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Analyzing nanostructures in mesogenic host–guest systems for polarized phosphorescence

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ABSTRACT

Feasibility of polarized phosphorescent organic light-emitting devices (OLEDs) had been previously demonstrated by combining a discotic Pt(II) complex with a glassy-nematic oligofluorene host to form a mesogenic host–guest phosphorescent emitting system. Previous photophysical studies suggested that in the host–guest film, the Pt(II) complex tended to aggregate into columnar stacks, exhibiting metal–metal-to-ligand charge transfer (MMLCT) emission. Both host molecules and guest aggregates in the host–guest films could be oriented by a conductive alignment layer, giving rise to polarized phosphorescence from the Pt(II) aggregates. Nevertheless, film morphologies and nanostructures of the mesogenic host–guest systems have remained to be elucidated. In this work, grazing incidence X-ray scattering (GIXS) was carried out to analyze nanostructures in both neat films of the discotic Pt(II) complex and mesogenic host–guest mixture films. In addition, confocal laser scanning microscopy (CLSM) was also utilized for visualization of the morphologies of mesogenic host–guest systems. The columnar axes of nanostructured Pt(II) stacks lying on the alignment-treated surfaces were found to be preferentially oriented perpendicular to the rubbing direction, which is responsible for the observed linearly polarized phosphorescence.

1. Introduction

The ability to organize nanostructures in ordered orientations over large areas is of primary importance for the bottom-up fabrication of nanostructure-based devices. By controlling the spatial arrangement and the degree of ordered nanostructures, it is possible to control polarization of light for optical information processing, such as displays, optical communication, optical storage, and stereoscopic (3D) imaging systems etc. [1,2]. For instance, polarized electroluminescence devices would be useful for backlights of liquid–crystal displays (LCDs) to make them more power efficient and for pixels of 3D displays to simplify their configurations [3–5]. As such, there have been substantial efforts in developing polarized organic light-emitting devices (OLEDs) [6–19]. With the strong intrinsic anisotropy in polymer chains, conjugated polymers that can form well aligned thin films [13–18,20], such as mesogenic polyfluorenes [21–24], represent a common class of active materials for polarized OLEDs. Meanwhile, with better control of molecular structures and material purity, mesogenic conjugated oligomers that can form well aligned films are another promising

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class of active materials for polarized OLEDs [6–12]. Liquid–crystalline (LC) oligofluorenes have been reported as hosts to guide molecular orientation of guest emitters, forming host–guest emitting systems for highly polarized and efficient OLEDs spanning the whole visible spectrum and white-light emission [8–11].

Most of previous efforts in polarized OLEDs, however, were mainly focused on fluorescence mechanisms. Yet, the development of OLEDs in recent years has largely shifted toward phosphorescent OLEDs [25,26], since phosphorescent OLEDs could effectively utilize both singlet and triplet excitons and realize essentially 100% internal quantum efficiencies [27,28]. As such, it is of both scientific and technical importance to explore the possibility of achieving polarized phosphorescent OLEDs. In a recent publication [29], we have reported an initial attempt to realize workable and functional polarized phosphorescent OLEDs by mixing a discotic mesogenic phosphorescent metal (Pt(II)) complex N200 (Fig. 1) with a glassy-nematic oligofluorene host (F(MB)5, Fig. 1) to form the corresponding mesogenic host–guest (phosphorescent) emitting system.

Spectral properties of the neat N200 spin-cast films suggest N200 molecules exhibit strong ground-state intermolecular interactions (instead of simply excited-state interaction, like excimers) and they tend to self-assemble to form aggregates in films [29]. Previous luminescence characterization of bulk samples of these Pt(II) complexes revealed that they exhibited red emission only in the columnar mesophase, while monomer-like green emission was observed in isotropic liquid state or dilute solution [30]. Thus the appearance of red emission in N200 samples is a good indication of columnar-like mesophase packing. Due to the columnar mesomorphic nature of N200 and the resemblance of photophysical properties in spin-cast films to those of bulk samples in the liquid crystal phase [30], presumably the square-planar N200 molecules also pack into a one-dimensional columnar stacking arrangement in spin-cast films.

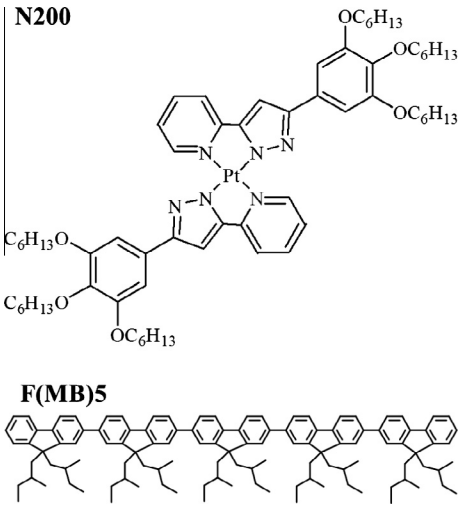

Fig. 1. The mesogenic materials, the Pt(II) complex N200 and the fluorene oligomer F(MB)5, used in this work.

To account for the observed mesomorphism, photophysical characteristics, and polarized transitions of these materials in various states and compositions, we proposed that N200 self-assemble into columnar stacking in the host–guest film, exhibiting metal–metal-to-ligand charge transfer (MMLCT) emission of the Pt(II) complex N200 [29,30]. Both the host molecules and guest aggregates in the host–guest films were successfully aligned on the rubbed conducting polymer alignment layer. With such alignment and effective host-to-guest energy transfer, polarized red phosphorescence and electrophosphorescence from the phosphorescent Pt(II) complex as aggregates were observed. Although this proposed scenario appeared consistent with all the physical and photophysical characterizations reported earlier, experimental observations are desired for film morphologies and nanostructures of the N200-oligofluorene host–guest systems. In this work, the grazing incidence X-ray scattering (GIXS) was performed to investigate morphologies and nanostructures in both neat N200 and its mixture with F(MB)5 films. In addition, the confocal laser scanning microscopy (CLSM) was also utilized for the visualization of morphologies of mesogenic host–guest systems.

2. Experiment

2.1. Materials

Fig. 1 shows the mesogenic materials, the Pt(II) complex N200 and the fluorene oligomer F(MB)5 used in this work. N200 is a $Pt(N^N)_2$ complex, in which N^N = 2-(3-(3,4,5-trihexoxyphenyl)-1H-pyrazol-5-yl) pyridine. It adopts the distinctive pyridyl azolate as ligands, which are known to form strong chelate bonding with Pt ions and render the molecule a square-plannar geometry, affording distinctive emission (phosphorescent) properties [30–32]. Indeed, such Pt(II) complexes exhibit rather efficient green phosphorescence at room temperature in dilute solutions [30]. Further attaching alkyloxyphenyl groups with the alkyl chain (i.e., 3,4,5-trihexoxyphenyl) onto the ligands imparts certain flexibility to the molecular core and mesomorphic characteristics, thereby yielding luminescent metallomesogens [30,33–36]. As studied by polarizing optical microscopy and differential scanning calorimetry, N200 shows liquid–crystalline properties across a wide temperature range. Upon heating the crystalline samples of these Pt(II) complexes, a transition from the solid to the columnar mesophase (as verified by X-ray diffraction [30]) and a transition from the mesophase to the isotropic liquid occurs at ~98 °C and ~342 °C, respectively. The details of syntheses and basic material properties of the Pt(II) complexes had been reported elsewhere [30].

Employed as the host, the fluorene oligomer F(MB)5 consists of five fluorene units on the backbone and two 2-methylbutyl substituents at C9 atoms [8,9]. F(MB)5 belongs to a class of glass-forming nematic oligofluorenes, that is, materials that exhibit the nematic mesophase at elevated temperatures and yet also the stable glass phase at room temperature [8–11]. As studied by polarizing optical microscopy and differential scanning calorimetry,