Journal of Engineering Science 09(2), 2018, 103-108

JES
an international Journal

SYNTHESIS AND OPTOELECTRONIC PROPERTIES OF FLUORINATED DIKETOPYRROLOPYRROLE: EXPERIMENTAL INVESTIGATION OF SUZUKI COUPLING REACTIONS

Ashis K. Sarker

Department of Chemistry, Mawlana Bhashani Science and Technology University, Tangail-1902, Bangladesh

Received: 25 September 2018 Accepted: 04 December 2018

ABSTRACT

High molar extinction co-efficient and low band gap small molecules are highly demanding for optoelectronic applications. In this work, a series of diketopyrrolopyrrole (DPP) with/without fluorine were designed and synthesized, and compared with their parent molecule DPP-Br. These molecules exhibited strong visible absorption (450-640 nm). Relative to the parent molecule DPP-Br, fluorinated DPP exhibited red-shifted and stronger absorption. We also investigated the effects of fluorine on Suzuki coupling reaction and the structures of newly synthesized molecules were confirmed by proton NMR and UV/Visible absorption spectroscopy.

Keywords: *Absorption, Diketopyrrolopyrrole, Fluorine, Molecules, Optoelectronics, Synthesis*

1. INTRODUCTION

Diketopyrrolopyrrole (DPP) is a based on the bicyclic heterocyclic compound, formulated by dihydropyrrolo [3, 4-c] pyrrol-1, 4-dione. DPP pigments are an important class of high-performance pigments used in inks, paints and plastic (Kaur *et al.,* 2015; Grzybowski *et al.,* 2012). More recently, their optical-electronic performance was discovered for photovoltaic applications and related uses (Mukhopadhyay *et al.,* 2016; Kanimozhi *et al*., 2012). Thermal stability of DPP is very high but not very good to acid and base (Grzybowski *et al.,* 2015; Glowacki *et al.,* 2014). DPP has attracted much attention because of easy synthesis and structural modification, high molar absorptivity, highly conjugated structure, strong π-π interaction and strong electron deficiency.

Recent efforts have focused on developing small band gap organic molecules that allow absorption of a larger part of the solar spectrum. A very successful strategy for lowering the optical band gap involves strong electron deficient moieties in the organic molecules. DPP can show endless tunability of the optical band gap and the frontier orbital energy levels. It has now become one of the most favored electron deficient units in organic molecules (Zhao *et al.,* 2012; Liang *et al.,* 2017; Li *et al*., 2015; Takimiya *et al.,* 2013). DPP derivatives are generally composed of three parts: (1) the DPP unit, (2) an adjacent aromatic substituent, and (3) alkyl side chains of the DPP unit. By varying the aromatic substituents, one can tune the optical and electronic properties of DPP molecules. The side chains attached to the DPP unit provide solubility for solution processing and a handle to modify and adjust the aggregation of the molecules during thin film deposition. Phenyl-substituted DPP molecules have been used for their distinct photoluminescence and electroluminescence but never afforded high efficiencies in organic solar cells. By use of thiophene as a strong electron donating substituent, the absorption onset of the DPP molecules can be shifted to the near-infrared region. Thiophene-substituted DPP also shows high hole and electron mobilities above 1 $cm^2V^{-1}s^{-1}$ (Pietro *et al.,* 2017). Furthermore, the energy levels of such conjugated materials can be adjusted to obtain p-type, n-type, or ambipolar or organic semiconductors with highly efficient charge transport properties, depending on the type of moieties incorporated. The molecular energy levels of conjugated molecules depend upon several factors including conjugation length, strength of electron-donating and electron-accepting power and electronic properties of substituent, etc. Among these factors, the substitution of fluorine atom in conjugated molecules has recently been a promising method to control the energy levels, because it can lower the HOMO energy level of materials (Kim *et al.,* 2017). A recent development in organic photovoltaic cells (OPVs) is the introduction of electron-withdrawing fluorine atoms within the conjugated backbone, which significantly improve the overall performances of OPVs (Kim *et al.,* 2017). Fluorine atoms lower both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of conjugated materials while inducing promising inter-or intra-molecular interactions through existing F-F and H-F bonding. In addition, the small size of fluorine substituents can efficiently suppress undesirable steric effects.

---

* Corresponding Author: ashischemru@gmail.com

In this work, we synthesized low band gap conjugated molecules composed of DPP as electron-accepting unit with benzene with/without fluorine to examine the effect of the number of substituted fluorine on their electronic properties. The molecules with tri-fluorinated benzene exhibit higher λ_{max} due to deeper HOMO energy levels than the molecule with non-fluorinated benzene.

2. EXPERIMENTAL

2.1 Materials

Diketopyrrolopyrrole (DPP), N-bromosuccinimide (NBS), $Pd(PPh_3)_4$, phenylboronic acid, 4- fluorophenylboronic acid, 4- (trifluoromethyl) phenylboronic acid were purchased from Sigma-Aldrich. Chloroform, Tetrahydrofuran (THF), Magnesium Sulfate ($MgSO_4$), Potassium carbonate (K_2CO_3) were purchased from Samchun chemicals. Column chromatography was performed using silica gel 230-300 mesh (purchased from Aldrich) as the solid support. All NMR spectra were recorded on a Bruker Advance DPX 400 MHz spectrometer at 25 °C in $CDCl_3$. ^1H NMR chemical shifts are reported in δ units, part per million (ppm) relative to the chemical shift of residual solvent. Deuterated solvents were used as received from Aldrich. Reference peaks for chloroform in ^1H NMR spectra were set at 7.18 ppm. The absorption spectra were measured on a SHIMADZU/UV-2550 model UV-visible spectrophotometer.

2.2 Synthesis

Synthesis of DPP-Br: To a stirred solution of 2,5-bis (2-ethylhexyl)-3,6-di (thiophen-2- yl) pyrrolo [3,4-c] pyrrole-1,4(2H,5H)-dione (5.00 g, 9.52 mmol) in dry chloroform (300 mL), N-bromosuccinimide (NBS, 1.69 g, 9.52 mmol) was slowly added at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the mixture of products was separated using column chromatography (silica gel, eluent gradient 8:2>5:5 hexane: DCM). The target compound (2.59 g) was obtained as a red flaky powder (yield = 2.59 g, 45%). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.90 (dd, J = 6.50, 1H), 8.63 (d, 1H), 7.64 (dd, J = 6.16, 1H), 7.28-7.26 (m, 1H), 7.22 (d, J = 6.04, 1H), 4.03-3.99 (m, 2H), 3.98-3.92 (m, 2H), 1.88-1.80 (m, 2H), 1.38-1.23 (m, 16H), 0.90-0.84 (m, 12H).

Synthesis of Compound 1: To a mixture of compound 1 (3.00 g, 4.97 mmol) and phenylboronic acid (1.04 g, 7.45 mmol) in dry THF (40 mL), $Pd(PPh_3)_4$(0.24 g, 0.21 mmol) and aqueous K_2CO_3 (2.0 M, 20 mL; N_2 bubbled before use) were added and the mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous MgSO4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: $CHCl_3$), recrystallized from chloroform/methanol, and dried under vacuum to afford compound 1 as a dark violet solid (yield = 3.23 g, 96%). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.97 (d, 1H), 8.90 (d, 1H), 7.69 (d, J =8.44, 2H), 7.63 (d, 1H), 7.47-7.36 (m, 4H), 7.28 (d, J = 7.32, 1H), 4.08-4.07 (m, 2H), 4.03-4.02 (m, 2H), 1.93- 1.87 (m, 2H), 1.40-1.27 (m, 16H), 0.93-0.85 (m, 12H).

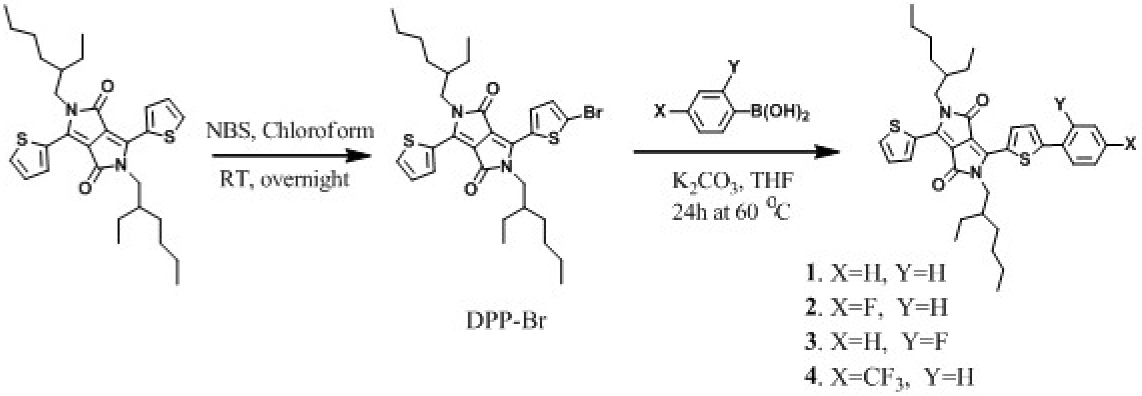
Synthesis of Compound 2: To a mixture of compound 1 (3.00 g, 4.97 mmol) and 4-fluorophenylboronic acid (1.04 g, 7.45 mmol) in dry THF (40 mL), $Pd(PPh_3)_4$(0.24 g, 0.21 mmol) and aqueous K_2CO_3 (2.0 M, 20 mL; N_2 bubbled before use) were added and the mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: $CHCl_3$), recrystallized from chloroform/methanol, and dried under vacuum to afford compound 2 as a dark violet solid (yield = 3.12 g, 92%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.93 (d, 1H), 8.90 (d, 1H), 7.67-7.60 (m, 4H), 7.40 (d, 1H), 7.15-7.10 (m, 2H), 4.07-4.02 (m, 4H), 1.90-1.87 (m, 2H), 1.38-1.25 (m, 16H), 0.92-0.85 (m, 12H).

Synthesis of Compound 3: To a mixture of compound 1 (3.00 g, 4.97 mmol) and 2-fluorophenylboronic acid (1.04 g, 7.45 mmol) in dry THF (40 mL), $Pd(PPh_3)_4$(0.24 g, 0.21 mmol) and aqueous K_2CO_3 (2.0 M, 20 mL; N_2 bubbled before use) were added and the mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: $CHCl_3$), recrystallized from chloroform/methanol, and dried under vacuum to afford compound 3 as a dark violet solid (yield = 3.12 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (d, 1H), 8.90 (d, 1H), 7.67-7.60 (m, 4H), 7.40 (d, 1H), 7.15-7.10 (m, 2H), 4.07-4.02 (m, 4H), 1.90-1.87 (m, 2H), 1.38-1.25 (m, 16H), 0.92-0.85 (m, 12H).

Synthesis of Compound 4: To a mixture of compound 1 (3.00 g, 4.97 mmol) and 4-(trifluoromethyl) phenylboronic acid (1.42 g, 7.45 mmol) in dry THF (40 mL), $Pd(PPh_3)_4$(0.24 g, 0.21 mmol) and aqueous K_2CO_3 (2.0 M, 20 mL; bubbled with N_2 before use) were added and the mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: $CHCl_3$), recrystallized from chloroform/methanol, and dried under vacuum to afford compound 4 as a dark violet solid (yield = 2.88 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (t, 2H), 7.77 (d, 2H), 7.69-7.63 (m, 2H), 7.54 (d, J = 8.32, 1H), 7.29-7.27 (m, 2H), 4.08-4.03 (m, 4H), 1.89 (m, 2H), 1.40-1.25 (m, 16H), 0.93-0.85 (m, 12H).

3. RESULTS AND DISCUSSION

DPP is synthesized by the reaction of aromatic nitrile with dialkyl succinate. The molecular frame of DPP has many reactive centers such as (i) the aryl rings that undergo electrophilic and nucleophilic reactions and (ii) the bicyclic lactam chromophoric unit with three different functional groups: (1) –C=C- double bonds, (2) carbonyl, and (3) secondary amine (=NH) groups that may potentially undergo structural modification for further derivatization. The significant advantages of DPP derivatives are as follows: (a) they can undergo several synthetic modifications (b) act as strong acceptor units, (c) exhibit high fluorescence quantum yields, and (d) possesses exceptional thermal and photostability, making them excellent building blocks for many applications. Owing to the above features, DPP and its derivatives have been widely used as high-performance pigments and exhibit outstanding semiconducting properties (Kaur *et al.* 2015).



Scheme 1: Synthetic route to fluorinated DPP-Br, **1**, **2**, **3** and **4**

In this work, we have synthesized fluorinated DPP starting form aromatic nitrile and dialkyl succinate. Parent DPP moiety was synthesized following the literatures (Grzybowski *et al.,* 2015). Synthesizing monobromo-DPP (DPP-Br) with high yield is challenging for the chemists. After bromination reaction, separation of monobromo compound is notoriously very big challenge by column chromatography. We optimize all the conditions to produce maximum yield of DPP-Br. At low temperature (-78 °C) the reaction does not move forward. The temperature has been increased to 0 °C and we observed tremendous change in TLC and found high yield product (45%) (Scheme 1). We performed this reaction at room temperature and found low yield because DPP is decomposed by NBS at room temperature and dibromo-DPP formed instead of DPP-Br. Now, to incorporate fluorinated benzene to DPP, we performed Suzuki coupling reaction with DPP-Br. Phenylboronic acid, 4- fluorophenylboronic acid, 2-fluorophenylboronic acid, 4- (trifluoromethyl) phenylboronic acid have been used for Suzuki coupling reactions. The yield of the reactions with phenylboronic acid was 96%, and the yield was found to be 92, 85 and 81% with 4-fluorophenylboronic acid, 2- fluorophenylboronic acid, and 4- (trifluoromethyl) phenylboronic acid, respectively (Table 1).

Table 1: Conditions for the synthesis of 1, 2, 3 and 4

Reactant	Time (h)	Temp (°C)	Yield (%)	Product
Phenylboronic acid	6	60	96	1
4-fluorophenylboronic acid	6	60	92	2
2-fluorophenylboronic acid	6	60	85	3
4-(trifluoromethyl) phenylboronic acid	6	60	81	4

The halogen substituted aromatic ring has an electron withdrawing effect, however, essentially no effect for fluorine even it has electron donating resonance dipole. Phenylboronic acid has no fluorine attached and phenyl is electron withdrawing group and boron also electron deficient so, the bond between boron and phenyl carbon turn into weak and phenyl group develop as strong nucleophile which made the yield superior. In case of 4-fluorophenylboronic acid, fluorine shares the electron with phenyl ring and increase the electron density in boron which has space for electron (Figure 1). Therefore, the bond between boron and phenyl carbon turn out to be strong and the creation of nucleophile become comparatively unfavorable and the yield of the reaction become low. In case of 2-fluorophenylboronic acid, fluorine shares the electron with phenyl ring and increase the electron density in boron which has space for electron. As a result, the bond between boron and phenyl carbon become strong as well as the fluorine and boron atom tend to close to each other and they have ionic interactions (Figure 1). Boron has positive in nature and fluorine has negative in nature. Because of these two phenomena, the nucleophilicity of 2-flurophenyl group exhibits less. Therefore, the rate of the reaction tends to be lowered. In case of 4- (trifluoromethyl) phenylboronic acid, it is obvious that it contains 3 fluorine atoms and force electron to the benzene ring and bond between boron and phenyl carbon become stronger and nucleophilicity become the least. That is the reason 4-(trifluoromethyl) phenylboronic acid showed the lowest yield compared to other fluorinated moieties.

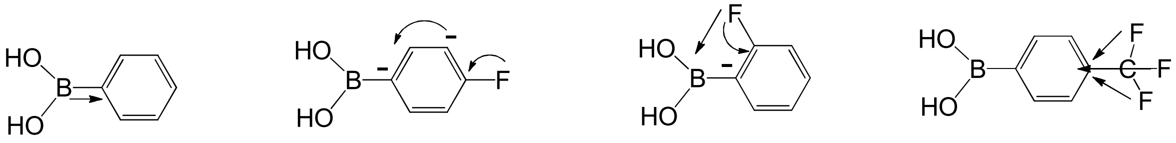


Figure 1: Effect on Suzuki coupling reaction by fluorine atoms

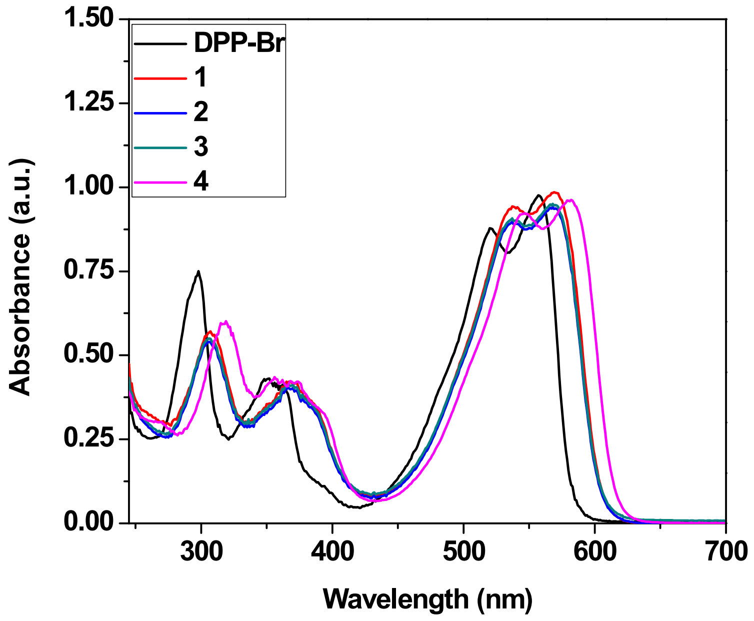


Figure 2: Comparison of absorption spectra of 1, 2, 3 and 4 together with DPP-Br in chloroform

DPP is an electron deficient moiety which absorbs in the range of 400-500 nm, and it may act as electron acceptor in the electronic devices. Whereas, benzene with fluorine and without fluorine absorbs in the range of 200-250 nm and it may act as electron donor in the moiety. The UV/Visible spectra of all fluorinated and without fluorinated moieties were recorded in chloroform and are presented in Table 2. The spectra of optical absorption of these fluorinated/without fluorinated phenyl-DPP-based materials in chloroform solution (10^{-6} M) are shown in Figure 2. DPP-Br exhibited absorption maxima at around 557-558 nm in solution while 1, 2 and 3 exhibited absorption maxima at 570-573 nm, respectively, additional CF_3 (4) led to an obvious red shift of (585 nm) 30-35 nm. Furthermore, the maximum extinction co-efficient of the extended molecules 4 were at least 1.2 times higher than the parent molecule. The red-shifted and stronger absorption of the extended molecules can be attributed to the elongated π conjugation length and strengthened intra-molecular charge transfer effect.

Table 2: UV/Visible absorption data of compounds DPP-Br, 1, 2, 3 and 4 in chloroform, the concentration was 10^{-6} M

Compound	Absorbance, λ_{max} (nm)			
DPP-Br	299	350	523	557
1	305	370	544	570
2	305	370	544	570
3	305	370	544	570
4	320	375	550	580

These fluorinated DPP can be used for numerous applications. We are currently investigating the uses of these molecules for photovoltaic applications. The results will be reported in due course.

4. CONCLUSION

In conclusion, we have synthesized high molar extinction co-efficient and low band gap small molecule DPP-Br and its derivatives 1, 2, 3 and 4 by Suzuki coupling reaction to benzene with/without fluorine. The effect of fluorine on Suzuki coupling reaction was investigated. Relative to the parent molecule DPP-Br, fluorinated DPP exhibited red-shifted and stronger absorption. These high molar extinction co-efficient and low band gap small molecules are very important for optoelectronic devices.

ACKNOWLEDGEMENT

The author appreciates Prof. Sung-Yeon Jang, Department of Chemistry, Kookmin University, South Korea, for NMR and UV/Visible absorption data.

REFERENCES

Glowacki, E. D., Coskum H., Forsythe M. A. B., Monkowius U., Leonat L., Grzybowski M., Gryko D., White M. S., Guzik A. A., and Sariciftci N. S., 2014. Hydrogen-bonded diketopyrrolopyrrole (DPP) pigments as organic semiconductors. Org. Electronics, 15, 3521.

Grzybowski, M., and Gryko D. T., 2015. Diketopyrrolopyrroles: Synthesis, Reactivity, and Optical Properties. Adv. Optical Mater., 3, 280.

Grzybowski, M., Mrowka E. G., Stoklosa T., and Gryko D. T., 2012. Bright, Color-Tunable Fluorescent Dyes Based on π-Expanded Diketopyrrolopyrroles. Org. Lett., 14, 2670.

Kanimozhi, C., Gross N. Y., Chou K. W., Amassian A., Anthonoulos T. D., and Patil S., 2012. Diketopyrrolopyrrole -Diketopyrrolopyrrole-Based Conjugated Copolymer for High-Mobility Organic Field-Effect Transistors. J. Am. Chem. Soc., 134, 16532.

Kaur, M., and Choi D. H., 2015. Diketopyrrolopyrrole: brilliant red pigment dye-based fluorescent probes and their applications. Chem. Soc. Rev., 44, 58.

Kim, I. B., Jang S. Y., Kim Y. A., Kang R., Kim I. S., Ko D. K., and Kim D.Y., 2017. The Effect of Fluorine Substitution on the Molecular Interactions and Performance in Polymer Solar Cells. ACS Appl. Mater. Interfaces, 9, 24011.

Li, W., Hendriks K. H., Wienk M. M., and Janssen R. A. J., 2015. Diketopyrrolopyrrole Polymers for Organic Solar Cells. Acc. Chem. Res., 49, 78.

Liang, N., Jiang W., Hou J., and Wang Z., 2017. New developments in non-fullerene small molecule acceptors for polymer solar cells. Mater. Chem. Front., 1, 1291.

Mukhopadhyay, T., Puttaraju B., Senanayak S. P., Sadhanala A., Friend R., Faber H. A., Anthopoulos T. D., Salzner U., Meyer A., and Patil, S., 2016. Air-Stable n-channel Diketopyrrolopyrrole-Diketopyrrolopyrrole Oligomers for High Performance Ambipolar Organic Transistors. ACS Appl. Mater. Interfaces, 8, 25415.

Pietro, R. D., Ermann T., Carpenter J. H., Wang N., Shivhare R. R., Formanek P., Heintze C., Voit B., Neher D., Ade H., and Kiriy A., 2017. Synthesis of High-Crystallinity DPP Polymers with Balanced Electron and Hole Mobility. Chem. Mater., 29, 10220.

Takimiya, K., Osaka I., and Nakano M., 2014. Π-Building Blocks for Organic Electronics: Revaluation of “Inductive” and “Resonance” Effects of π-Electron Deficient Units. Chem. Mater., 26, 587.

Zhao, B., Sun K., Xue F., and Ouyang J., 2012. Isomers of dialkyldiketo-pyrrolo-pyrrole: Electron-deficient units for organic semiconductors. Org. Electronics., 13, 2516.