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Synthesis of Diketopyrrolopyrrole (DPP) using ionic liquid as a co-solvent

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Abstract

Diketopyrrolopyrrole as an important monomer, precursor for many synthesis conjugated polymers and organic pigments. Herein, we modify the synthesis DPP preparation method, using ionic liquid as a co-solvent. In this study, Furan DPP, Thiophene DPP and Pyridine DPP are synthesized at 70 ^{0}C with improved yield reported by previous method. The effect of ionic liquid on the yield is monitored by changing the volume of ionic liquid and t-amyl alcohol. These DPPs are characterized by ^{1}H NMR and ^{13}C NMR. The optical properties are recorded and textures of DPP films are also analyzed.

Keyword: Diketopyrrolopyrrole, Ionic liquid, and 1-methylimidazolium hydrogen sulphate

1. Introduction

Diketopyrrolopyrroles (DPPs) are one of the most recently discovered groups of organic pigments [1-3]. Due to their relatively simple synthesis and other advantageous properties, such as their intense color, excellent stability, and low solubility, DPPs have been rapidly adopted for numerous industrial applications such as pigments in paints, varnishes, and high quality printing ink [4-9]. The DPP has attracted considerable research interest over the last few years. DPP has a planar structure and can induce strong intermolecular H-bonding and p–p stacking with neighboring molecules [10-13]. The molecular frame of DPP has many reactive centers that may potentially undergo structural modification for further functionalization. An easy synthesis procedure even makes this material attractive and common among the researcher [14-15]. Over the time, it was revealed that, through N -alkylation, DPP pigments can be easily transformed into soluble dye which widen the scope in the solution processable applications [12, 16-18]. Intense investigation soon resulted in a large number of scientific reports showing that DPP derivatives can be applied as functional dye in dye sensitized solar cell [19-22]. The planar structure and chromophoric nature of DPP renders a remarkable starting material for synthesis of active materials for organic field effect transistor (OFET) and organic solar cell (OSC) [10, 23-31].

DPPs are structurally based on 2, 5-dihydropyrrolo [4, 3- c] pyrrolo-1,4-dione -(figure 1), the aromatic substitution at position 6 and 3 makes it even more useful material for organic electronics. Strong hydrogen bonding

between lactum units reduces the solubility of the solubility of this chromophore. The optical properties of DPP are described by the charge transfer between electronic rich aromatic ring to the electron deficient 2, 5-dihydropyrrolo [4, 3- c] pyrrolo-1,4- dione unit. Hence, optical properties of DPPs are modified by aromatic substitution at position 6 and 3. In recent past different aryl DPP derivative and their polymers are being synthesized and used as organic semiconductors. Until now, many reports discussed about the structure property relationship DPP based small or polymers, however; only little attention has been paid toward optimization of synthesis of DPP conjugated core. Normally, DPP are synthesized by condensation of aryl cabonitrile with dialkyl suucinate in presence of base, known as Iqbal method. In this report, we modified the synthetic procedure of DPPs by adding ionic liquid as a co-solvent, the volume of ionic liquid is optimized to ensure the solubility of the reactants. Herein, we synthesized series of DPPs using modified synthetic procedure, and compared with previously reported procedure (without ionic liquid), the yield of DPP is improved when ionic liquid was applied to reaction mixture.

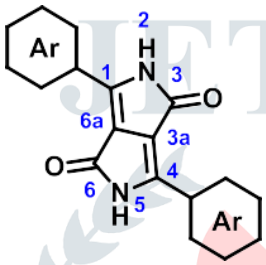
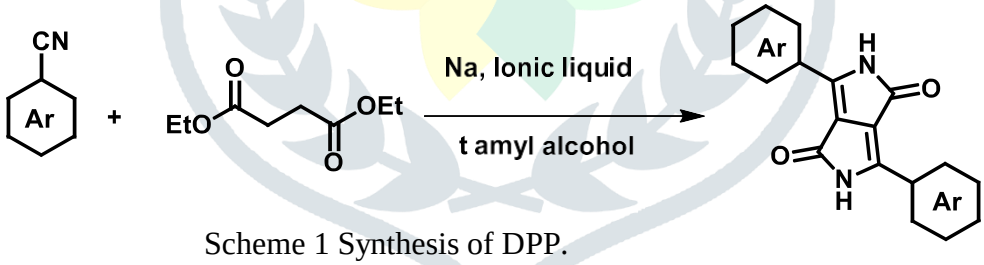


Figure 1: General structure of DPP with atom labeled

2. Result and discussion



Scheme 1 Synthesis of DPP.

The synthesis of DPP is outlined in scheme 1. In the previous reports, Diketopyrrolopyrroles were synthesized by reacting aryl cabonitrile with diethyl suucinate under basic condition in t amyl alcohol at 100 ^{0}C. Herein, we introduced an ionic liquid as a co- solvent in the reaction medium and reduce the reaction temperature to 70℃.

The name of ionic liquid used in this series is 1-methylimidazolium hydrogen sulphate ([Hmim]HSO_4). Further, we systematically optimized the volume [Hmim]HSO_4 being added in the reaction mixture by altering t amyl alcohol to [Hmim]HSO_4 ratio such as 100:0, 90:10, 80:20, 70:30, 60:40, 50:50. We examine that addition of ionic liquid more than 50% in the reaction medium reduced the solubility of the reactants and hence the product formation. The highest yield was achieved when the solvent ratio 20% (t amyl alcohol: ionic liquid) as shown in figure 3. The TDPP, FDPP and PyDPP (figure 2) were synthesized by reacting corresponding aryl cabonitrile with diethyl suucinate under basic condition.

The yield of all DPPs was 70-80 %. The structure of DPPs was conformed using 1HNMR and 13CNMR spectra. Please note that the solubility of PyDPP is very low in polar solvent therefore we could not record the ^{13}C NMR of PyDPP, in this case the product conformation is done by solid state ^{1}H NMR only.

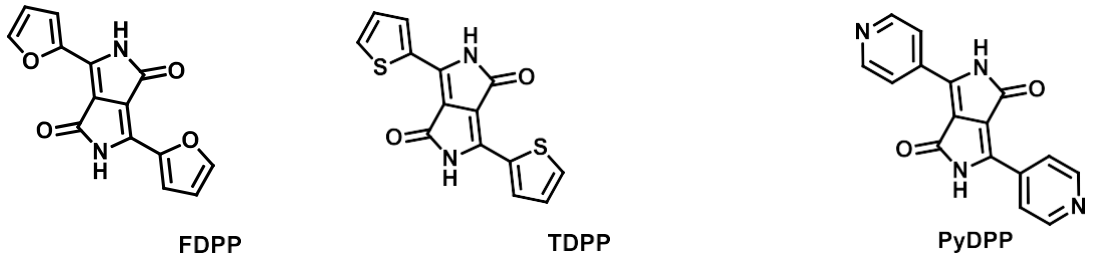
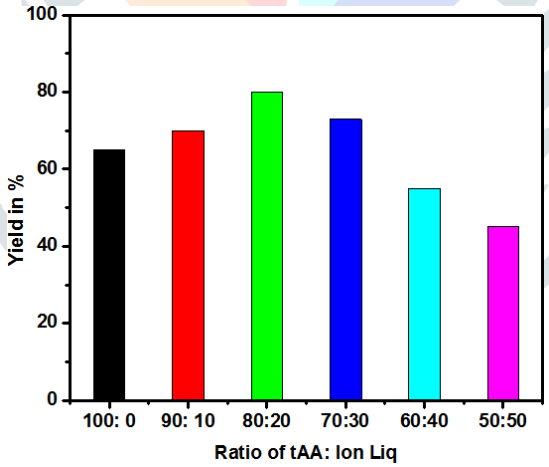


Figure 2 structures of FDPP, TDPP and PyDPP

Since the DPP are used as a pigment in paints, useful to record the optical properties. The absorption and emission spectra of DPPs were shown in figure 4 and summarized in table 1. Optical properties of all DPPs were recorded in DMF solution. The optical properties of DPP are ascribed by the charge transfer between electron rich aromatic units to electron deficient Bislactum unit. Therefore, aromatic unit in DPPs has differentiating impact on optical properties. The absorption profiles of all DPP are identical in nature, having one high energy transition along with a charge transfer band at lower wavelength. The lower energy transition (at higher wavelength) is corresponds to charge transfer between aromatic unit to the electron deficient Bislactum unit which can be varied depending upon aromatic unit.

Figure 3: The graph of ratio of t-amyl alcohol: and Ionic liquid used as a solvent to corresponding yield for



synthesis of TDPP.

The λmax of FDPP, TDPP and PyDPP is 520 nm, 531 nm and 513 nm respectively. The band gap of DPPs were calculated using λonset using formula E = hc /λ. The band gap of FDPP, TDPP and PyDPP is 2.34 eV, 2.20 eV and 2.39 eV respectively.

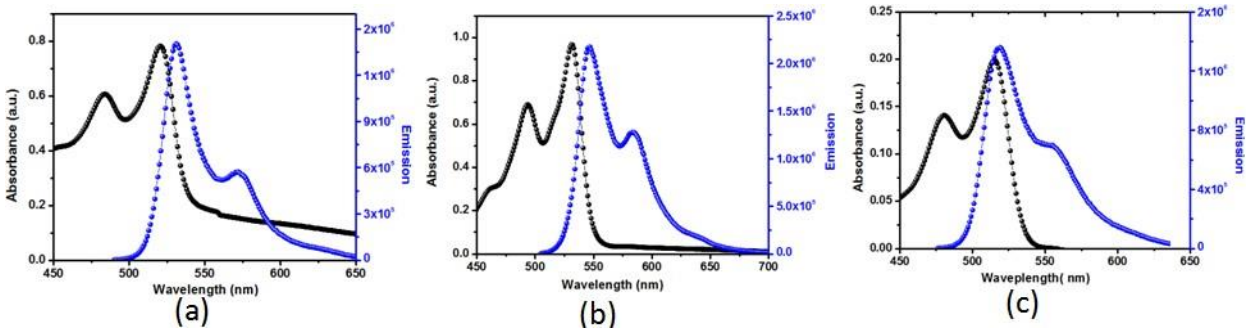


Figure 4: Absorption and emission spectra of (a) FDPP, (b) TDPP and (c) PyDPP.

The emission spectra of all DPPs are having identical profile, having a strong emission band with additional weak emission at higher wavelength. The λemission of FDPP, TDPP and PyDPP is 530 nm, 546 nm and 520 nm respectively. Figure 4 has shown the pictures of DPP in the normal light, in ultraviolet light and in solid state. The pictures of DPP were recorded in DMF solution. As shown in figure 4a, the solution of DPPs is possessed color in normal-visible light. The solution of DPP in ultraviolet light possesses strong fluorescence evident from figure 4b. In the solid state all the synthesized DPPs are red in color.

Figure 5 Picture of solution of DPP in DMF in visible (normal) light (a), in ultraviolet light (b), in solid state (c).

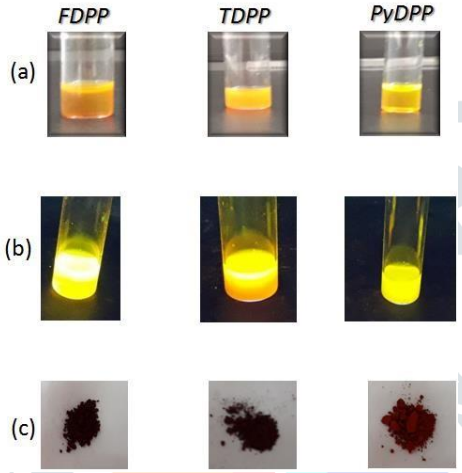


Table 1 summary of optical properties of synthesized DPPs.

Sr.No	λabs (nm)	λonset (nm)	λemission (nm)	Band gap (Eg) (eV)
FDPP	520	530	540	2.34
TDPP	531	546	550	2.20
PyDPP	513	520	532	2.39

White light interferometry based surface profiling (WLISP) provide valuable information about the surface texture of thin films over a large area (mm^2). Quantitative information on the three dimensional topography of surfaces are obtained by interference pattern of light waves with the surfaces. For these experiments, the sample was prepared by dissolving DPP in dimethylformamide and drop casted on glass slide. The sample was dried for 24 h prior to the measurements. The film texture of DPPs was shown in figure. Evidently, aromatic unit in DPPs have significant impact on their film texture. The FDPP has a sharp needle like texture while TDPP forms a small crystalline particles and film of PyDPP has not possess a define texture. The texture of DPP films, perhaps, could

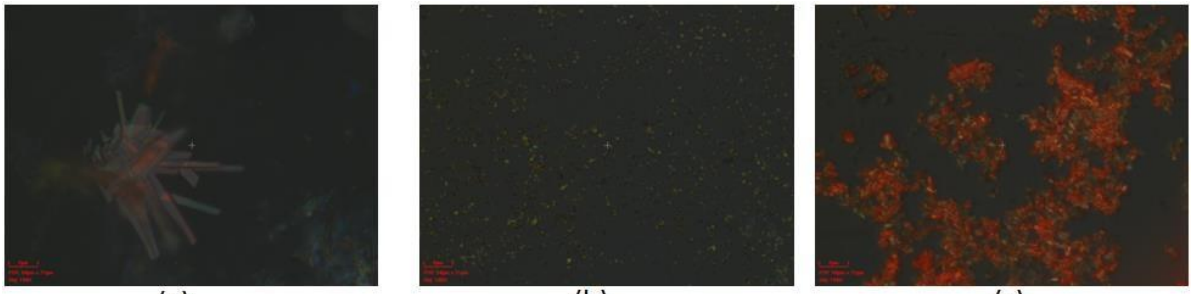
be due to degree of distortion in the DPP structure.

Figure 6: Optical microscopy images of (a) FDPP, (b) TDPP and (C) PyDPP

3. Materials and Methods

Materials

2 thiophene carbonitrile, 2 furocarbonitrile, 4 cyannopyridine and diethyl succinate were purchased from Aldrich chemicals. The ionic liquid [Hmim]HSO_4 is also purchased from Aldrich. The solvent were dried by following reported procedures. 1H-NMR and 13C NMR spectra were recorded using 200 and 400 MHz Brucker NMR spectrophotometer in CDCl3 / DMSO-d6 containing small amount of TMS as internal standard. UV-Vis



spectra were recorded using Perkin Elmer Lambda-35 UV-Vis spectrophotometer. White light interferometry based surface profiling (WLISP) provide valuable information about the surface texture of thin films over a large area (mm^2). For these experiments, SiO_2 substrates were used.

General procedure for synthesis of DPPs (TDPP)

In a 100 ml two neck oven dried round bottom flask mixture of t- amyl alcohol and ionic liquid HMIM]HSO_4 were added under inert atmosphere. To the solvent mixture Na metal (4mmol) was added slowly (caution: addition of Na to ionic liquid may catch the fire). The resulting solution was heated at 50- 70 C, dissolved the Na metal as much as possible. The aryl carbonitrile (2mmol) then added to the reaction mixture and heat the mixture at same temperature for two hours followed by addition of diethyl suucinate (1mmol) to it. Before cooled down to room temperature reaction mixture was stirred 70 ˚C for 6 h. The reaction mixture was neutralized by adding the mixture of acetic acid and methanol to it. The mixture was then filtered off and wash with hot water and methanol two to three time to get red color solid DPP.

TDPP (70%) ^{1}H NMR (200 MHz, DMSO) δ 8.06 (d, J = 3.7 Hz, 2H), 7.80 (d, J = 4.9 Hz, 2H), 7.15 (t, J = 4.4 Hz, 2H).

^{13}C NMR (50 MHz, DMSO) δ 161.71, 136.30, 132.55, 131.55, 130.51, 128.69, 108.64.

FDPP (65%): ^{1}H NMR (200 MHz, DMSO) δ 11.17 (s, 2H), 8.03 (s, 2H), 7.68 (d, J = 3.5 Hz, 2H), 6.82 (s, 2H).

^{13}C NMR (50 MHz, DMSO) δ 161.16, 146.76, 143.77, 131.25, 116.94, 113.58,
107.73.

PyDPP (72%): ^{1}H NMR (200 MHz, DMSO) δ 8.83 (d, J = 5.9 Hz, 4H), 7.87 (d, J = 4.6 Hz, 4H).

4. Conclusion

In conclusion, we synthesized the three different derivative of DPP i.e. FDPP, TDPP and PyDPP using ionic liquid as a co-solvent. We optimized the yield of DPP by changing the solvent ratio i.e. t amyl alcohol to ionic liquid. The maximum yield was obtained when solvent ratio is 80:20. Finally we characterized the structure of DPP using different spectroscopic techniques. We performed the optical characterization and morphological study.

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