITIC-2F, confirming the observation that the photodegradation product accumulates more quickly in ITIC-DM films consistent with reported changes in the IR absorption spectra after long term illumination of ITIC-DM.

As we have previously reported, at 514 nm excitation the Raman spectra of degraded ITIC is due to growing signal from the degradation product. Therefore, the difference spectra between the fresh and degraded films are equivalent to the degradation product being formed. We therefore plot the Raman difference spectra in Figure S2, Supporting Information, which shows that the spectral changes in all the neat films are identical (it should be noted that with longer degradation...
times, neat ITIC-2F shows similar spectral changes to the other acceptors), indicating that the nature of degradation is the same regardless of derivative. However, it indicates that ITIC-2F is the most stable derivative whilst ITIC-DM is the least.

2.2. Blend Photodegradation

To understand how this absorption quenching proceeds in the blend, blend films, and a neat polymer film were degraded under the same conditions as above with the fresh and aged absorption spectra being given in Figure 2a. The fresh spectra in the blends are dominated by two peaks, the acceptor peak around 700 nm, and the polymer peak around 640 nm. Compared to the neat films the ITIC acceptor peak is blue shifted by 11 nm suggesting that ITIC crystallinity is disrupted by blending with the polymer, consistent with the previous reports.[31] ITIC-DM is less miscible with the PBDB-T polymer,[7] and as such the acceptor peak shifts by only 5 nm in the blend. Interestingly, the ITIC-2F peak maintains its position, indicating that its crystallinity is undisturbed in the blend.

Upon white light LED degradation both the polymer and acceptor peaks are quenched in PBDB-T:ITIC and PBDB-T:ITIC-DM, with a clear increase in high energy absorption in the ITIC-DM blend. Meanwhile, the ITIC-2F blend shows only minor quenching of the acceptor peak whilst the polymer peak is stabilized. The neat polymer shows some quenching upon ageing, and an increase in signal below the bandgap due to an increased film roughness leading to an increase in scattering. Looking at the difference spectra in Figure S2, Supporting Information, it is apparent that upon photo-ageing of the blend both the acceptor bleaching and new product formation are observed, although at much lower intensities, with ITIC-DM showing the largest change, followed by ITIC, whilst ITIC-2F shows the smallest bleach and minimal product absorption growth. Additionally, a second bleach at 634 nm corresponding to polymer absorption loss indicates that the PBDB-T polymer is also prone to degradation in the blend. This is observed when degrading neat films of the polymer, in which a strong bleach at 630 nm and an increase in absorption...
at 500 nm are observed indicating some conjugation breaking, additionally below the bandgap there is an increase in scattering. More interestingly, the lower energy peak centered at 630 nm is selectively quenched (grey trace in Figure S2, Supporting Information). This peak has a strong contribution from polymer aggregation,[32] indicating either that the aggregated form of the polymer is more prone to photodegradation, or that photodegradation results in disruption of polymer packing, that is, some conformational or morphological changes. In the blend the acceptor bleach is much sharper than in the neat films, and as such linear deconvolution of polymer and acceptor contributions is not possible. However, despite the overlap of the donor and acceptor components there is clear quenching of the polymer in the ITIC and ITIC-DM blends, whilst in the ITIC-2F blend there is negligible polymer quenching.

To probe the degradation product in the blends accelerated degradation was also conducted; with the spectra and extracted peak intensity changes shown in Figure 2. The fresh blend spectra are dominated by the polymer peaks due to the wider bandgap of PBDB-T being more resonant (neat PBDB-T spectra are shown in Figure S3, Supporting Information). Upon degradation of the blends there is an increase in Raman intensity in both the ITIC and ITIC-DM blends, with the latter showing the largest increase, whilst the ITIC-2F blend is stable. This is confirmed by again extracting the intensity of acceptor peaks at 1577 and 1456 cm⁻¹, and the polymer peak at 1427 cm⁻¹. The rate of peak increase is again dependent on the acceptor, with ITIC-DM blends showing the fastest increase, and ITIC-2F showing negligible changes. The rate of change of the polymer peak is similar to the acceptor peaks suggesting that the increase in this peak is actually due to the increase in overlapping acceptor intensity.

The difference spectra between fresh and degraded ITIC and ITIC-DM blends (Figure S2, Supporting Information) show the same spectral shape as the neat film degradation product, albeit at about half the intensity, indicating a slower rate of degradation in blends. These spectral changes, signifying acceptor degradation, indicate that the ITIC derivatives are sensitive to photodegradation even when blended with PBDB-T, and therefore are likely to contribute to the losses seen upon device degradation. Like the neat films, the ITIC-2F blend shows only small changes, highlighting the photostability of both ITIC-2F and PBDB-T when blended together, consistent with the stable absorption spectra. The small negative peak seen in the ITIC-2F blend correlates to quenching of the polymer thiophene peak at 1430 cm⁻¹. For the ITIC and ITIC-DM blends there is also a slight reduction in intensity between the neat and blend spectra around 1425, 1488, and 1540 cm⁻¹ (grey lines in Figure S2, Supporting Information), which correlate to the bleaching of polymer peaks (Figure S3, Supporting Information), consistent with the quenching of polymer absorption in these blends. The different degrees of degradation of the acceptors in the blends observed here match those observed from the absorption quenching.

2.3. Identifying the Nature of the Degradation Product

Having established all ITIC derivatives show the same degradation product, we now investigate the nature of this degradation product. Previously, we have assigned the Raman spectral changes upon degradation to INCN end-group rotation away from planarity and possible loss of end-groups.[14] However, Che et al. have recently suggested that upon illumination of ITIC and ITIC-2F in an inert environment there is a multistep triplet mediated isomerization.[16] This isomerization proceeds via a cis–trans isomerization (which is also detailed elsewhere)[15] that requires end-group rotation away from the minimum energy structure. This is followed by an electrocyclization and hydride shift to give the product P1, which is identified experimentally with NMR spectroscopy. The structure of P1 is shown in Figure 3a, with the newly formed ring highlighted in red. A further degradation can occur if both ends of the ITIC acceptor undergo this isomerization. It is important to note that an alternative but similar isomerization is possible via the formation of a pyran ring. However, this can confidently be ruled out as a primary degradation product, details of which are given in Figure S6, Supporting Information.

In order to identify the nature of the product we simulated the Raman spectra of P1 and compare it to ITIC as shown in the bottom of Figure 3a. The main changes upon this conversion are highlighted with arrows: the main thiophene C–C single bond peak at 1425 cm⁻¹, the phenyl peak at 1600 cm⁻¹, and the carbonyl peak at 1750 cm⁻¹ are shifted to higher frequencies; there is a quenching of the peak corresponding to the

![Figure 3](image-url)
alkene connecting the indanone to the malonitrile at 1522 cm\(^{-1}\) and a shift and increase in relative intensity of the vinylene bond to higher frequencies appearing at 1580 cm\(^{-1}\); and a new alkene peak at 1620 cm\(^{-1}\) corresponding to the double bond in the new 6-membered ring. It should be noted that the simulated spectra are based on single molecules in the gas-phase without accounting for any resonant peak enhancement, and as such give well-defined frequencies of vibration. In the solid state there are a range of ITIC environments and conformations that give rise to much broader peaks, and different relative peak intensities. However, despite these expected differences between simulated and measured spectra, the important features observed upon P1 formation are evident in the experimental spectra (Figure 3a, top). When we compare fresh ITIC with the degradation product the quenching of the alkene peak between malonitrile and indanone is particularly significant. The striking similarity between the simulated and experimental spectra upon P1 formation clearly indicate that this is the degradation product we are observing for all three ITIC derivatives in both neat and blend films. The simulated spectra of the P1 degradation product for ITIC-DM and ITIC-2F are given in Figure S5, Supporting Information.

To check if the photocyclization reaction pathway to form this P1 product is different between these derivatives, further Density functional theory (DFT) calculations were performed as previously described.\cite{16} As shown in the Figure 3b and Table S2, Supporting Information, the activation energy required for the isomerization of all three derivatives is very similar. Therefore, the much faster photodecomposition of ITIC and ITIC-DM cannot be directly attributed to differences in the single molecule photocyclization reaction pathway.

2.4. Morphological Stability

In addition to probing the formation of this degradation product we also probe the photoluminescence (PL) spectra of the BHJ blends, as this provides valuable information about blend morphological stability, with PL intensity being quenched by effective charge separation which is more significant in highly intermixed blend morphologies. The PL spectra of the blends as a function of laser illumination times are shown in Figure 4a. All fresh blends show two peaks: one at 675 nm corresponding to neat polymer emission, and a lower energy peak corresponding to neat acceptor emission at 780, 765, and 805 nm for ITIC, ITIC-DM, and ITIC-2F, respectively. Compared to neat acceptor films the acceptor emission is quenched significantly in the blend, predominantly due to charge transfer at the donor/acceptor interface, driven by the energetic offset between polymer and acceptor. Comparing the fresh blends with the neat acceptor films, the PL of ITIC-DM shows the least quenching (84%) whilst the emission of ITIC and ITIC-2F is nearly completely quenched (96% and 98%, respectively). The absolute intensity of the polymer peak is highest in the ITIC-DM blend and lowest in the ITIC-2F blend. The relatively poor quenching and high polymer emission in the ITIC-DM blend suggest that the charge transfer in this blend is less efficient than the other blends, this likely arises from a more phase-separated morphology with larger grains, and less interfaces formed between the donor and acceptor molecules. This is consistent with the surface morphology observed in AFM images of ITIC-DM blends, which show a rougher morphology with larger grains than the other two blends (Figure S7, Supporting Information).

Similar to the in situ Raman measurements above, here we use a 514 nm laser to degrade the sample at an accelerated rate as we have demonstrated before, details can be found in the Experimental Section.\cite{14,22} Upon illumination there is a fast initial drop in acceptor emission in all blends, with this drop being particularly significant (~75%) for ITIC-DM, indicating a rapid change in optoelectronic properties. ITIC shows an initial drop of 25% before acceptor PL begins to increase after a delay. ITIC-2F has a fast initial drop of 15% after which acceptor PL remains stable. In all blends the polymer PL increases with increased illumination time with PBDB-T:ITIC-DM showing the fastest increase, doubling in intensity after 50 s. The ITIC blend is slightly slower, taking twice as long to double in intensity, whilst the ITIC-2F blend is relatively stable increasing <25% after 300 s. The increase in polymer PL suggests a change in blend morphology that results in less effective charge transfer at the donor/acceptor interface,\cite{14,33} likely driven by phase segregation of small molecule acceptors from donor.
polymer domains. Upon illumination the initial reduction in acceptor PL could indicate improved excited state quenching at the heterointerface, but this is unlikely considering the increase seen in polymer PL. Instead, we attribute this quenching to the observed chemical instability of the ITIC derivatives, with neat acceptor films showing a quenching of emission with ITIC degradation. More interestingly, after this initial drop three different situations occur: in the ITIC-DM blend the acceptor PL continues to drop due to the acceptor itself being very unstable; in the ITIC blend the PL begins to rise which is consistent with a morphological change which is also observed upon degradation by Du et al.; finally, in the ITIC-2F blend PL remains stable indicating both a stable blend morphology and an intrinsically photostable acceptor.

So far, we have observed significant differences in the intrinsic photostability of different ITIC derivatives but have shown this is not driven by differences in the reaction pathway of single molecules. We have also observed different blend morphological stability depending on acceptor. In order to identify the origin of these stabilities we investigate the acceptor molecular structure effects in more detail, and how these influence intermolecular interactions in the solid state.

2.5. Intermolecular Interactions

To explore the molecular origins as to why the ITIC-2F is intrinsically more photo-stable and its blend more morphologically stable than other ITIC derivative blends, DFT simulations and energetic measurements were carried out.

All ITIC acceptors have a planar backbone structure that maximizes $\pi$-electron delocalization along the conjugated backbone. The potential energy scans (PESs) of the ITIC derivatives are performed as a function of the dihedral angle about the C–C single bond between the core and end-groups (Figure S8, Supporting Information). The scans of all ITIC derivatives are similar except a very small difference in the barrier heights for ITIC-DM to rotation. Due to the similarity in PESs we conclude that this is not the main factor contributing to differences in photostability in which an initial conformational change is required prior to cis–trans isomerization.

In addition, the frontier molecular orbitals of all acceptors are similar, being delocalized across the whole molecule but with the HOMO being more confined to the electron-rich core and the LUMO to the electron-deficient end-groups (Figure S9, Supporting Information). As consistent with previous studies, methylation is shown to raise both the HOMO and LUMO with the HOMO being more confined to the electron-rich core and the LUMO to the electron-deficient end-groups (Figure S9, Supporting Information). Deeper frontier orbitals are shown this is not driven by differences in the reaction pathway of single molecules. We have also observed different blend morphological stability depending on acceptor. In order to identify the origin of these stabilities we investigate the acceptor molecular structure effects in more detail, and how these influence intermolecular interactions in the solid state.

Due to the symmetrical design of these ITIC acceptors there are negligible dipoles in these molecules (Table S3, Supporting Information, which is in contrast with the banana-shaped Y6 family of acceptors which possess strong dipoles). Thus the long-range order is more dependent on the quadrupole moment of the molecules, particularly the contribution that is in the direction of the close $\pi$–$\pi$ stacking between molecules.[37,38] The quadrupole moment of a molecule is governed by the spatial distribution of partial charges within the molecule and as such is sensitive to the addition of electronegative or inductive moieties, particularly at the periphery of the molecule. Therefore, fluorination of the end-groups increases the molecular quadrupole moment, whilst demethylation leads to a reduction compared to ITIC. The increased quadrupole moment will enhance the strength of coupling between molecules, as evidenced by the tighter $\pi$–$\pi$ stacking, higher coupling constant, and higher electron mobility observed for ITIC-2F versus ITIC.[40] These stronger interactions also result in a stronger propensity of ITIC-2F to pack as evidenced by the stronger diffraction peaks observed for ITIC-2F compared to ITIC in as-cast films (using the same conditions used here).[41] This increased crystallinity in ITIC-2F films is also likely to reduce the amount of triplet formation,[42,43] closing off the triplet mediated isomerization.[16] The improved packing of ITIC-2F would also inhibit any conformational or isomeric changes due to the close packing of molecules restricting molecular motion and improving ITIC-2F photostability in the solid state relative to ITIC and ITIC-DM.

To gain further insight into the strong intermolecular interactions induced by the large $Q_x$ of ITIC-2F, we apply APS to probe the HOMO level of the polymer in the neat and blend films. The difference between neat and blend polymer HOMO levels is expected to arise due to interactions with the acceptor, with the larger the difference, the larger the interaction between the two (Figure 5b). Interestingly, only ITIC-2F shows deepening of the HOMO level of PBDB-T, indicating strong interactions between ITIC-2F and PBDB-T.

To understand this further we simulate the electrostatic potential of the acceptors and polymer, as shown in Figure 5c. Due to the bulky sidechains attached to the core of the molecule, the end-groups (circled) are more available for intermolecular interactions leading to end-group $\pi$–$\pi$ stacking,[44,45] although face-to-edge packing has also been reported in single crystals of ITIC-2F.[40] The fluorinated molecule shows more positively charged phenyl in the end-groups due to the strong electron-withdrawing effect of the fluorine, this is likely to affect $\pi$–$\pi$ interactions between ITIC molecules, with fluorination leading to an increase in coupling between ITIC molecules. This is also consistent with the increase in quadrupole moment discussed above, which will increase the quadrupole–quadrupole interaction strength between molecules. More importantly, interactions with the donor polymer are also likely to be affected by this changing ESP landscape. We propose that the acceptor/polymer interactions are strongest for ITIC-2F due to this more electron-deficient end-groups interacting strongly with the electron-rich backbone of PBDB-T. This is
consistent with reports that chlorination of the acceptor Y6, which increases polarity of the molecule, increases interaction strength with the donor polymer.\(^\text{[46]}\) These strong intermolecular interactions stabilize the heterointerface between the two components stabilizing charge separation and interfacial morphology leading to the stable PL upon illumination, as evident in Figure 4. This stable heterointerface also leads to stabilization of PBDB-T against photobleaching. Efficient excited state quenching is observed in the initial ITIC-2F/PBDB-T blend PL spectra, in which ITIC-2F shows the highest acceptor quenching and PBDB-T shows the lowest polymer emission. This effective quenching of the polymer and acceptor excited state may also close off excited state degradation pathways that are seen in other organic semiconductors.\(^\text{[34]}\) ITIC-DM on the other hand shows the coarsest initial morphology and highest PL, indicating poor excited state quenching, which could contribute to the higher rate of degradation seen in its blend. This is also consistent with ITIC-DM being less miscible with PBDB-T than other ITIC derivatives.\(^\text{[7]}\)

Our simulations and experimental results demonstrate that the superior stability of the PBDB-T:ITIC-2F blend arises from two main factors: good intrinsic acceptor photostability and strong intermolecular interactions between the donor and acceptor. Both of these can arise from the strong molecular quadrupole moment which enhances intermolecular interactions. This results in close packing of molecules that can then resist the conformational and isomeric changes observed upon degradation of the other ITIC acceptors. Whilst in the blend, strong intermolecular interactions between ITIC-2F and the donor PBDB-T polymer result in a highly intermixed stable blend morphology, and effective excited state quenching. The poor photostability of ITIC-DM on the other hand results from a lower \(Q_\pi\) which causes weaker interactions between acceptor molecules and with the polymer, allowing for conformational and isomeric changes to occur, and a coarse, unstable morphology to form in the blend. ITIC itself, with a \(Q_\pi\) value in between the other derivatives, is more photostable than ITIC-DM but still shows instability, particularly in the blend as the heterointerface is not stabilized as it is with ITIC-2F.

Hence, we hypothesize that strong intermolecular interactions induced by large quadrupole moments enable
conformational, and consequently energetic disorder. [23]

restrict any conformational distortion around this linkage, degradation indicating excellent photostability. This is further supported by the stable absorption spectra of IEICO-4F and Y6 compared to ITIC following 24 h of 1 sun white light LED degradation in an inert environment (Figure S11, Supporting Information). We note that in addition to the strong quadrupole moment, the improvement in Y6 photostability is also related to the undecyl side-chains on the periphery of the core unit that inhibits the isomerization pathway presented above due to the hydride shift no longer being possible, consistent with previous reports.[16] These alkyl side chains also restrict any conformational distortion around this linkage, closing off other potential degradation pathways and reducing conformational, and consequently energetic disorder.[21] Despite these nuances, our results show that the photostability of INCN containing acceptors correlates to the strength of the molecular quadrupole, which in effect is determining the intermolecular interactions.

Figure 6. a) Raman spectra of IEICO-4F and Y6 neat films before and after 9 min of in situ 633 nm laser degradation. b) The molecular structure of IEICO-4F with the electron withdrawing end-groups in blue, separated by d and the electronegative fluorine atoms highlighted in red.

Finally, to formulate potential molecular design rules for enhancing the quadrupole moment in A–D–A type acceptors, we perform DFT calculations on modified acceptor molecules and compare their $Q_a$ values. First, the comparison of the quadrupole moment ($Q_a$) of ITIC-2F and ITIC (232.4 and 130.3 $e a_0^2$, respectively) as well as simulated Y6 with and without fluorination (191.7 and 125.2 $e a_0^2$, respectively) suggest that addition of strongly electronegative atoms can increase the quadrupole moment in these NFAs. Further, by investigating a series of Y6 derivatives terminated by F (191.7 $e a_0^2$), Cl (175.7 $e a_0^2$), and Br (171.9 $e a_0^2$) atoms, it can be seen that this effect increases with increasing electronegativity of the terminating atoms. However, when substituting the end-groups with inductive methyl groups the reverse effect is realized, with the quadrupole moment of ITIC-DM (77.2 $e a_0^2$) being lower than ITIC.

Second, to investigate the role of the D–A–D Y6 core in determining the quadrupole moment two Y6 derivatives with alternative cores are simulated (Figure S12, Supporting Information). First, the electron-withdrawing sp² nitrogen atoms from the benzothiadiazole are replaced with carbon to disrupt the D–A–D structure (Y6*), and second all the nitrogen in the core are replaced with carbon (Y6**). As we make these changes the core becomes more electron rich and more donor like, losing its D–A–D character and enhancing the overall A–D–A structure. This is demonstrated by the increase in dipole upon substitution of nitrogen (Figure S4, Supporting Information). However, the quadrupole moments of Y6* and Y6** are 195.1 and 193.6 $e a_0^2$, respectively, which are similar to Y6 itself (191.7 $e a_0^2$), indicating that the D–A–D core structure does not contribute significantly to the overall quadrupole.

Third, calculations were also used to rationalize the greater $Q_a$ of IEICO-4F (282.1 $e a_0^2$) compared to ITIC-2F despite only small differences in their chemical structures (structures given in Figures 1,6). IEICO-4F has a longer but less fused donor core than ITIC-2F, increasing the effective conjugation length of the molecule and increasing the distance between the electron accepting end-groups. We note that although IEICO-4F has an unfused thiophene in the core, the minimized energy structure is essentially planar, similar to the ITIC derivatives. On this unfused thiophene there are also alkoxy side chains which do not appear in ITIC-2F. Upon removal of the alkoxy side chains the quadrupole moment of IEICO-4F is increased (297.3 $e a_0^2$), suggesting that these side chains are not responsible for the enhanced quadrupole moment. Instead, the increased physical separation between the acceptor regions in the backbone of IEICO-4F compared to ITIC-2F may be responsible for the difference observed. To test this we modeled an extended version of alkoxy-free IEICO-4F (Figure S13, Supporting Information) that utilizes an IDTT core (similar to ITIC) rather than indacenodithiophene (IDT). The resultant molecule has a larger quadrupole moment (353.7 $e a_0^2$) than the shorter IEICO-4F, confirming that increased separation of the acceptor units enhances the molecular quadrupole moment.

In summary, we have identified two key features to enhance the quadrupole moment in A–D–A type acceptors: a chemical effect (addition of strongly electronegative atoms or groups) and a physical effect (extending the distance between acceptor regions of the NFA molecule). These are highlighted on the IEICO-4F structure in Figure 6b.
3. Conclusion

To investigate the role of end-group substitution of ITIC on stability, the stability of ITIC, ITIC-DM, and ITIC-2F have been investigated. All ITIC derivatives are found to degrade via a photoinduced isomerization, with ITIC-2F being the most stable and ITIC-DM the least. This difference in stability is rationalized via considering the different intermolecular interactions and packing of the acceptors in the solid state. The close packing in ITIC-2F is suggested to inhibit the conformational and isomeric changes observed. In the blend, the strong molecular quadrupole and ESP distribution of ITIC-2F lead to strong interactions with the PBDB-T polymer which stabilizes the donor/acceptor heterointerface and effectively quenches the excited state, which closes off excited state driven degradation routes. This hypothesis is further tested on two other high quadrupole acceptors, Y6 and IEICO-4F, which both show impressive photostability. Our results demonstrate that intrinsic photodegradation pathways can be significantly influenced by the packing in the solid state and highlight the important role that NFA quadrupoles may play in understanding the photostability of OPV devices.

4. Experimental Section

Film Preparation and Degradation: Films were fabricated on clean indium tin oxide (for APS measurements) or quartz substrates (for absorption and Raman spectroscopy measurements) by spin-coating in an ambient atmosphere in a cleanroom. Solutions for spin coating were made in chlorobenzene with 0.5 vol% of diiodooctane (except Y6 which was spun from chloroform). Concentrations and spin conditions were kept consistent for all comparable films. Polymer and blend films had a thickness of 70–80 nm, whilst neat ITIC films were roughly 30 nm. Films were degraded in a sealed N2 atmosphere under an array of white LEDs (100 mW cm\(^{-2}\)). The spectrum of the LED array is given in Figure S7, Supporting Information.

Absorption Spectroscopy: A Shimadzu UV-2550 UV/visible spectrophotometer was used to measure steady state thin film transmittance and was converted to absorption taking into account the substrate but ignoring reflectance and scattering effects.

Raman Spectroscopy: Raman spectroscopy and PL measurements were taken using a Renishaw inVia Raman microscope in a backscattering configuration with a 50× objective and holographic notch filters to remove Rayleigh scattered light. A diffraction grating with 2400 l mm\(^{-1}\) was defocused during degradation so that the spectrum of the LED array is given in Figure S7, Supporting Information.

4.1. Absorption Spectroscopy

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

intermolecular interactions, non-fullerene acceptors, organic photovoltaics, photostability, quadrupole

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