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Molecular structure–intrinsic photostability relationships for thiophene-benzothiadiazole alternating type conjugated polymers

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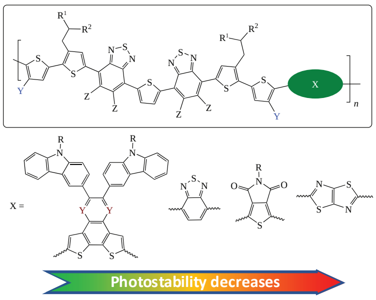
A systematic study of the UV light-induced degradation of a series of structurally similar conjugated polymers revealed important relationships between the molecular structure of the used building blocks and photostability of the resulting materials. These findings form a set of important guidelines for future rational design of new absorber materials for efficient and stable organic solar cells.



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Organic solar cells (OSCs) represent a highly promising emerging photovoltaic technology. A low efficiency of organic solar cells has been the main obstacle for their practical implementation for many years.[1] However, the recent tremendous progress in the materials design has brought the performance of OSCs a competitive level: the best laboratory small-area cells demonstrated power conversion efficiencies of 19.2%, which is close to the characteristics of the best cadmium telluride (22.4%) and copper indium gallium selenide (23.6%) solar cells, which had been commercialized long time ago.[2–5] Thus, the practical implementation of organic solar cells depends now mostly on the progress in their upscaling and achieving sufficiently long operational lifetimes.[6–9]

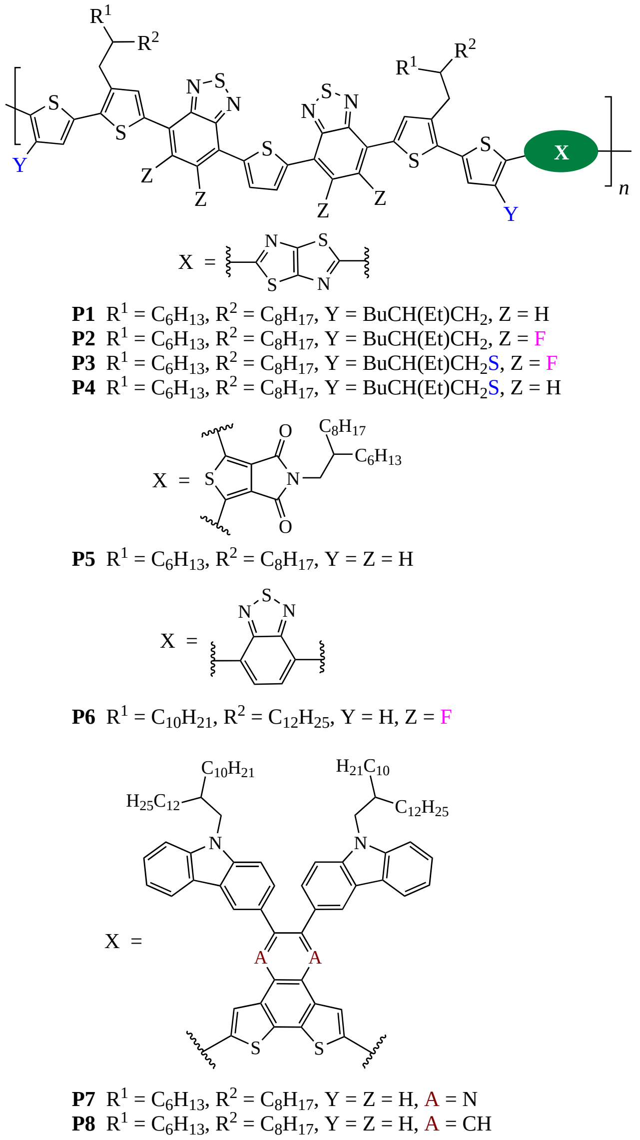
The stability of OSCs is quite a critical issue since organic semiconductors are very labile and undergo multiple aging pathways under exposure to elevated temperatures, light and other stress factors.[10] Surprisingly, very little attention has been paid so far to the exploration of intrinsic stability of different types of organic semiconductor materials, while the understanding of the corresponding aging pathways currently is very limited.[6,7,11–13] The most common approach to study photostability of organic semiconductor materials was based on the exposure of their films to light under ambient conditions in the presence of oxygen and moisture.[14–16] However, the observed photooxidation of organic materials is not relevant to the operational conditions of organic solar cells, which have to be properly encapsulated and thus well protected from the contact with ambient species.[17–19]

More recently, it has been discovered that both electron acceptor fullerene derivatives and electron donor small molecules are prone to the photochemical degradation involving [2 + 2] cycloaddition pathway that leads to the formation of the heavily cross-linked species.[20, 21] This kind of photochemical degradation is very unfavorable since it creates the defects in the active layer of OSCs, facilitates non-radiative recombination of charge carriers and thus results in a substantial decrease in the device efficiency.[22–25]

One of the first attempts to study the intrinsic photostability of conjugated polymers and to reveal stability–structure relationships was based on using electron spin resonance (ESR) spectroscopy.[26,27] Indeed, many conjugated polymers form stable radical species under exposure to light and, hence, some correlations could be drawn between the concentration of radicals (and their formation rates) and the material photostability. However, further studies revealed that there were many materials that degraded rapidly under exposure to light without forming any stable radicals.[21] Thus, ESR spectroscopy cannot be used as a tool to quantify the intrinsic stability of organic semiconductors. Other attempts involved the application of impedance spectroscopy and gel permeation chromatography techniques, but they also have severe limitations.[21,28]

To address the aforementioned challenge, we have proposed recently to study the light-induced degradation of different types of organic semiconductors under exposure to UV light (254 nm) under anoxic conditions inside the glove box. This methodology turned out to be a powerful tool for rapid assessment of intrinsic photostability of organic conjugated molecules and revealing correlations with their molecular structures.[29,30]

Herein, we applied the developed methodology to study the intrinsic photostability of a series of (X-TTBTBTT)$_n$-type (where T represents thiophene and B – benzothiadiazole units) conjugated polymers to unravel the impacts of different building blocks X and various side chains attached to polymer backbone. The molecular structures of the studied materials **P1–P8** are presented in Figure 1. It should be noted that (X-TTBTBTT)$_n$ is



P1 $R^1 = C_6H_{13}$, $R^2 = C_8H_{17}$, $Y = BuCH(Et)CH_2$, Z = H
P2 $R^1 = C_6H_{13}$, $R^2 = C_8H_{17}$, $Y = BuCH(Et)CH_2$, Z = F
P3 $R^1 = C_6H_{13}$, $R^2 = C_8H_{17}$, $Y = BuCH(Et)CH_2S$, Z = F
P4 $R^1 = C_6H_{13}$, $R^2 = C_8H_{17}$, $Y = BuCH(Et)CH_2S$, Z = H

P5 $R^1 = C_6H_{13}$, $R^2 = C_8H_{17}$, Y = Z = H

P6 $R^1 = C_{10}H_{21}$, $R^2 = C_{12}H_{25}$, Y = H, Z = F

P7 $R^1 = C_6H_{13}$, $R^2 = C_8H_{17}$, Y = Z = H, A = N
P8 $R^1 = C_6H_{13}$, $R^2 = C_8H_{17}$, Y = Z = H, A = CH

Figure 1 Molecular structures of the studied polymers **P1**–**P8**.

the type of conjugated polymers which have been intensively developed as promising materials for OSCs due to favorable combination of their optoelectronic properties induced by alternating thiophene and benzothiadiazole units, enhanced stability and good device performances.[31,32] The description of the experimental setup and used experimental conditions are given in Online Supplementary Materials.

The degradation behavior of the polymer films was assessed through periodic measurements of their UV-VIS absorption and photoluminescence (PL) spectra (excitation wavelength 450 nm) directly in the same glove box (see Online Supplementary Materials, Figure S1), which excludes any contact with ambient species (oxygen or moisture) during the sample transfer. UV light causes photobleaching of the polymer films due to the gradual decrease in their conjugation length and degradation of some functional groups in the building blocks incorporated in the polymer structure.

Figure 2(*a*) shows the evolution of the absorption spectra of the thin films of polymer **P6** under UV light exposure. One could notice that the absorption band demonstrates blue shift and decrease in the intensity due to the progressing polymer aging. Similarly, the PL spectra exhibit gradual decay in the emission band intensity due to the formation of defects acting as deep traps and promoting nonradiative recombination of excitons and charge carriers [Figure 2(*b*)].

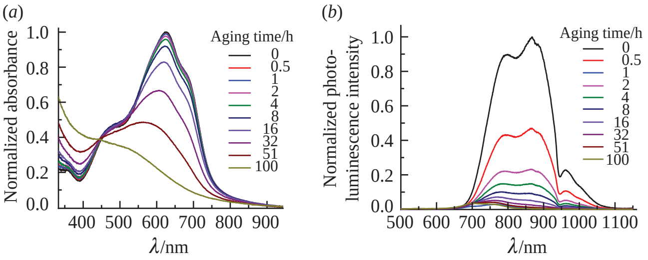


Figure 2 Evolution of the (*a*) UV-VIS and (*b*) PL spectra of **P6** films upon aging.

While analyzing the obtained sets of the UV-VIS spectra, we extracted the values of the normalized absorbance at the band maximum for each polymer and plotted it as a function of the aging time [Figure 3(*a*)]. Similarly, we also plotted the logarithm of the PL intensity as a function of the aging time [Figure 3(*b*)]. These two plots shown in Figure 3 feature the aging dynamics of polymers **P1**–**P8** and may be used to reveal some correlations between the materials molecular structure and photostability.

First, one can notice that polymers **P3** and **P4** are the least stable materials and undergo very fast degradation as it is evident from the rapid decay of their films' absorbance [see Figure 3(*a*)]. Notably, very similar polymers **P1** and **P2** show a considerably higher stability due to the fact that they bear alkyl side chains instead of alkylthio substituents present in **P3** and **P4**. Thus, alkylthio groups dramatically reduce photostability of conjugated polymers, which is in line with our previous observations made for materials having alkylthio-substituted benzodithiophene building blocks.[30] The conclusions made on the basis of UV-VIS spectra evolution are supported also by the PL dynamics: the emission of thin films of **P3** and **P4** is quenched almost immediately after their exposure to UV light and then becomes stabilized at the very low intensity [Figure 3(*b*)].

Interestingly, we did not observe any negative effect of the fluoro substituents in the series of polymers **P1**–**P4** on the intrinsic photostability of these materials, though such effect was evident for two other groups of polymers studied before. We believe that in the case of polymers **P1**–**P4** the overall material degradation is controlled by the decomposition of the thiazolothiazole blocks, which occurs faster than the fluorinated or non-fluorinated benzothiadiazole units become involved. Thus, we may conclude that using thiazolothiazole as a building block for conjugated polymers might be not very promising since it causes substantial reduction in the material photostability.

The most stable polymers according to the UV-VIS spectroscopy data were **P6**–**P8** since they demonstrate similar or weaker degradation than the reference poly[[9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) polymer within the first 50 h of UV light exposure. The PL dynamics also strongly suggests that polymers **P7** and **P8** are much more resistant to UV light as compared to other studied materials. The common feature of the structures of **P7** and **P8** is the presence of two pendant carbazole units, which seem to be responsible for the observed superior photostability. It should be noted that PCDTBT is also a carbazole-based copolymer which is commonly considered as one of the most stable conjugated polymers ever reported.[33] Thus, the carbazole units in contrast to the thiazolothiazole blocks improve the intrinsic photostability of conjugated polymers.

Polymer **P6** with benzothiadiazole X block also demonstrated high stability comparable to those of polymers **P7** and **P8**. This result is expectable since multiple benzothiadiazole units are already incorporated into the structure of the TTBTBTT

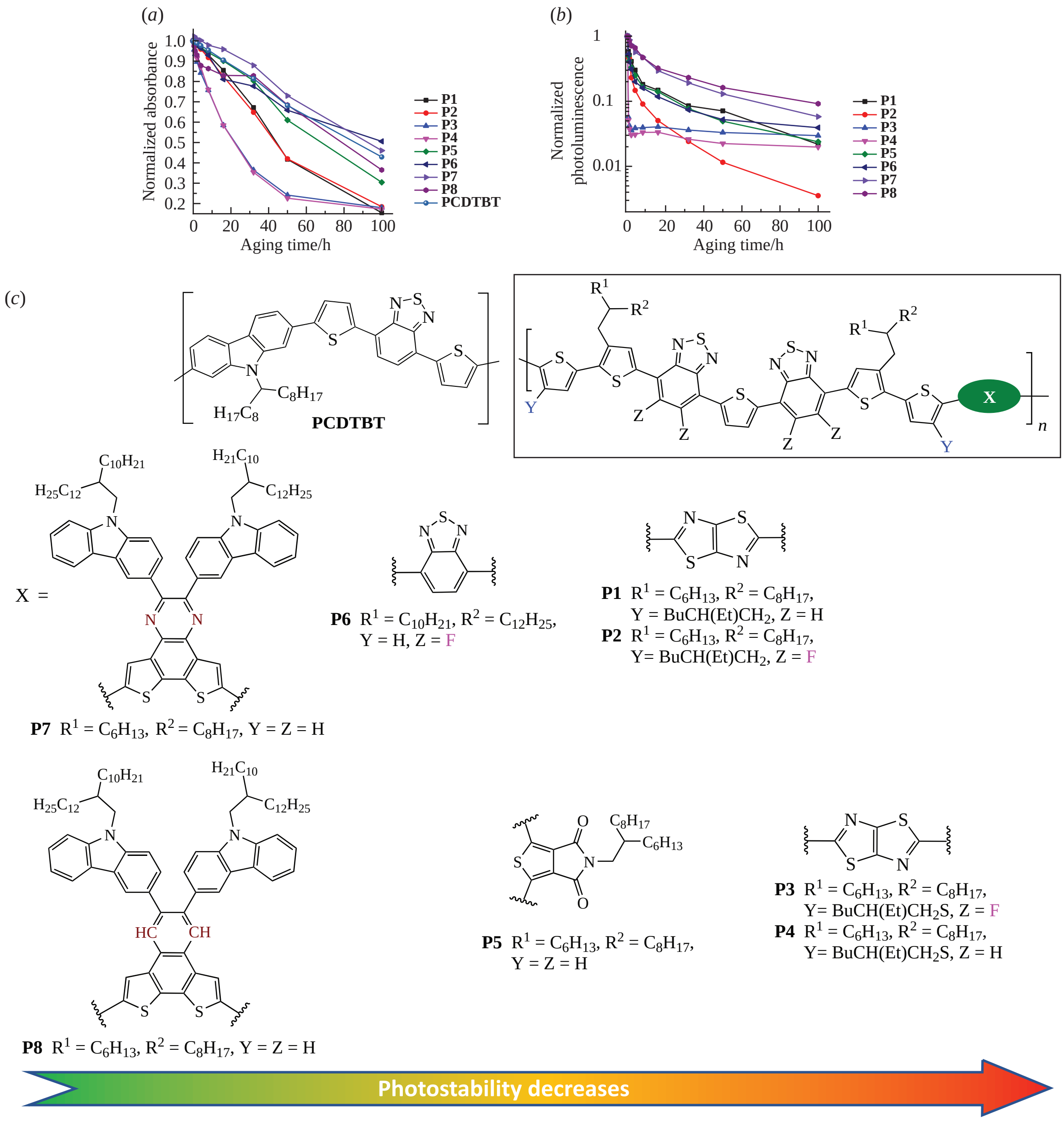


Figure 3 The dynamics of the (*a*) UV-VIS and (*b*) PL characteristics of thin films of **P1**–**P8** upon aging. (*c*) The ranking of polymers **P1**–**P8** with respect to their photostability.

frameworks, so their use as X block should not bring any new aging phenomena. Finally, polymer **P5** with the X block based on thienopyrroledione units showed a decent stability, which was much superior in comparison with **P1**–**P4** and inferior as compared to **P6**–**P8**. The obtained results allowed us to rank the building blocks X in terms of their effect on the photostability of conjugated polymers: from the stabilizing carbazole-loaded blocks integrated in polymers **P7**, **P8** to the least stable thiazolothiazole units present in **P1**–**P4** [Figure 3(*c*)].

To summarize, we explored for the first time the intrinsic photostability of a series of (X-TTBTBTT)$_n$-type polymers and demonstrated that it is strongly dependent on the molecular structure of the X block. Furthermore, we confirmed that using alkylthio substituents ruins the photostability of conjugated polymers and results in their fast degradation under the exposure to light. We strongly believe that these findings would provide valuable guidelines to polymer chemists and materials scientist in general that can be used for rational design of new organic absorber materials with substantially improved stability to achieve the desired long operational lifetimes of organic solar cells.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.04.009.

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