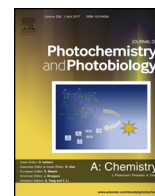




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Invited feature article

Synthesis and characterization of coumarin-biphenyl derivatives as organic luminescent materials

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ABSTRACT

Three new coumarin derivatives containing biphenyl group have been successfully synthesized and characterized by EA, IR and NMR. The photophysical properties of all derivatives were investigated by UV–vis and photoluminescence spectroscopic analysis. Their thermal stabilities were demonstrated by TGA. The doped light-emitting devices using the coumarin derivatives as dopants were fabricated. The results show that one of coumarin derivatives with coumarin-biphenyl skeleton would serve as promising luminescent materials.

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1. Introduction

Coumarins are important class of organic heterocyclic molecules [1]. Many natural and synthetic coumarin derivatives have been extensively studied due to their several activities. In addition to a wide variety of biological activities [2–4], they exhibit favorable photophysical properties such as large Stokes shifts, high fluorescence quantum yields, excellent light stability, visible excitation and emission wavelengths and nontoxicity [5,6]. Undeniably, the coumarin derivatives used extensively as potential fluorescence materials, and widely used as emissive dopants in organic light-emitting diodes (OLEDs) application [7,8].

The photophysical properties of the coumarin derivatives are strongly related to the electron-donating or electron-withdrawing capacity of the substituents attached to their core and the conjugation degree of molecules. The longer π -conjugation dye molecules generally achieve a longer absorption maximum and extend the absorption region [9]. The extension of the π -delocalized system will lead to molecules showing more promising fluorescent behavior [10]. As reported, biscoumarin analogues extend the absorption and emission wavelength ranges, by increasing the electron conjugated system [11,12].

Biphenyl exhibits planar configuration, which expects full delocalization of the π -system over the two rings [13]. Because of photophysical and opto-electronic properties, biphenyl derivatives

are widely used as hole-transport and host materials and sometimes as blue-emitting materials [14,15]. Combining biphenyl moiety with coumarin may afford new chemical entities, which would possess simultaneously the superior properties of biphenyl and coumarin. Furthermore, biphenyl with coumarin ring containing a diethylamino group as a donor moiety increases the conjugation of the chromophore.

In view of the above mentioned findings, the present work describes the synthesis and characterization of three new coumarin-biphenyl derivatives (4,4'-di(coumarin-3-yl)-biphenyl, 4-(coumarin-3-yl)-4'-(7-diethylaminocoumarin-3-yl)-biphenyl and 4,4'-di(7-diethylaminocoumarin-3-yl)-biphenyl), aiming at obtaining new materials with higher fluorescent properties. The photophysical, electrochemical properties and thermal stabilities of the derivatives were investigated. Furthermore, the electroluminescence devices made using codeposition of the derivatives and TBADN films as emitters were fabricated to investigate the electroluminescence properties of the derivatives.

The synthetic routes of the coumarin-biphenyl derivatives is outlined in Scheme 1.

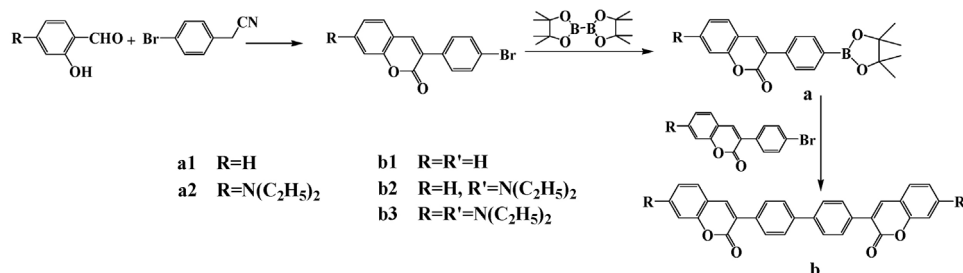
2. Experimental

2.1. Materials and instruments

All materials and reagents were of AR grade and directly used. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

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Scheme 1. Synthesis of coumarin-biphenyl derivatives.

IR spectra were taken with a Shimadzu IR Prestige-21 FT-IR spectrophotometer. ¹H NMR spectra were obtained on Varian Mercury Plus 400 MHz and Agilent Technologies DDZ 600 MHz Spectrometer with tetramethylsilane as the internal standard. Elemental analyses were performed on an Vario-EL automatic elemental analysis instrument. Absorption spectra were recorded by a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS-55 spectrometer. MS was obtained from a Thermo Scientific Orbitrap Elite mass spectrometer. Fluorescent lifetime and quantum yield were recorded on a FLSP920 type steady-state/transient fluorescence spectrometer (Edinburgh Instruments Ltd). Cyclic voltammetry (CV) was carried out on a CH Instruments 760B with a three electrode system (a Pt working electrode, a Pt-wire counter electrode, and a Ag/AgCl reference electrode) in the presence of *n*-Bu₄NPF₆ (0.1 mol L⁻¹) as a supporting electrolyte in CH₂Cl₂.

2.2. Synthesis and characterization

3-(4-Bromophenyl)coumarin and 3-(4-Bromophenyl)-7-(*N,N'*-diethylamino) coumarin were prepared according to the procedure as previously described [16].

2.2.1. Preparation of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-coumarin (**a1**)

The suspension of 3-(4-Bromophenyl)coumarin (1.5 g, 4.98 mmol), bis(pinacolato) diboron (2.0 g, 7.87 mmol), potassium acetate (0.8 g, 8.15 mmol) and Pd(dppf)Cl₂ (0.1 g, 0.14 mmol) in absolute 1,4-dioxane (100 mL) was placed in a three-necked flask. The mixture was heated up to 95 °C and stirred for 24 h under N₂. After solvent was evaporated under vacuum, the mixture was dissolved in dichloromethane, washed with water (3 × 20 mL). The organic layer was dried over MgSO₄ and concentrated in vacuum. The residue was chromatographed on silica, eluting with EtOAc/ether(1:30-1:10 gradient, v/v) to form white solid (yield 84%). m. p.: 178–179 °C. Anal. Calcd. for C₂₁H₂₁BO₄ (%): C 72.44, H 6.08. Found (%): C 72.31, H 6.10. ¹H NMR (400 MHz, CDCl₃) δ: 7.89 (d, *J*=8.0 Hz, 2H, Ar-H), 7.85 (s, 1H, coumarin H), 7.73 (d, *J*=8.0 Hz, 2H, Ar-H), 7.54 (t, *J*=8.7 Hz, 2H, coumarin H), 7.37 (d, *J*=8.3 Hz, 1H, coumarin H), 7.30 (t, *J*=7.4 Hz, 1H, coumarin H), 1.36 (s, 12H).

2.2.2. Preparation of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-7-(*N,N'*-diethylamino)coumarin (**a2**)

The preparation of **a2** was similar to that described for **a1**, which was obtained through the reaction of 3-(4-Bromophenyl)-7-(*N,N'*-diethylamino)coumarin (1.0 g, 2.69 mmol) with bis(pinacolato)

diboron (1.10 g, 4.33 mmol). The crude was purified by chromatography on silica gel using EtOAc/CH₂Cl₂/petroleum ether (1:8:30, v/v/v) to form yellow solid (yield 74%). m.p.: 212–214 °C. Anal. Calcd. for C₂₅H₃₀BNO₄ (%): C 71.61, H 7.21, N 3.34. Found (%): C 71.53, H 7.29, N 3.30. ¹H NMR (400 MHz, CDCl₃) δ: 7.85 (d, *J*=7.9 Hz, 2H, Ar-H), 7.73 (s, 2H, Ar-H), 7.71 (s, 1H, coumarin H), 7.32 (d, *J*=8.8 Hz, 1H, coumarin H), 6.59 (dd, *J*=8.8, 2.1 Hz, 1H, coumarin H), 6.53 (s, 1H, coumarin H), 3.43 (q, *J*=7.0 Hz, 4H, CH₂), 1.35 (s, 12H, CH₃), 1.22 (t, *J*=7.0 Hz, 6H, CH₃).

2.2.3. Preparation of 4,4'-di(coumarin-3-yl)-biphenyl (**b1**)

Absolute toluene (100 mL) was added under N₂ to the mixture of **a1** (1 g, 2.87 mmol), 3-(4-Bromophenyl)coumarin (1.4 g, 4.65 mmol), Na₂CO₃ (1 g, 9.43 mmol), TBAB (0.05 g, 0.16 mmol) and Pd(pph₃)₄ (0.2 g, 0.17 mmol). The suspension was heated up to 110 °C and stirred vigorously. After 10 min, distilled water (2 mL) was added. The resulting mixture was stirred 110 °C for 24 h. After solvent was evaporated under vacuum, the mixture was dissolved in dichloromethane, washed with water (3 × 20 mL). The organic layer was dried over MgSO₄ and concentrated in vacuum. The residue was chromatographed on silica, eluting with EtOAc/CH₂Cl₂/petroleum ether (1:100:300, v/v/v) to form white solid. Yield: 68%. m.p. > 280 °C. Anal. Calcd. for C₃₀H₁₈O₄ (%): C 81.44, H 4.10. Found (%): C 81.40, H 4.13. IR (KBr), cm⁻¹: 1722 (ν_{C=O}), 1114 (ν_{C-O}), 1610 and 1455 (ν_{C=C}), 809 (δ_{Ar-H}). ¹H NMR (600 MHz, CDCl₃) δ: 7.82 (s, 2H, coumarin H), 7.62–7.57 (m, 8H, Ar-H), 7.57–7.54 (m, 4H, coumarin H), 7.38 (d, *J*=8.7 Hz, 2H, coumarin H), 7.32 (d, *J*=7.5 Hz, 2H, coumarin H).

The preparation of 4-(coumarin-3-yl)-4'-(7-diethylaminocoumarin-3-yl)-biphenyl (**b2**) and 4,4'-di(7-diethylaminocoumarin-3-yl)-biphenyl (**b3**) were similar to that described for **b1**.

b2 was synthesized through the reaction of 3-(4-Bromophenyl)coumarin (0.5 g, 1.67 mmol) with **a2** (0.46 g, 1.09 mmol). The crude was purified by chromatography on silica gel using EtOAc/CH₂Cl₂ (1:100, v/v) to form yellow solid (yield 74%). m.p. > 280 °C. Anal. Calcd. for C₃₄H₂₇NO₄ (%): C 79.51, H 5.30, N 2.73. Found (%): C 79.53, H 5.31, N 2.71. IR (KBr), cm⁻¹: 2970 (ν_{C-H}), 1715 (ν_{C=O}), 1138 (ν_{C-O}), 815 (ν_{Ar-H}), 1275 (ν_{C-N}). ¹H NMR (400 MHz, CDCl₃) δ: 7.89 (s, 1H, coumarin H), 7.82 (dd, *J*=8.4, 1.4 Hz, 4H, Ar-H), 7.78 (s, 1H, coumarin H), 7.71 (dd, *J*=12.6, 8.5 Hz, 4H, Ar-H), 7.56 (dd, *J*=15.6, 7.2 Hz, 2H, coumarin H), 7.40 (d, *J*=8.7 Hz, 1H, coumarin H), 7.37–7.28 (m, 2H, coumarin H), 6.64–6.49 (m, 2H, coumarin H), 3.45 (dd, *J*=13.6, 6.5 Hz, 4H, CH₂), 1.27–1.19 (m, 6H, CH₃). MS (ESI) *m/z* 514.20 [M+H]⁺, calculated for C₃₄H₂₇NO₄, 513.58.

b3 was obtained from the reaction of 3-(4-Bromophenyl)-7-(*N,N'*-diethylamino) coumarin (0.46 g, 1.24 mmol) with **a2** (0.4 g, 0.95

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