Synthesis and Characterization of N-Coumarin Derivatives for Organic Light-Emitting Diodes (OLEDs)

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Abstract

In this work, a series of new emissive materials based on pyrene substituted thiophenyl N-coumarins was developed for use in organic light-emitting diodes. The designed four molecules namely **CTnP** and **CTnCP** (n = 1-2) having thiophene moieties in the molecules up to two units were synthesized using a combination of condensation, bromination, Suzuki cross-coupling and Ullmann coupling reactions. Their chemical structures were confirmed by NMR techniques. The optical properties were measured by UV-Vis and fluorescence spectroscopy. Major absorption and emissive bands at λ_{max} 420-480 nm and λ_{max} 520-535 nm were observed, respectively. These peaks exhibit a red shift as the number of thiophene moiety increasing from 1 to 2 units. They are highly fluorescence with emission colors varying from green to orange. With the same the thiophene unit, molecules bearing carbazole-pyrenes substituent showed blue shifted spectra compared to those having pyrene. The CV measurements exhibited reversible oxidation at potential of 0.6-1.2 V and irreversible reduction at potential of -1.6-(-1.8) V.

Keywords : N-coumarins, carbazole, dendrimer, hole-transporting material, light-emitting material, organic light-emitting diode

1. Introduction

Organic light-emitting diodes (OLEDs) hold the potential to make affordable full color large-flat-panel displays on low-cost flexible substrates (Promarak *et. al.* 2007). Coumarins are important class of naturally occurring and synthetic compounds which have been extensively investigated for electronic and photonic applications, such as fluorescence probe, charge-transfer agents, solar energy collectors, and nonlinear optical properties due to their high emission yield, excellent photo-stability, extended spectral range, good solubility and their relative ease of synthesis (Kele *et. al.* 2002; Wang *et. al.* 2005; Kitamura *et. al.* 2007, Sheng *et. al.* 2008; Serin *et. al.* 2002; Potjanasopa *et. al.* 2010). As emitting materials, their fluorescent wavelength and the fluorescence quantum yield strongly depend on the nature, the position of the substituent and also on the rigidity of the molecule (Yu *et. al.* 2009). Pyrene derivatives have been used in OLEDs in order to improve hole transporting ability because of its electron-rich property (Tang *et. al.* 2006). Due to its unique optical, electrical, and chemical properties, carbazole has been widely employed as a functional building block or substituent in the construction of organic semiconductors (Promarak *et. al.* 2007; Arivuoli 2001; Promarak *et. al.* 2007; Kappaun *et al.* 2008). Moreover, thermal stability and glassy state durability of these organic molecules were found to be significantly improved upon incorporation of a carbazole moiety in the structure.

In this work, we synthesize a series of new emissive materials based on N-coumarin-thiophene end-capped with either pyrene or carbazole-pyrenes for using as light-emitting materials in OLEDs. The structure-physical properties were investigated.

2. Methodology and Experiment

2.1 General procedures

^{1}H-NMR spectra were recorded on Brüker AVANCE (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on Brüker AVANCE (75 MHz) spectrometer and were fully decoupled. $CDCl_3$ was used as a solvent in all cases with TMS as the internal reference. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), doublet (d), doublet of doublet (dd), triplet (t) and multiplet (m). UV-visible spectra were measured in CH_2Cl_2 on a Perkin-Elmer UV Lambda 25 spectrometer. Fluorescence spectra were recorded as a dilute solution of CH_2Cl_2 on a Perkin-Elmer LS 50B Luminescence Spectrometer. The electrochemistry was performed using an AUTOLAB spectrometer. All measurements were made at room temperature on sample dissolved in freshly distilled CH_2Cl_2 with 0.1 M n-Bu_4NPF_6 as supporting electrolyte. The solutions were degassed by bubbling with argon. CH_2Cl_2 was washed with concentrated sulfuric acid and distilled from calcium hydride. A glassy carbon working electrode, platinum wire counter electrode, and a Ag/AgCl/KCl (Sat.) reference electrode were used. All quantum chemical calculations were performed by using density functional theory (DFT) at the B3LYP/6-31G(d,p) level, as implement in Gaussian 03 program. The excitation energies of the low lying states were calculated using the time-dependent density functional theory (TD-DFT/B3LYP) at the same level.

2.2 Synthesis

2.2.1 Synthesis of **CT1P**

A mixture of **2** (0.50 g, 1.32 mmol) and pyrene-1-boronic acid (0.32 g, 1.32 mmol), $Pd(PPh_3)_4$ (0.048 g, 0.039 mmol), Na_2CO_3 (2.80 g, 26.43 mmol) in THF (20 ml) and water (13 ml) was degassed with N_2 and heated at reflux for 24. After being to room temperature, the mixture was extracted with CH_2Cl_2 (50 ml x 2). The combined organic layer washed with water (100 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatograph eluted with hexane : dichloromethane (3:2) to give an orange solid (0.64 g, 96%). 1H NMR ($CDCl_3$, 300 MHz): δ 1.33 (t, 6H), 3.44 (q, 4H), 6.61 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 7.37 (m, 2H), 7.83 (d, *J* = 3 Hz, 1H), 8.06 (m, 5H), 8.59 (d, *J* = 10.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.43, 45.25, 76.59, 77.01, 77.21, 77.43, 97.21, 109.78, 124.65, 125.10. 125.62, 127.75, 128.41, 129.80, 131.50, 136.38, 138.31, 142.75, 155.52.

2.2.2 Synthesis of **CT1CP**

A mixture of **2** (0.30 g, 0.79 mmol) and **5** (0.45 g, 0.79 mmol), CuI (0.075 g, 0.39 mmol), (±)-*trans*-1,2-diaminocyclohexane (0.045 g, 0.39 mmol), K_3PO_4 (0.42 g, 1.98 mmol) in toluene (20 ml) was degased with N_2 and heated at reflux for 48 hr. After cooling, the reaction was quenched by adding water and then was extracted with CH_2Cl_2 (50 ml x 2). The combined organic layer was washed with water (100 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatograph eluted with hexane : dichloromethane (3:2) to give a yellow solid (0.26 g, 38%). ($CDCl_3$, 300 MHz): δ 1.26 (t, 6H), 3.45 (q, 4H), 6.68 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 7.39 (m, 2H), 7.76 (m, 5H), 8.1 (m, 20H), 8.4 (d, *J* = 9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.30, 45.95, 76.59, 77.22, 110.46, 122.28, 123.88, 124.76, 125.57, 127.47, 128.86, 129.37, 130.42, 131.54, 134.05, 135.50, 136.50, 138.84, 141.63, 155.43, 160.31.

2.2.3 Synthesis of **CT2P**

A mixture of **3** (0.30 g, 0.65 mmol) and pyrene-1-boronic acid (0.16 g, 0.65 mmol), $Pd(PPh_3)_4$ (0.037 g, 0.032 mmol), Na_2CO_3 (1.38 g, 13.03 mmol) in THF (20 ml) and water (15 ml) was degased with N_2 and heated at reflux for 24 hr. After cooling, being to room temperature, the mixture was extracted with CH_2Cl_2 (50 ml x 2). The combined organic layer washed with water (100 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatograph eluted with hexane : dichloromethane (3:2) to give an red solid (0.12 g, 33%). 1H NMR ($CDCl_3$, 300 MHz): δ 1.24 (t, 6H), 3.44 (q, 4H), 6.58 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 7.37 (m, 2H), 7.61 (d, *J* = 3.9 Hz, 1H), 7.88 (m, 9H), 8.59 (d, *J* = 9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.44, 45.22, 76.59, 77.21, 97.68, 109.79, 123.93, 124.67, 125.38,126.18, 127.84, 128.81, 129.41, 130.98, 131.48, 136.35, 137.45, 138.45, 141.47, 155.45.

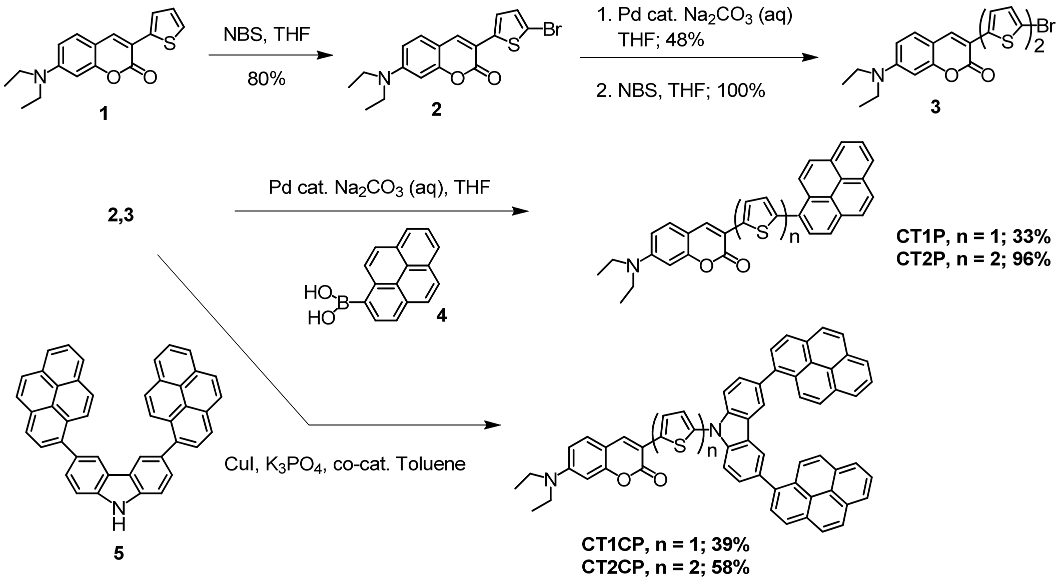
2.2.4. Synthesis of **CT2CP**

A mixture of **3** (0.30 g, 0.65 mmol), **5** (0.40 g, 0.71 mmol), CuI (0.062 g, 0.32 mmol), (±)-*trans*-1,2-diaminocyclohexane (0.037 g, 0.32 mmol), K_3PO_4 (0.34 g, 1.62 mmol) in toluene (20 ml) was degased with N_2 and heated at reflux for 48 hr. After cooling, the reaction was quenched by adding water and then was extracted with CH_2Cl_2 (50 ml x 2). The combined organic layer was washed with water (100 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatograph eluted with hexane : dichloromethane (3:2) to give a red-orange solid (0.35 g, 58%). 1H NMR ($CDCl_3$, 300 MHz): δ 1.25 (t, 6H), 3.41 (q, 4H), 6.57 (s, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 7.34 (m, 9H), 8.15 (m, 20H), 8.4 (d, *J* = 9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.43, 45.25, 76.61, 77.21, 109.79, 110.38, 122.33, 123.88, 124.66, 125.25, 127.47, 128.83, 129.44, 130.43, 131.53, 134.14, 136.30, 137.00, 138.17, 141.63, 155.47.

3. Results and Discussion

The synthetic route to the target molecules is shown in Scheme 1. Coumarin intermediate **1** was first formed by condensation of diethylamino-2-hydroxy benzaldehyde and 2-thiopheneacetonitrile in the presence of piperidine as base. It was then selectively brominated at the most nucleophilic 2-position of thiophene ring with NBS in THF to give a key intermediate **2** in good yield. Cross coupling of **2** with 2-thiopheneboronic acid under Suzuki coupling conditions with $Pd(Ph_3P)_4$ as catalyst and Na_2CO_3 as base in THF/water followed by selective bromination of the resultant at 2-position of the terminal thiophene ring with NBS gave an intermediate **3** in reasonable yield over two steps. The target molecules **CT1P** and **CT2P** were then formed by Suzuki cross-coupling between the corresponding intermediates **2** and **3** bearing 1 and 2 thiophene rings in molecules, respectively, and pyrene-1-boronic acid. They were obtained in reasonable yields as orange and red solids, respectively. On the other hand, target molecules **CT1CP** and **CT2CP** were synthesized in different manners. Ullmann coupling reaction between intermediate **5** and arylbromides **2** and **3** in the present of CuI as catalyst, (±)-*trans*-1,2-diaminocyclohexane as co-catalyst and K_3PO_4 as base in toluene at reflux. They were obtained in moderate yields as yellow and red-orange solids, respectively.

The chemical structures of **CTnP** and **CTnCP, n = 1-2** were confirmed NMR technique. The ^1H-NMR spectra in $CDCl_3$ revealed the H_8 proton of coumarin ring as singlet peak at of 6.6 ppm and H_3 proton of pyrene ring as doublet peak at chemical shift around 8.3-8.6 ppm. The H_4 and H_5 protons of carbazole ring appeared as singlet peak at chemical shift of 8.4 ppm. The $–CH_3$ and $–CH_2–$ protons of the diethylaminos were observed as triplet peak at chemical shift of 1.2 ppm and quartet peak at chemical shift of 3.4 ppm, respectively. These materials are well soluble in most organic solvents. This should allow a high quality thin film to be prepared by simple solution casting process.



Scheme 1 Synthetic route to of **CTnP** and **CTnCP, n = 1-2**

The UV-Vis absorption spectra of the **CT1P** and **CT2P** having pyrene terminus showed the same observable single absorption peak at 447and 464 nm, respectively (Figure 1 and Table 1). It is assigned to the π-π^* transition of the entire coumarin-pyrene conjugated backbone. While **CT1CP** and **CT2CP** having carbazole-pyrene terminus exhibited the same two observable absorption peaks. Absorption band at 346 nm corresponds to the π-π^* transition of the carbazole-pyrene moiety and absorption band at longer wavelength around 436-453 nm corresponds to the π-π^* transition of the entire coumarin-carbazole-pyrene conjugated backbone.

The PL spectra of **CTnP** and **CTnCP, n = 1-2** with excitation at absorption wavelength of the conjugated backbone (435-460 nm) showed observable single bands at 521, 509, 533 and 527 nm, respectively as show in Figure 1 and summarized in Table 1. When **CT1CP** and **CT2CP** were excited the absorption wavelength of carbazole-pyrene moiety (346 nm) the identical single emission peak was observed at 533 and 527 nm, respectively. This indicates that there is an efficient electron transfer from higher energy carbazole-pyrene to lower energy coumarin-thiophene resulting in the emission of such moiety.

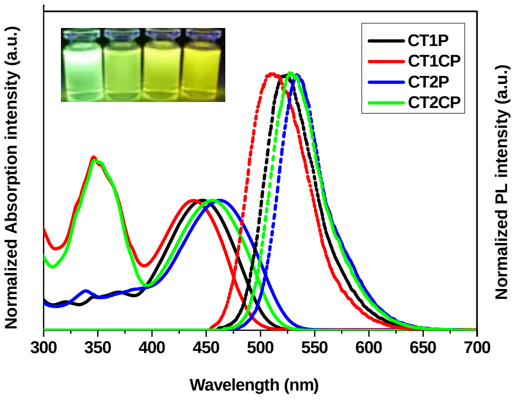


Figure 1 UV-Vis absorption and photoluminescence (PL) spectra of **CTnP** and **CTnCP, n = 1-2** measured in dilute CH_2Cl_2 solution.

Table 1 Optical properties, electrochemical data and molecular energy levels of **CTnP** and **CTnCP, n = 1-2**

Comp.	E_g (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]	λ_{abs} (nm)[d]	λ_{em} (nm)[d]	E_{ox} (V)[f]	E_{red} (V)[f]	CIE (x, y)
CT1P	2.46	-5.19	-2.73	472	632	0.88, 1.10	-1.74	0.235, 0.580
CT1CP	2.53	-5.19	-2.66	452	602	0.87, 0.98	-1.74	0.194, 0.550
CT2P	2.35	-5.11	-2.76	508	654	0.76, 1.06	-1.70	0.299, 0.617
CT2CP	2.41	-5.12	-2.71	493	641	0.79, 0.89	-1.68	0.274, 0.616

[a] Estimated from the onset of absorption ($E_g = 1240/\lambda_{onset}$).

[b] Calculated using the empirical equation: HOMO = -4:44 + E^{ox}_{onset}.

[c] Calculated from LUMO = HOMO - E_g.

[d] Measured in dilute CH_2Cl_2 solution.

[e] Excited at the absorption maxima.

[f] Measured using a glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and SCE as a reference electrode in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte.

The optical properties of these materials were tuned by the number of thiophene rings and type of terminus groups in the molecules. A red shift of absorption and emission spectra are observed when either number of thiophene unit increase or pyrene terminus is used. Increasing number of thiophene unit in molecule increases the π-conjugation length of the molecule. Pyrene substituent can adopt more planar conformation to the coumarin plan than the carbazole-pyrene substituent as observed in the optimized molecular geometry (Figure 2). The carbazole-pyrene plan twists nearly perpendicular to the coumarin plan due to sterric hindrance. Therefore, **CTnPs** will hold longer π-conjugation length than that of the corresponding **CTnCPs**. Although, it has been reported that electron from carbazole can delocalize over the carbazole ring and its connective ring through the lone pair electron of the N-atom, even they have a perpendicular conformation (Promarak *et. al.* 2007). These materials show strong fluorescence emission. Their emission colors are varying from green to yellow. Their energy gaps (E_g) calculated from the absorption edge range from 2.41 to 2.53 eV (Table 1).

The electronic configurations were further examined by theoretical models implanted in Gaussian 03 program. Their molecular geometries were optimized by using B3LYP/6-31G* basis set. The orbitals of both ground and excited states were computer calculated by time-dependent density functional theory (TDDFT) with B3LYP functional. The electron density of the HOMO of **CTnP** is delocalized over the entire coumarin-pyrene backbone, while that of **CTnCP** is mainly on the carbazole-pyrene moiety. This indicates that there is a strong electron conjugation (interaction) between coumarin unit and pyrene unit in **CTnP** than that in **CTnCP** as observed in the optical spectra. The electron density of the LUMO is localized on the coumarin ring due the presence of the electron acceptor carbonyl group (Figure 2).

CV curves of **CTnP** and **CTnCP, n = 1-2** showed one irreversible reduction and two oxidations. The former corresponds to a reduction of a carbonyl group of the coumarin ring. The reduction potentials are around 50 mV increase when number thiophene increase, but slight increase when change from pyrene to carbazole-pyrene terminus (Figure 3). The first oxidation process can be attributed to the removal of electrons from the peripheral carbazole moiety and the other corresponds to the removal of electrons from the interior thiophene backbone. The first oxidations are around 80 mV increase when number thiophene increase, but slight increase when change from pyrene to carbazole-pyrene terminus. The HOMO and LUMO energy levels of these coumarin derivatives were determined using the onset positions of the oxidation and energy gap (E_g) and are summarized in Table 1. The determined HOMO levels are in the range of -5.11 to -5.19 eV, which match well with the work function of gold (Au) or indium tin oxide (ITO) electrodes, favoring injection and transport of holes.

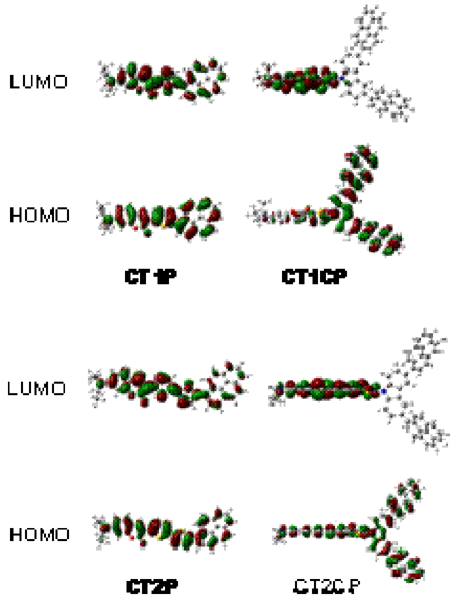


Figure 2 Computer calculated frontier orbitals of **CTnP** and **CTnCP, n = 1-2**

4. Conclusions

A series of new emissive materials based on N-coumarin derivatives were successfully synthesized using a combination of condensation, bromination, Suzuki and Ullmann coupling reactions. The conformation of the coumarin plan and the terminus plan plays an important role in tuning the optical and electronic properties of these materials. Their absorption and emission spectra are red shifted when either number of thiophene unit increase or pyrene terminus is used. These materials display strong fluorescence and should be promising light-emitting materials for OLED devices.

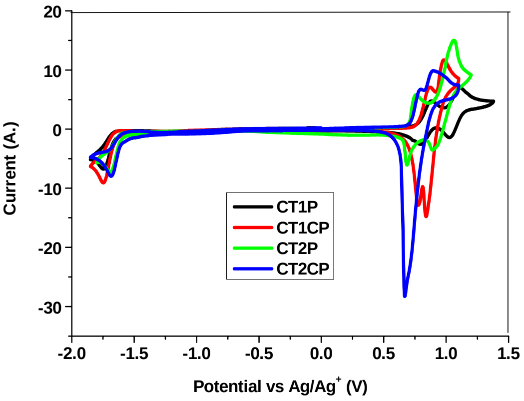


Figure 3 CV curves of **CTnP** and **CTnCP, n = 1-2** measured in CH_2Cl_2 solution with n-Bu_4NPF_6 as supporting electrolytes at scan rate of 50 mV/s

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