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SYNTHESIS AND ELECTRON TRANSPORT PROPERTY OF NICKEL (II) PERFLUOROPHTHALOCYANINE

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A metal perfluorophthalocyanines compound $NiPcF_{16}$ was synthesized and characterized. The energy gap and electron energy levels were studied by UV-vis absorption and cyclic voltammetry mathods. The measurement results indicated that the $NiPcF_{16}$ compound embodies low LUMO level for electron injection. Thermal analysis showed the compound has excellent thermal stability with decomposition temperature about 400 ^{o}C. The dual-layer photoreceptor containing oxotitanium phthalocyanine ($TiOP_C$) as the charge generation material (CGM) and $NiPcF_{16}$ as the charge transportation material (CTM) was fabricated. The photosensitivity measurement showed that the $NiPcF_{16}$ compound was a promising electron transportation material in organic optoelectronic fields.

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Keywords: Phthalocyanines, Electron transportation, Photosensitivity, Hole

1. Introduction

Organic photoconductive materials have several advantages over their inorganic counterparts, such as light weight, low cost and easy processing, mechanical flexibility, property tuning by molecular engineering, and ready fabrication into transparent photosensitive thin films. Hole transport materials have been widely used in organic photoconductor devices duo to their excellent photo conductive properties. In the printing process, due to high-voltage corona discharge, oxygen in the air is ionized into ozone, which can lead to environmental pollution. Therefore, all countries attach great importance to the development of electronic transport materials to eliminate environmental pollution and reduce production costs. At the same time, the electron transport materials can be applied to the study of organic electroluminescent (OLED), thus study on the synthesis and properties of such materials has become a hot field in recent years.

Phthalocyanines (Pcs) have attracted much attention for many decades because they exhibit excellent photoelectrochemical properties [5, 6]. Phthalocyanine compound are widely used as photoelectric materials for organic photoconductors, photovoltaic solar cells, organic field effect transistors, optical switches, optical storage, etc. Most of the unsubstituted phthalocyanines show the properties of hole transport properties while some metal perfluorophthalocyanines, such as $CuPcF_{16}$, exhibit electron transport characteristic due to the strong electron-withdrawing effect of the -F substituent [7, 8].

Synthesis and characterization of copper hexadecafluorophthalocyanine ($CuPcF_{16}$) were reported in Ref. [7, 9]. And the electron mobility of the $CuPcF_{16}$-based organic field effect

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transistors was 0.07cm^2/V s. However metal perfluorophthalocyanines used as electron transport materials in photoconductor devices are rarely reported. In this paper, nickel (II) perfluorophthalocyanine (shown in Fig. 1) was synthesized and their optical, electrochemical and thermal properties were characterized in detail. And $NiPcF_{16}$-based photoconductive devices (shown in Fig. 2) were fabricated and their photoconductivity properties were also investigated.

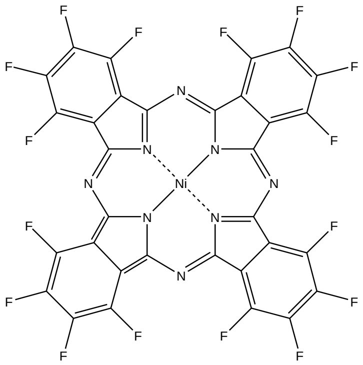

Fig. 1. Molecular structure of $NiPcF_{16}$.

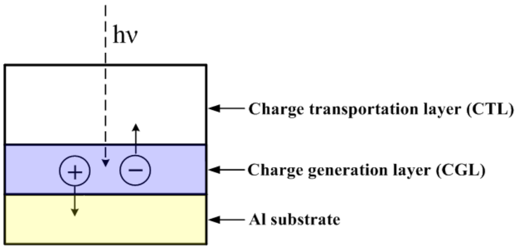

Fig. 2. Configuration of the dual-layer photoreceptor.

2. Experiment

The $NiPcF_{16}$ compound was synthesized using a procedure similar to that previously reported [6, 7, 9]. An equimolar 4:1 ratio mixture of 3, 4, 5, 6-tetrafluorophtalo-1, 2-dinitrile and Nickel (Ⅱ) acetate was filled in a glass vessel and sealed under vacuum (1.33×10^{-3} Pa). After heating for 8 h at 200 ^{o}C the dark blue product was washed with ethanol and acetone to remove the soluble organic admixtures. The $NiPcF_{16}$ compound was recrystallized from sulfuric acid and isolated in 56.1% yield. ($NiPcF_{16}$, IR (KBr) 1624, 1530, 1470, 1160, 846 and 752 cm^{-1}. MS (TOF, m/e 855.802.)

Photoconductivity was studied in function-separated dual-layer photoreceptors (Fig. 2). The photoreceptors were made by coating the charge generation layer (CGL) and the charge transportation layer (CTL) in that order on an aluminum substrate. The CGL was formed with 0.5 μm thickness from the dichloroethane slurry containing 30 wt. % TiOPc in polyvinylbutyral matrix. The CTL consisted of 40 wt. % $NiPcF_{16}$ in polycarbonate matrix, and the thickness was 7 μm. Photoconductive measurements were carried out by an SP-428 model photoconductivity measuring device, and the photoinduced discharge curve of the device was recorded, from which the parameters such as V_o, V_r, R_d, and $E_{1/2}$ could be obtained. Here, V_o was the surface charged potential; V_r was the residual potential; R_d was the rate of dark discharge; and $E_{1/2}$ was the photosensitivity, the lower the $E_{1/2}$ value, the higher was the photosensitivity of the material.

3. Results and discussion

3.1 UV-vis and fluorescence spectra

Fig. 3 shows the UV-vis absorption spectra of 0.5×10^{-5} mol L^{-1} $NiPcF_{16}$ solutions in 1, 2-dichlorobenzene (DCB), pyridine and dimethylformamide (DMF), respectively. The absorption spectra were measured by an EVOLUTION300 spectrometer. The absorption maxima for Q band are seen at 667 nm for $NiPcF_{16}$ dissolved in DCB and 669 nm for $NiPcF_{16}$ dissolved in pyridine. With the increase of the polarity of solvents, the Q band shift to a shorter wave length to some extent, which originates from the increasement of the transition energy gap in the π-π* transition system. In polar solvent such as DMF, the Q-band peak is observed at about 625 nm. It is well known that the phthalocyanine compounds are blue-shifted by dimerization. Thus, $NiPcF_{16}$ aggregate in DMF solvent according to reference literature [7, 9, 10].

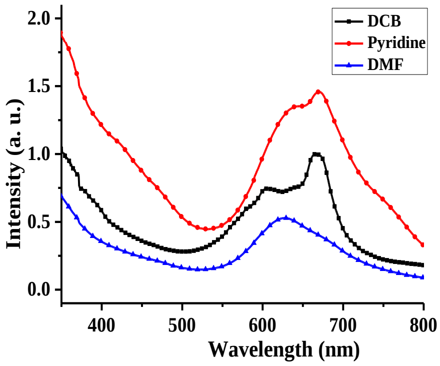

Fig. 3. The UV-vis spectra of $NiPcF_{16}$ in different solvents.

The fluorescences pectrums of $NiPcF_{16}$ in DMF were measured on a CARYE clipse fluorescence spectrophotometer, as shown in Fig. 4. The emission maxima is observed at 696 nm for $NiPcF_{16}$ corresponding to the red light emission. The absorption edges of $NiPcF_{16}$ in DMF is found around 757 nm, from which the optical band gap energies of $NiPcF_{16}$, *Eg*, is estimated to be 1.64 eV.

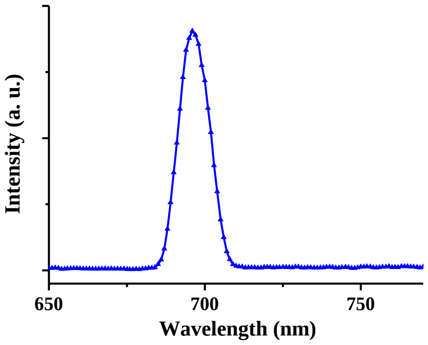

Fig. 4. Fluorescence emission spectrum of $NiPcF_{16}$ in DCB.

3.2 C-V curve

The electrons transport ability and electrochemical properties of the $NiPcF_{16}$ compound were examined by solution cyclic voltammetry (CV). The cyclic voltammogram (Fig. 5) were collected on a CHI760E electrochemistry workstation at room temperature in DMF measured against a saturated calomel electrode (SCE) with tetrabutylammonium perchlorate (Bu_4NClO_4, 0.10 M) as the supporting electrolyte. As shown in Fig. 5, the chemical oxidation and reduction peaks of E_{OX} = -0.79 V and E_{RE}= -0.62 V are observed for $NiPcF_{16}$. The reductive process started at -0.24 V. The energy level of the lowest unoccupied molecular orbital, E_{LUMO}, can be estimated from the reductive onset potential to be -4.50 eV [12, 13]. The low LUMO energy level is favorable for electron injection and transport; in other words, $NiPcF_{16}$ should be a good electron transport material. The energy level of the highest occupied molecular orbital, E_{HOMO}, can be calculated by adding E_g from E_{LUMO} as determined by the electrochemistry curve. This leads to an estimation of E_{HOMO} to be -6.14 eV for $NiPcF_{16}$.

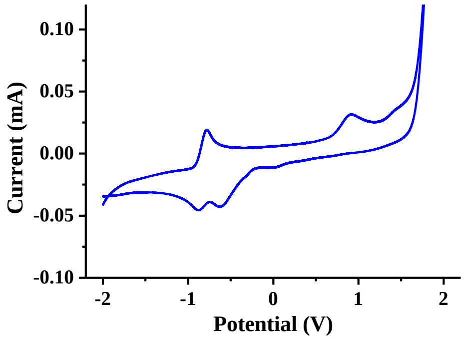

Fig. 5. Cyclic voltammogram of $NiPcF_{16}$ in DMF.

3.3 Thermal properties

The thermal stability of $NiPcF_{16}$ compound was tested by thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The TGA curves were measured by a TG 209 F3 thermo gravimetric analyzer. As shown in Fig. 6, the $NiPcF_{16}$ compound possess excellent thermal stability properties with high decomposition temperature (T_d) of about 400 °C, (T_d, correspond to a 10% mass loss).

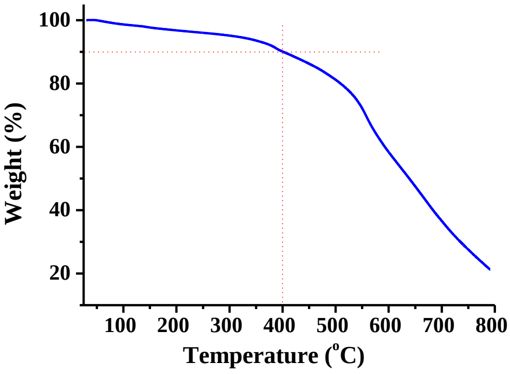

Fig. 6. TGA curve of $NiPcF_{16}$.

3.4 Photoconductive property

In order to demonstrate the electron transport property of NiPcF16, the photoconductivity was studied in the dual-layer photoreceptor device, where TiOPC was used as CGM and F16NiPc acted as CTM. TiOPc has been proved to be a good charge generation material and marketed as a CGM in photoreceptors for copiers and laser printers. Device photoconductive performance parameters *V*o, *V*r, *R*d, and *E*1/2 were 350 V, 263 V, 52 V s-1 and 32 lx s, respectively. According to the cyclic voltammetry measurement, the LUMO energy level of NiPcF16 is -4.50 eV, and the LUMO energy level of TiOPc is -3.91 eV in the literature [14]. Under light exposure, electrons in TiOPc jump from HOMO to LUMO, realizing the separation of electron-hole pairs. With introduction of the -F substitutes, LUMO energy level of NiPcF16 becomes lower than that of TiOPc, which will facilitate the electrons transportation from TiOPc to NiPcF16.

4. Conclusions

In summary, the NiPcF16 compound with low LUMO energy level was synthesized by the solid state reaction. The compound has good thermal stability and strong absorption in visible region. The electronic structure was studied by UV-vis absorption and cyclic voltammetry methods.

The photosensitivity study shows that NiPcF16 with the electron-acceptor group (-F) has better electron transport property. The results here suggest a promising application of NiPcF16 in organic optoelectronics.

Acknowledgements

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