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# Progress in perylene diimides for organic solar cell applications

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Compared to fullerene materials, non-fullerene acceptor materials have in recent years been more widely used in organic solar cell devices due to their optical properties and due to the ease of carrying out syntheses to tune their electronic energy levels. Non-fullerene acceptors constitute a major focus of research in the development of bulk-heterojunction organic solar cells. Recent developments have yielded increased power conversion efficiency (PCE) levels for non-fullerene acceptor materials, with the PCE levels now shown to exceed 20%. Perylene diimide (PDI), a non-fullerene acceptor material, has been widely studied because of its good transmission capacity and strong electron affinity. This paper summarizes the application of PDI molecules as acceptor materials in organic solar cells in recent years, detailing the strategies and approaches of molecular design and their application effects.

## 1 Introduction

Solar cells are used to generate energy from solar power. Despite the current availability of various new photovoltaic technologies, such as quantum dot solar cells and perovskite-type solar cells,<sup>1–3</sup> organic solar cells still have many advantages,<sup>4–6</sup> including (1) low cost, light weight, good mechanical flexibility, and roll-to-roll production, offering the possibility of large-area industrial production, and (2) the ability to modulate the relevant energy levels by performing organic synthesis. The materials used at present for organic solar cell acceptors can be divided into fullerenes and non-fullerenes. Solar cells made with fullerene acceptor materials are mainly based on fullerenes and their derivatives, which are expensive and their energy levels are difficult to alter by means of chemical modification.<sup>7,8</sup>

The absorption spectra of non-fullerene acceptor materials can complement that of the donor material in the visible and near-infrared regions to achieve effective charge separation. Also, compared to fullerene acceptor materials, the non-fullerene acceptor materials can yield a better morphology in the mixed film with the donor and as a result show high charge mobility and improved charge transfer efficiency. Organic solar cells based on perylene materials were first reported in 1986.<sup>9</sup> Compared to the bilayer system, the bulk heterojunction solar cell structure greatly increases the contact area between the donor and acceptor, hence facilitating the diffusion and dissociation of excitons in the active layer and improving cell performance. Bulk heterojunction solar cells with non-fullerene acceptor materials are gradually becoming a hot research topic.<sup>10–18</sup>

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## 2 Result and discussion

Since 2015, the efficiency of solar cells with non-fullerene acceptor materials has been significantly improved and various non-fullerene acceptor materials have been studied extensively.<sup>19–24</sup> Perylene diimide (PDI) materials have become a hot topic due to their high electron mobility levels. They show good photostability, thermal stability and chemical stability, show good absorption in the visible range, and are easily chemically modified. However, for a single layer of PDI solar cell devices, the efficiency is very low. Several studies have shown that the self-aggregation of PDI molecules leads to a restriction of electron transport channels, which affects the efficiency of the device.<sup>25</sup> To overcome the self-aggregation of PDI molecules, controlling the formation of molecular  $\pi$ - $\pi$  stacking and maintaining a sufficient overlap of energy levels for better electron transport are effective methods. Also, reducing the planarity of the molecules by introducing bridging groups can lessen self-aggregation.

As shown in Fig. 1(b), the PDI molecule is quite symmetric. It mainly possesses three active positions: modification of PDI units at the nitrogen position can result in a linking together of two or more PDI units, and a destruction of the self-aggregation and an inhibition of intermolecular packing; modification at the harbor position can be used to increase the conjugation length and improve the absorption properties of the molecule, thus modulating the molecular energy level; and modification at the shoulder can enhance  $\pi$ - $\pi$  stacking and improve the mobility of the molecule. This paper focuses on the progress made in research about PDI molecules in recent years, in particular involving these modifications, and their applications in organic solar cells.

### 2.1 Nitrogen position modification

Substitution at the nitrogen atom is the simplest modification that does not cause distortion of the molecular plane. This substitution results in a vertical conformation of the molecular arrangement due to the spatial site resistance of the oxygen atoms.<sup>26–33</sup> Molecules with two or more PDI units linked at the nitrogen position have been reported to yield relatively high device efficiencies (Fig. 2).<sup>26,27,32,33</sup>

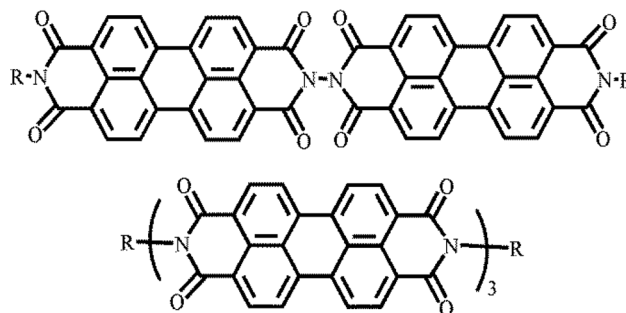


Fig. 2 Structures of PDI molecules modified at the nitrogen position.

### 2.2 Harbor position modification

**2.2.1 Single bond linking.** As shown in Fig. 3, PDIs linked directly by a carbon-carbon single bond at the harbor position show a certain degree of distortion.<sup>34–36</sup> The Wang group synthesized a PDI-containing molecule by linking two single PDI molecules through different bonds, and the power conversion efficiency (PCE) reached 4.39%.<sup>37,38</sup> When replacing the donor with the polymer PTB7-TH, the PCE reached 5.90%.<sup>34</sup> Subsequently, sulfur and selenium atoms were introduced into the PDI dimer molecule, and PCEs of, respectively, 7.16% and 8.42% were achieved.<sup>34,35</sup> The gradual increase in PCE was mainly due to the molecular structure of the dimer having become non-planar and the two PDI units having become related by a dihedral angle resulting in a hindering of face-to-face stacking between molecules and inhibiting strong aggregation between PDI molecules. In addition, the dimer molecules were shown to achieve intermolecular electronic and orbital interactions between the individual PDIs, leading to nanoscale phase separations in the film and increasing the efficiency.

#### 2.2.2 Planar and non-planar linking

**2.2.2.1 Planar and non-planar dimers.** Harbor position modifications can also involve connections by a planar or non-planar unit as a bridge. The Hou Jian-hui and Yao Jian-nian group reported a PDI molecular dimer with thiophene as the bridging unit<sup>39</sup> and yielding an efficiency of 4.03%, and the Yan He group reported a PDI molecular dimer with spirofluorene as the bridging unit<sup>40</sup> and yielding an efficiency of 9.5% (Fig. 4).

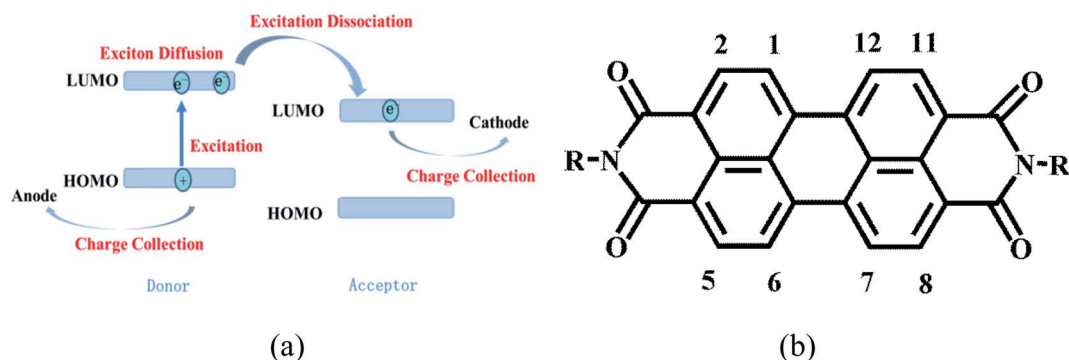


Fig. 1 (a) Schematic of the working mechanism of a BHJ solar cell. (b) Molecular structure of PDI.



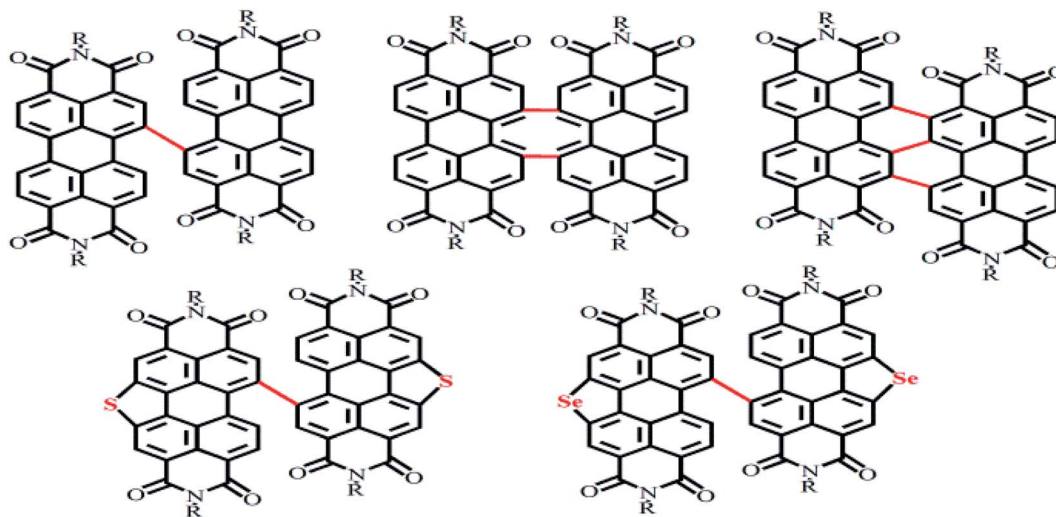


Fig. 3 Structures of PDI units linked together at their harbor positions by single bonds.

**2.2.2.2 Planar and non-planar trimers.** For the fullerene acceptor, the electron transport is homogeneous due to the approximate spherical shape of fullerene. For PDI molecules, the different orientation of each PDI molecular unit not only suppresses the self-aggregation in the large conjugation plane, but also promotes nano-sized phase formation, which is more conducive to intermolecular charge transport.<sup>41–43</sup> The Chen Hong-zheng group reported a PDI trimer with a benzene as a planar unit and yielding an efficiency of 5.65%.<sup>44</sup> A trimer of PDI molecules with triphenylamine as the bridge was reported by the Zhan Xiao-wei group to display a PCE of 3.32%.<sup>45</sup> The Peng Qiang group reported trimers of PDI molecules with 1,3,5-triazine as the bridge and yielding an efficiency of 9.15%.<sup>46</sup> 1,3,5-Triazine is an electron-deficient group with relatively broad spectral absorption and a small twist angle in its molecular structure, which improves the crystallinity of the molecule and provides for improved  $\Pi$ - $\Pi$  stacking for intermolecular electron transport (Fig. 5).<sup>41</sup>

**2.2.2.3 Planar and non-planar tetramers.** The Yan He group reported three kinds of 3D-structured PDI acceptor materials with, respectively, tetraphenylcarbon, tetraphenylstyrene and

tetraphenylpyrazine as the bridge<sup>47</sup> and analyzed the effects of the three molecular structures on their photovoltaic properties. For these molecules, self-aggregation and electron mobility were found to gradually increase with decreasing rotational freedom and the distortion of the molecule. The results showed the larger nucleus of tetraphenylpyrazine resulting in lower free rotation angles of the PDI unit—and hence a reduced distortion of the molecule. However, the electron mobility was increased due to the enhanced aggregation. The highest efficiency obtained for the molecule containing tetraphenylpyrazine as the central group was 7.1%. In addition, PDI molecules with, respectively, spirothiophene and tetraphenylpyrazoloquinoxaline have also been reported (Fig. 6).<sup>48,49</sup>

**2.2.3 Fused-ring PDI molecules.** Fused-ring PDI molecules have been obtained by performing closed-loop reactions of PDI units through their harbor positions. They have a relatively extensive conjugation and good planarity to facilitate intermolecular stacking, thus improving carrier mobility. Fused-ring compounds with two PDI molecules were first reported in 2014, with an efficiency of 6.05%.<sup>50</sup> The compounds with three and four PDI units were reported by the Chen Yong-

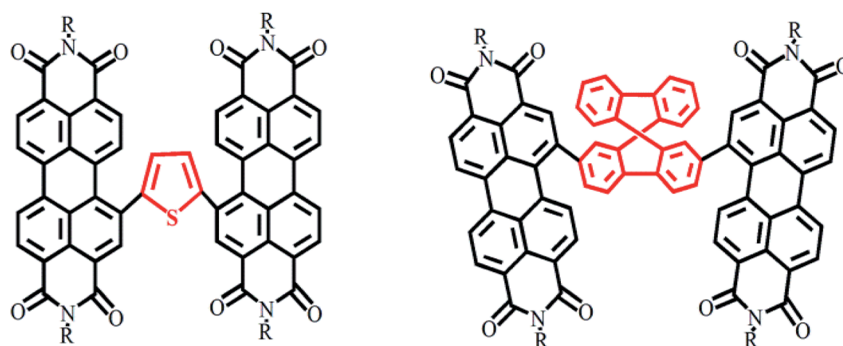


Fig. 4 Structures of planar (left) and non-planar (right) PDI molecular dimers.



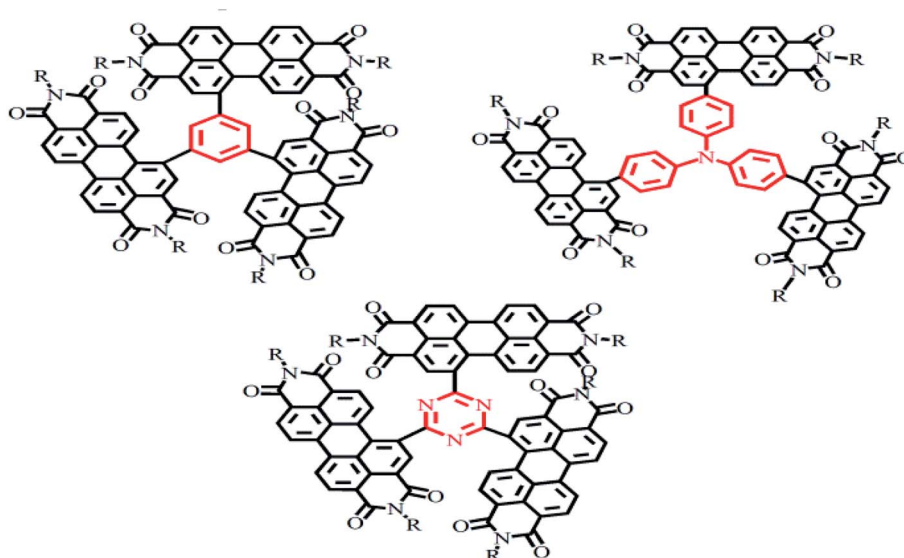


Fig. 5 Structures of planar (top left and bottom) and non-planar (top right) molecular trimers.

sheng group to yield efficiencies of 7.9% and 8.3%, respectively.<sup>51</sup> As the number of PDI units was increased, the absorption signals of the fused-ring compounds red-shifted and broadened, due to the corresponding increase in extent of conjugation, and their electron affinity increased significantly as well (Fig. 7).

Fused-ring PDI molecules made with, respectively, furan, thiophene and selenium atoms were reported by the Alex K.-Y. Jen group of the University of Washington. The results

showed that as the radius of the central atoms was changed, the dihedral angle relating the two PDI units also changed, affecting the packing arrangement and the morphology and crystallinity of the mixed film.<sup>28</sup> A single-bonded PDI compound based on a thiophene moiety was reported by the Yang Chu-luo group to yield a maximum efficiency of 5.84%.<sup>30</sup> A tetrameric benzene-group-containing PDI-like fused-ring compound was reported by the Wang Zhao-hui group. The photovoltaic performances resulting from this compound and a from a selenium derivative

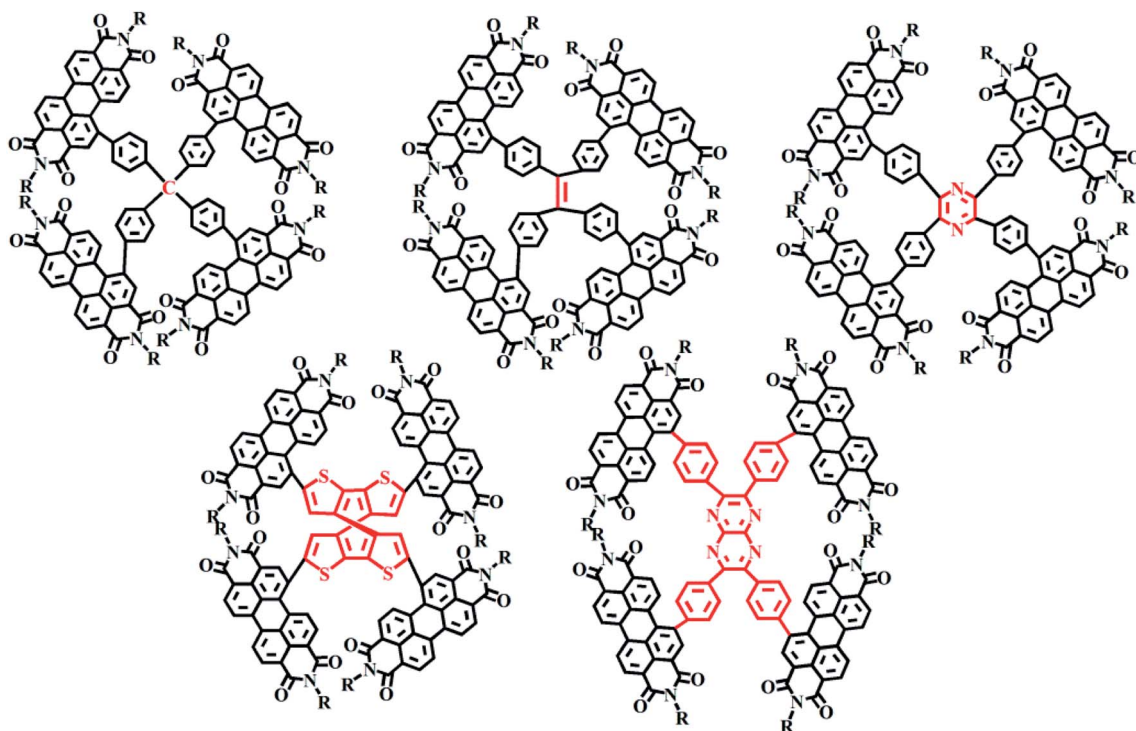


Fig. 6 Structures of non-planar (top left and bottom left) and planar (rest) PDI-like molecular tetramers



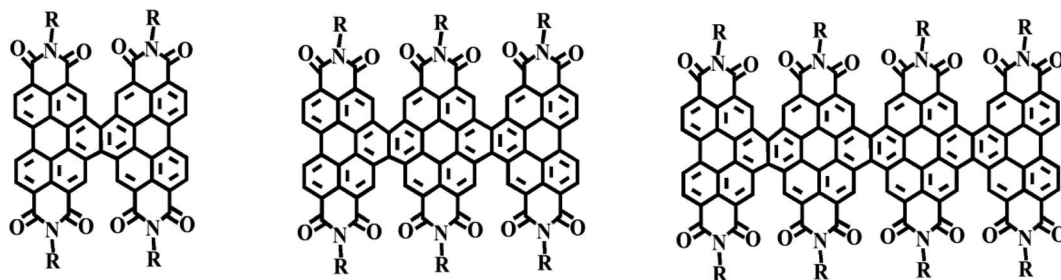


Fig. 7 Structures of fused-ring PDI molecules.

of this compound were compared, and showed device efficiencies of 8.28% and 9.28%, respectively (Fig. 8).<sup>52</sup>

### 2.3 Shoulder position modification

It is more difficult to carry out a substitution at the shoulder position of PDI than at the harbor and N positions. Nevertheless, alkyl-chain substitutions of PDI molecules at their shoulders were reported by Müllen.<sup>53</sup> Their impacts in solar cell devices were compared with those of N-position-modified PDI molecules. The introduction of an alkyl chain improved the solubility of PDIs and modulated the photophysical properties of the solid-state films.

The efficiency effects of branched chains, stacking behavior and the morphology on the shoulder position are reported by Guo Xugang.<sup>54</sup> The Yu Lu-ping group of the University of Chicago<sup>55</sup> compared the differences between the harbor position and the shoulder position. The results indicated that the inclusion of the shoulder position groups distorted the whole molecule, but it ensured the extensive planarity of the PDI unit, which is conducive to the stacking of molecules and to high charge mobility. A 3D structure of a PDI compound modified at the shoulder position was reported. The more planar molecules resulting from shoulder position modification than from harbor position modification facilitated a tighter stacking of the  $\pi$ -conjugated structure. The

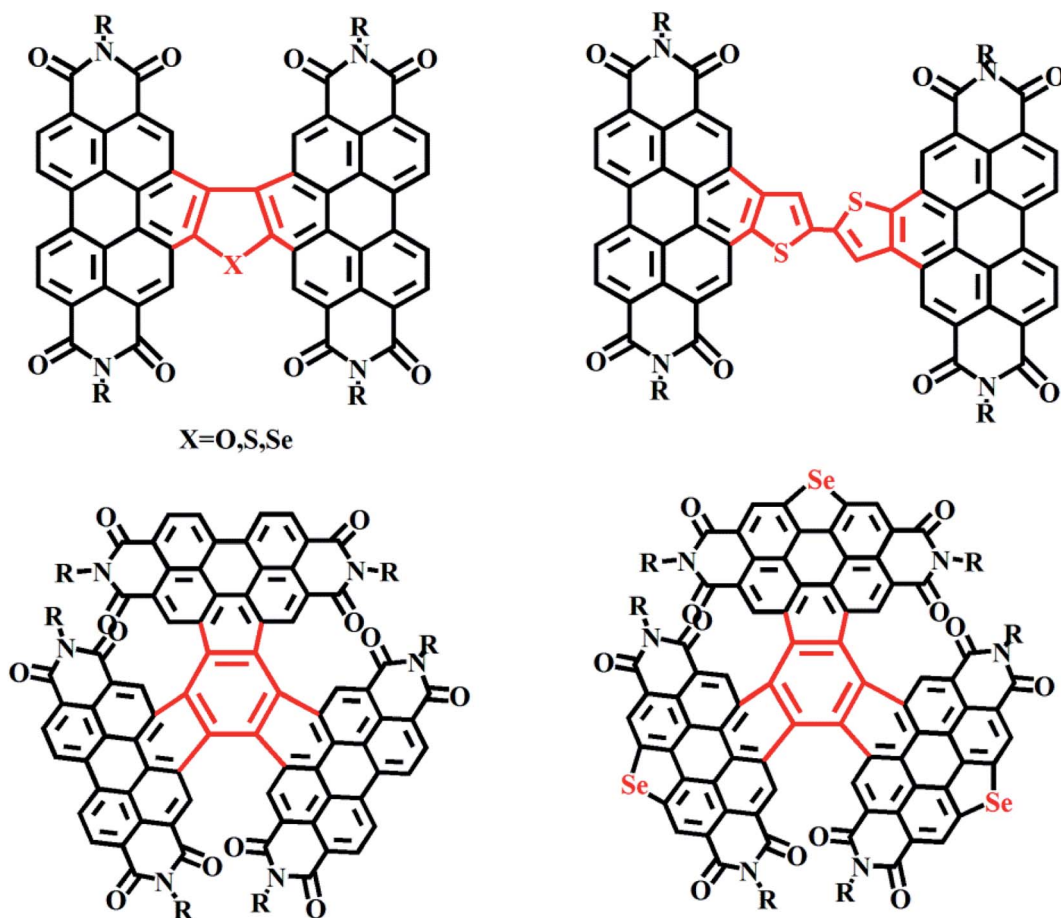


Fig. 8 Structures of fused-ring PDI molecules with different central groups.



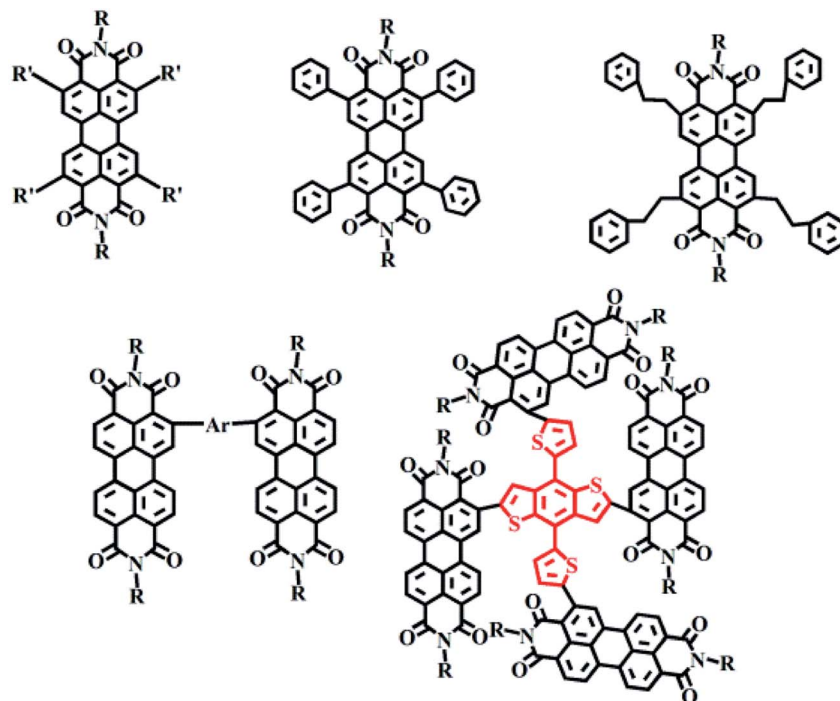


Fig. 9 Structures of PDI molecules modified at the shoulder position.

efficiency for this structure reached 8.47%,<sup>56</sup> attributed to a certain degree of distortion of this structure inhibiting self-aggregation of the molecules and facilitating film formation (Fig. 9).

### 3 Summary

In this paper, some of the main methods used to modify the PDI molecule have been introduced. In order to suppress the self-aggregation of PDI molecules, modifications at N, harbor, and shoulder positions have been reported. The modified compounds showed a broadened range of wavelengths absorbed, adjusted energy levels, and improved electron mobility, enhancing their application in photovoltaics. Therefore, the main idea has been to introduce different groups, in particular at the imide position or the harbor position, in order to control the energy levels and aggregation abilities of the molecules. In particular, PDI molecules with non-planar structures showed unique advantages due to the conformation of the molecule, which inhibit the stacking and self-aggregation and suppress the crystallization. Increasing the extent of conjugation in the structure and broadening the range of wavelengths absorbed by the molecule are expected to be very significant considerations for future design of the structures of PDIs.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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