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Synthesis and application in photovoltaic device of the porphyrin derivatives with liquid crystal properties

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ABSTRACT

A series of porphyrin derivatives with four meso-substituted amide groups and their zinc coordination compounds have been synthesized and characterized. The thermal behavior and morphology of these compounds were investigated using thermogravimetry (TG), differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffraction (XRD), and Atom Force Microscopy (AFM). The ligands exhibited a columnar mesophase. However, their corresponding zinc coordination compounds showed only a crystalline state. DSC and XRD data indicated that the ligands were amorphous while the complexes were crystalline at room temperature. Using the porphyrin derivatives as donor materials and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) as the acceptor material, organic photovoltaic devices were fabricated. The device structure was ITO/porphyrin derivative:PTCDA/Al. The relationship between the morphology and photovoltaic properties was investigated. It was found that the crystalline morphology of the film was beneficial for improving the efficiency of the devices.

1. Introduction

Porphyrin and porphyrin-metal complexes are important for biochemical reactions,[1] and have been extensively investigated. These compounds are also an interesting class of functional material for light-emitting diodes,[2–7] field-effect transistors,[8–11] and photovoltaic cells,[12–14] etc.. Among porphyrin derivatives, those with liquid crystalline properties are particularly interesting for device applications. Since the first liquid crystalline porphyrin was synthesized by Goodby et al.,[15] and showed a very narrow mesomorphic temperature, liquid crystalline porphyrins have aroused considerable research interest.

In general, columnar discotic liquid crystals consist of rigid polyaromatic cores surrounded by flexible arms.[16] Porphyrin derivatives having appropriate side chains can form columnar discotic liquid crystals. Based on the position of the side chains (β- and meso-position), porphyrin derivatives can be classified into two broad categories. Porphyrins with multiple substituents at the β-position of the pyrrole rings tend to exhibit columnar mesophases,[17] although these compounds are difficult to synthesize. However, porphyrins with meso-substituted side chains tend to form atypical columnar or lamellar phases,[18] and these compounds are easier to obtain. Columnar phases are important because their one-dimensional (1D) aromatic π–π stacking[19] leads to one-dimensional charge conduction,[20] which may improve the charge-carrier mobility. A molecular assembly is formed when the columns pack in parallel in a two-dimensional (2D) lattice.[21] The columnar phases that formed are classified according to the order of molecular stacking of the columnar packing.[22] These arrangement types include hexagonal, rectangular, oblique, plastic, helical, and lamellar columnar phases,[21] with hexagonal and rectangular columnar phases being the most common types.

Under certain conditions, a hexagonal columnar phase can be converted to a rectangular columnar phase by changing the molecular shape from disc-like to rod-like.[23] Many liquid crystalline porphyrin derivatives with a variety of different side chains, such as alkyl,[24] alkoxy,[25] and acyloxy[26] have been reported; however, alkylamide substituents are rare. Because the substituent of porphyrin is acylamino, intermolecular hydrogen bonding interaction can exist between molecules. This will be beneficial to improve the molecule orientation of the film.[27] Liquid crystal compounds are not regularly used as photovoltaic materials. However, some researchers have found that the properties of liquid crystals can be used to grow oriented crystalline films for

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photovoltaic materials.[28,29] In our previous work, we found that intermolecular hydrogen bonding between the donor and acceptor contributes to a high open-circuit voltage and photoelectric conversion efficiency (PCE).[27] We also found that donor materials with mesogenic properties or crystalline morphologies can promote forward interfacial electron transfer and transport, and improve the performance of organic photovoltaic devices. Conversely, donor materials that have an amorphous morphology do not improve performance in organic photovoltaics.[30,31]

In this paper, we investigate the relationship between liquid crystal and photovoltaic properties. We report the synthesis of meso-tetra(4-acylaminophenyl) porphyrins (4NC$_n$-TPP) and 4NC$_n$-TPPZn ($n = 14, 16, 18$) (Fig. 1), and fabricated organic photovoltaic devices using these porphyrin derivatives as donor materials and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) as an acceptor material. The relationship between the morphology of the vacuum-evaporated organic films and the photovoltaic performance was investigated.

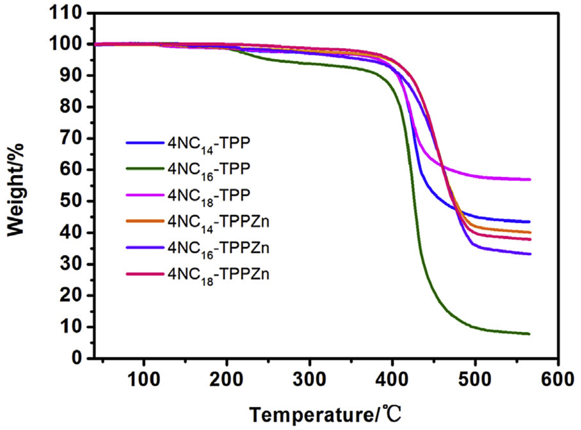


Fig. 2. TG curves of porphyrin derivatives.

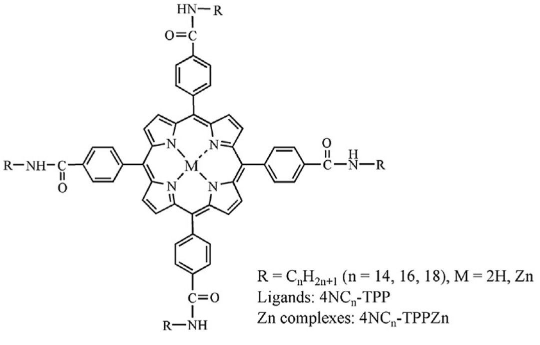
2. Results and discussion

2.1. Thermal properties and morphology

The thermal stability of the porphyrin derivatives was investigated by TG, as shown in Fig. 2. The onset decomposition temperatures of the porphyrin derivatives were 385 °C for 4NC$_{14}$-TPP, 397 °C for 4NC$_{14}$-TPPZn, 255 °C for 4NC$_{16}$-TPP, 370 °C for 4NC$_{16}$-TPPZn, 385 °C for 4NC$_{18}$-TPP, 399 °C for 4NC$_{18}$-TPPZn. The decomposition temperatures were high except for 4NC$_{16}$-TPP, which showed a slight weight loss from ~200 °C. The onset decomposition temperatures of 4NC$_{14}$-TPP and 4NC$_{18}$-TPP were same, higher than that of 4NC$_{16}$-TPP, so the thermal stability of the moleculars were better when the side chain were myristylamide or octadecylamide. This might be because of the loss of water of crystallization.[32] Unlike the ligands without zinc in the center of the porphyrin core, the TG curves of the complexes with zinc remained constant before 370 °C. This is because the whole molecule becomes more stable when the ligands are coordinated with metal atoms.

The thermal phase behaviors and morphologies of the porphyrin derivatives were investigated by a combination of DSC, POM, and XRD. These results showed that the metal-free ligands 4NC$_n$-TPP ($n = 14, 16, 18$) had liquid crystalline properties. Moreover, the range of the liquid crystalline phase dramatically widened as the length of the side chain increased. However, the coordination compounds 4NC$_n$-TPPZn ($n = 14, 16, 18$) did not show liquid crystalline properties.

The DSC curve of 4NC$_{14}$-TPP from 40 to 350 °C (Fig. 3a), showed three endothermic peaks. The small peak at 65 °C is the glass transition temperature. The second phase transition from crystalline to liquid crystalline occurred at 167 °C and the liquid crystal to isotropic phase transition occurred at 291 °C. During the cooling process, the phase transitions occurred at 275, 155, and 62 °C. The POM image in Fig. 4a shows an unusual flower-like dendritic texture.[1,33] After chelating with the metal atom, 4NC$_{14}$-TPPZn showed only one melting and crystallization peak at 330 and 290 °C in the heating and cooling curves (Fig. 3b), respectively. The very small inverse peak at 108 °C is a possible crystalline modification transformation. When slowly cooling from the isotropic phase only a large area sphaerocrystal appeared (Fig. 4b), and the weak fluidity gradually disappeared. 4NC$_{14}$-TPPZn did not show any liquid crystalline properties.



R = C$_n$H$_{2n+1}$ (n = 14, 16, 18), M = 2H, Zn
Ligands: 4NC$_n$-TPP
Zn complexes: 4NC$_n$-TPPZn

Fig. 1. Molecular structure of 4NC$_n$-TPP and 4NC$_n$-TPPZn ($n = 14, 16, 18$).

The DSC curves of 4NC$_{16}$-TPP and 4NC$_{18}$-TPP (Figs. S1A and S1C) are similar to that of 4NC$_{14}$-TPP. However, the POM images show a fan-shaped texture (Figs. S2a and S2c), which is evidence of a columnar phase.[34] After molecules form a single column, they can produce two types of phase structure: a straight hexagonal columnar phase or a tilted phase (Fig. 5). The columnar phases of 4NC$_{16}$-TPP and 4NC$_{18}$-TPP are tilted. The DSC curves of 4NC$_{16}$-TPPZn and 4NC$_{18}$-TPPZn (Figs. S1B and S1D) show two and three pairs of endothermic and exothermic peaks, respectively. The POM image of 4NC$_{16}$-TPPZn (Fig. S2b) shows a sphaerocrystal, like that of 4NC$_{14}$-TPPZn. The crystals of 4NC$_{18}$-TPPZn (Fig. S2d) showed a fan-shaped texture; however, the fluidity disappeared when the texture formed. All of the phase transition temperatures from the DSC curves and the corresponding enthalpies are listed in Table 1. From the structure of the porphyrins, we know that there is an amide group in the molecule. Intermolecular interactions between N and H atoms might allow hydrogen bonds to form, which drive the liquid crystalline properties.[16,30]

The XRD results are shown in Fig. 6 and Fig. S3. The porphyrin derivatives were vacuum-deposited with a film thickness of ~150 nm on quartz glass. These results show that the free ligands tended to be amorphous. However, the metal complexes (except 4NC$_{18}$-TPPZn) showed some diffraction peaks in small or wide-angle regions, which indicated molecular ordering. The XRD pattern of 4NC$_{14}$-TPPZn showed three obvious peaks with d-spacings of 2.14, 1.54, and 1.34 Å. The arrangements of the molecules of 4NC$_{14}$-TPPZn and 4NC$_{16}$-TPPZn were similar. The XRD results agree with the DSC results. However, 4NC$_{18}$-TPPZn is different from the other metal complexes, and the XRD showed that the diffraction peaks were very weak.

2.2. Photoelectric properties

2.2.1. UV–vis absorption spectra and fluorescence spectra

Thin film absorbance is an important parameter for