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Rational synthesis and comparative investigation on a series of fluorinated aryl substituted diketopyrrolopyrrole

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ABSTRACT

We novelly designed and synthesized a set of fluorinated diphenyl-diketopyrrolopyrrole (DPP) compounds by varying the position and amount of fluorine atom, and to the best of our knowledge, it is the first time a difluoromethyl group and perfluoroalkyl chains had been introduced into the DPP unit in good yields. We investigate the optical/electrochemical properties of all the compounds. Density functional theory (DFT) calculations were applied to explore orbital energy value of these compounds. The results demonstrated that the perfluorocarbon chains substituted DPPs with larger red-shift in both absorption and emission spectra and narrower bandgap.

1. Introduction

Fluorination of conjugated organic molecules for optoelectronic applications has attracted increasingly research interest over the years.[1] The introduction of fluorine atom could lead excited state switching[2] and hyper- or hypochromic effects (i.e. in-/decrease of absorbance), as well as significant batho-(red) or hypsochromic (blue) shifts of the optical spectra to the whole molecules.[3,4] Furthermore, due to fluorine with the highest electronegativity (EN), C—F bond could break the symmetry of the molecular orbitals (MOs) and lower the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO).[5,6] These fluorinated compounds could achieve higher open circuit voltages in organic solar cells,[7] promote tuning of p-type towards n-type semiconductors.[8] Consequently, a more detailed investigation on the impact of fluorine on the structure-property relationship is vital.[9]

Diketopyrrolopyrrole (DPP) unit has a large planar π surface, exhibits strong π-π interactions and an electron-deficiency.[10] Furthermore, DPP derivatives have advantageous optical properties, such as strong absorption and emission in visible region, high photostability and large Stokes shift.[11] But fluorination of DPP-based compounds are rarely reported.[12] Herein, we originally varied the level of fluorination and position of substitution, and constructed seven DPP-based fluorinated compounds (**pFDPP**, **mFDPP**, **2mFDPP**, **CF_2HDPP**, **CF_3DPP**, **R_f4CDPP** and **R_f6CDPP**, as shown in Scheme 1, "**p**" and "**m**" refer to the fluorine atoms oriented *para*- and *meta*-to the DPP core, "**R_f**" refer to perfluoro) to compared with two non-fluorinated compounds (**HDPP** and **CH_3DPP**) in the optical/electrochemical properties. To the best of our knowledge, it is the first time a difluoromethyl group and perfluoroalkyl chains had been introduced into the DPP unit in good yields. Besides, the electron-withdrawing, optical and electrochemical properties of these DPP derivatives was systematically studied.

2. Results and discussion

2.1. Design and synthesis

The seven targeted compounds **IDPP~2mFDPP** (1-1~1-7) were

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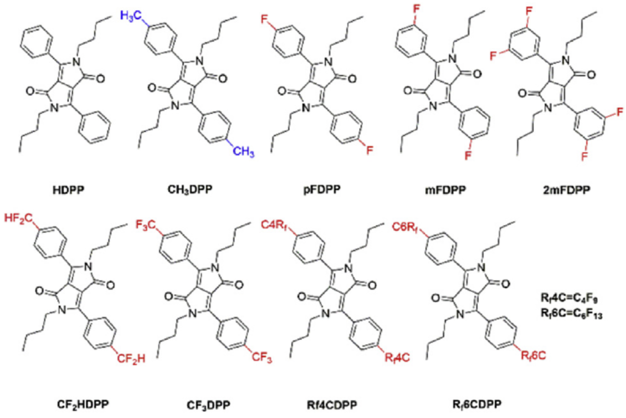
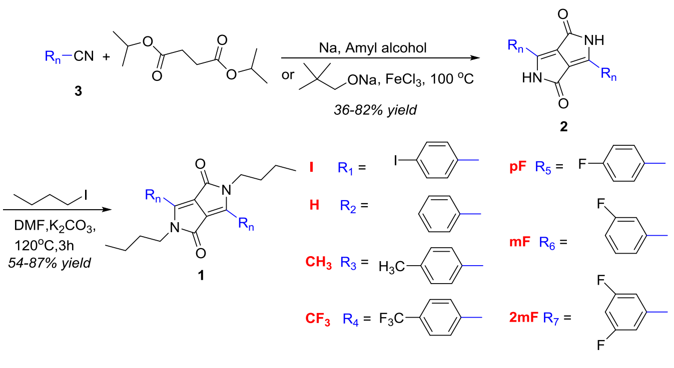


Scheme 1. The chemical structures of fluorinated and non-fluorinated diphenyl-DPP compounds.

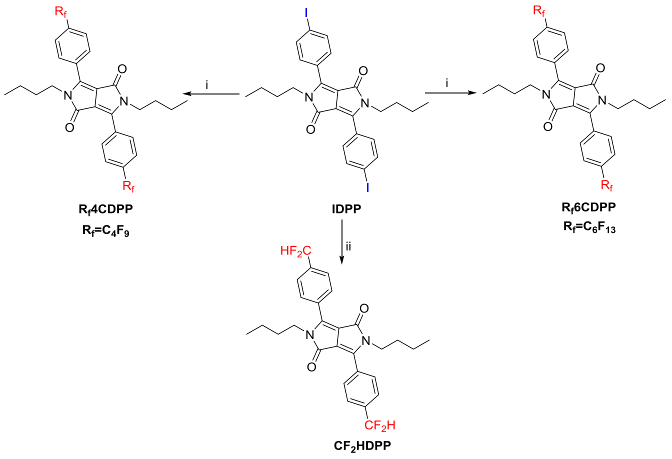
designed and synthesized according to the synthetic route shown in Scheme 2. Intermediate DPP dye (**2**) was prepared according to the published literature.[11] According to the synthetic route shown in Scheme 3, compound **CF$_2$HDPP** was obtained by the reaction of **IDPP** with (difluoromethyl)-trimethylsilane (TMSCF$_2$H) which is according to the relevant literature.[13] Compounds **R$_f$4CDPP** and **R$_f$6CDPP** were obtained by the similar reaction of **IDPP** with perfluorobutyl or perfluorohexyl iodide in the prescence of DMF using activated copper.[14]

2.2. *Optical properties of targeted compounds*

Fig. 1 shows the absorption spectra of nine targeted DPP derivatives in DCM (0.1 mM). The maximum absorption bands of **HDPP**, **pFDPP**, **CH$_3$DPP**, **mFDPP**, **CF$_2$HDPP**, **2mFDPP**, **CF$_3$DPP**, **R$_f$4CDPP** and **R$_f$6CDPP** were 463, 463, 467, 470, 472, 474, 475, 479, 480 nm, respectively. Among the fluorinated DPPs, the increasing electro-withdrawing ability of substituent on aryl ring resulted in a gradual red-shift of the absorption maxima. Surprisingly, the maximum absorption band of **pFDPP** was equal to **HDPP**, but slightly blue-shifted compared to the compound **mFDPP**, which indicates that para-substituted fluorine atoms affected weakly the absorption spectra. Interestingly, the maximum absorption of **CF$_3$DPP** and **2mFDPP** are slightly red-shifted compared to **CF$_2$HDPP** and **mFDPP** respectively due to the difference of the amounts of fluorine atoms. Moreover, the maximum absorption of **R$_f$4CDPP** and **R$_f$6CDPP** are red-shifted by 16 nm, 17 nm relative to that of **HDPP** due to the electron-withdraw properties of two perfluoroalkyl chains substituents.



Scheme 2. The synthetic routes of compounds **IDPP~2mFDPP** (**1-1~1-7**).



Scheme 3. The synthetic route of compounds (**CF$_2$HDPP, R$_f$4CDPP, R$_f$6CDPP**) (i) CF$_3$CF$_2$CF$_2$CF$_2$I or CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$I/Cu, DMF, 125 °C; (ii) TMSCF$_2$H, CuCl, Phen, t-BuOK, DMF, r.t., 10 h.

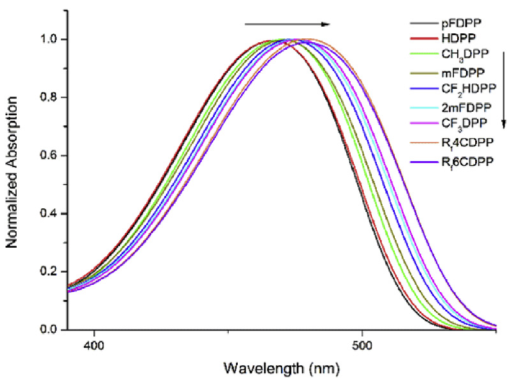


Fig. 1. Absorption spectra of all targeted compounds in DCM.

The fluorescence spectra of DPP derivatives in DCM (0.1 mM) were shown in Fig. 2. All of emitted intense fluorescence and the maximum bands ranged from 524 nm to 550 nm. In accordance with the absorption spectra, the maximum emission of **mFDPP**, **CF$_2$HDPP**, **2mFDPP** and **CF$_3$DPP** show the relatively redshifted by 7, 12, 12, 14 nm compared to **HDPP**. However the maximum emission of **pFDPP** is blue-shifted by 3 nm to **HDPP** due to the repulsion between the neighboring fluorine atoms, causing larger steric hindrance, reducing the planarity of the molecule and affecting the

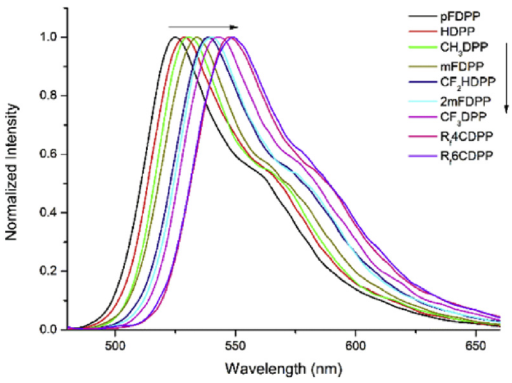


Fig. 2. Emission spectra of all targeted compounds in DCM.