



# A phosphorescent copper(I) complex: Synthesis, characterization, photophysical property, and oxygen-sensing behavior

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## ABSTRACT

In this paper, we report the synthesis, crystal structure, photophysical properties, and electronic nature of a phosphorescent Cu(I) complex of  $[\text{Cu}(\text{Phen-Np})(\text{POP})]\text{BF}_4$ , where Phen-Np and POP stand for 2-(naphthalen-1-yl)-1H-imidazo[4,5-f][1,10]phenanthroline and bis(2-(diphenylphosphanyl)phenyl) ether, respectively.  $[\text{Cu}(\text{Phen-Np})(\text{POP})]\text{BF}_4$  renders a yellow phosphorescence peaking at 545 nm, with a long excited state lifetime of 4.69  $\mu\text{s}$ . Density functional calculation reveals that the emission comes from a triplet metal-to-ligand-charge-transfer excited state. We electrospun composite nanofibers of  $[\text{Cu}(\text{Phen-Np})(\text{POP})]\text{BF}_4$  and polystyrene (PS), hoping to explore the possibility of using the composite nanofibers as an oxygen sensing material. The finally obtained samples with average diameter of  $\sim 300$  nm exhibit a maximum sensitivity of 7.2 towards molecular oxygen with short response time of 7 s due to the large surface-area-to-volume ratio of nanofibrous membranes. No photobleaching is detected in these samples.

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## 1. Introduction

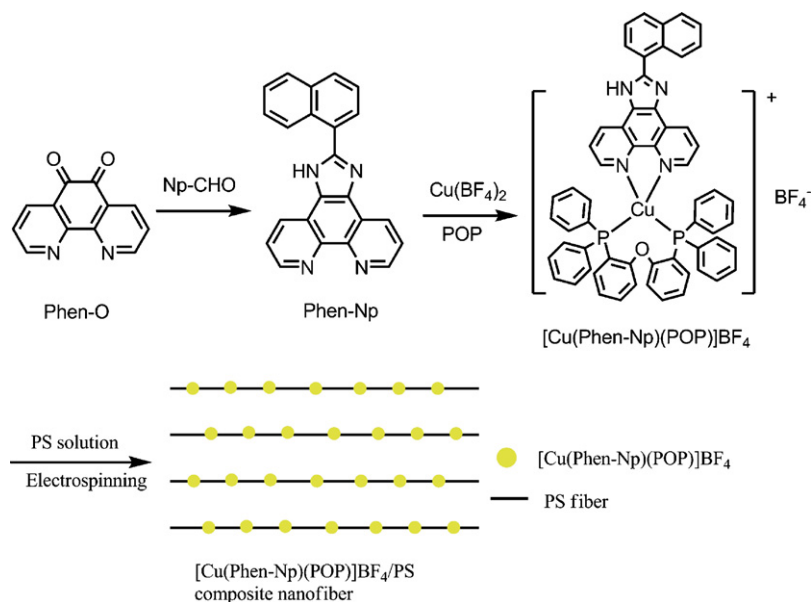
Recently, the synthesis and research on luminescent transition metal complexes have attracted much attention due to their favorable optical and electrical properties, making them in general perfect candidates for electro-optical applications, such as optical sensors [1,2]. Owing to the advantages of simple, rapid, and non-destructive characteristics, optical sensor technology is much simpler in instrumental implementation and sample preparation compared with traditional ones for detecting oxygen, metal ions, and so on. Recently, many sensor systems have been reported since such sensors can offer advantages in terms of size, electrical safety, costs, not requiring a reference element, and the fact that analytical signals are free of interference from electromagnetic field as well as easy to transmit over a long distance [3,4]. Among them, the development of optical sensors for oxygen detection has attracted considerable attention in recent years, because it is an important analytical problem to determine the molecular oxygen concentrations in gas phase, liquid phase, or both in different branches of chemical and food industries, medicine, analytical chemistry, and environmental monitoring [5,6].

For practical applications in optical oxygen sensing devices, it is necessary to embed sensors into solid matrix acting as a supporting medium, allowing oxygen transportation from surroundings. The commonly used matrixes are silica-based materials, polymers, and Langmuir–Blodgett films. Indeed, the support may have quite stringent criteria for suitable performances [7]. For example, a high diffusion coefficient is necessary for a rapid response, while, an effective local-quenching around the sensor molecule is necessary for good sensitivity, and long distance on-line monitoring necessitates a high degree of photostability. Thus, the exploration for sensors with intense luminescence, long excited state lifetime, high photostability, and good compatibility with supporting matrix is still a challenge.

Phosphorescent Cu(I) complexes, as a new class of optoelectrical material, have drawn much attention due to their advantages of less toxic, low cost, redundant resource, and environmental friendliness. Recently, a series of new mixed-ligand copper(I) complexes of  $[\text{Cu}(\text{N-N})(\text{POP})]^+$  [POP = bis(2-(diphenylphosphanyl)phenyl) ether] which are superior emitters have been synthesized [8–10]. For a typical phosphorescent Cu(I) complex, its HOMO and HOMO-1 have predominant metal Cu d character, while, LUMO and LUMO+1 are essentially  $\pi^*$  orbitals localized on the diimine ligand [9]. The photoluminescence corresponds to the lowest triplet  $T_1$  and is thus assigned as a character of metal-to-ligand-charge-transfer  $^3\text{MLCT}$  [ $d(\text{Cu}) \rightarrow \pi^*(\text{diimine ligand})$ ]. The MLCT excited states of cuprous diimine compounds are

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**Scheme 1.** A synthetic route for [Cu(Phen-Np)(POP)]BF<sub>4</sub> and [Cu(Phen-Np)(POP)]BF<sub>4</sub>/PS composite nanofibers.

often luminescent and play important roles in photoinduced electron and energy transfer process.

In this paper, we report a phosphorescent Cu(I) complex of [Cu(Phen-Np)(POP)]BF<sub>4</sub>, where Phen-Np stands for 2-(naphthalen-1-yl)-1H-imidazo[4,5-f][1,10]phenanthroline. Its crystal structure, photophysical properties, and electronic nature are discussed in detail. In addition, we dope [Cu(Phen-Np)(POP)]BF<sub>4</sub> into a polymer matrix, hoping to explore the possibility of using the composite material as an oxygen sensing material.

## 2. Experimental

A synthetic route for [Cu(Phen-Np)(POP)]BF<sub>4</sub> and the corresponding composite material of [Cu(Phen-Np)(POP)]BF<sub>4</sub>/PS is shown in Scheme 1. PS, POP, Cu(BF<sub>4</sub>)<sub>2</sub>, and 1-naphthaldehyde (NP-CHO) were purchased from Aldrich Chemical Co. and used without further purifications. Organic solvents were purified through standard procedures. The starting material of 1,10-phenanthroline-5,6-dione (referred as Phen-O) was synthesized according to the literature procedure [7,11]. All organic solvents were purified using standard procedures.

### 2.1. Synthesis of Phen-Np

A typical synthetic route for Phen-Np is described as follows. The mixture of 20 mmol of Phen-O, 22 mmol of Np-CHO, 15.40 g of NH<sub>4</sub>Ac, and 30 mL of HAc was stirred at 90 °C for 4 h. Then the mixture was poured into cold water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. After the evaporation of solvent, the crude product was further purified by recrystallization from EtOH. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ [ppm]: 11.62 (s, 1H), 9.13 (m, 2H), 8.79 (m, 1H), 8.54 (m, 1H), 7.94 (m, 3H), 7.72 (m, 1H), 7.63 (m, 1H), 7.56 (m, 4H). Anal. Calcd for C<sub>23</sub>H<sub>14</sub>N<sub>4</sub>: C, 79.75; H, 4.07; N, 16.17. Found: C, 79.62; H, 3.96; N, 16.29. IR (KBr pellet): ν 3037, 1615, 1558, 885, 783, 767, 725 cm<sup>-1</sup>.

### 2.2. Synthesis of [Cu(Phen-Np)(POP)]BF<sub>4</sub>

[Cu(Phen-Np)(POP)]BF<sub>4</sub> was synthesized according to the classic literature procedure [10]. Its identity was confirmed by <sup>1</sup>H NMR, elemental analysis, IR spectra, and single crystal XRD (CCDC-717869). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ [ppm]: 12.66 (s, 1H), 9.28 (m,

3H), 8.57 (m, 2H), 8.34 (m, 1H), 7.90 (m, 2H), 7.65 (m, 4H), 7.51 (m, 1H), 7.30 (m, 2H), 7.23 (m, 4H), 7.10 (m, 8H), 7.07 (m, 4H), 7.02 (t, 8H), 6.80 (m, 2H). Anal. Calcd for C<sub>59</sub>H<sub>42</sub>BCuF<sub>4</sub>N<sub>4</sub>OP<sub>2</sub>: C, 68.45; H, 4.09; N, 5.41. Found: C, 68.53; H, 4.13; N, 5.63. IR (KBr pellet): ν 3514, 3061, 1558, 1424, 1251, 1074, 776, 745, 691, 515 cm<sup>-1</sup>.

### 2.3. Fabrication of [Cu(Phen-Np)(POP)]BF<sub>4</sub>/PS composite nanofibers

A typical procedure for the electrospinning composite nanofibers is described as follows. PS with a number-average molecular mass of 100,000 was dissolved in N,N'-dimethyl formamide (DMF) to form a 22 wt% solution. Then [Cu(Phen-Np)(POP)]BF<sub>4</sub> was added into the solution under stirring to form [Cu(Phen-Np)(POP)]BF<sub>4</sub>/PS homogeneous solutions. The final solutions were then electrospun to be composite nanofibers of [Cu(Phen-Np)(POP)]BF<sub>4</sub>/PS. For electrospinning, the mixed solution was placed in a 5 mL glass syringe, with the opening end connected to a plastic needle (inner diameter=0.6 mm) as the nozzle [12]. The anode terminal of a high-voltage generator was connected to a copper wire inserted into the polymer solution in the glass syringe. A piece of Al foil was used as the collector plate and connected to the grounding electrode. The driving voltage was 18 kV, with the tip-to-target distance of 25 cm.

### 2.4. Methods and measurements

Density functional theory (DFT) and singlet excitation calculations using time-dependent density functional theory (TD-DFT) were performed on [Cu(Phen-Np)(POP)]<sup>+</sup> at RB3PW91/SBKJ level. The initial geometry was obtained from its single crystal. All computations were finished by GAMESS software package.

The IR spectra were recorded using a Magna560 FT-IR spectrophotometer. Excited state lifetimes were obtained with a 355 nm light generated from the Third-Harmonic-Generator pumped, using pulsed Nd:YAG laser as the excitation source. The Nd:YAG laser possesses a line width of 1.0 cm<sup>-1</sup>, pulse duration of 10 ns and repetition frequency of 10 Hz. A Rhodamine 6G dye pumped by the same Nd:YAG laser was used as the frequency-selective excitation source. All photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer.

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