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ARTICLE TYPE

Synthesis and Characterization of Heteroatom Substituted Carbazole Derivatives: Potential Host Materials for Phosphorescent Organic Light-emitting Diodes

Jian Sun, Hong-ji Jiang [*a], Jin-long Zhang, Ye Tao, and Run-feng Chen

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A series of novel heteroatom substituted carbazole derivatives based on 9-ethyl-carbazole, diphenylamine, carbazole, phenoxazine, phenothiazine, and phenothiazine-S,S-dioxide units were successfully developed, and a comparative study on their thermal and photoelectrical properties were investigated by differential scanning calorimetric measurement, thermogravimetric analysis, UV-vis absorption, photoluminescent spectra, cyclic voltammetry, and phosphorescent spectra. All the synthesized compounds were found to have high thermal decomposition temperature in the range of 304-344 ^{o}C (except for C-SO, 145 ^{o}C) and showed a remarkable improvement when compared with 9-ethyl-carbazole (180 ^{o}C). The emission properties can be effectively tuned by systematically changing the substituent units. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital(LUMO), and triplet energy (E_T) of the synthesized compounds were determined both theoretically by quantum chemical calculations and experimentally by examination. Their energy levels can also be tuned by the change of the moieties connected to the 3-position through C-N coupling reaction. The experimental values of ionization potentials range from 5.37 to 5.46 eV. Some of these compounds exhibit high E_T, and C-SO achieves the highest E_T value of 2.79 eV, which exhibits a marked improvement than that of 4,4'-bis(9-carbazolyl)-biphenyl (2.6 eV). Green phosphorescent devices using tris (2-phenylpyridine) iridium as guest and C-O as host show excellent performances. Remarkably, one device hosted by C-O exhibits the best performance with a maximum luminance of 10270 cd m^{-2}, a maximum current efficiency of 34.8 cd A^{-1}, a maximum power efficiency of 26.0 lmW^{-1}. The results illustrate that the introduction of heteroatoms into carbazole can result in significant change in their optoelectronic characteristics. The low LUMO, high HOMO, suitable E_T and thermal stability of the carbazole derivatives endow them with potential as green, red, and even blue host materials for phosphorescent organic light-emitting diodes.

1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have recently attracted considerable attention mainly because it is possible to increase the internal quantum efficiency of the devices up to 100% as a result of their harvesting of both singlet and triplet excitons. [1] Generally, in order to suppress concentration quenching, a phosphorescent emitter is dispersed in a suitable host material to obtain a high photoluminescent (PL) quantum yield. Good host materials used in PHOLEDs commonly have the following properties: (1) a triplet energy(E_T) larger than that of the phosphorescent guest, which facilitates an efficient energy transfer from the host to the guest and prevents reverse energy transfer from the guest back to the host; (2) appropriate values of highest occupied molecular orbital (HOMO) energy and lowest occupied molecular orbital (LUMO) energy to facilitate charge injection from adjacent hole-transporting and electron-transporting layers, which is also the key to balance the transporting of holes and electrons; (3) high glass transition temperatures (T_g) and thermal decomposition temperatures (T_d) confer better device endurance.

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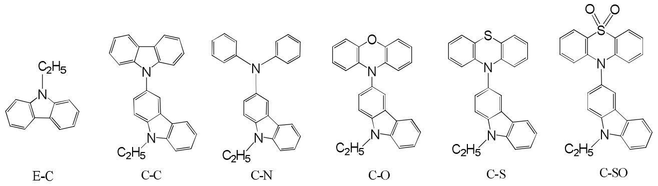
Among host materials, carbazole-based materials have received special attention for their sufficient E_T (up to 3.05 eV) and excellent hole-transporting properties, well-positioned HOMO[2-9].The most commonly used host material of carbazole derivatives in organic light-emitting diodes(OLEDs) is 4,4'-bis(9-carbazolyl)-biphenyl, which is used along with the iridium(III) bis[[4,6-difluorophenyl] pyridinato-N,C2] picolinate to fabricate blue PHOLEDs with high quantum efficiency.[10] So far, many host materials, such as carbazole derivatives containing diarylamine units,[11] phenylsilane[12,13] and phosphine oxide moieties,[14,15] heterofluorenes,[16] and heterocyclic cores,[17-22] carbazole-based conjugated dendrimer units,[23] and noncoplanar units,[24] with high T_g values have been reported, where the carbazoles were substituted on the 2,7-position, 1,8-position, 3,6-position or N-position, respectively.

Recently, phenoxazine and phenothiazine derivatives were synthesized in an attempt to modify the HOMO/LUMO energy level and further improve the device performance [25-26]. The meterials containing phenothiazine and phenoxazine have been mainly developed as p-type or ambipolar materials that can transport hole and/or electron in OLEDs. Especially, the materials, which were incorporated with heterocyclics and heteroatoms to break points of π-conjugation, have attracted more attention. The chemical modification of the heterocyclic could induce new desired properties to the material. These attractive features can promise tremendous opportunities as a host material in PHOLEDs. However, there is still room for improvement, as these host materials still present issues related to large band gaps, unbalanced charge transporting, and low device power efficiency.



Scheme 1. The chemical structure of heteroatom substituted carbazole derivatives E-C, C-C, C-N, C-O, C-S and C-SO

Therefore, in an attempt to address the above problems, we reported in this work the synthesis of six types of heteroatom substituted carbazole derivatives, which were modified with carbazole (C-C), biphenylamine (C-N), phenoxazine (C-O), phenothiazine (C-S), and phenothiazine-S,S-dioxide (C-SO) moieties on the 3-positions of 9-ethyl-carbazole(E-C) (Scheme 1). We also address the effects of different units on the energies of the frontier molecular orbitals, thermal stability and T_1 of these carbazole-based derivatives, one phosphorescent device hosted by C-O exhibits the excellent performance.

2. Experimental Section

2.1 Materials and measurements

Materials purchased from commercial suppliers were used without further purification. The common solvents were purified according to their standard methods.

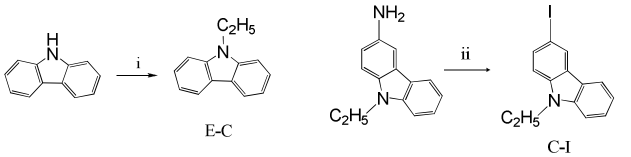
Both ^1H NMR and ^{13}C NMR spectra were measured on a Varian Mercury Plus 400 spectrometer with $CDCl_3$ as solvent and tetramethylsilane as internal reference. Chemical shifts were reported in ppm relative to $CDCl_3$ as internal standard, which was set to be 7.26 ppm, and coupling constant (J) was expressed in hertz. The signals have been designed as follows: s (singlet), d (doublet), t (triplet), m (multiplets). Matrix assistant laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrometry was performed on a Buker Daltonics flex Analysis. Elemental analysis of carbon, hydrogen and nitrogen was obtained on Elementar Vario MICRO elemental analyzer. UV-Vis absorption spectra were recorded on an UV-3600 SHIMADZU UV-Vis-NIR spectrophotometer. PL spectra were recorded on a RF-5301PC spectro fluorophotometer with a xenon lamp as a light source. The concentration of these compounds solution (in $CHCl_3$) was adjusted to be about 0.01 mg/mL or less. The thin solid films were prepared by spin-coating on quartz substrates from solution in $CDCl_3$ at a spin rate of 3500 rpm. The phosphorescence spectra of the compounds were measured using an Edinburgh LFS920 fluorescence spectrophotometer at 77 K, with a 5 ms delay time between the excitation with a microsecond flash lamp. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer Diamond DSC at a heating rate of $10^0C\ min^{-1}$ from room temperature to 500 ºC under nitrogen. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 ºC min^{-1}. Cyclic voltammetric measurements were carried out on the Chi660e system in a conventional typical three-electrode cell with a Pt work electrode (glass carbon), a platinum-wire counter electrode and a Ag/Ag^+ reference electrode (referenced against ferrocene/ferrocenium (FOC)) in a acetonitrile solution of Bu_4NPF_6 (0.10 M) at a sweeping rate of 100 mV/s. The HOMO and LUMO were measured by CV and calculated according to the formula: HOMO=$-E_{oxi}+0.0042 - 4.8$, LUMO=$-E_{red}-0.061 - 4.8$, where the 0.0042 and -0.061 are the E_{oxi} and E_{red} of FOC respectively. E_{oxi} , E_{red} are the values of compounds.

2.2 Synthesis

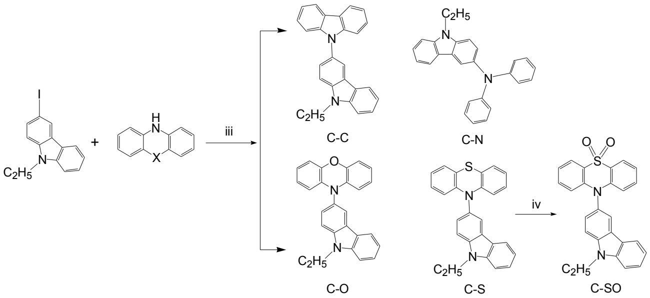
9-Ethyl-carbazole (E-C). E-C was synthesized through the N-H alkylation reaction[27] as shown in Scheme 2. Carbazole (0.21 g, 1.25 mmol), bromoethane (0.54 g, 5.02 mmol), NaOH (aq, 12.5 mol/L, 5 ml, 62.5 mmol) and catalytic amount of tetrabutyl ammonium bromide (0.05 g, 0.14 mmol) was charged in a flask. The flask was heated at 70 ºC continuously for 8 h. After the completion of the reaction monitored by thin-layer chromatography, the reaction mixture was cooled to room temperature, and extracted with dichoromethane. The organic layer was washed with water and dried over anhydrous sodium sulfate (Na_2SO_4). The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with petroleum ether/ dichloromethane (2:1) as eluent. The recovered yield of the solid was 0.20 g (83%). ^1H NMR (400MHz, $CDCl_3$, ppm):δ 8.15 (d, J=8.0 Hz, 2H), 7.52 (t, J=15.2 Hz, 2H), 7.44 (d, J=8 Hz, 2H) ,7.28 (t, J=14.8 Hz, 2H), 4.43-4.37 (m, 2H, $-\underline{CH_2}CH_3$), 1.47 (t, J=14.4 Hz, 3H, $-CH_2\underline{CH_3}$). ^{13}CNMR (100MHz, $CDCl_3$, ppm) :δ 139.96, 125.62, 122.95, 120.44, 118.76, 108.44, 37.52, 13.82. MALDI-TOF, m/z cacld for $C_{14}H_{13}N$, 196.0; Found: 196.7. Elemental analysis: calcd (%) for

$C_{14}H_{13}N$: C 86.12, H 6.71, N 7.17; Found: C 86.04, H 6.58, N 7.12.

3-Iodo-9ethyl-carbazole (C-I). C-I was synthesized through Sandmeyer reaction[28] as shown in Scheme 2. A solution of 3-amine-9-ethyl-carbazole (10.68 g, 50.8 mmol) and concentrated HCl (37.2 mL) in water (42.8 mL) was cooled to 0 ºC. Next, 5.32 g (77.12 mmol) of $NaNO_2$ in 26.8 mL of water was added dropwise to the diamine solution over a period of 30 min, keeping the temperature at 0 ^{0}C. After the addition of $NaNO_2$ was completed, the resulting mixture was stirred for an additional 30 min, and an aqueous solution of KI (12.48 mol/L, 100 ml, 1.25 mol) was added dropwise over 30 min at -5 ºC. The reaction mixture was then stirred for 1 h at room temperature and 3 h at 60 ºC, giving a dark brown solution. The solution was then cooled to 25 ^{0}C and the brown precipitate was collected by filtration. The crude brown solid was then purified by column chromatography (petroleum ether/ dichloromethane=6:1) yielding the title compound as a white solid in a yield of 4.56 g (28 %). ^{1}HNMR (400MHz, $CDCl_3$, ppm): δ8.41 (s, 1H, Ar), 8.03 (d, J=8 Hz,1H, Ar), 7.72-7.70 (m, 1H, Ar), 7.50 (t, J=15.6 Hz, 1H, Ar), 7.39 (d, J=4 Hz,1H, Ar), 7.26 (t, J=14.8 Hz, 1H, Ar), 7.17 (d, J=8.4 Hz, 1H, Ar), 4.34-4.29 (m, 2H, $-\underline{CH_2}CH_3$), 1.41 (t, J=14.4 Hz, 3H, $-CH_2\underline{CH_3}$). ^{13}CNMR (100MHz, $CDCl_3$, ppm): 139.93, 139.06,133.81, 129.27, 126.37, 125.63, 125.49, 121.69, 120.61, 119.33, 110.53, 108.66, 37.62, 13.76. MALDI-TOF, m/z cacld for $C_{14}H_{12}IN$, 322.0; found, 323.7.



Scheme 2. Synthesis of compounds E-C, C-I. i: Tetrabutyl ammonium bromide, NaOH(aq). ii: $NaNO_2$, HCl, KI.



Scheme 3. Synthesis of compound C-C, C-N, C-O, C-S and C-SO. iii: K_2CO_3, Cu, $PhNO_3$, reflux, 190 ºC, 24h. iv: CH_3COOH, H_2O_2, 5h.

General Procedure. The new carbazole derivative C-C, C-N, C-O and C-S were synthesized by substituting the C-I on the 3-position through Ullmann C-N coupling reaction[29] (Scheme 3) with different units. Take the synthesis of C-O as an example: C-I (2.00 g, 6.2 mmol), phenoxazine (1.32 g, 7.2 mmol), copper powder (0.09 g, 1.41 mmol), anhydrous potassium carbonate (1.74 g, 12.59) and nitrobenzene (44.5 mL) were placed into a round-bottom flask. The mixture was refluxed for 24 h under argon. After evaporation of the solvent in vacuo, distilled water was added into and the reaction mixture was extracted with dichoromethane. The combined organic layers were collected, dried over anhydrous Na_2SO_4, filtered and evaporated to remove the solvent. The resulted crude product was chromatographed on a silica gel column with petroleum ether/dichloromethane (6:1) as eluent. Recrystallize several times from ethanol or hexane to afford the pure solid compounds in a yield of 1.64 g (70 %).

9-Ethyl-9H-3,9'-bicarbazole (C-C). C-C was prepared according to the general procedure. C-I (0.53 g, 1.64 mmol), carbazole (0.63 g, 3.79 mmol), copper powder (0.05 g, 0.78 mmol), anhydrous potassium carbonate (0.91 g, 6.61 mmol). The resulting solid product was purified by column chromatography with petroleum ether/ dichloromethane (6:1) as eluent. Yield: 0.51 g (85%). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 8.35-8.26 (m, 3H, Ar), 8.12 (d,J=8 Hz, 1H, Ar), 7.67-7.47 (m, 8H, Ar), 7.39-7.30 (m, 3H, Ar), 4.51-4.46 (m, 2H, $-\underline{CH_2}CH_3$), 1.59-1.55 (t, J=14.4 Hz, 3H, $-CH_2\underline{CH_3}$). ^{13}CNMR (100MHz, $CDCl_3$, ppm): δ142.13, 140.69, 139.18, 128.92, 126.45, 125.94, 125.33, 123.96, 123.19, 122.67, 120.79, 120.36, 119.76, 119.65, 119.38, 109.98, 109.51, 108.93, 37.87, 14.01. MALDI-TOF, m/z cacld for $C_{26}H_{20}N_2$ 361.1; found, 361.6. Elemental analysis: calcd (%) for $C_{26}H_{20}N_2$: C 86.64, H 5.59, N 7.77; found C 86.53, H 5.66, N 7.69.

9-Ethyl-N,N-diphenyl-9H-carbazol-3-amine (C-N). C-N was prepared according to the general procedure. C-I (0.50 g, 1.56 mmol), diphenylamine (0.31 g, 1.81 mmol), copper powder (0.02 g, 0.31 mmol), anhydrous potassium carbonate (0.44g, 3.18 mmol). The resulting solid product was purified by column chromatography with petroleum ether/ dichloromethane (5:1) as eluent in a yield of 0.45 g (80%). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 8.02 (d, J=8 Hz, 1H, Ar), 7.93 (d, J=1.6 Hz, 1H, Ar), 7.58 (t, J=18 Hz, 2H, Ar), 7.41 (t, J=15.6 Hz, 1H, Ar), 7.21 (t, J=15.6 Hz, 5H, Ar), 7.10 (t, J=15.2 Hz, 1H, Ar), 6.97-6.89 (m, 6H, Ar), 4.43-4.38 (m, 2H, $-\underline{CH_2}CH_3$), 1.31 (t, J=14 Hz, 3H, $-CH_2\underline{CH_3}$). ^{13}CNMR (100 MHz, $CDCl_3$, ppm): δ148.66, 140.52, 139.07, 137.52, 129.69, 126.43, 126.16, 123.70, 122.35, 121.92, 121.12, 119.50, 119.16, 110.81, 109.63, 37.53, 14.25. MALDI-TOF, m/z cacld for $C_{26}H_{22}N_{2,}$ 363.1; found, 362.2. Elemental analysis: calcd (%) for $C_{26}H_{22}N_2$: C 86.15, H 6.12, N 7.73; found C 86.62, H 5.59, N 7.58.

10-(9-Ethyl-9H-carbazol-3-yl)-10H-phenoxazine (C-O). C-O was prepared according to the general procedure. C-I (0.50 g, 1.55 mmol), phenoxazine (1.32 g, 1.8 mmol), copper powder (0.02 g, 0.34 mmol), anhydrous potassium carbonate (0.43 g, 3.14 mmol). The resulting solid product was purified by column chromatography with petroleum ether/ dichloromethane (6:1) as eluent in a yield of 0.41 g (70%). ^{1}H NMR (400MHz, $CDCl_3$, ppm):δ 8.05 (d, J=8 Hz, 2H, Ar),7.60 (d, J=8.8 Hz, 1H, Ar), 7.55-7.47 (m, 2H, Ar), 7.41-7.38 (m, 1H, Ar), 7.29-7.25 (m, 1H, Ar), 6.72-6.54 (m, 6H, Ar), 5.95 (d, J=7.6 Hz, 2H, Ar), 4.47-4.42 (m, 2H, $-\underline{CH_2}CH_3$), 1.52 (t,J=8.0 Hz, 3H, $-CH_2\underline{CH_3}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.05, 140.47, 139.36, 135.36, 129.85, 127.77, 126.38, 124.89, 123.23, 122.79, 122.56, 121.01, 120.72, 119.39, 115.25, 113.51, 110.76, 108.86, 37.83, 13.93. MALDI-TOF, m/z cacld for $C_{26}H_{20}N_20$, 377.1; found, 376.5. Elemental analysis: calcd (%) for $C_{26}H_{20}N_2O$: C 82.95, H 5.35, N 7.44; found C 83.01, H 5.38, N 7.45.

10-(9-Ethyl-9H-carbazol-3-yl)-10H-phenothiazine (C-S). C-S was prepared according to the general procedure. C-I (2.00 g, 6.23 mmol), phenothiazine (1.44 g, 7.22 mmol), copper powder (0.09 g, 1.41 mmol), anhydrous potassium carbonate (1.74 g, 12.59 mmol). The resulting solid product was purified by column chromatography with petroleum ether/ dichloromethane (7:1) as eluent in a yield of 1.59 g (65%). ^{1}HNMR (400MHz, $CDCl_3$, ppm): δ 8.14 (d, J=1.6 Hz, 1H, Ar), 8.07 (d, J=8 Hz, 1H, Ar), 7.62 (d, J=8.4 Hz, 1H, Ar), 7.54-7.46 (m, 3H, Ar), 7.27 (t, J=13.6 Hz, 1H, Ar), 7.03-7.01 (m, 2H, Ar), 6.80 (t, J=7.2 Hz, 4H, Ar), 6.25-6.23 (m, 2H, Ar), 4.49-4.43 (m, 2H, $-\underline{CH_2}CH_3$), 1.54 (t,J=14.4 Hz, 3H, $-CH_2\underline{CH_3}$). ^{13}CNMR (100MHz, $CDCl_3$, ppm): δ145.12, 140.51, 139.26, 131.81, 128.46, 126.80, 126.52, 126.38, 124.70, 123.18, 122.65, 122.14, 120.74, 119.47, 119.39, 115.90, 110.35, 108.87, 37.86, 13.96. MALDI-TOF,m/z cacld for $C_{26}H_{20}N_2S$, 393.0; found, 394.1. Elemental analysis: calcd (%) for $C_{26}H_{20}N_2S$: C 79.56, H 5.14, N 7.14; found C 79.61, H 5.15, N 7.09.

10-(9-Ethyl-9H-carbazol-3-yl)-10H-phenothiazine-S,S-dioxide (C-SO). C-SO was obtained from the oxidation of C-S in the presence of hydrogen peroxide. C-S (0.4 g, 1.0 mmol) was dissolved in acetic acid (8.1 mL) and hydrogen peroxide (2.4 mL) was carefully added and the solution was refluxed for 5 h at 130 ºC. A further 1.6mL of hydrogen peroxide was added and the solution was refluxed over night. After cooling, water was added and the resultant solid was filtered and washed with water. The solid was dissolved in dichloromethane and washed with brine, dried ($MgSO_4$), filtered and concentrated. The resulting solid product was purified by column chromatography with petroleum ether/ dichloromethane (2:1) as eluent to give the targeted solid compound C-SO in a yield of 0.37 g (86%). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 8.19 (d, J=8 Hz, 2H, Ar), 8.10 (d, J=2 Hz, 1H, Ar), 8.05 (d, J=8 Hz, 1H, Ar), 7.67 (d, J= 8.41 Hz,1H, Ar), 7.59-7.51 (m, 2H, Ar), 7.42-7.21 (m, 6H, Ar), 6.70 (d, J=8.4 Hz, 2H, Ar), 4.53-4.47 (m, 2H, $-\underline{CH_2}CH_3$), 1.56 (t, J=14.4 Hz, 3H, $-CH_2\underline{CH_3}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ141.60, 140.68, 139.74, 132.66, 129.79, 127.04, 126.90, 124.84, 123.27, 122.45, 122.33, 122.31, 121.82, 120.83, 119.78, 117.68, 110.74, 109.08, 37.96, 13.95. MALDI-TOF, m/z cacld for $C_{26}H_{20}N_2O_2S$, 425.1; found 425.9. Elemental analysis: calcd (%) for $C_{26}H_{20}N_2O_2S$: C 73.56, H 4.75, N 6.60; found C 73.69, H 4.72, N 6.51.

2.3 Device fabrication and measurement

The hole injection material MoO_3, hole transporting material 1,4-bis[(1-naphthylphenyl)amino]biphenyl(NPB), electron/exciton-blocking material 4,4',4''-tri(N-carbazolyl) triphenylamine (TCTA) and electron-transporting material 1,3,5-tris(Nphenylbenzimidazol-2-yl)benzene (TPBI) were commercially available. Commercial indium tin oxide (ITO) coated glass with sheet resistance of 10 Ω per square was used as the starting substrate. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by oxygen plasma for 2 min. Then the sample was transferred to the deposition system. MoO_3 (8 nm) was firstly deposited to ITO substrate, followed by NPB (50 nm), TCTA (5 nm), emissive layer, and TPBI (25 nm). Finally, a cathode composed of lithium fluoride (1 nm) and aluminium (100 nm) was sequentially deposited onto the substrate in the vacuum of 10^{-6} Torr. The L-V-J of the devices was measured with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The electroluminescent (EL) spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

3. Results and Discussion

The new compound C-C, C-N, C-O and C-S, which are based on E-C, were synthesized using an optimized Ullmann C-N cross-coupling reaction between the C-I and carbazole, diphenylamine, phenoxazine, phenothiazine. The optimized Ullmann reaction proceeded in refluxing nitrobenzene in the presence of copper bronze as catalyst and K_2CO_3 as base and produced the desired compounds in relative high yields. C-SO was obtained from the oxidation of C-S in the presence of hydrogen peroxide.

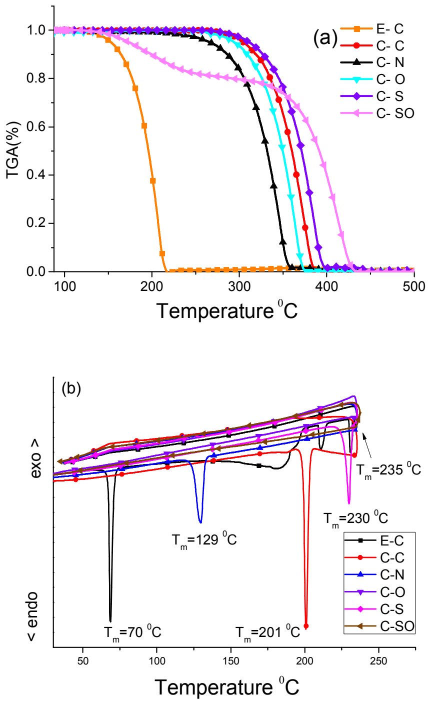


Figure 1. TGA (a), DSC (b) traces of compounds E-C, C-C, C-N, C-O, C-S and C-SO

All the target compounds were purified on a silica column and recrystallized to yield pure solid compounds. The chemical structures of the synthetic compounds were confirmed by ^{1}H NMR, ^{13}C NMR (supporting information), elemental analysis and MALDI-TOF-MS. All these compounds were readily soluble in common organic solvents such as chloroform, dichloromethane at room temperature. The thermal stabilities of the compounds were studied by DSC and TGA under a nitrogen atmosphere, and the details were summarized in Table 1 and Figure 1. All the synthesized compounds demonstrated high thermal stability. The DSC measurements revealed melting points (T_m) ranging from 129 to 235 °C for carbazole derivatives, which were higher than that of E-C (70 ^{0}C), and the T_m of C-O and C-S are 235 °C, 230 °C respectively, which are the highest of all. All the values of T_d confirmed by TGA with a heating rate of 20 °C /min were higher than 304 °C (except C-SO). The values of C-O and C-S are 318 °C, 344 °C respectively, and that of compound C-S is the highest of all. This shows that the incorporation of carbazole, diphenylamine, phenoxazine, phenothizine can significantly improve the T_d and T_m of E-C.

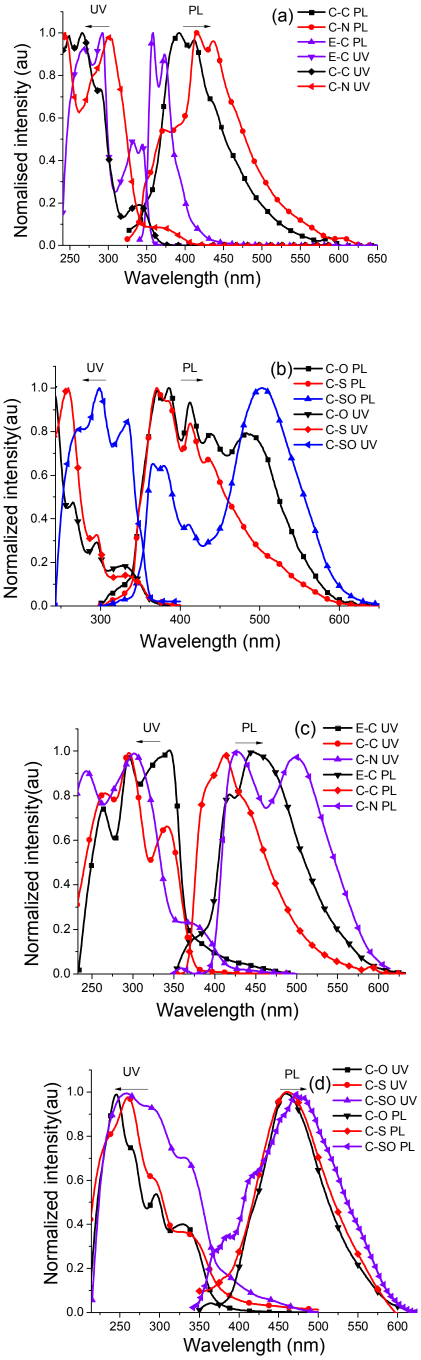


Figure 2. Normalized UV-vis and PL emission spectra of compounds E-C, C-C, C-N, C-O, C-S and C-SO in chloroform (a, b) and thin solid films (c, d)

Table 1. Absorption, PL emission spectra and thermal characteristics of compounds E-C, C-C, C-N, C-O, C-S and C-SO.

Compound	CHCl$_3$			thin solid film					
	λ_{abs}	λ_{em}	E_g[a]	λ_{abs}	λ_{em}	E_g[a]	T_d[b]	T_m[b]	η [c] （%）
E-C	292	358	3.47	345(295)	446	3.34	180	70	1.36
C-C	266	392	3.39	295	412	3.29	334	201	7.92
C-N	300	416	3.02	302	427(499)	3.00	304	129	2.2
C-O	265	370	3.40	245	458	3.34	318	235	1.25
C-S	259	371	3.41	260	460	3.27	344	230	2.16
C-SO	298	503	3.43	258	472	3.32	145	-	5.97

[a]Optical band gaps obtained from the absorption edge; [b] T_m and temperatures at which 5% loss of mass (T_d); [c] absolute PL quantum yields.

Table 2. Experimental and theoretical HOMO, LUMO, energy band gaps of the compounds (eV)

Compound	HOMO[a]	LUMO[a]	E_g[a]	E_T[b]	HOMO[c]	LUMO[c]	E_g[c]
E-C	-5.58	-2.34	3.24	2.61	-5.29	-0.60	4.70
C-C	-5.44	-1.89	3.55	2.70	-5.04	-0.87	4.17
C-N	-5.45	-1.99	3.46	2.49	-4.64	-0.58	4.06
C-O	-5.46	-1.84	3.62	2.57	-4.67	-0.68	2.76
C-S	-5.37	-1.86	3.51	2.34	-4.75	-0.68	2.79
C-SO	-5.38	-2.03	3.35	2.79	-5.42	-1.15	3.15

[a] Results obtained from the CV curves on spin-coated films; [b] Results obtained from phosphorescent spectra; [c] Results obtained from the theoretical calculations at B3LYP/6-31G*.

The optical properties of the derivatives in chloroform and in thin solid film were investigated and summarized in Table 1 and Figure 2. The first absorption band around 290 nm can be assigned to the carbazole-centered n-π* transition, and the other long wavelength absorption around 330-343 nm is attributed to the π-π* transition of the entire conjugated backbone. An absorption peak at around 245 nm and a shoulder at 265 nm can be attributed to π-π* and n-π* transitions of arylenes respectively, which belong to carbazole, diphenylamine, phenothizine, phenothizine, and phenothiazine-S, S-dioxide. The UV-vis absorption maxima in the solution state were 292, 266, 300, 265, 259, 298 nm for E-C, C-C, C-N, C-O, C-S and C-SO respectively, and 245, 295, 302, 245, 260, 258 nm for E-C, C-C, C-N, C-O, C-S and C-SO respectively, in the film state. The UV-vis spectra of these compounds displayed virtually slight changes on going from the solution to the film state, as a result of the dihedral angle between the carbazole and the hetrocyclics which can prevent the aggregation in the films. However, the absorption maxima and the position of absorption edges changed obviously. The optical energy band gaps (E_g) of the new compounds determined from the onset of the UV-vis spectra in solid film are in a range of 3.00-3.34eV. For the PL emission spectra, the emission maxima in the solution were 358, 392, 416, 370, 371, 503 nm for E-C, C-C, C-N, C-O, C-S and C-SO respectively, and 446, 412, 427, 458, 460, 472 nm for E-C, C-C, C-N, C-O, C-S and C-SO, respectively, in the film state. A bathochromic shift of the PL spectra is found when heteroatoms are introduced into the arylenes. The emission in the thin solid film was generally red-shifted about 50 nm as a result of the stronger intermolecular interactions in the solid state. For C-O, C-S, C-SO in the dilute $CHCl_3$ solutions, more PL peaks appear and the spectra are quite complicated, however, the three compounds have only one emission peak in the film state. It was interesting to notice that the absolute PL quantum efficiency of C-C and C-SO in thin solid film was relatively higher than that of compound E-C, C-N, C-O and C-S, and the potential mechanism is still unclear at this stage.

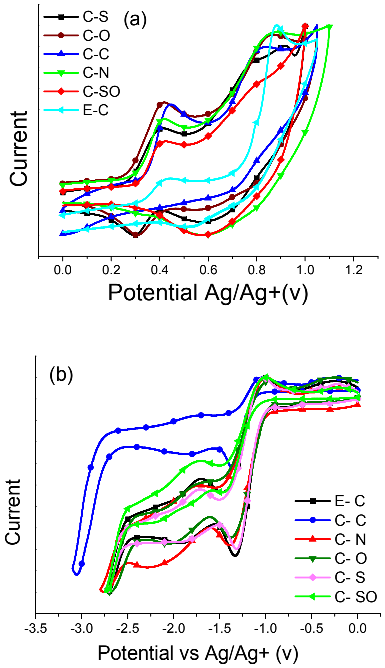


Figure 3. Oxidative CV (a) and reductive CV (b) curves of the compounds in the film state.

The electrochemical behaviors of synthesized compounds were investigated by cyclic voltammetry (CV), and the HOMO/LUMO values were determined. The electrochemical waves are showed in Figure 3. On the basis of these results, the HOMO and LUMO energy levels were calculated and summarized in Table 2. Carbazole derivatives have clearly localized frontier orbitals with HOMO predominately localized in heterocyclic moieties and LUMO in E-C moieties. The HOMO of carbazole derivatives have the close values ranging from -5.46 to -5.37 eV, which are higher than that of E-C (-5.58 eV), and C-S have the highest of all (-5.37 eV), showing that the units, especial hetetocyclics on the 3-position, can improve the HOMO and may enhance the hole transporting ability of these compounds. The LUMO values range from -2.03 to -1.89 eV, which have a strong improvement when compared with E-C (-2.34 eV), and target compounds C-O, C-S have the highest LUMO value. It is obvious that the incorporation of carbazole, diphenylamine, especially heterocyclic penoxazine, phenothizine can improve the HOMO/LUMO energy levels of the derivatives and may endow them with excellent hole transporting ability. The E_g estimated from the corresponding HOMO and LUMO has the similar values ranging from 3.35 to 3.62 eV. The HOMO and LUMO orbitals are shown in Table 3. As can be seen from the molecular orbital distribution of the compounds, the LUMO contour of the compounds are all localized on the carbazole units of E-C, while the HOMO contour of compound C-C, C-N, and C-S have covered the whole molecular framework, and the HOMO contour of compound C-O and C-SO are both localized on the phenoxazine and phenothiazine-S,S-dioxide units. There might exist obvious intramolecular charge transfer in compounds C-O and C-SO, and compounds C-O and C-SO might have potential applications as bipolar host materials in PHOLEDs. The variation tendency of band gaps obtained from DFT calculations for compounds E-C, C-C, C-N, C-O, C-S, C-SO is approximately consistent with those of obtained from experimental characterization.

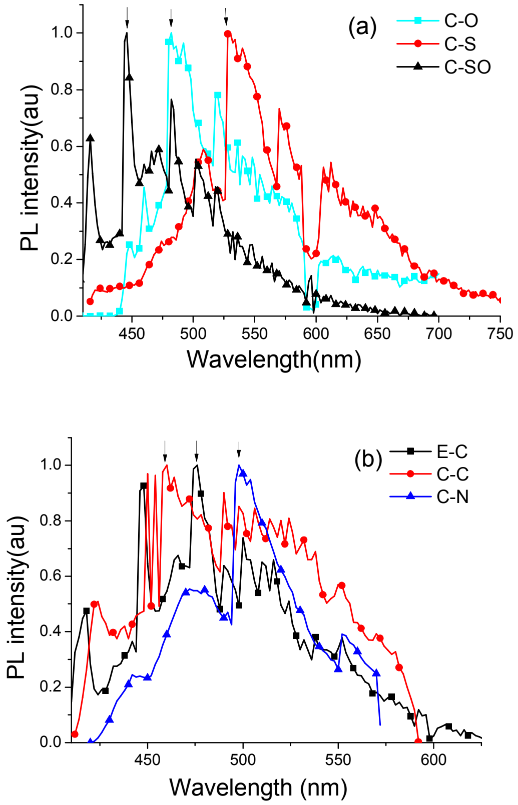
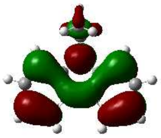
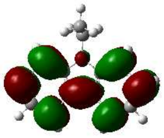
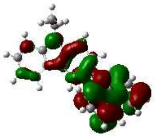
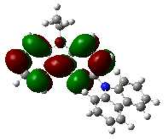
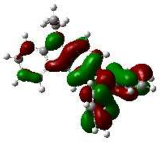
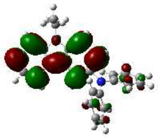
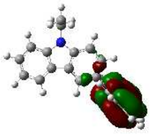
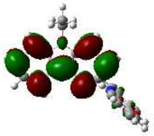
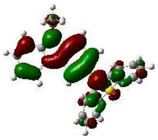
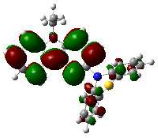
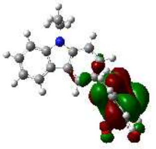
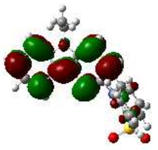


Figure 4. Normalized phosphorescent spectra of compounds E-C, C-C, C-N, C-O, C-S and C-SO at 77 K with 5 ms delay.

As shown in Figure 4, the phosphorescent spectra of synthesized compounds were detected at 77K with 5 ms delay. The E_T was determined by taking the highest energy peak of phosphorescence spectra as the transition energy of T_1-S_0. The carbazole derivatives showed high E_T (2.34-2.79 eV), and C-SO exhibited the highest value of all, which showed that the introduction of heterocyclics, especial phenothiazine-S,S-dioxide, could remarkably improve the E_T value. When the oxygen atom in phenoxazine group is changed into sulfur atom, the E_T value would have a clear decrease.

Table 3. The molecular orbital contours of HOMO and LUMO energy levels (b) of compounds E-C, C-C, C-N, C-O, C-S, C-SO from DFT calculations.

Compound	HOMO	LUMO
E-C		
C-C		
C-N		
C-O		
C-S		
C-SO		

However, when the phenothiazine is oxidized into phenothiazine-S,S-dioxide, the E_T shows an increase of about 0.45eV. This may be attributed to different sizes and inductive effects from different atoms. The phenomena indicate that these compounds with high E_T are promising host materials for green, red and even blue PHOLEDs. To evaluate the utility of these compounds as host materials for green phosphor tris (2-phenylpyridine) iridium(Ir(ppy)$_3$), we initially fabricated green devices A–C by using C-O as the host and Ir(ppy)$_3$ as the guest with the configuration of ITO/MoO$_3$ (8 nm)/NPB (50 nm)/TCTA (5 nm)/host C-O: Ir(ppy)$_3$ (10 nm)/TPBI (25 nm)/LiF (1 nm)/Al (100 nm).

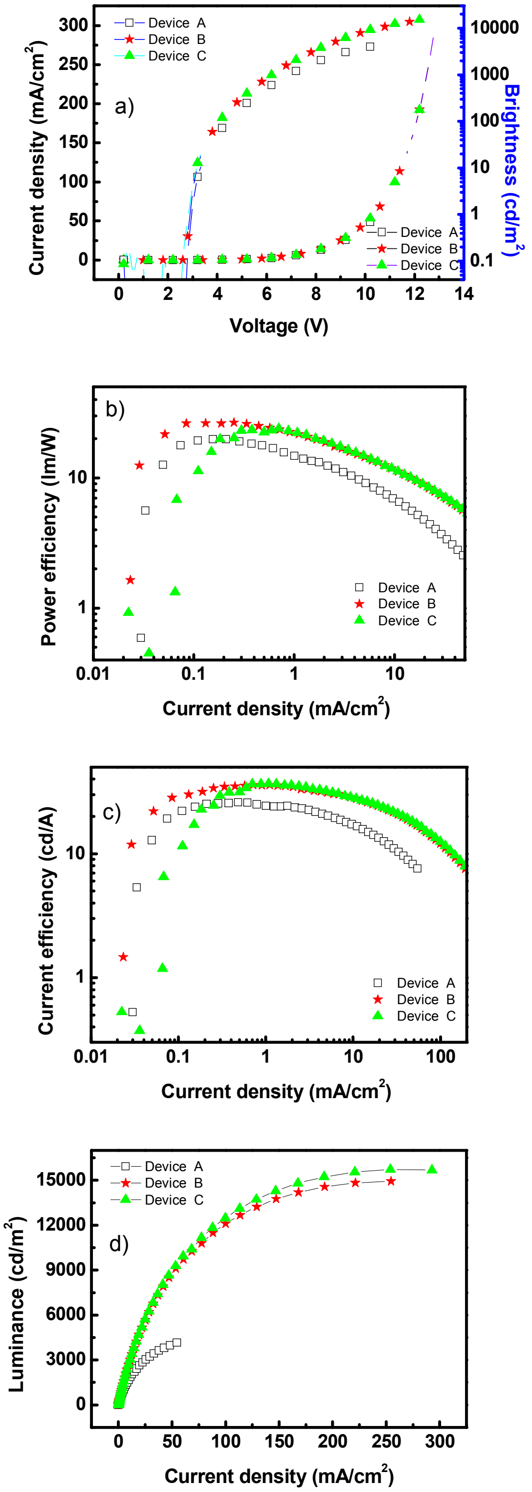


Figure 5. a) Current density-voltage-brightness characteristics for devices

A–C. b) Power efficiency versus current density for devices A–C. c) Current efficiency versus current density for devices A–C. d) luminance versus current density for devices A–C.

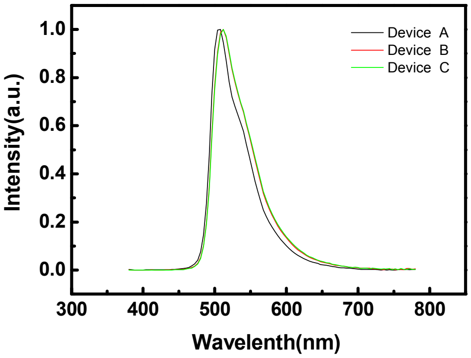


Figure 6. EL spectra of devices A–C

Table 4. Electroluminescence characteristics of the devices.[a]

Device	V^b/V	I^c/ mA cm^{-2}	$L_{max}{}^d$/cd m^{-2}	$\eta_{c.max}{}^e$/cd A^{-1}	$\eta_{p.max}{}^f$/lm W^{-1}
A	4.6	0.5	125	26.0	17.7
	7	5.2	1049	20.3	9.1
	10.4	54.7	4157	7.6	2.3
B	4.2	0.3	117	**34.8**	**26.0**
	6.2	3.0	998	33.3	16.9
	8.8	22.0	5162	23.4	8.4
	10.6	68.6	10270	15.0	4.4
C	4.2	0.4	119	31.3	23.4
	6.4	3.5	1151	33.4	16.4
	8.8	21.9	5195	23.7	8.5
	10.6	68.3	10406	15.2	4.5

[a] Device configuration: ITO/MoO_3 (8 nm)/NPB (50 nm)/TCTA (5 nm)/host C-O: $Ir(ppy)_3$ (10 nm)/TPBI (25 nm)/LiF (1 nm)/Al (100 nm). [b] Voltages. [c] Current density. [d] Maximum luminance. [e] Maximum current efficiency. [f] Maximum power efficiency.

NPB and TPBI were used as the hole-and electron transporting layers, respectively; TCTA was used as the electron/exciton-blocking layer; MoO_3 and LiF served as hole- and electron-injecting layers, respectively; $Ir(ppy)_3$ doped in host C-O was used as the emitting layer. Figure 5 shows the current density-voltage-brightness (J-V-L) characteristics, efficiency versus current density curves and Luminance versus current density curves for the devices. The electroluminescence (EL) data are summarized in Table 4. Device A with 5% $Ir(ppy)_3$ doped in host C-O achieves a maximum current efficiency ($\eta_{c.max}$) of 26.0 cd A^{-1}, and a maximum power efficiency ($\eta_{p.max}$) of 17.7 lm W^{-1}. In comparison, device C with 10% $Ir(ppy)_3$ doped in host C-O exhibits higher efficiencies with $\eta_{c.max}$ of 31.3 cd A^{-1}, and $\eta_{p.max}$ of 23.4 lm W^{-1}. Device B, with 8% $Ir(ppy)_3$ doped in host C-O, achieves the highest performance with a maximum luminance of 10270 cd m^{-2}, a maximum current efficiency ($\eta_{c.max}$) of 34.8 cd A^{-1}, and a maximum power efficiency ($\eta_{p.max}$) of 26.0 lm W^{-1}. It is worth noting that these devices show high efficiencies and low efficiency roll-off at high luminance. For example, when the brightness reaches 1000 cd m^{-2}, η_c still remains as high as 20.3 cd A^{-1} for device A, 33.3 cd A^{-1} for device B , and 33.4 cd A^{-1} for device C. EL spectra of devices A–C are shown in Figure 6. Devices A–C show the same main peak at 509 nm.

4. Conclusions

In conclusion, a series of derivatives obtained by substituting E-C with different units in the 3-position were synthesized through Ullmann C-N coupling reaction. Their energy levels including HOMO, LUMO and E_T can be effectively tuned by the choice of substituent moieties. Especilly the incorporation of heterocyclics can further optimize the HOMO/LUMO and E_T of these carbazole derivatives. The properties of carbazole derivatives were further validated by theoretical calculations. We have successfully fabricated highly efficient green electrophosphorescences by using C-O as host material, with a maximum luminance of 10270 cd m^{-2}, a maximum current efficiency ($\eta_{c.max}$) of 34.8 cd A^{-1}, and a maximum power efficiency ($\eta_{p.max}$) of 26.0 lm W^{-1}. New bipolar molecules capable of transporting both electrons and holes have been obtained while maintaining a desired energy gap for using as the host for both singlet and triplet emitters. These carbazole derivatives have potential as green, red, and even blue host materials for PHOLEDs. This can serve as an excellent exploratory example for fine band gap and optoelectronic control principle through the heteroatom replacement of carbazole derivatives.

Acknowledgements

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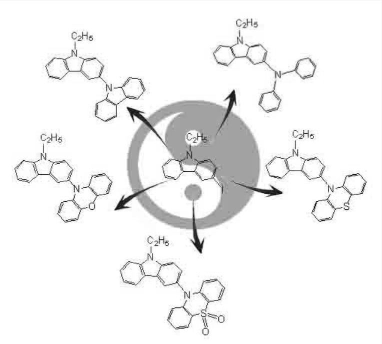
A series of carbazole derivatives based on 9-ethyl-carbazole substituted on the 3-position with different units were synthesized through Ullmann C-N coupling reaction. Their energy levels can be effectively tuned by the choice of suitable moieties. Especilly the incorporation of heterocyclics can further optimize the highest occupied molecular orbital / lowest unoccupied molecular orbital and triple energy levels of these carbazole derivatives. New bipolar molecules capable of transporting both electrons and holes have also been obtained while maintaining a desired energy gap for using as the host for both singlet and triplet emitters. One phosphorescent device hosted by C-O exhibits the excellent performance, and these carbazole derivatives have the potential as green, red, and even blue host materials for phosphorescent organic light-emitting diodes.



Synthesis and Characterization of Heteroatom Substituted Carbazole Derivatives: Potential Host Materials for Phosphorescent Organic Light-emitting Diodes.