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## COORDINATION COMPOUNDS

# Synthesis and 1.1 μm Near-Infrared Electrophosphorescence Properties of a Phenoxy-Substituents Copper Phthalocyanine[1]

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**Abstract**—A novel copper phthalocyanine bearing phenoxy-substituents was prepared and characterized by MS and Elemental analysis. Its UV/Vis absorption and photoluminescence (PL) spectra were investigated. Organic light-emitting devices (OLEDs) were demonstrated by employing this copper phthalocyanine doped into 4, 4'-N,N'-dicarbazole-biphenyl (CBP). Room-temperature electrophosphorescence was observed at about 1.1 μm due to transitions from the first excited triplet state to the singlet ground state ($T_1$–$S_0$) of this CuPc. The intensity of NIR emission at lower doping concentrations (about 10 wt %) was extremely high compared with devices doped with fluorescent dyes. The results indicated that direct charge trapping appears to be the dominant mechanism.

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Since the first report of multi-layer organic light-emitting diodes (OLEDs) by Tang and Van Slyke [1] OLEDs have been developed remarkably because their applications in full-color flat-panel displays [2–4]. Most of the research focused on devices that emitted visible light. Recently NIR OLEDs have received attention due to their potential application in laser technology, optical sensors and optical communication. However, most of materials for use in NIR OLEDs were organic complexes with trivalent rare earth ions such as $Er^{3+}$, $Nd^{3+}$, $Tm^{3+}$ and $Yb^{3+}$ [5–11]. Only few organic materials containing no rare earth ions showed EL characteristic in near-infrared region [12].

Phthalocyanine, which was first developed as a pigment, has found widespread applications in materials science. Many potential applications are expected for these molecular materials which have a high thermal and chemical stability, for instance, solar cell functional materials [13], gas sensors [14], nonlinear optical limiting devices [15], photodynamic therapy agents [16]. Recently, Pcs have been used as light-emitting material.

In this paper, a novel copper-tetra (2-isopropyl-5-methylphenoxy)phthalocyanine (TIMP PcCu) was synthesized and characterized by MS, elemental analysis and UV/Vis absorption. In order to study its electroluminescent (EL) properties, we prepared single-layer devices and multiple-layer devices.

## EXPERIMENTAL

### *Instruments*

Mass spectrum (MS) was obtained on a LDI-1700-TOF mass spectrometer (Linear Scientific Inc., USA). $^1$H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 500 spectrometer. Elemental analysis was performed on a Flash EA1112 Elemental Analyzer (ThermoQuest, Italy). UV/Vis spectra were carried out on a UV-3100 UV-Vis-NIR Recording Spectrophotometer (SHIMADZU, Japan). Current (I) versus voltage (V) measurements were obtained on a Keithley 2400 current-voltage source. The NIR photoluminescence (PL) spectra were determined on a PL9000 Photoluminescence System (BIO-RAD Micromeasurements Ltd, UK). The NIR EL signals were focused into a monochromator and detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques.

### *Synthesis of 4-(2-isopropyl-5-methylphenoxy)phthalonitrile*

A mixture of 2-isopropyl-5-methylphenol (1.5 g, 10 mmol), 4-nitrophthalonitrile (1.73 g, 10 mmol) and LiOH · $H_2O$ (0.42 g, 10 mmol) in anhydrous DMSO (30 mL) was stirred at room temperature for 72 h. The reaction mixture was poured into NaCl solution (10%, 400 mL) and the precipitate was isolated by filtration. Further purification was achieved by column chromatography on silica gel with petroleum/ether (9 : 1) as the mobile phase to afford colorless crystals. Yield: 83%. $^1$H NMR (500 MHz,

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CDCl3): d = 7.708 (d, 1 H, J = 8.5 Hz, ArH), 7.295 (d, 1 H, J = 8.5 Hz, ArH), 7.219 (s, 1 H, ArH), 7.189 (d, 1 H, J = 8 Hz, ArH), 7.109 (d, 1 H, J = 8 Hz, ArH), 6.745 (s, 1 H, ArH), 2.958 (m, 1 H, CH), 2.331 (s, 3 H, $ArCH_3$), 1.154 (d, 6 H, J = 6.5 Hz, $2CH(CH_3)_2$).

### *Synthesis of Copper-Tetra (2-isopropyl-5-methylphenoxy)phthalocyanine*

A mixture of 4-(2-isopropyl-5-methylphenoxy)phthalonitrile (1.104 g, 4 mmol), $Cu(OAc)_2$ (0.20 g, 1 mmol), 1-pentanol (6 mL) and a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was heated to 135°C for 12 h. After cooling to room temperature the reaction mixture was poured into 100 mL of methanol, precipitation was collected and adequately extracted by anhydrous methanol in a Soxlet extractor. The obtained mixture was purified by column chromatography on silica gel. The target product was eluted twice by $CHCl_3$/methanol (40 : 1) as a blue band. Yield: 607 mg, (52%). UV-Vis (chloroform, λ max/nm) 340, 616, 684; MS (LDI-TOF): m/z 1168.6 ($M + H^+$); anal., calcd. for $C_{72}H_{64}CuN_8O_4$ (1168.4): C, 73.87; H, 5.51; N, 9.57. Found: C, 73.54; H, 5.70; N, 9.23.

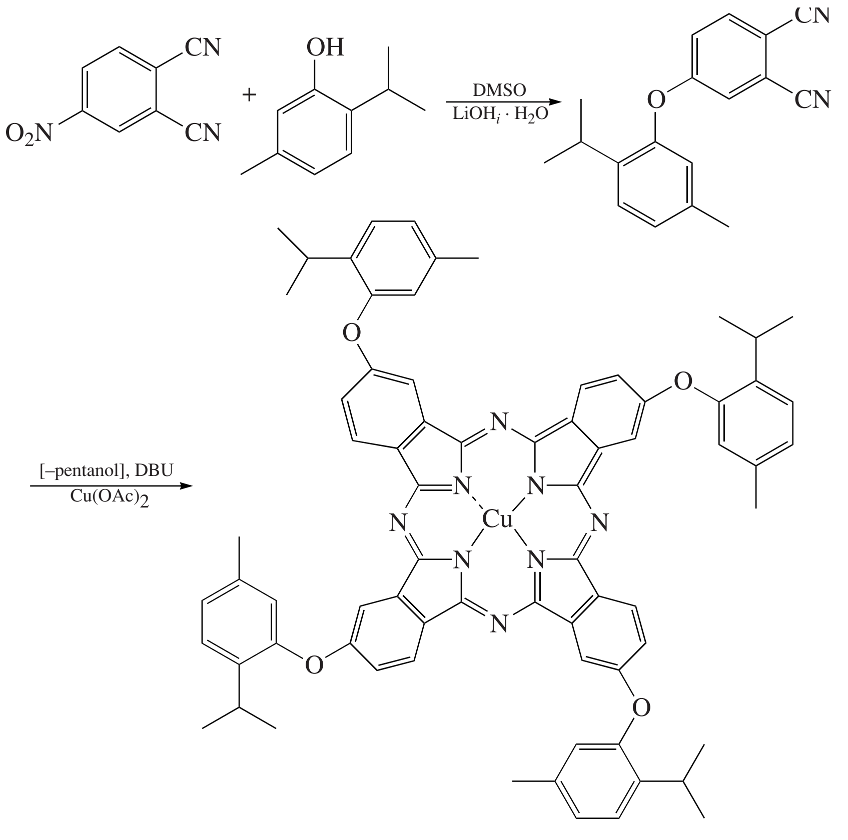
### *Device Preparation and Characterization*

The structure of devices used in this study is traditional. The indium-tin-oxide (ITO) with a resistance of 10 Ω/cm on glass was cleaned sequentially by acetone, ethanol, deionized water and supersonic treatment. The OLEDs of single-layer and the type ITO/NPB/CBP: CuPc/$Alq_3$/Al were fabricated by vacuum evaporating with a base pressure of $3 \times 10^{-4}$ Pa. A 35-nm-thick film of N, N'-di-1-naphthyl-N, N'-diphenylbenzidine (NPB) served as the hole-transport layer (HTL). A 30-nm-thick TIMP PcCu doped CBP layer was deposited as light-emitting-layer (EML) by simultaneous evaporation from two separate sources. A 15-nm-thick 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was deposited as hole-blocking layer (HBL). After that, a 20-nm-thick tris-(8-hydroxyquinoline) aluminum ($Alq_3$) was used to electrons-transport-layer (ETL). Finally a shadow mask with 2 × 2 mm openings was used to define the 120-nm-thick Al cathode.

## RESULTS AND DISCUSSION

### *Synthesis*

The synthetic route of TIMP PcCu is outlined in Scheme 1. Copper-tetra(2-isopropyl-5-methylphenoxy)phthalocyanine was synthesized according to the previous published methods [17] with the corresponding phthalonitrile derivatives, namely 4-(2-isopropyl-5-methylphenoxy)phthalonitrile. Tetrasubstituted phthalocyanines are usually obtained as a mixture of four constitutional isomers ($D_{2h}$ : $C_s$ : $C_{2v}$ : $C_{4h}$). According to reports of Prof. M. Hanack [18, 19] its isomers should be in the expected statistical proportion ($D_{2h} : C_s : C_{2v} : C_{4h} = 1 : 4 : 2 : 1$). The conclusions of this paper do not depend on having a pure isomer.



**Scheme 1.** The synthetic route of copper-tetra (2-isopropyl-5-methylphenoxy)phthalocyanine.

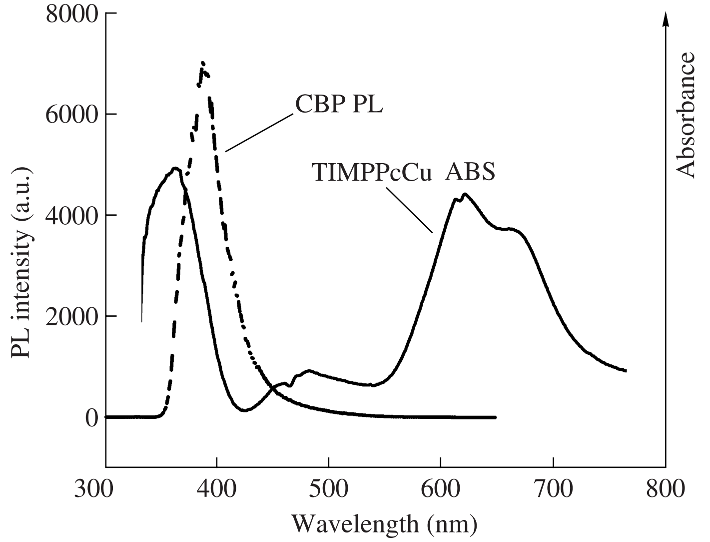


**Fig. 1.** The absorption spectrum of TIMPPcCu film and PL spectrum of CBP at room temperature (excited using 325 nm line from a He–Cd laser).

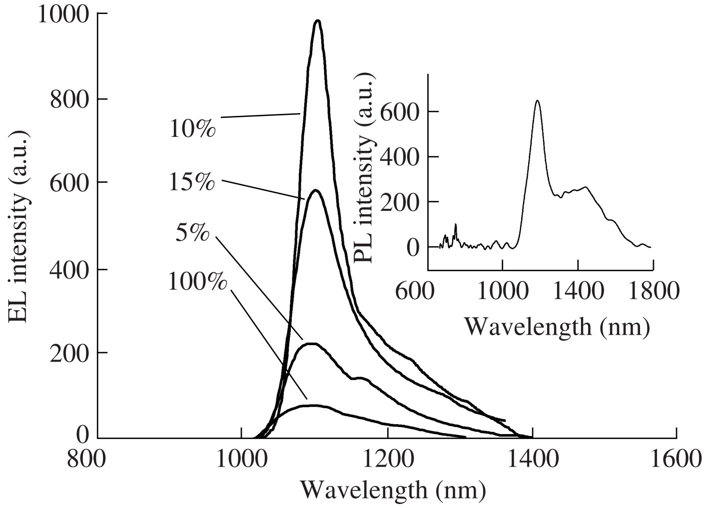


**Fig. 2.** The NIR EL spectra of devices based on TIMPPcCu with different concentrations in CBP (measured under the same conditions). Inset: The PL spectra of TIMPPcCu tablet excited using the 488 nm line from an $Ar^+$ laser at 10 K temperature.

### *Optical Properties*

The UV-Vis absorption spectra of TIMPPcCu film and PL spectrum of CBP presented in Fig. 1. The absorption spectrum exhibit the characteristic B band (corresponding to 340 nm) and Q band (the region of 600–700 nm) of phthalocyanines, which assigned to be $\pi$-$\pi^*$ transition of conjugated systems. Figure 1 also shows the PL spectrum of CBP. There was an overlap between the PL spectrum of CBP and the B band of the TIMPPcCu which indicated that the CBP (host) doped with TIMPPcCu (guest) system may meet the requirement for efficient Förster energy transfer [20] from the singlet excited state of the host to the singlet excited state of the guest.

The inset of Fig. 2 shows the PL spectrum of TIMPPcCu tablet excited using the 488 nm line from an $Ar^+$ laser at 10 K temperature. The tablet emitted a sharp peak centered at around 1180 nm. There exists a broad band at 1300–1400 nm which can not be assigned. According the repot before [21], the luminescence of CuPc without any substituents is due to transitions from the first excited triplet state to the ground state ($T_1$–$S_0$). Phenoxy-substituents does not change the large spin-orbit coupling, the center metal (Cu) atom is not changed yet. So we can conclude the luminescence

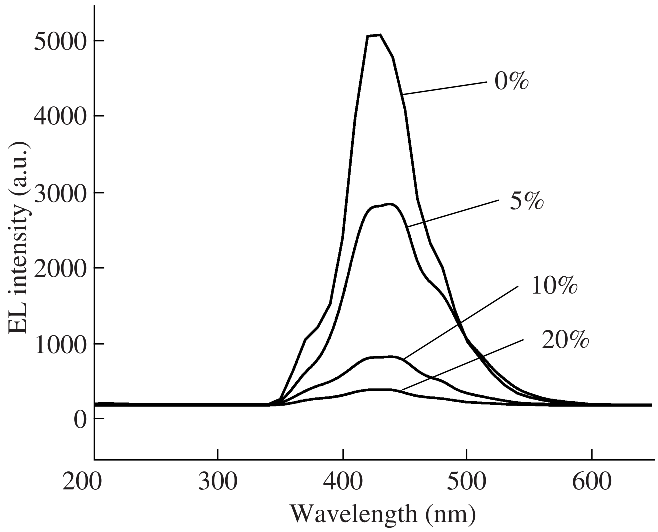


**Fig. 3.** The UV-vis EL spectrum of the doped OLEDs with different TIMPPcCu concentrations.

of TIMPPcCu tablet can be attributed to the phosphorescence of the first excited triplet state to the ground state ($T_1$–$S_0$). PL spectrum at room temperature shows almost no emitting, which can also prove that the luminescence of TIMPPcCu tablet is phosphorescence.

### *Electroluminescent Properties*

The single-layer devices of TIMPPcCu between ITO and Al electrodes do not show any measurable EL, the reason for which we attribute to unbalanced charge injection and transport at the electrode/organic interface. Figure 2 shows the NIR EL spectra of the devices made by different concentrations of TIMPPcCu doped in CBP at 10 mA at room temperature. As can be seen, the emission at about 1.1 μm coincides with the PL spectra of TIMPPcCu. The difference of wavelength between EL and PL is about 80 nm. This difference can be attributed to the form (tablet or film) and even the crystal type (α, β, single crystal or polycrystal [21]). When the concentration of TIMPPcCu is low (<10 wt %), the intensity of NIR emission increases with the increasing doping concentration. When the concentration of TIMPPcCu is high (>10 wt %), the intensity of NIR emission decreases with the increasing doping concentration. The reason may be that the effect of triplet-triplet annihilation becomes remarkable at higher concentration. The optimum concentration is 10 wt %, which is extremely high compares with devices doped with other fluorescence dyes.

There are two possible ways for electrically exciting TIMPPcCu in the doped OLED: either by direct carrier trapping and exciton formation on the TIMPPcCu, or by exciton formation in the host and energy transfer to TIMPPcCu guest by Förster [20] or Dexter [22] process. Figure 3 shows the UV-vis EL spectrum of the doped OLEDs with different TIMPPcCu concentrations. There exists the blue emitting of NPB centering at about 440 nm in all the devices. In the doped devices there almost exists no emitting of CBP centering at about 380 nm. The results can be understood as follows. In the case of the low doping concentrations hole injection from the NPB highest occupied molecular orbital (HOMO) into the CBP HOMO was energetically unfavorable because of the large energy difference between the HOMO levels of NPB and CBP (0.8 eV) (Fig. 4b). The recombination of the holes accumulated at the interface of NPB, CBP and electrons injected from CBP layer leads to blue NPB emission. The HOMO and lowest unoccupied molecular orbital (LUMO) of TIMPPcCu are –4.97 eV and –3.3 eV (measured by CV), falling within the band gap of the CBP. So the TIMPPcCu functioned as both a hole trap and an electron trap. Thus, we concluded that exciton formation occurred on TIMPPcCu by sequential electron and hole capture. It is more efficient with increasing of TIMPPcCu concentrations, which leading to the decrease of NPB EL intensity. The weak emission of CBP from undoped device indicated that only a small number of exciton (singlet or triplet) formation occurred on CBP molecules. That is to say only a small number of exciton (singlet or triplet) can be involved in energy transfer of the host (CBP) to guest (TIMPPcCu). The results suggested that Förster and Dexter energy transfers play a minor role in these devices, and direct charge trapping appears to be the dominant mechanism.

The I–V characteristics of OLEDs (Fig. 4a) also present an evident of the direct charge trapping process. In the case of lower doping concentrations (<10 wt %) there appear to be higher driving voltages. When the doping concentrations were higher than 10 wt % direct hole injection from NPB into TIMPPcCu and direct electron injection from BCP into TIMPPcCu may lead

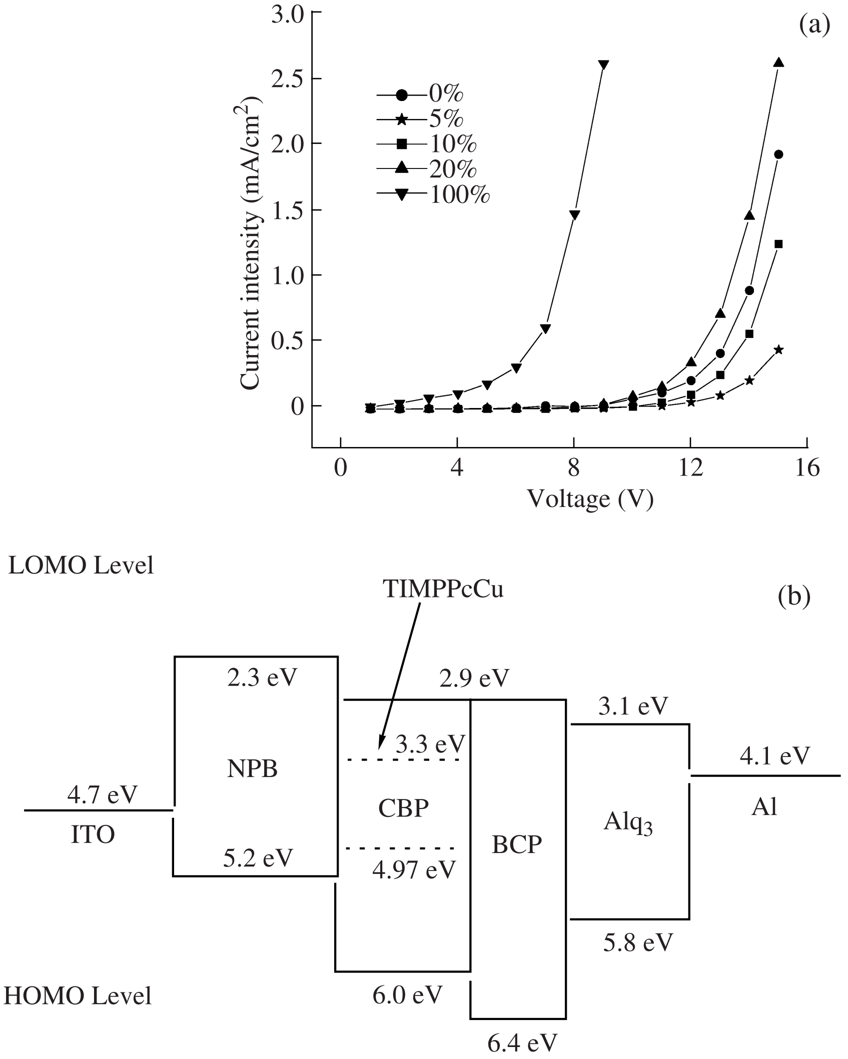


**Fig. 4.** (a) The current-voltage characteristics of OLEDs based on TIMPPcCu. (b) The energy level diagram of the devices containing TIMPPcCu.

to the lower driving voltage. When the doping concentration was 100%, the driving voltage is lowest.

In summary we have prepared a copper-tetra(2-isopropyl-5-methylphenoxy)phthalocyanine which was characterized by MS and Elemental analysis. We have fabricated the NIR OLEDs emitting at about 1.1μm by employing the TIMPPcCu. The dominant mechanism in NIR EL should be direct charge trapping.

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