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Photochemical stability of π -conjugated polymers for polymer solar cells: a rule of thumb⁺

Matthieu Manceau, Eva Bundgaard, Jon E. Carlé, Ole Hagemann, Martin Helgesen, Roar Søndergaard, Mikkel Jørgensen and Frederik C. Krebs*

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A comparative photochemical stability study of a wide range of π -conjugated polymers relevant to polymer solar cells is presented. The behavior of each material has been investigated under simulated sunlight (1 sun, 1000 W m⁻², AM 1.5G) and ambient atmosphere. Degradation was monitored during ageing combining UV-visible and infrared spectroscopies. From the comparison of the collected data, the influence of the polymer chemical structure on its stability has been discussed. General rules relative to the polymer structure–stability relationship are proposed.

Introduction

Polymer-based solar cells (PSCs) have the potential to become one of the future's renewable and environmentally friendly energy sources. Combining several attractive properties-flexibility, low manufacturing costs, low capital investment in equipment, a low thermal budget and the use of only abundant elements in the active layer-they open up a variety of new market opportunities and applications and have thus been under intense research focus during the last decade.¹⁻⁶ This development has led to a significantly improved device power conversion efficiency, that now exceeds 8%.7 To reach this, many classes of new polymers have been designed, synthesized, characterized and incorporated into photovoltaic devices.^{1,2,8-11} Consequently, a very broad range of material families have already been investigated in order to create polymers with good solubility, small band-gap, strong absorbance, appropriate HOMO and LUMO energy levels and high charge carrier mobilities.

However efficient and promising these materials are, their practical use in large-scale PSC production can only be successful if they also provide a good processability, a sufficient photochemical stability and device stability.^{12,13} So far, this last point has received limited attention and the literature is still scarce. As a result, the relationship between the polymer chemical structure and the expected device efficiency is rather well explored, the chemical structure–photochemical stability relationship, however, remains largely unknown. From a simplified chemical point of view, polymers for organic solar cells can be described as the combination of a rigid π conjugated backbone regularly substituted by side-chain groups ensuring their solution processability. Previously published papers already identified the critical role of the side-chain in the polymer degradation processes.^{14–16} A large difference in terms of the stability between MDMO–PPV and P3HT—two of the most studied polymers in the field—was also reported, P3HT being much more stable whatever the ageing conditions.¹⁷ However, to our knowledge, no detailed studies have yet been dedicated to the influence of the backbone nature on the polymer stability.

In this work, we present a photochemical stability study in air on 24 different polymers (34 including the thermo-cleaved derivatives) relevant to PSCs. Samples were selected to cover a very broad range of polymer types (purely donor, donor/ acceptor, thermo-cleavable, *etc.*) and chemical structures. Many of the moieties commonly used in the PSCs field are thus included in this paper. As all the experiments were conducted under the same conditions, comparison of the collected data was possible and the influence of different points is discussed (donor and acceptor group nature, side-chain type). This screening finally allowed for the description of general rules for the π conjugated polymer photochemical stability.

Experimental

Samples preparation

Synthetic procedures and characterization data for the materials have either been described in detail elsewhere^{18–24} or are given in the ESI[†]. Molecular weights and optical band-gaps of the samples are collected in Table S1, ESI[†] (where available, power conversion efficiencies have been added).

Pure polymer samples were spin-coated on KBr plates from chlorobenzene solutions. The polymer concentration in the

Risø National Laboratory for Sustainable Energy, Technical University of Denmark, P.O. Box 49, DK-4000 Roskilde, Denmark. E-mail: frkr@risoe. dtu.dk; Fax: +45 46 77 47 91; Tel: +45 46 77 47 99

[†] Electronic supplementary information (ESI) available: Characterization data of the polymers, list of abbreviations, thermal cleavage conditions and IR spectra recorded along ageing. See DOI: 10.1039/c0jm03105d

spin-coating solutions were adjusted to get a maximum peak absorbance of about 0.8 for each material.

Thermal cleavage was performed in the inert atmosphere of a glove box and the reaction progress was checked by IR spectroscopy. The heating step was kept as short as possible to avoid undesirable thermal degradation reactions. For cleavage temperatures and durations, see Table S2, ESI⁺.

Ageing and characterization

Samples were illuminated under 1 sun and ambient air with monitoring of the relative humidity (but no control) using a standard solar simulator from Steuernagel Lichttechnik (KHS 575, AM 1.5G, 1000 W m⁻², 85 °C, $30 \pm 10\%$ RH). The samples were removed periodically and UV-visible absorbance and IR spectra were recorded to monitor the degradation. UV-visible absorbance spectra were recorded from 200 to 1100 nm using a UV-1700 spectrometer from Shimadzu. IR spectroscopy was conducted with a Spectrum One from PerkinElmer operating in transmission mode (4 cm⁻¹ resolution, 32 scans summation).

Stability evaluation

To quantitatively compare all the materials, the total amount of absorbed photons (N_{Tot}) was monitored *versus* ageing time over the range $\lambda_1 - \lambda_2$ by summation over the polymer absorption peaks (Table S1, ESI†). This value was calculated according to the following equation:

$$N_{
m Tot}^t = \sum_{\lambda_1}^{\lambda_2} N_0(\lambda) imes \left(1 - 10^{-A^{t(\lambda)}}
ight)$$

where $A^{t}(\lambda)$ is the absorbance at a given wavelength (λ) and time (t), and $N_{0}(\lambda)$ is the incident photon flux. $A^{t}(\lambda)$ was directly extracted from the UV-visible absorbance spectra of the sample at the corresponding ageing time (t). The ASTM G173 standard was used as a reference for the incident photon flux.²⁵

At the end of the degradation, the quantity of absorbed photons systematically reached a constant value (N_{Tot}^{∞}) after which no absorbance evolution followed. This value was always above zero due to the absorption, reflection and scattering of the KBr substrate. Finally, the normalized number of photons absorbed by the polymer was calculated by:

$$N_{\rm Photons}^t = \frac{N_{\rm Tot}^t - N_{\rm Tot}^\infty}{N_{\rm Tot}^0 - N_{\rm Tot}^\infty}$$

For a great majority of the experiments, $N_{\text{Photons}'}$ exhibited a linear decay. In that case, the experimental data were then fitted with a straight curve. Quantitative comparisons of the respective stability of different samples were then established using the slopes of these curves. In some cases a logarithmic time scale was used for the sake of clarity.

Naming of compounds

Different abbreviations can often be found in the literature for the same material due to the very complex IUPAC names that these materials generally present. We have employed the most commonly employed abbreviations for these materials and also provide a list of the studied chemical units along with their full IUPAC names and the abbreviations in the ESI[†].

Results and discussion

Pure donor polymers

During the last decade, two polymer families have played a major role in the development of PSCs: polyphenylenevinylene derivatives and polythiophene. For example, polymers such as poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH–PPV), poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4phenylenevinylene) (MDMO–PPV) and poly(3-hexylthiophene) (P3HT) have been widely studied as they used to give the best device performances. A few reports on the photochemical stability of these materials have been published.^{14–17} Some of these studies revealed that polyphenylenevinylene derivatives are extremely unstable under photo-oxidative conditions.¹⁴ This behavior has been attributed both to the presence of the vinylene bond and of the alkoxy substituents. Conversely, P3HT has been shown to be much more stable.¹⁷

In this first part of the study, we compare the photochemical behavior in air of two donor conjugated polymers: MEH– PPV and poly(2,2'-(2,5-bis(2-hexyldecyloxy)-1,4-phenylene)dithiophene) (JC1) (Fig. 1).

Both materials are comprised of a dialkoxybenzene unit alternating either with a vinylene bond (MEH–PPV) or a bithiophene group (JC1). P3HT data were also added and used as a benchmark. From the results presented in Fig. 1, it is very clear that JC1 is much more stable than MEH–PPV. This result confirms that the exocyclic double bond has a very strong detrimental effect on the MEH–PPV stability. This very low stability is due to the fact that vinylene bonds can be easily saturated by the radicals formed after side-chain cleavage.¹⁴ Owing to its aromaticity, thiophene is much more difficult to saturate. Replacing the vinylene unit by a bithiophene thus greatly enhances the whole polymer stability.

Very interestingly, JC1 is observed to be as stable as P3HT which could be surprising as alkoxy side-chains are well-known for their poor stability. It should, however, be recalled that P3HT instability has been ascribed to the *hexyl* side-chains. The presence of two unsubstituted thiophene rings in JC1 then probably balances the presence of the alkoxy substituents on the *phenyl* ring and explains our finding.

Donor-acceptor copolymers, backbone composition effect

Presently, strong efforts are directed towards the synthesis of materials absorbing at longer wavelengths (*i.e.* with lower bandgaps) that can harvest a larger fraction of the solar spectrum. The most common strategy to control the band-gap is to alternate the electron-rich (donor) and electron-poor (acceptor) groups in the main chain of the polymer.^{8,26–28} An Internal Charge Transfer (ICT) from the donor to the acceptor occurs and a reduction of the band-gap is achieved. In this part of the study, attention will be focused on these so-called donor/acceptor polymers.

Influence of the donor group. Five series of polymers were aged to investigate the influence of the donor group on the stability of



Fig. 1 (Left) Chemical structure of the investigated samples, (right) evolution of the normalized amount of absorbed photons during photochemical ageing. Note how MEH–PPV degrades very quickly.

the polymer. For a given series of compounds, the only difference between the samples was the nature of the donor moiety.

Dithienylthienopyrazine series. Materials belonging to this first class are copolymers based on dithienylthienopyrazine bearing thermo-cleavable tertiary esters on the pyrazine ring, alternating with different donor groups: fluorene, carbon-bridged cyclopentadithiophene (CPDT), silicon-bridged cyclopentadithiophene (Si-CPDT) and thiophene (Fig. 2).

Fig. 3 presents the evolution of the normalized amount of absorbed photons *versus* ageing time for each polymer. As clearly observed, the stability ranking from the lowest to the highest is as follows: fluorene–CPDT–Si-CPDT–thiophene. It is also worth noting that an identical ranking is obtained with the cleaved materials but on a very different timescale (Fig. 3). This second point will be discussed in detail later. Different comments can be made based on this ranking. First of all, the two least stable polymers contain a quaternary carbon atom in their backbone. As this type of site can be readily oxidized,^{29,30} this can explain the poor stability of these two polymers that are completely bleached after less than 100 hours. Secondly, it can be noticed

Fig. 2 Chemical structure of the materials in the series of materials using a thermo-cleavable dithienylthienopyrazine (shown left). The X in the polymer backbone designates one of four donor groups shown to the right of the broken line.

that the substitution of this quaternary carbon atom by a silicon atom results in a significant improvement in the stability. One could imagine that this increase originates from a lowering of the HOMO level when carbon is replaced by silicon, as a deeper HOMO enhances the oxidative stability.³¹ However, Scharber et al. and Chen et al. previously showed that the nature of the bridging atom (C or Si) had almost no influence on the HOMO and LUMO levels of the polymer.^{32,33} This implies that the observed stability improvement cannot result from a lower HOMO level. But, it could be explained by the presence of the silicon atom which is known to be less easily oxidized than the carbon. Finally, using unsubstituted thiophene as a donor group highly improves the photochemical stability. More than 600 hours of irradiation are necessary to achieve full degradation. It is likely that this increase comes from the absence of both the quaternary site and side-chain in this donor moiety.

In parallel, the behavior of the non-cleaved samples was monitored by IR spectroscopy all along the ageing process (see Fig. S1, ESI[†]). Interestingly, very similar modifications are observed for the different polymers albeit on different timescales. Indeed, one can systematically notice: (i) a decrease in the intensity of the signals coming from the alkyl side-chains (3000- 2850 cm^{-1} ; (ii) the development of a broad signal in the carbonyl range (1800-1600 cm⁻¹) and (iii) the appearance of signals characteristic for sulfinic esters (1115 and 620 cm⁻¹). As reported in the case of P3HT, the observation of these latter bands indicates that the final degradation stages of the thiophene rings is reached.¹⁵ Their appearance is then a good indicator of how advanced the sample degradation is. Here we noticed that such signals appeared very quickly for the fluorene and CPDT-based compounds (about 20 hours). On the contrary, they were only detected after 200 hours for the thiophene.

As for cleaved materials, the behavior was very similar to the pristine polymers, but changes in the IR spectrum were much slower after cleavage. This is in good agreement with our previously published results.³⁴

Dithienylbenzothiadiazole (Series 1). To check the consistency of the previous results, three of the four previous donor



Fig. 3 Evolution of the normalized amount of absorbed photons during photochemical ageing. (Left) Pristine polymers, (right) cleaved polymers.

groups—thiophene, CPDT and Si-CPDT—were investigated in a second set of experiments. Here, samples were based on an electron-deficient benzothiadiazole group with two flanking thiophene rings substituted by a cleavable ester moiety (Fig. 4). From Fig. 4, it is obvious that the stability ranking remains identical to the one reported in the previous section.

This means that even though different parameters can influence the stability of a polymer (*e.g.* molecular weight, regioregularity, purity) the chemical nature remains the most important one.

Dithienylbenzothiadiazole (Series 2). In a third step, three new electron-rich moieties were introduced—dialkoxybenzene, carbazole, thienoimidazolone—and compared to thiophene and CPDT. These donor moieties were copolymerized with a central benzothiadiazole flanked by two unsubstituted thiophene rings (Fig. 5). Here again, the evolution of the amount of absorbed photons has been recorded all along ageing and results are shown in Fig. 5. IR data are also provided in the ESI (Fig. S2[†]). The thienoimidazolone-based sample appeared to be as unstable as the one based on CPDT. This is related to the presence of the imide group that is photochemically unstable.³⁵ As evidenced by *Arnaud et al.*, irradiation of this unit causes the homolysis of the C–N bonds which leads to the degradation of the whole unit through oxidation of the formed radicals. This is confirmed here, as the IR bands characteristic for the imide group (1725 and 1560 cm⁻¹) disappeared after only a few hours of irradiation. As the donor unit is quickly degraded, the ICT is prevented and a rapid absorbance loss takes place.

Attention should also be drawn to the fact that the polymers containing the carbazole and dialkoxybenzene groups were more stable than polymers containing the CPDT moiety. However, they all degrade relatively quickly as complete photo-bleaching was achieved after less than 100 hours. A rapid decrease in the IR bands coming from carbazole moieties (*e.g.* 1600 cm⁻¹) was evidenced confirming the limited stability of this moiety. This can be ascribed to various phenomena. First, it is due to the presence of the C_{sp3}–N bond that can be easily cleaved as previously reported.³⁶ A carbazoyl radical is generated, that can further



Fig. 4 Chemical structures of the investigated polymer samples (left). The X denotes one of the three donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).



Fig. 5 Chemical structure of the investigated polymer samples (left). The X denotes one of the five donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).

react with oxygen. This ends up in the degradation of the carbazole group, and thus in the interruption of the π -conjugated system. The C–N bond cleavage was confirmed by the IR monitoring, as signals characteristic for alkyl side-chains ($\nu_{C-H} \approx 3000$ to 2850 cm⁻¹) and C_{sp3}–N bonds ($\nu_{C-N} \approx 1330$ cm⁻¹) quickly vanished. *Pfister and Williams* also suggested that irradiation of the carbazole group leads to the formation of quinonic oxidized structures after reaction with the superoxide anion O₂^{-,37} This second pathway can also contribute to the photodegradation of the sample.

The dialkoxybenzene-based polymer appeared to be approximately as stable as the carbazole-based sample. This finding can seem rather surprising as alkoxy side-chains are usually known for their very negative impact on the polymer stability. The C–O bond is indeed readily cleavable under irradiation³⁸ and as expected, the intensity of the IR bands coming from the side-chains ($\nu_{C-H} \approx 3000$ to 2850 cm⁻¹ and ν_{C-O} 1385 cm⁻¹) gradually

decreases all along ageing. However, the breaking of this bond does not affect the conjugated backbone of the polymer directly as it is the case for C–N homolysis in the carbazole moiety. This could explain why the dialkoxybenzene unit gives a photochemical stability comparable to that of the carbazole.

Finally, and as one could have expected, the thiophene-based polymer was once again shown to be the most stable among the investigated materials although it was substituted by a carboxylic acid. This is due to the simultaneous absence of breakable bonds (C–O, C–N), of the quaternary carbon and of cleavable sidechain.

Dithienylbenzothiadiazole (Series 3). This fourth class is similar to the previous one except that the benzothiadiazole unit bears two solubilizing alkoxy side-chains (Fig. 6). Three donor units have been studied—CPDT, Si-CPDT, carbazole—and the results are presented in Fig. 6. First, it is further confirmed that



Fig. 6 Chemical structure of the investigated polymer samples (left). The X denotes one of the three donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).

the use of Si-CPDT provides a greater stability than CPDT. This finding is consistent with the previously discussed data.

Secondly, we observe that carbazole is less stable than Si-CPDT. As deduced from these results, the stability ranking from the lowest to the highest for this series of compounds is: CPDT– Carbazole–Si-CPDT.

Benzothiadiazole series. So far the unsubstituted thiophene ring has been shown to be the most stable moiety especially because this moiety is side-chain free. So, in a last series of experiments, different unsubstituted aromatic donor groups were investigated: thiophene, benzodithiophene and dithienothiophene. Samples were based on a benzothiadiazole unit bearing solubilizing alkoxy side-chains without flanking thiophenes (Fig. 7).

As observed in Fig. 7, the change of the thiophene by a benzodithiophene results approximately in a twofold stability increase. One can also easily notice that the dithienothiophene derivative provides by far the highest stability. Obviously, the use of unsubstituted polycyclic aromatic units is thus beneficial in terms of the photochemical stability.

In summary, a combination of all the results collected so far enables the formulation of a global stability ranking for the investigated donor groups as shown in Fig. 8. One can conclude that the presence of a quaternary carbon atom or an easily cleavable bond leads to a rather low stability. Conversely, donor units that provide the highest stability are those without any sidechain.

Influence of the acceptor group. In a similar fashion, the influence of the acceptor group on the photochemical stability of conjugated polymers was investigated.

Dithienocyclopentadithiophene series. To begin, we studied benzothiadiazole (BTD) and thienopyrazine (TPz) units. As illustrated in Fig. 9, samples were based on a dithienocyclopentadithiophene electron-rich group. In order to minimize the effects of the side-chain, we chose to study a TPz unit substituted by the carboxylic acid (*i.e.* thermo-cleaved).

From Fig. 9, it is very clear that the sample containing the TPz unit is significantly more stable. This effect cannot be explained by the presence of side-chains or by a difference in the samples HOMO position. *Blouin et al.* reported that the substitution of a BTD unit by a TPz should theoretically lead to an increase in the polymer HOMO energy level.³⁹ This was confirmed experimentally by *Bijleveld et al.* and should engender a lower oxidative stability of the TPz-based compound.⁴⁰ The superior stability of the sample based on the TPz moiety must then come from a greater intrinsic photochemical stability of this unit.

Si-bridged cyclopentadithiophene series. A second set of polymers was then studied. This one was based on the Si-CPDT unit associated either with a benzothiadiazole (BTD) unit or an ester-substituted thienothiophene (Fig. 10). This latter has recently given very good results in terms of efficiencies.^{10,11}

According to the results presented in Fig. 10, the BTD-based polymer appears to be much more stable than the thienothiophene. However, it should be emphasized that, whereas the BTD group is not substituted, the thienothiophene unit bears a primary ester side-chain. It is thus very likely that the rather fast degradation originates from this group as IR monitoring of the degradation shows a decrease in the signals pertaining to this ester moiety (e.g. $\nu_{C-O} \approx 1350 \text{ cm}^{-1}$, see Fig. S3, ESI†). In addition, signals characteristic for the degradation of the sulfurcontaining rings appeared quickly (around 1115 and 620 cm⁻¹). As previously stated, the observation of such signals implies an opening of the ring and thus an advanced degradation level. The presence of this side-chain is, however, required to adjust the position of the energy levels.¹⁰ It should be added that very good performance has also been obtained using the thienothiophene group substituted by a ketone.¹¹ Ketones are well-known to be highly unstable under irradiation as they readily evolve through Norrish reactions.⁴¹ It can be anticipated that the photochemical stability of the whole sample will be rather limited.

As for the previous section dedicated to the donor group, the different data were combined to establish the stability ranking given in Fig. 11. Here again the most stable moieties are the ones without side-chains or readily cleavable bonds.



Fig. 7 Chemical structure of the investigated polymer samples (left). The X denotes one of the three donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).



Fig. 8 Donor group stability ranking.



Fig. 9 Chemical structure of the investigated polymer samples (left). The X denotes one of the two acceptor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).



Fig. 10 Chemical structure of the investigated polymer samples (left). The X denotes one of the two acceptor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).

Side-chain effect

Influence of the nature of side-chains. The presence of sidechains is necessary to ensure a sufficient solubility of the sample and thus allows the solution-processability of the PSCs active layer. However, side-chains can also be used to tune other properties of the materials such as the positions of the HOMO and LUMO levels or the packing of the macromolecular chains.¹⁰

To begin, we studied different alternating polymers based on a dithienocyclopentadithiophene unit associated with a benzothiadiazole group. This latter was either unsubstituted or substituted with one of the following side-chains: ether or ester (Fig. 12). As in the previous experiments, the total number of absorbed photons was recorded all along ageing and the results are presented on Fig. 12.

According to these results, the stability ranking from the lowest to the highest is as follows: $CO_2R < OR < H$. As expected, the unsubstituted BTD demonstrates the highest stability among the three samples although the durability difference with the other samples is surprisingly low. On the contrary, ester and alkoxy substituents gave a lower stability, the latter being slightly more stable.

Thermo-cleavable polymers. As described in previously published papers^{14–16} and also shown before in this study, side-chains have a negative influence on the polymer photochemical stability. In addition, in a previous paper we showed that side-chain thermal cleavage systematically lead to a strong increase in the sample photochemical stability.³⁴ Here, the study was extended to various new thermo-cleavable polymers, and a total of 8 different samples were investigated.

Whatever the sample nature, thermo-cleavage systematically led to an increase in the stability as exemplified on Fig. 3. In every case, the amount of absorbed photons exhibited a quasi-linear decay and the experimental data were thus fitted with a straight curve. The stability improvement provided by thermal cleavage was then estimated quantitatively for each sample by comparing the slope of the curves before and after side-chain cleavage. These results are reported in the ESI (Table S2[†]). Depending on the backbone chemical structure, it was noticed that thermocleaved samples are approximately between 2 and 20 times more stable than corresponding pristine materials. This set of results further confirms the higher potential stability offered by thermocleaved conjugated polymers. Among the investigated materials, the beneficial effect of thermal cleavage surprisingly appeared to be more pronounced for those which are the most stable before cleavage. This is of course a very interesting and fortunate result.

It should finally be mentioned that some of the thermo-cleaved polymers exhibited a very high photochemical stability. For example, 1000 hours irradiation of the polymer based on a thienopyrazine unit and three thiophene rings only lead to a 20% decrease in the amount of absorbed photons.

Summary

As clearly demonstrated in the present work, slight changes in the material's chemical structure can result in huge variations in the photochemical stability. Indeed, polymer durability was shown to cover a very broad range of values, from very few hours (*e.g.* MEH–PPV) to several thousands of hours (*e.g.* thermo-cleaved samples). Several crucial parameters influencing the stability have been identified through this study and the main findings have been summarized in the following basic rules.

1. The use of exocyclic double bonds in the main backbone (MEH–PPV, MDMO–PPV) leads to a poor stability and should be avoided,

2. Moieties containing a quaternary site are very unstable (*e.g.* fluorene, cyclopentadithiophene) because of the oxidazability of this site,

3. The presence of readily cleavable bonds (such as C–N or C– O) also limits stability,

4. Side-chains play a key role in conjugated polymer degradation and their cleavage largely improves stability,

5. Aromatic polycyclic units generally exhibit a good photochemical stability.

Indirectly, it was also shown that the position of the HOMO level for the polymers is not a sufficient criterion to conclude on the photochemical stability.



Fig. 11 Acceptor group stability ranking.



Fig. 12 Chemical structure of the investigated polymer samples (left). The X denotes one of the three substituents shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).



Fig. 13 Most stable donor (top) and acceptor units (bottom) identified within this study.

Fig. 13 provides a list of the most stable donor and acceptor building blocks we identified. Assembly of these units into larger aromatic ones is also expected to lead to stable blocks as evidenced by the behavior of the dithienothiophene group. Finally, for the side-chains, a good rule of thumb is to keep their amount as low as possible whatever their chemical nature.

Conclusions

In conclusion, we have mapped the photochemical stability in air for a wide range of π -conjugated polymers relevant to PSCs. By comparing the data collected for more than 25 different samples, various points critical for the polymer stability have been identified. This enabled us to rationalize how variations in the chemical structure of π -conjugated polymers impact the photochemical stability. Our results thus provide a better description of the structure–stability relationship, as well as important insight that will prove useful to anyone in the process of designing new materials for PSCs. We are of course fully aware that the photochemical stability is only one aspect of the complex PSC stability problem and that stable but inefficient polymers are rather useless. However, we believe that this study can provide meaningful help if ones aim is to synthesize new good candidates for PSCs that unite efficiency and stability.

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