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Synthesis, Optical Properties and Morphology of Film of Novel Bridged Double Benzimidazole Perylene Derivative

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A bridged double benzimidazole perylene derivative (BIDP) was synthesized from 3,4,9,10-perylenetetracarboxylic dianhydride. UV-visible spectrum and fluorescence spectrum of BIDP were studied in DMF, which showed that the maximum absorption peak was at 525 nm and the other characteristic absorption peaks were at 498 and 566 nm and the emission peak was at 540 and 580 nm. Then the film of BIDP was made by the electrodeposition. The optical physical properties, morphology and aggregation structure were investigated by UV-visible and fluorescence spectra. The characterization were investigated by UV-visible, fluorescence spectrum, SEM and XRD. Finally, the electrodeposition films that had ordered morphology were got by DMF vapour annealing.

Keywords: Bridged double benzimidazole perylene derivative, Electrodeposition, Film, Optical physical properties, Aggregation structure.

INTRODUCTION

A two-layer organic photovoltaic cell, which was fabricated from copper phthalocyanine and *bis*(benzimidazo)perylene (BZP), was reported by Tang[1], *bis*(benzimidazo)perylene has become increasingly attractive in recent years. The *bis*(benzimidazo)perylene presented remarkable electron-donor characteristics and it also has high charge-carrier mobilities, high thermal, chemical and photostability and superior light absorption in the wavelength range of visible light[2-5]. In general, perylene bisimide derivatives (PTCD) have electronic absorption bands spanning the 400-600 nm spectral range, with the vibronic structure superposed on the π-π* transition that is characteristic of the PTCD chromophore[6]. However, *bis*(benzimidazo)perylene derivatives are transparent in the near-infrared region[7]. Hence, their strong absorption in the visible spectral range makes them potential candidates for applications as organic semiconductors, photoconductors and laser materials[8,9]. But *bis*(benzimidazo)perylene derivatives are also reported that they have relatively poor solubility, which influence their development in the field of organic photovoltaic, so designing perylenediimide with high solubility is a problem to be solved.

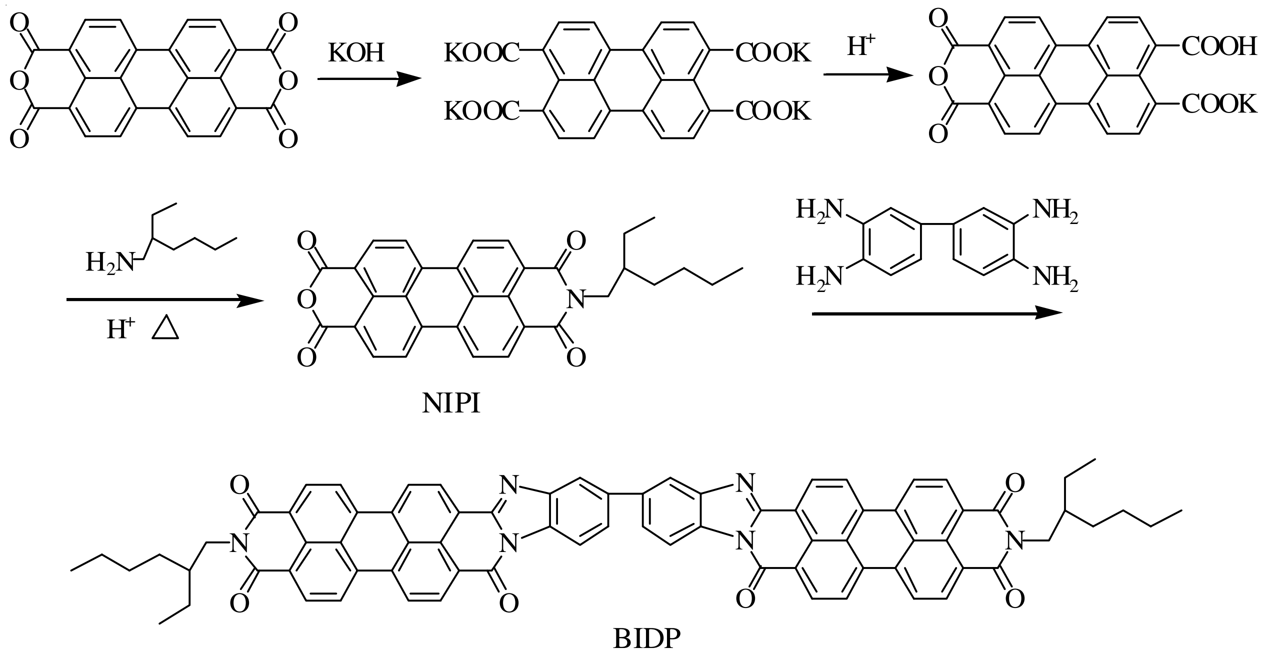
We reported in present study, the synthesis of a bridged double benzimidazole perylene derivative (BIDP) shown in **Scheme-I**. There is a wide range of absorption in the UV-visible absorption spectrum of BIDP. And then the film of BIDP was made by the electrodeposition and ordered morphology in the film was obtained though DMF vapour annealing.

EXPERIMENTAL

The synthetic route of BIDP has been as shown in **Scheme-I**. The synthesis, purification and characterization of the NIPI are described elsewhere[10]. And then, BIDP was synthesized by NIPI and 3,3'-diaminobenzidine (DAB)[11] and characterized by IR spectrum and UV-visible absorption spectrum.

Preparation of solution and electrodeposition film: The concentration of BIDP was 1×10^{-4} mol/L in DMF and then added hydrazine hydrate solution (the volume content of 25 %) as electrolyte. The condition of electrodeposition is that the foil and conductive glass (ITO) respectively do the cathode and anode and constant potential 8 v was for electrodeposition and then the samples were dried in the vacuum oven for 12 h at 90 °C. The characterization of these films were investigated by UV-visible, fluorescence spectrum, SEM and XRD.

Characterization of NIPI: FT-IR (KBr, ν_{max}, cm^{-1}): 3078 (Ar, H), 2959 (CH_3), 2931, 2856 (CH_2), 1765, 1733 (C=O, anhydride), 1693, 1652 (C=O, imide), 1404, 1323 (C-N), 1242, 1126, 1016 (C-O-C). ^1H NMR (500 MHz, $CDCl_3$): δ 8.67-8.71 (d, 6H, *J* = 7.1 Hz, Ar-H), 8.62-8.65 (d, 2H, *J* = 8.6 Hz, Ar-H), 4.16-4.19 (m, 2H, $-CH_2-$), 1.95-1.97 (m, 1H, $-CH_2-$), 1.26-1.42 (m, 8H, $-CH_2-$), 0.92-0.96 (t, 3H, *J* = 7.5 Hz, $-CH_3$), 0.85-0.89 (t, 3H, *J* = 6.3 Hz, $-CH_3$).



Scheme-I: Synthetic route of BIDP

The FT-IR spectra of NIPI and BIDP were shown in Fig. 1, compared with NIPI, in the FT-IR spectra of BIDP, stretching vibration peak of anhydride (C=O) disappeared at 1767 cm^{-1} and 1731 cm^{-1} and appeared stretching vibration peak of imide (C=O) at 1654 cm^{-1} and 1692 cm^{-1} and also appeared stretching vibration peak of C-N at the 1353 cm^{-1}. The characteristic peak of imidazole (C=N) was at 1589 cm^{-1}. So chemical structure of BIDP was consistent with theoretical structure by the characteration FT-IR spectra.

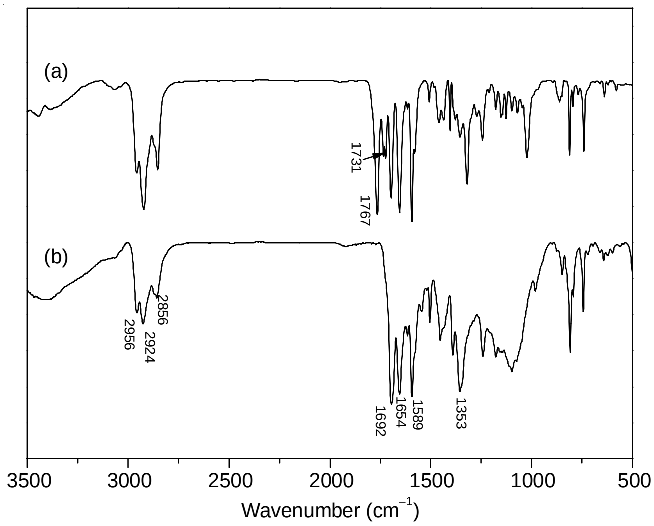


Fig. 1. FT-IR spectra of NIPI (a) and BIDP (b)

UV-visible absorption spectra of NIPI and BIDP (10^{-5} mol/L) in DMF was in Fig. 2. The maximum absorption of NIPI is at 525 nm (perylene imide 0-0 transition) and the mimimum absorption is at 489 nm (perylene imide 0-0 transition) and its 0-2 peak appears at 457 nm, So NIPI is a typical derivative of perylene imides. By comparing with NIPI, BIDP showed different absorption spectra. Its absorption spectra was similar to PPDI that formed dimers, which transformed into a π-stacked aggregated form upon one-electron. The main band of PPDI in water was found at 500 nm, with a lower intensity band at 540 nm[12]. This inversion in the relative intensity of the vibrational bands was observed, indicating the dimerization of the dye. Absorption spectrum of BIPD was very similar to PPDI forming dimers, So the structure of BIPD is similar to chemical structure of dimerization of PPDI. However, BIPD is one bridged double benzimidazole perylene derivative, the main absorption band appeard red shift at 527 nm (similar to 0-1 transition of perylene imides) and maximum wavelength absorption was at 574 nm (similar to 0-0 transition), This obvious red shift shows that the length of conjugation has effective increase and also suggests that two benzeneimidazole perylene have been linked by covalent bond.

RESULTS AND DISCUSSION

Optical physical properties of BIDP solution and film: Fig. 3a is UV-visible absorption of BIDP solution and electrodeposition film. Compared with the absorption spectrum of BIDP solution, half peak width of electrodeposition film obvious increase and the peak shape disappeared and there is "black" characteristic absorption (> 600 nm), This absorption is caused by aggregation by face to face way between the molecules in BIDP film and is caused by stronger charge transfer of intermolecular. Fig. 3b is photo-luminescence spectra of BIDP solution and electrodepositon film (excitation wavelength λ_{exc} = 525 nm). The maximum emission peak is at 560 nm in BIDP solution and shows stronger yellow fluorescent, electrodeposition film of BIDP has no obvious fluorescence absorption, which is caused by π-π aggregation of intermolecular that leads to fluorescence quenching phenomenon.

Crystallization mechanism of BIDP electrodeposition film: Fig. 4 shows SEM photograph of the thin film of BIDP at different electrodeposition time. Electrophoretic deposition process of crystal growth process of BIDP can be seen more

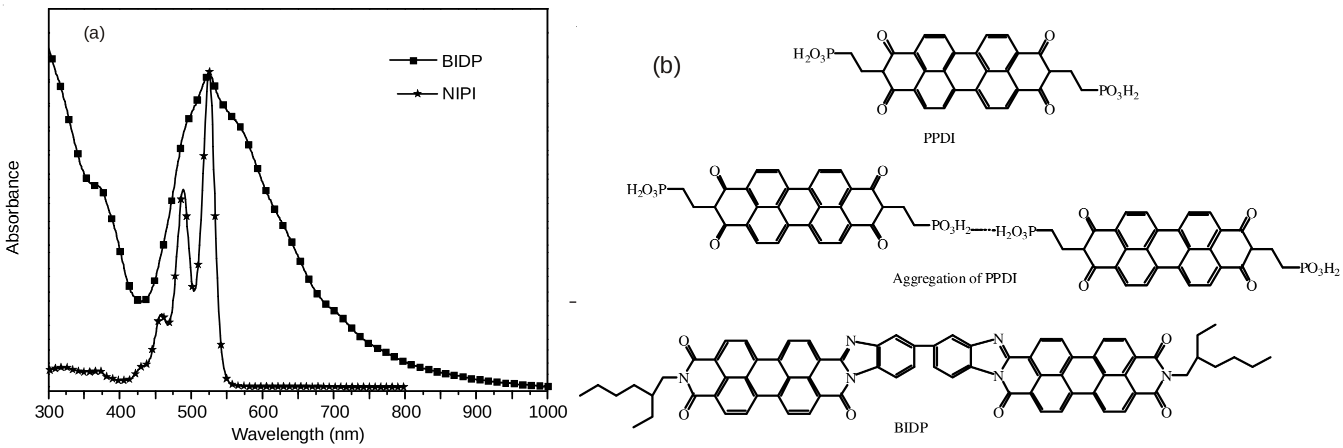


Fig. 2. (a) UV-visible absorption of NIPI and BIDP in DMF; (b) Structure and aggregation of PPDI and BIDP

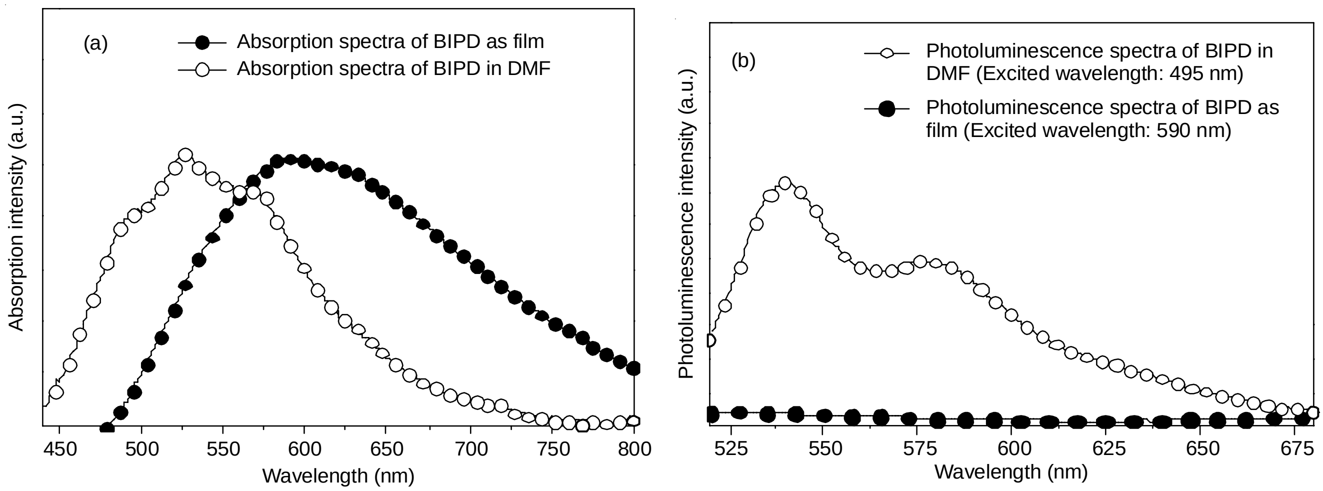


Fig. 3. UV-visible absorption (a) and photoluminescence spectra (b) of BIDP

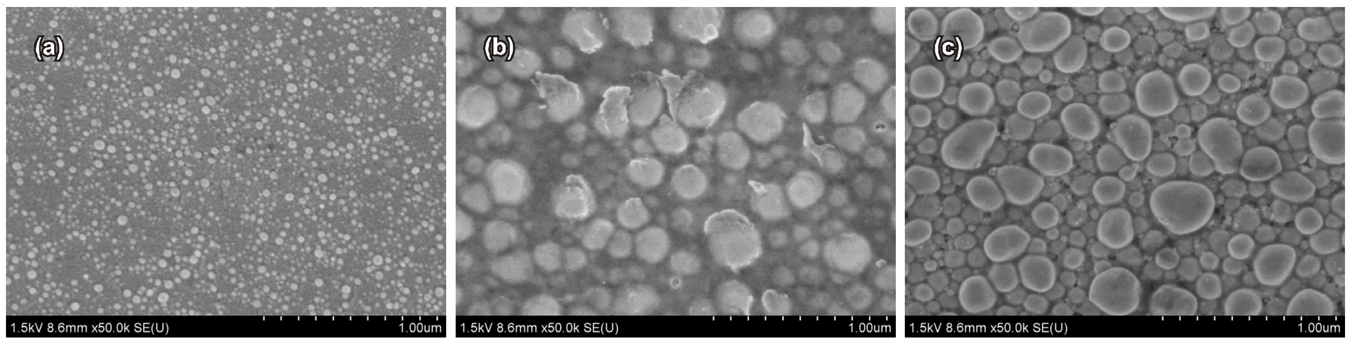


Fig. 4. SEM photograph of the thin film of BIDP at different electro-deposition time: (a) 1 min (b) 5 min (c) 10 min

clearly in the figure. If the deposition time was 1 min, which was beginning time of the film growth, the bare ITO glass was seen and the film wasn't fully covered and the crystalline size was very small (about 0.03-0.04 μm). If the deposition time was 5 min, the crystalline size increased significantly (the maximum size is 0.3 μm) and the film was relatively complete covered, but the shape of crystalline grain was not very unified. It is that crystalline growth of molecular aggregation was unfinished in the crystal growth process. If the deposition time was 10 min, the film was complete covered and the crystalline size was gradually unified (the maximum size is 0.4 μm) and it's shape was relatively unitied.

XRD of electrodeposition film of BIDP: Fig. 5 shows XRD of electrophoretic deposition film of BIDP at different electrodeposition time. In the figure, the electrodeposition films of BIDP in 5 min and 10 min have multiple diffraction peaks. It is because that the molecules aren't in a complete plane, crystal growth crossed each other between the molecular layer is leading to different spacing in the electrodeposition and film has good single crystal. Compared with 5 min and 10 min, it's found in XRD of 10 min that $2\theta = 32.742°$, $35.137°$ and $39.242°$ diffraction peak position was unchanged and the intensity was just changed, but in the XRD of 10 min, diffraction peaks, which was in $2\theta = 30.157°$ and $2\theta = 21.147°$

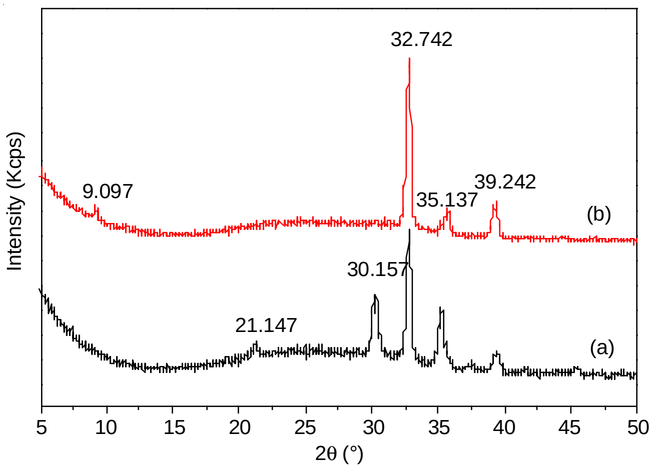


Fig. 5. XRD of the thin film of BIDP at different electrodeposition time: (a) 5 min (b) 10 min

disappeared and 2θ = 9.097° appeared a new diffraction peak, it shows that the order of the film increases, with the extension of electrophoretic deposition time and consistent with in Fig. 5b and 5c.

Solvent steam annealed BIDP electrodeposition film: Vapour annealing can change morphology of the electrodeposition film and the morphology of the film has a certain influence on the photoelectric device applications, so the thin films were processed by different solvent steam. By acetone, benzene, petroleum ether and DMF solvent steam annealing, we found that the effect of DMF vapour on the morphology of BIDP film is relatively obvious, Fig. 6 is SEM photograph

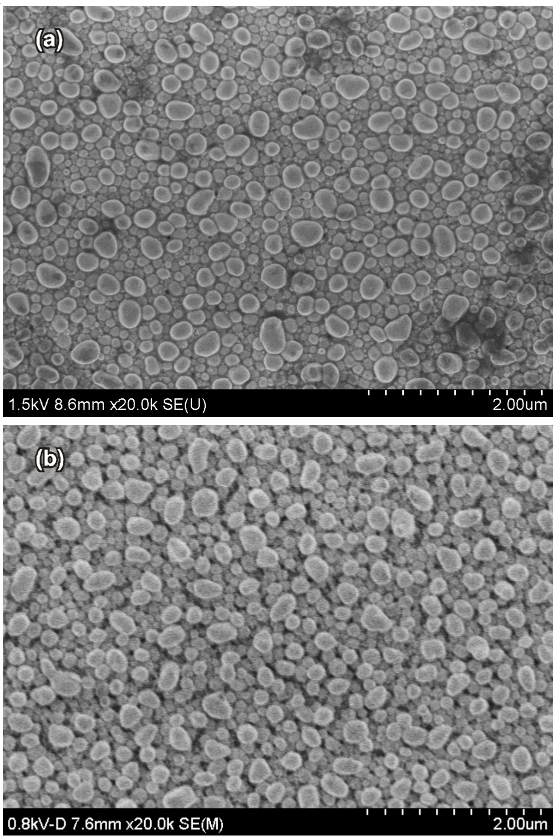


Fig. 6. SEM photograph of the thin film of BIDP (a) and annealing thin film of BIDP (b)

of electrodeposition film of BIDP in 10 min and it was treated by annealing in DMF solvent steam and this figure shows that the film morphology is more neat and grain size is more uniform after annealing.

Conclusion

A bridged double benzimidazole perylene derivative-BIDP was successfully synthesized, in DMF. It covers the 400 to 700 nm in wide absorption and yellow red emission spectrum. The electrodeposition film of BIDP shows that it can almost cover all visible spectrum (450-800 nm) and the wide absorption shows that BIDP may become a kind of potential solar cell materials.

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