



Full Length Article

Room-temperature electrophosphorescence from an all-organic material

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ABSTRACT

Materials displaying both fluorescence and phosphorescence emission in solutions and solid state at room temperature are described. The present materials comprise diphenylphosphino and bromo-substituents that cause intersystem crossing and corresponding triplet emission without the presence of heavy metals. Electroluminescence with a significant contribution of phosphorescence was observed in the experimental (Ph)OLEDs.

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1. Introduction

The phosphorescence in organic materials originates in forbidden transitions [1]. In OLEDs, due to the spin statistics of electron-hole recombination, the electrical excitation generates three triplets for every singlet exciton [2]. Thus, this feature makes the triplet-based electro-luminescence properties an area of high interest [3]. In organic materials, triplet radiative decay rates are low, and therefore the triplet decay is often difficult to observe, particularly at room temperature where nonradiative decay often predominates [4].

However, by employing molecules with high phosphorescence quantum yields, the quantum efficiency of OLEDs may be significantly improved [5]. Such phosphorescent molecules often include heavy-metal atoms that improve the harvesting of singlets and their intersystem crossing (ISC) to triplet states, a process which further increases the observable electrophosphorescence [6]. On the other hand, the phosphorescence quantum yield of organic materials is usually very low due to negligible heavy-atom effect and a corresponding lack of ISC [7]. Nevertheless, phosphorescence at room temperature (RTP) has been reported for various polycyclic aromatic hydrocarbons in fluid solutions in the presence of a high concentration of heavy atoms such as thallium [8,9], or in cases where the nonradiative triplet deactivation is prevented by the formation of inclusion complexes with cyclodextrins [10] or incorporation of the luminophore into a crystal lattice [11]. Thus, RTP has been used to identify organic compounds [12]. However, the determination of traces of hydrocarbon

compounds requires that these molecules are adsorbed onto a solid substrate or included in rigid matrixes [13–15].

In solid state devices, Baldo *et al.* reported phosphorescence sensitization improving the emission efficiency of small-molecule-based OLEDs [16]. Similarly, triplet excitons were observed to transfer energy from the phosphorescent complex bis[2-(4,6-difluorophenyl)pyridinato-*C*²,*N*](picolato)iridium(III) (FIrpic) to 4,4'-*N,N'*-dicarbazole-biphenyl (CBP) with a lower triplet energy which then resulted in CBP triplet-sensitization [17]. Goushi *et al.* reported the phosphorescence enhancement of 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (α -NPD) using *fac*-tris(2-phenylpyridine) iridium(III), a donor with higher triplet energy than that of α -NPD [18]. The phosphorescence of 4,4'-*N,N'*-dicarbazole-biphenyl (CBP), 4,4'-bis-[*N*-(*p*-tolyl)-*N*-phenyl-amino]biphenyl (TPD), 1,1-bis[(di-4-tolylamino)phenyl]cyclo-hexane (TAPC) and tris(8-hydroxyquinoline) aluminum (III) (Alq₃) have also been sensitized by phosphorescent donor molecules [18,19]. However, the phosphorescence emission observed for these films was obtained at very low temperatures, in most cases at 8 K. In the present study, however, we show the phosphorescence and electrophosphorescence originating from all-organic materials at room temperature.

2. Experimental

2.1. General procedures

¹H NMR and ¹³C NMR spectra were recorded using a Bruker 300 MHz spectrometer. ³¹P NMR spectra were recorded using a

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Varian 400 MHz. MALDI MS spectra were recorded using a MALDI-TOF Bruker Omiflex using 2',5'-Dihydroxyacetophenone matrix.

Cyclic voltammetry measurements were carried out using a three-electrode cell (Pt working electrode) with Pt wire as an auxiliary electrode. Millimolar DCM solutions containing 0.1 M tetrabutylammonium perchlorate were used. All potentials were referenced against the Ag/AgNO₃ reference electrode and each measurement was calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox system. Under these conditions the ferrocene/ferrocenium couple potential was determined to be +0.240 V vs Ag/AgNO₃.

The UV-vis spectra were recorded using an HP diode array spectrophotometer. The absorbance of the measured solutions was between 0.1 and 0.3. Emission spectra were recorded using an Edinburgh Analytical Instruments (FL/FS 900) spectrofluorimeter. The fluorescence quantum yields of the luminophores were measured as a function of the excitation wavelength using Tryptophan in water at pH 7 as a standard ($\Phi=0.20$) by the method described by Crosby [20].

The devices were fabricated using indium tin oxide (ITO) coated glass slides (sheet resistance 20 Ω /square) according to our published procedure [21]. The ITO substrates were cleaned using surfactant, water, 2-propanol, and acetone, then dried and exposed to ozone plasma. A 25 nm film of PEDOT:PSS was spin-coated from a 1.25% aqueous dispersion of Clevis[®] P and dried at 145 °C for 10 min. The OLED layers were deposited by resistive evaporation at a rate of 1 Å/s . The thicknesses of the individual layers are described below. The electroluminescent (EL) characteristics were measured using a Keithley 2400 source-meter and a Hamamatsu Photonic multi-channel analyzer C10027 (PMA-12) and an integrating sphere. All measurements were carried out under nitrogen at room temperature.

2.2. Synthesis and characterization

2.2.1. Synthesis of 2-bromo-7-diphenylphosphine-9,9'-bis(2-ethylhexyl)fluorene. (1)

A solution of 2,7-dibromo-9,9'-bis(2-ethylhexyl)fluorene (5.0 g, 9.1 mmol) in THF (160 ml) was cooled down to $-70\text{ }^{\circ}\text{C}$ in an acetone-dry ice bath. *n*-butyllithium (3.7 ml, 9.25 mmol) was added to the solution, and the resulting solution was stirred at $-70\text{ }^{\circ}\text{C}$ for 1 h. After that, the temperature was allowed to increase slowly to room temperature. The solution was stirred at room temperature for 3 hours before cooling down to $-70\text{ }^{\circ}\text{C}$ again. After 20 min chlorodiphenylphosphine (3.6 ml, 20.0 mmol) was added. The resulting mixture was stirred overnight allowing the temperature to increase slowly to room temperature. The reaction mixture was poured into methanol. The mixture was filtered through a filter paper, and the filtrate was transferred to a round bottom flask. After solvent evaporation, the resulting oil was digested in hexanes, and the solvent was evaporated. The resulting oil was digested in a mixture of dichloromethane and methanol. The solvents were evaporated and a clear oil was obtained. The oil was purified by column chromatography using a mixture of hexane and dichloromethane as eluent (9:1). Yield (4.15 g, 70%). ¹H NMR (CDCl₃), δ (ppm): 0.42 (td, 5 H, $J=2.07, 7.15$ Hz); 0.50 (td, 3 H, $J=1.69, 7.15$ Hz); 0.71 (m, 15 H); 0.877 (m, 9 H); 1.83 (m, 2 H); 7.33 (m, 11 H); 7.22 (dd, 1 H, $J=3.57, 8.10$ Hz); 7.43 (dd, 1 H, $J=7.72, 1.69$ Hz); 7.47 (t, 1 H, $J=1.88$ Hz); 7.53 (d, 1 H, $J=8.10$ Hz); 7.63 (d, 1 H, $J=7.72$ Hz). ¹³C APT NMR (CDCl₃), δ (ppm): 10.00 CH₃, 10.42 CH₃, 13.99 CH₃, 14.02 CH₃, 22.68 CH₂, 22.75 CH₂, 26.59 CH₂, 27.17 CH₂, 27.97 CH₂, 28.32 CH₂, 33.50 CH₂, 33.85 CH₂, 34.59 CH, 34.66 CH, 44.27 CH₂, 44.51 CH₂, 55.18 C, 119.63 CH, 120.89 C, 121.02 CH, 121.14 CH, 126.57 C, 127.35 CH, 127.45 CH, 128.37 CH, 128.47 CH, 128.64 CH, 129.91 C, 130.07, 132.25 C, 133.51 C (d, $J=2.19$ Hz), 133.77 C (d, $J=2.19$ Hz), 135.19 C, 137.34 C, 139.68 C. ¹³C DEPT135 NMR (CDCl₃), δ (ppm): 10.06 CH₃, 10.53 CH₃, 14.11 CH₃, 18.53 CH₂,

22.83 CH₂, 26.67 CH₂, 27.25 CH₂, 28.03 CH₂, 28.39 CH₂, 33.58 CH₂, 33.92 CH₂, 34.66 CH, 44.32 CH₂, 44.57 CH₂, 58.57 C, 119.62 CH, 121.03 CH, 121.54 CH, 127.32 CH, 128.39 CH, 128.47 CH, 128.65 CH, 129.91 CH, 133.51 C (d, $J=1.64$ Hz), 133.75 C (d, $J=1.64$ Hz). ³¹P NMR (CDCl₃), δ (ppm): -2.88 . MALDI-TOF Calculated C₄₁H₅₀P₁Br₁: 653.23. MALDI-TOF Experimental: 654.27.

2.2.2. Synthesis of 2-bromo-7-diphenylphosphineoxide-9,9'-bis(2-ethylhexyl)fluorene. (2)

A solution of 2-bromo-7-diphenylphosphine-9,9'-bis(2-ethylhexyl)fluorene (3 g, 4.6 mmol) in 30 ml of dichloromethane was prepared and stirred. After 15 min, 0.5 ml of hydrogen peroxide were added dropwise to the solution. The resulting solution was stirred at room temperature overnight, and the reaction mixture was poured into distilled water. The mixture was extracted 3 times with 30 ml of dichloromethane. The organic layers were combined and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The resulting oil was dried under vacuum for 12 hours. Yield (2.76 g, 90%). ¹H NMR (CDCl₃), δ (ppm): 0.38 (td, 4 H, $J=3.01, 7.15$ Hz); 0.51 (dd, 2 H, $J=2.26, 7.72$ Hz); 0.54 (dt, 2 H, $J=2.07, 6.9$ Hz), 0.71 (m, 16 H); 0.83 (m, 9 H); 1.88 (m, 2 H); 7.46 (m, 6 H); 7.52 (m, 3 H); 7.59 (d, 1 H, $J=8.1$ Hz); 7.66 (m, 5 H); 7.75 (m, 1 H). ¹³C NMR (CDCl₃), δ (ppm): 9.98, 10.41, 14.02, 22.70, 26.52, 27.10, 27.22, 28.07, 28.37, 33.53, 33.99, 34.68, 44.27, 44.55, 55.50, 119.68, 121.04, 121.74, 121.95, 127.41, 127.56, 127.66, 128.38, 128.51, 130.08, 130.24, 131.87, 132.06, 132.15, 139.09. ³¹P NMR (CDCl₃), δ (ppm): 30.27. MALDI-TOF Calculated C₄₁H₅₀O₁P₁Br₁: 669.43. MALDI-TOF Experimental: 669.43.

3. Results and discussion

3.1. Synthesis

The synthesis of **1** and **2** (Fig. 1) was performed following the outline in Scheme 1.

Thus, the starting material, 2,7-dibromo-9,9'-bis(2-ethylhexyl)fluorene (DBEHF), was treated with 1 equiv. of *n*-butyllithium followed by the addition of chlorodiphenylphosphine according to the modified procedure previously used to synthesize bis-phosphinated compounds such as compound **3** [22]. The 2-bromo-7-diphenyl-phosphine-9,9'-bis(2-ethylhexyl)fluorene **1** product was then treated with hydrogen peroxide to obtain the corresponding phosphine-oxide material **2**. Compound **3** was synthesized using a similar procedure.

3.2. HOMO-LUMO and electronic structure

The values of HOMO and LUMO (Table 1) for compounds **1** and **2** were determined from electrochemistry and compared to the previously published data for compound **3** [23].

The obtained experimental values showed that the phosphine group in **1** induced a stronger stabilizing effect while reducing the

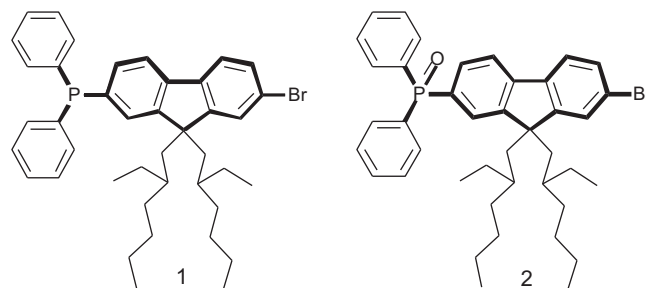


Fig. 1. Structure of compounds 1 and 2.

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