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Mixture of Ionic Liquids as Novel Media for Green Synthesis of Diketopyrrolopyrrole Pigments

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ABSTRACT

A green method for the synthesis of high-performance diketopyrrolopyrrole pigments using diethyl succinate in the presence of mixture of ionic liquids is reported. Although, alkaline condition is needed in the succinate ester route for synthesis of the pigments, in the present study, the replacement possibility of conventional organic base by mixture of [BMIM][OH] and [BMIM][BF4] ionic liquids was investigated. One of the points in this approach is the utilization of diethyl succinate, a commercially available and low-cost reagent instead of di-t-butyl or t-amyl succinate as bulky esters which are recommended in conventional methods. The obtained results were compared with the results of synthesis in the presence of each of ionic liquids solely with sodium t-amyloxide. Prog. Color Colorants Coat. 6(2013), 81-86. © Institute for Color Science and Technology.

1. Introduction

Since most of chemical reactions in laboratories and industries carried out in solution form, selection of a proper solvent is an important parameter [1-3]. In the recent times, ionic liquids have attracted a great attention due to their special physical and chemical properties [4-7]. Ionic liquids are salts consist of cations and anions which exist in liquid form at room temperature [8]. Because of their very low vapor pressure, ionic liquids are not volatile and belong to a class of green chemistry solvents [9-10]. They could solve both organic and inorganic, even polymeric compounds and recycle easily [11-13]. Ionic liquids were studied as solvent for various organic and inorganic reactions [12-15]. Ionic liquids with counter ion of OH^- have basic properties and PF_6^- and BF_4^- cause neutral ionic liquids [16-18].

By the way, diketopyrrolopyrroles (DPPs) as innovative in high-performance pigments, have fascinated a lot of attention due to excellent properties such as high thermal stability, good weather and light fastnesses and other special characteristics including photoluminescence, high conductivity and color strength [19-23] for applying in industries such coloring, fibers and surface coatings like paints, prints, and inks. Nowadays they are used in color filters due to their color

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strength and high stability, laser dyes [22-26], erasable optical memory devices and organic solar cells [27-29].

Considering the properties of ionic liquids and efficiency of DPP pigments, and in continuous of our previous studies [30-32], in this study, 1, 4-diketopyrrolopyrrole (pigment red 255), 4, 4′-*para*-chloro-1, 4-diketopyrrolopyrrole (pigment red 254), and 4,4′-*para*-bromo-1,4-diketopyrrolopyrrole is synthesized in mixed ionic liquids of [BMIM][BF4] and [BMIM][OH] in absence of sodium t-amyloxide as well as any other organic solvents.

2. Experimental

2.1. Materials

The chemicals were purchased from Merck (Germany) and Fluka Chemical Company (Buchs Switzerland) and used without further purification. Ionic liquids and sodium *t*-amyl oxide were synthesized according to [27] and [1], respectively.

2.2. Instruments

Melting point measurements were carried out with a Perkin Elmer Pyris 6 differential scanning calorimeter (DSC) from 0 to 400°C at the rate of 10°C/min. The UV-Vis spectra of the pigments were obtained with a Cecil 9200 double beam spectrophotometer. The samples were dissolved in dimethyl sulfoxide. FT-IR spectra of the neat DPPs samples between KBr discs were obtained with a Perkin-Elmer Spectrum One BX FTIR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker Drx-500 Avance spectrometer at 500 MHz. The samples were dissolved in deuterated chloroform or dimethyl sulfoxide and TMS was used as the internal standard. A Scanning Electron Microscope (SEM, LEO 1455 VP) was used to analyze the pigments morphology. A small amount of the pigments were placed on aluminum stubs and sputter coated with gold. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an acceleration voltage of 10 keV.

2.3. Synthesis

2.3.1. Synthesis of the pigments in the mixed ionic liquids via succinate route in lack of organic base

In a three-necked flask equipped with thermometer and a reflux condenser tube, benzonitrile or its derivatives (20 mmol) was slowly added to diethyl succinate (2 mL, 10 mmol) at 50˚C, different portions of ionic liquids [BMIM][BF4] and [BMIM][OH] (totally 0.5 ml) was added to the reaction mixture. Reactions were stirred in 24 hours at room temperature and monitored by TLC. Afterward, the pigments were precipitated using 20 mL water and filtrated. Filter cakes was rinsed by methanol to remove the remained ionic liquids and dried at 80 ˚C in vacuum.

DPP (1a)

1a: Yellowish-red powder; m.p. > 300˚C; FT-IR (KBr) (ν_{max} cm^{-1}): 3439 (NH); 2947(CH); 1654(C=O); 1346, 1225(C-N); λ_{max}/nm (DMSO) 506, 473; ^{1}HNMR (500 MHz, $CDCl_3$): δ_H 7.33-7.70 (10H, m, 10 CH), 10.43(2H, s, NH).

Cl-DPP (1b):

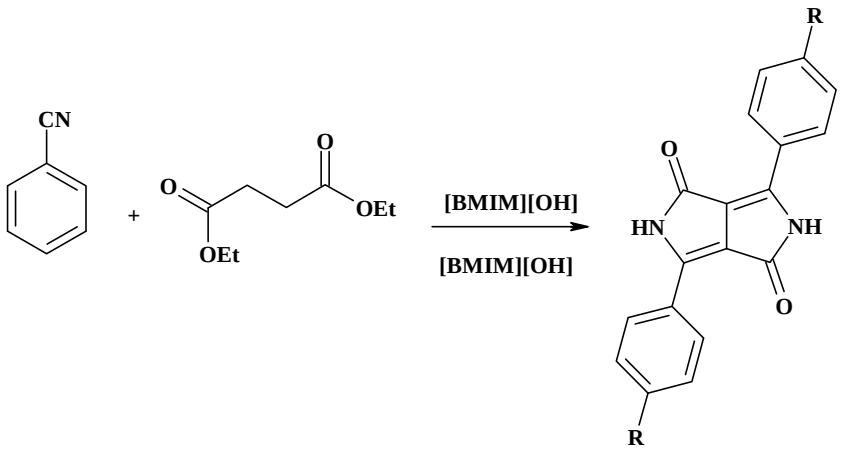
1b: Red powder; m.p. > 300˚C; IR (KBr) (ν_{max} cm^{-1}): 3436 (NH); 2931(CH); 1635 (C=O); 1392, 1169(C-N); λ_{max}/nm (DMSO) 520, 482; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 7.65 (4H, d, J_{HH} 13.3 Hz, 4CH), 7.87 (4H, d, J_{HH} 13.3 Hz, 4 CH).

3. Results and discussion

The reaction between diethyl succinate and two equimolar benzonitrile and its derivatives (4-chloro benzonitrile and 4-bromo benzonitrile) in the presence of 1-butyl and 1-hexyl-3-methylimidazolium hydroxide as media in lack of organic base (sodium *t*-amyl oxide) has been accomplished and resulted in two pigments of 1,4-diketopyrrolopyrrole (DPP) and 4,4′-dichloro-1, 4-diketopyrrolopyrrole (Cl-DPP), although 4,4′-dibromo-1, 4-diketopyrrolopyrrole (Br-DPP) was not obtained in this conditions. The pigments were compared with those obtained in the presence of each ionic liquid solely under alkaline condition [32]. The procedure is depicted in Scheme 1.

In the absence of sodium *t*-amyloxide, based on succinate ester route, the synthesis has been carried out by mixing different proportions of two ionic liquids, i.e. [BMIM][OH] and [BMIM][BF_4], under solvent-free condition (Scheme 1). The data are illustrated in Table 1.

According to the results presented in Table 1, synthesis of these high performance pigments have been accomplished in a green condition without using conventional solvent and organic base.



Compound	R	Pigment
1a	H	DPP
1b	Cl	Cl-DPP
1c	Br	Br-DPP

Scheme 1: Synthesis of DPP pigments by succinate ester route in the presence of ionic liquid media without organic base.

Table 1: Efficiencies of the syntheses in different proportions of the ionic liquids.

[BMIM][BF_4] / [BMIM][OH] (ml)	Cl-DPP Obtained Yield (%)	DPP Obtained Yield (%)
0.2 / 0.8	23	24
0.4 / 0.6	25	43
0.5 / 0.5	30	32
0.6 / 0.4	28	24
0.8 / 0.2	18	22
1 / 0 0 / 1	0 0	0 0

In the presence of two ionic liquids of [BMIM][OH] and [BMIM][BF_4] with the ratio of 0.4:0.6, DPP was obtained in 43% yield under alkaline condition using ionic liquid of [BMIM][BF_4] [32]. Cl-DPP was obtained up to 30% yield with equal proportions of the ionic liquids. Br-DPP was not obtained in this approach.

3.1. Crystal morphology of the pigments

The crystal morphology of the pigments was investigated by Scanning Electron Microscopy (SEM). The SEM images in Figures 1 and 2, show the crystallinity of the products in the presence of two ionic liquids of [BMIM][OH] and [BMIM][BF_4].

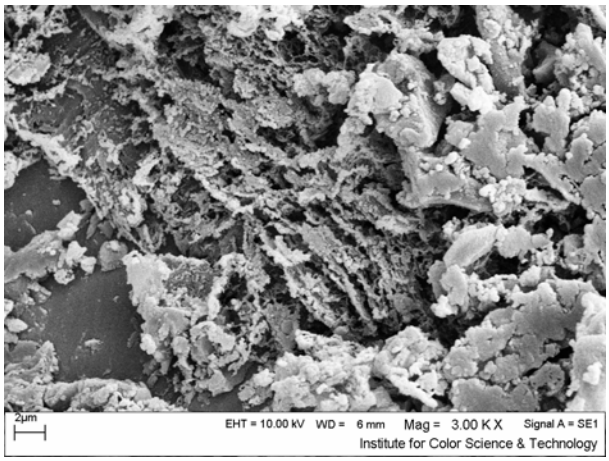


Figure 1: SEM images of the synthesized Cl-DPP at equal ratio of [BMIM][OH] and [BMIM][BF_4] in the absence of sodium *t*-amyl oxide.

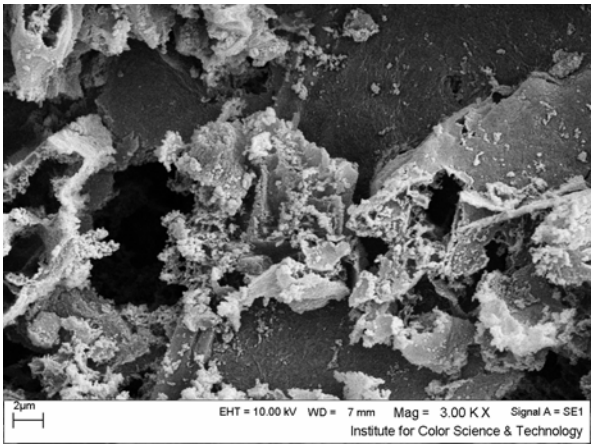


Figure 2: SEM images of the synthesized DPP at 0.6:0.4 ratio of [BMIM][OH] and [BMIM][BF_4] in the absence of sodium *t*-amyl oxide.

According to Figure 2, amorphous pigments were obtained in the absence of sodium amyl oxide.

4. Conclusions

In conclusion, green synthesis of DPP pigments by succinate route in the mixture of [BMIM][OH] and [BMIM][BF_4] in equal ratio and absence of sodium *t*-amyl oxide under solvent-free conditions was successful. The maximum yield of Cl-DPP was 30% at 0.6/0.4 ratio of [BMIM][OH] and [BMIM][BF_4] in the absence of sodium *t*-amyl oxide. The pigments were obtained in amorphous crystal morphology in the mentioned media.

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