



Geometric relaxation in a copper complex and its limitation by polymer immobilization: Structure, characterization and photophysical analysis



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ABSTRACT

A diamine ligand having an electron-pulling oxadiazole ring in its molecular structure was synthesized. Its Cu(I) complex was established using PPh₃ as an auxiliary ligand. Geometric structure, electronic transition and photophysical feature of this Cu(I) complex were reported and discussed in detail. It followed a traditional tetrahedral coordination field and suffered from geometric relaxation badly. Aiming at an effective limitation for this geometric relaxation, this Cu(I) complex was immobilized into a polymer matrix via electrospinning technique. A full comparison between solid sample, solution sample and composite sample suggested that such geometric relaxation was effectively limited by polymer immobilization effect. A detailed analysis indicated that polymer host offered a rigid and protective microenvironment for dopant molecules, limiting their geometric relaxation in excited state. As a consequence, photophysical performance was improved, including emission blue shift, long emissive lifetime and improved photostability.

1. Introduction

Recently, much research attention has been focused on nanocomposite materials owing to their promising and attractive performance in optoelectronic field, including nanofibers, nanobelts and nanorods [1–3]. As an effective and low cost way to obtain nanofibers, electrospinning method has shown its virtues of controllable morphology and suitable mechanical strength [4–8]. To meet numerous demands in practical application, these electrospinning fibers are usually functionalized with co-dopants of organic dyes and sensitizers which generally have good emission yields, controllable emission energy, high stability, long excited state lifetime and acceptable compatibility with host matrix [9–15].

It seems that luminescent transition metal complexes may well satisfy above points, especially phosphorescent Cu(I) complexes having a general molecular formula of [Cu(N-N)(P-P)] [14–17]. Here N-N and P-P denote a diamine ligand and a phosphorous ligand, respectively. As suggested by literature reports, their occupied frontier molecular orbitals (FMOs) are generally composed of metal center contribution, while their unoccupied ones consist of diamine ligand [18,19]. In this case, electronic transitions between these FMOs should have a mixed character of metal-to-ligand-charge-transfer (MLCT).

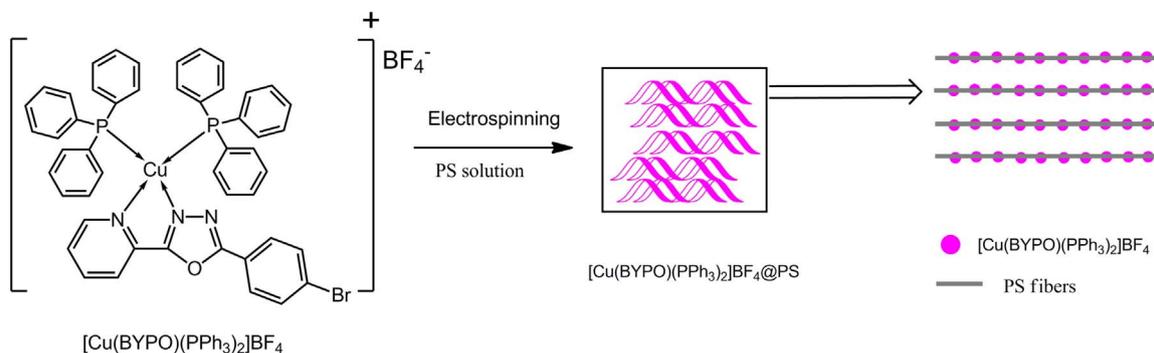
Later experimental result suggests that there is a tight correlation between such MLCT excited state and photophysical performance of [Cu(N-N)(P-P)]. Owing to its triplet character, a MLCT excited state is

usually a long-lived one with lifetime of a few hundreds of microseconds. Its emissive energy is controllable by modifying and adjusting N-N ligand. Never the less, a MLCT excited state is usually affected by surrounding environment and geometric relaxation. As a consequence, this MLCT excited state loses its energy through a non-radiative decay path, compromising its emissive performance [18–20]. Given electron-pulling groups in diamine ligand, such non-radiative decay shall be decreased, improving emissive performance [20]. Aiming at even better photophysical performance, geometric relaxation of MLCT excited state should be effectively limited. Precursive efforts have suggested some valid methods, such as modifying ligand with groups of steric hindrance, increasing rigidity of microenvironment around [Cu(N-N)(P-P)] molecules, and dispersing them into a rigid matrix such as polymer host [17–22].

Bearing above consideration in mind, this paper is focused on a diamine ligand (BYPO) having an electron-pulling oxadiazole ring in its molecular structure, as shown in Scheme 1. Its Cu(I) complex is established using PPh₃ as an auxiliary ligand. With electron-pulling effect from this diamine ligand and large steric hindrance from this phosphorous ligand, promising emissive performance is desired from [Cu(BYPO)(PPh₃)₂]⁺BF₄⁻. To further limit its geometric relaxation, this complex is doped into polystyrene (PS) matrix through electrospinning method. A full analysis on the obtained fibrous samples, along with solution sample and bulk sample, is performed.

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Scheme 1. Molecular structure of dopant $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$ and preparation strategy for its co-doping fibrous samples $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4@\text{PS}$.

2. Experimental section

2.1. General information

Scheme 1 depicts molecular structure of dopant $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$ and preparation strategy for its co-doping fibrous samples $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4@\text{PS}$. Corresponding reagents for sample preparation and synthesis were provided by Aldrich Chemical Co. (China) and used as received, including 4-bromobenzoyl chloride, picolinonitrile, NaN_3 , ZnCl_2 , triphenylphosphane (PPh_3), $\text{Cu}(\text{BF}_4)_2$, Cu powder and PS. Solvents used for sample preparation, including MeCN, N,N' -dimethylformamide (DMF), pyridine, CH_2Cl_2 and deionized water, were purified before usage. These samples were characterized by below equipments. NMR and mass spectra were determined by a Varian INOVA 300 spectrometer and a Agilent 1100 MS spectrometer (COMPACT), respectively. UV–Vis absorption and emission spectra were recorded through a HP 8453 UV–Vis–NIR diode array spectrophotometer and a Hitachi F-7000 fluorescence spectrophotometer, respectively. Excited state lifetimes were measured on a two-channel TEKTRONIX TDS-3052 oscilloscope which used pulsed YAG laser (355 nm) as excitation source. Scanning electron microscopy and fluorescence microscopy images were taken on a Hitachi S-4800 microscope and a Nikon TE2000-U fluorescence microscopy, respectively. Single crystal data were collected with a Siemens P4 single-crystal X-ray diffractometer and a Smart CCD-1000 detector. Graphite-monochromated Mo K α radiation was applied at 298 K. H atoms were calculated. Density functional theory calculation was performed on single crystal structure at RB3LYP/SBKJC level in vacuum, using GAMESS. FMOs were plotted with wxMacmolplt software package under contour value of 0.025.

2.2. Synthesis of diamine ligand BYPO

Diamine ligand BYPO was prepared following a literature method [15]. Firstly, 2-(2H-tetrazol-5-yl)-pyridine was synthesized following below procedure. A mixture of NaN_3 (10 mmol) and picolinonitrile (5 mmol) in DMF (25 mL) was allowed to react at room temperature for 1 h. Then ZnCl_2 (1 g) was slowly added. This final mixture was allowed to react at room temperature for 1 h and then at 90 °C for 12 h under N_2 protection. Finally, this mixture was cooled and poured into water ice. Crude product was purified on a silica gel column (n -hexane: $\text{CH}_2\text{Cl}_2 = 30:1$). ^1H NMR (300 MHz, CDCl_3): δ 7.61 (1, m), 7.83 (1H, m), 8.05 (1H, d, $J = 6.0$), 8.52 (1H, m). MS m/z : $[\text{m}]^+$ calc. for $\text{C}_6\text{H}_5\text{N}_5$, 147.0; found, 147.5.

A mixture of above obtained 2-(2H-tetrazol-5-yl)-pyridine (5 mmol) and 4-bromobenzoyl chloride (6 mmol) in anhydrous pyridine (40 mL) was at 120 °C for 2 days under N_2 protection. Then this mixture was cooled and poured into water ice. Crude product was purified on a silica gel column (n -hexane: $\text{CH}_2\text{Cl}_2 = 30:1$). ^1H NMR (300 MHz, CDCl_3): δ 7.53 (1H, m), 7.67 (2H, m), 8.07 (1H, m), 8.19 (1H, t), 8.26 (1H, t), 8.39 (1H, d, $J = 6.0$), 8.78 (1H, d, $J = 3.5$). MS m/z : $[\text{m}]^+$ calc. for

$\text{C}_{13}\text{H}_8\text{N}_3\text{OBr}$, 301.0; found, 301.1.

2.3. Synthesis of $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$

Firstly, $\text{Cu}(\text{BF}_4)_2$ (30 mmol) and excess Cu powder were added into MeCN (100 mL). This mixture was heated at 90 °C for 10 h under N_2 protection to obtain $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ [18,19]. Under stirring, $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (2 mmol) and PPh_3 (4 mmol) were mixed with CH_2Cl_2 (10 mL). After being stirred for 30 min, this solution was filtered off. BYPO (2 mmol) was added. This resulting solution was stirred at room temperature for 30 min. Natural evaporation of solvent gave $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$ as bulk crystals. ^1H NMR: δ 7.23 (18H, m), 7.30 (4H, m), 7.42 (8H, m), 7.54 (1H, t), 7.92 (2H, d, $J = 6.0$), 8.05 (1H, t), 8.17 (1H, d), 8.33 (1H, t), 8.46 (1H, m), 8.82 (1H, m). MS m/z : $[\text{m}]^+$ calc. for $\text{C}_{49}\text{H}_{38}\text{CuF}_4\text{N}_3\text{OBrP}_2$, 977.1; found, 977.5.

2.4. Construction of co-doping fibrous samples $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4@\text{PS}$

Our desired co-doping fibrous samples (denoted as $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4@\text{PS}$) were prepared through electrospinning method by doping $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$ into PS host. A typical run is described as follows. A transparent solution of PS in DMF was prepared (5 mL, 20 wt%). Dopant $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$ was carefully weighed and mixed with this PS solution, and then stirred at room temperature for 10 min. Later, this homogeneous solution was poured into a glass syringe connected with a plastic needle (inner diameter = 0.6 mm). The anode terminal of a high-voltage generator was connected by a copper wire which was soaked into this solution. Driving voltage was set as 18 kV. A sheet of Al foil was connected to grounding electrode and placed under this glass syringe with tip-to-target distance of 30 cm, serving as collecting substrate.

3. Results and discussion

3.1. Single crystal structure of $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$

Fig. 1A shows single crystal structure of $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$, which consequently confirms the successful synthesis of BYPO ligand and $[\text{Cu}(\text{BYPO})(\text{PPh}_3)_2]\text{BF}_4$. A typical tetrahedral coordination sphere is formed by two N atoms from a BYPO ligand and two P atoms from two PPh_3 ligands. Cu ion is localized at the center of this coordination field. A large coplanar conjugation is observed for BYPO ligand which is composed of three components, including pyridine ring, oxadiazole ring and bromobenzene ring. Their steric hindrance and electron-pulling effect may limit geometric distortion of MLCT excited state, which consequently improves MLCT photophysical performance. The free σ rotation makes one of PPh_3 phenyl rings align nearly parallel to BYPO conjugation plane, with minimal face-to-face distance of 3.42 Å and intersection angle of 0.95°, respectively. In addition, the face-to-face π - π attraction between BYPO planes makes every two neighboring [Cu

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