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# Graphical abstract



# Synthesis and Optical Characterization of Novel Carbazole Schiff Bases

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Abstract: In this study, newly substituted carbazole derivatives of S1; (Z)-4-((9-isobutyl-9H-carbazol-3ylimino)methyl)phenol, S2; (Z)-9-butyl- N-(2,3,4-trimethoxybenzylidine)-9H-carbazol-3-amine, S3; (Z)-4-((9-octyl-9Hcarbazol-3-ylimino)methyl)benzene-1,2-diol and S4; (Z)-3-((9-octyl-9H-carbazol-3-ylimino)methyl)benzene-1,2-diol compounds are synthesized by using condensation reaction between carbazole amines and aromatic aldehydes. All synthesized carbazole Schiff bases are purified by crystallizing from chloroform. The structural and optical characterizations of synthesized compounds are investigated by FT-IR (Fourier Transform-Infrared Spectroscopy), <sup>1</sup>H-NMR (Proton Nuclear Magnetic Resonance), <sup>13</sup>C-NMR (Carbon Nuclear Magnetic Resonance), LC-MS (Liquid Chromatography-Mass Spectrometry) and temperature dependent PL (Photoluminescence) measurements. The formations of synthesized Schiff bases were confirmed by FT-IR, NMR and microanalysis. Due to stronger  $\pi$ -conjugation and efficient charge transfer from host material, the broad and complex bands centered at about ~2.16 and ~1.76 eV are observed in PL spectra for all samples. Their relative intensities depend on functional groups associated with the carbazole. These newly synthesized Schiff bases could be considered as an active emissive layer for organic light emitting diodes.

Keywords: Carbazole, Carbazole Schiff Base, Synthesis, Optical Characterization, Photoluminescence, OLED.

# **1. INTRODUCTION**

Carbazoles and its derivatives have been received a great deal of interest due to their specific optical and electrochemical properties, which could potentially be explored to some device applications, such as organic lightemitting diodes (OLEDs) [1], organic photovoltaic devices (OPVs) [2], organic field-effect transistors (OFETs) [3], as wells as fundamental points of view [4,5]. Since the carbazole derivatives have high triplet energy and efficient energy transfer processes from hosts to doped triplet emitters, they can be used as host materials in highly efficient blue, green, or red electro-phosphorescent devices [6-10]. Numerous ways of functionalization of carbazoles or covalently linking to other molecules such as 3,6- or 2,7linking of carbazole molecules into dimers, trimers or oligomers [11,12], addition of enamine [13], and others [14-18] are reported for the enhancement of their conjugated  $\pi$ electron system and hence for the efficient light emitter.

Polycarbazoles and their nanocomposite films (polycarbazole/nanoZn and polycarbazole/nanoclayfilms) show protection of anodic corrosion on modified electrodes to form metal conserved region [19].

Carbazole Schiff bases demonstrate that they have superior fluorescence emission and also their  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  complexes show extra fluorescence emission [20-23].

For the synthesis of carbazole Schiff bases, a solvent free method were used and showed luminescence properties [24].

In current work, since Schiff bases containing carbazolyl groups are expected to have stronger conjugated system, higher intramolecular electron transfer efficiency and more stable structure than the general Schiff bases, four novel carbazole based Schiff bases referred as S1, S2, S3 and S4 were synthesized by condensation reaction between carbazole amines and aromatic aldehydes, and characterized by FT-IR, NMR, LC-MS, elemental analysis and temperature dependent PL spectroscopy.

# 2. MATERIALS AND METHODS

# 2.1. General

In this study, all starting materials were purchased from Merck, Sigma-Aldrich and Fluka Co., and used after further analytical purifications of solvents and chemical materials. A silica gel with column chromatography was used for chromatographic purifications. FT-IR spectra were taken using Perkin Elmer BX 2 FTIR spectrometer. Both <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) spectra were obtained from CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>OD solvents. LC-MS spectra were recorded on Agilent Technologies-1260 Infinity (LC) 6130 Quadropole (MS) Mass Spectrometry using acetonitrile as a solvent. Microanalyses were performed with a Thermo

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Scientific Flash 2000 elemental analyzer. Finally, temperature dependent photoluminescence measurements were carried out on powders placed in a close-cycled cryostat in the temperature range of 10–300 K and excitation densities between 0.01 and 1.04 W/cm<sup>2</sup>. A frequency tripled Nd:YLFQ-switched pulse laser at 349 nm were used for the

excitation. The luminescence was collected by suitable lenses and then dispersed with a 500 mm spectrometer using 1200 line/mm grating and detected by Intensified Charge Coupled Device (ICCD) camera.



Figure 1: Synthesis of the original carbazole Schiff bases (S1, S2, S3 and S4)

### 2.2. Experimental

General Procedure for Synthesis of Precursor Compounds: The N-substituted carbazoles were prepared according to the procedure reported in the literature [25]. Carbazole, alkyl halide, tetra butyl ammonium iodide and 50 % sodium hydroxide are refluxed at 77 °C. After a general work-up, the crude products are obtained and then purified over a silica gel column chromatography (1-3). The N-substituted mononitrocarbazoles (4-6) were prepared according to the procedure described in the literature [26]. The N-substituted carbazolyl is nitrated with concentrated nitric acid below 10 °C. The N-substituted monoamine carbazoles (7-9) were synthesized by using Pd/C and hydrazine hydrate [27]. The original carbazole Schiff bases were synthesized using Nsubstituted monoamine carbazoles with aromatic aldehydes by condensation reaction, Figure 1 (S1-S4).

General Procedure for Synthesis of Carbazole Schiff Bases: The original carbazole Schiff bases were synthesized using N-substituted monoamine carbazoles (7-9) with aromatic aldehydes by condensation reaction. N-substituted monoaminocarbazoles (7-9) (1.398 mmol) and aromatic aldehyde (1.398 mmol) were dissolved in 10 ml THF (Tetrahydrofuran) and refluxed in a 100 ml reaction flask for 24 hours. After that, one drop of acetic acid was added to solvent as a catalyst. As a result of condensation reaction reddish color was observed. The target compound was separated by precipitation with the addition of water. The crude product was filtered and washed with aqueous 5% of NaHCO<sub>3</sub>. The product was washed out with water and then dried. The final product was purified by recrystallization with chloroform, Figure 1.

3-(imine-p-hydroxybenzen)-N-isobutylcarbazole (S1).

S1 was obtained from p-hydroxybenzaldehyde and Nisobutyl-3-amine carbazole (7) following the general procedure for 5-6 h and then purified by recrystallization with chloroform (80%. m.p.: 223-224 °C). FT-IR ( $\gamma$  cm<sup>-1</sup>): 1619 (conjugated) -CH=N- stretch, 1545 aromatic -C=Cstretch, 743 1,2-disubstituted carbazolyl ring's bend, 822 and 858 1,2,4-trisubstituted carbazolyl ring's bend. <sup>1</sup>H-NMR (400 *MHz*, *CD*<sub>3</sub>*OD*): δ (Chemical Shift) 0.92 (t, 6H), 1.83 (m, H), 4.30 (t, 2H), 5.33 (s, H), 6.91 (d, 2H), 7.18 (m, 2H), 7.20 (m, H), 7.40 (m, 2H), 7.77 (m, 3H), 7.95 (s, H), 8.07 (d, H), 8.53 (s, H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD):δ 20.33, 30.98, 53.20, 108.87, 109.07, 111.76, 115.62, 118.61, 119.61, 120.16, 122.68, 123.21, 125.73, 130.48, 139.05, 143.63, 153.8, 159.34, 160.38. Anal. Calc. for  $C_{23}H_{22}N_2O$  (MW=342.43): C, 80.67; H, 6.48; N, 8.18. Found: C, 80.10; H, 6.60; N, 8.10%. LC-MS (m/z): 342.9 (M<sup>+</sup> "Molecular Ion Peak", CH<sub>3</sub>CN, Error % = 0.1834).

### 3-(imine-2,3,4-trimethoxybenzene)-N-butylcarbazole (S2).

S2 was obtained from 2,3,4-trimethoxybenzaldehyde and Nbutyl-3-amine carbazole (8) following the *general procedure* 5-6 h and then purified by recrystallization with chloroform (71%, m.p.: 44-45 °C). *FT-IR* ( $\gamma$  cm<sup>-1</sup>): 1627 (conjugated) – CH=N- stretch, 1601 aromatic –C=C- stretch, 745 1,2disubstituted carbazolyl ring's bend, <sup>8</sup>34 and 894 1,2,4trisubstituted carbazolyl ring's bend. <sup>1</sup>*H-NMR* (400 *MHz*, *CDCl<sub>3</sub>*): δ 0.96 (t, 3H), 1.42 (m, 2H), 1.87 (m, 2H), 3.94 (s, 9H), 4.30 (t, 2H), 6.82 (d, H), 7.24 (m, 2H), 7.41 (d, H), 7.46 (m, 2H), 7.48 (m, H), 8.02 (m, H), 8.14 (d, H), 8.95 (s, H). <sup>13</sup>*C-NMR* (100 *MHz*, *CDCl<sub>3</sub>*): δ 13.92, 20.58, 31.18, 53.48, 56.11, 60.99, 62.13, 108.0, 109.0, 112.4 (d), 118.8, 120.5, 122.5, 123.0, 123.5, 126.0, 139.1, 141.0, 142.0, 144.6, 153.8, 155.5, 156.1. Anal. Calc. for C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub> (MW=416.51): C, 74.97; H, 6.78; N, 6.73. Found: C, 75.00; H, 6.75; N, 6.70%. *LC-MS* (*m*/*z*): 415.0 (M<sup>+</sup>, CH<sub>3</sub>CN, Error % = 0.3625).

### 3-(imine-3,4-dihydroxybenzene)-N-octylcarbazole (S3).

S3 was obtained from 3,4-dihydroxybenzaldehyde and Noctyl-3-amine carbazole (9) following the general procedure for 5-6 h and then purified by recrystallization with chloroform (53%, m.p.: 126-127 °Č). FT-IR (y cm<sup>-1</sup>): 1625 (conjugated) -CH=N- stretch, 1594 aromatic -C=C- stretch, 743 1,2-disubstituted carbazolyl ring's bend, 867 and 900 1,2,4-trisubstituted carbazolyl ring's bend. <sup>1</sup>H-NMR (400 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>): δ 0.87 (t, 3H), 1.28 (m, 10H), 1.84 (m, 2H), 4.24 (t, 2H), 5.32 (s, 2H), 6.92 (d, H), 7.14 (t, H), 7.24 (m, 2H), 7.42 (m, 2H), 7.67 (d, 2H), 8.38 (d, H), 8.75 (s, H). <sup>13</sup>*C*-*NMR* (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 13.78, 22.56, 27.21, 28.93, 29.13, 29.32, 31.75, 43.20, 108.57, 109.26, 115.38 (2C), 117.80, 120.09, 125.30, 125.35, 125.78, 125.92, 126.06, 126.21, 135.0, 136.0, 139.0, 141.0, 145.0, 150.0, 163.0. Anal. Calc. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> (MW=414.54): C, 78.23; H, 7.29; N, 6.76. Found: C, 78.10; H, 7.15; N, 6.60%. LC-MS (m/z): 414.23 (M<sup>+</sup>, CH<sub>3</sub>CN, Error % = 0.0748).

### 3-(imine-2,3-dihydroxybenzene)-N-octylcarbazole (S4).

S4 was obtained from 2,3-dihydroxybenzaldehyde and Noctyl-3-amine carbazole (9) following the general procedure for 5-6 h and then purified by recrystallization with chloroform (78 %, m.p.: 105-106 °C). FT-IR ( $\gamma \ cm^{-1}$ ): 1619 (conjugated) -CH=N- stretch, 1600 aromatic -C=Cstretch, 740 1,2-disubstituted carbazolyl ring's bend, 822 and 982 1,2,4-trisubstituted carbazolyl ring's bend. <sup>1</sup>H-NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  0.88 (t, 3H), 1.30 (m, 10H), 1.90 (m, 2H), 4.33 (t, 2H), 5.33 (s, 2H), 6.85 (m, 2H), 7.03 (d, H), 7.26 (t, 3H), 7.50 (m, 3H), 8.12 (d, H), 8.14 (s, H), 8.81 (s, H). <sup>13</sup>C-NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):δ 13.78, 22.57, 27.21, 28.91, 29.14, 29.31, 31.74, 43.27, 109.15, 109.43, 112.46, 116.64, 118.55, 118.71, 119.09, 119.29, 120.40, 122.60, 123.36, 126.18, 138.0, 139.0, 141.0, 145.0, 150.0, 159.0. Anal. Calc. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> (MW=414.54): C, 78.23; H, 7.29; N, 6.76. Found: C, 78.12; H, 7.16; N, 6.80%. LC-MS (m/z): 414.23 (M<sup>+</sup>, CH<sub>3</sub>CN, Error % = 0.0748).

### 4. RESULTS

The synthesized novel substituted carbazole derivatives (S1, S2, S3 and S4) by condensation reaction as described above are characterized by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, LC-MS and temperature dependent PL measurements.

In FT-IR spectra, while the N-H stretch of Alkylated carbazolyl amine and aromatic aldehite carbonyl C=O expected at 3355 cm<sup>-1</sup> and 1800 cm<sup>-1</sup>, respectively were disappeared, typical azomethine -CH=N- bond stretch at 1625±10 cm associated with carbazole Schiff base were clearly observed indicating their formation (see Figure 1g-h, Figure 2f-g, Figure 3d-e, Figure 4d-e in supporting information for S1, S2, S3 and S4, respectively). In addition, aldehyde's carbonyl stretch (1723 cm<sup>-1</sup>) and amine's  $-NH_2$  stretch (3300 cm<sup>-1</sup>) which seems a double band disappeared.

These compounds showed 'H-NMR peaks for different kinds of protons on their spectral data. In <sup>1</sup>H-NMR spectra, –CHO proton band of aldehyde and -NH<sub>2</sub> proton band of amine peaks expected at 9.88 ppm and 6.58 ppm were vanished. The formation of syntheses Schiff bases were confirmed by observing –CH=N- proton band at ~8.5-8.9 ppm (singlet) for azomethine proton. Similarly, in <sup>13</sup>C-NMR spectra, –CHO

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carbonyl band of aldehyde peak expected at 191 ppm was vanished. The formation of the syntheses Schiff bases were confirmed by observing –CH=N- carbon band at ~155.5-163.0 ppm for azomethine (see Figure 1a-f, Figure 2a-e, Figure 3a-c, Figure 4a-c of the supporting information for S1, S2, S3 and S4, respectively).

Furthermore, in LC-MS spectra the molecular ion band were observed at  $(M^+)$  342.17, 416.21, 414.23 and 414.23 g/mol for S1, S2, S3, and S4, respectively. Finally, elemental analysis data verify the molecular structures of novel carbazoly shift bases. Synthesized and characterized all of the original carbazole Schiff bases have an uninterrupted electron delocalization.

The pure powders placed in closed cycle cryostat were examined by PL over the temperature range of 10 to 300 K and excitation power density of 0.01 and 1.04 W/cm<sup>2</sup>. The PL spectra at 300K are shown in Figure 2 along with reference sample containing only carbazole for comparison. The reference sample has several relatively narrow peaks over the spectral range between 2.5 and 3.3eV with the most intense peak situated at 2.95 eV. The PL spectra of S1, S2, S3 and S4 show completely different character compared to reference carbazole. Due to stronger  $\pi$ -conjugation and efficient charge transfer from host material to conjugated part of compounds, broad and complex bands centered at about ~2.16 and ~1.76 eV are observed in PL spectra for all samples.



Figure 2: PL spectra of S1-S4 compared to carbazole taken at room temparature.

The temperature and excitation density dependency of PL spectra were examined for all four samples, and the results are shown in Figure 3. As seen from the figures, the overall emission characters such as peak positions and shape of spectra do not significantly change with temperature. The peak intensities of two broad bands of samples S1, S3 remain almost constant over the entire temperature ranges. On the other hand, they increase very slightly as the temperature increases for sample S2. For sample S4, the peak intensity of the first broad peak centered at about  $\sim 2.16$ eV decreases, whereas that of second broad peak centered at about  $\sim 1.76$  eV increases slightly initially from 10 K to 60 K.

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Figure 3. Temperature dependent PL spectra for S1 (a), S2 (b), S3 (c) and S4 (d). The inset shows an example of Gauss fitting used for peak identification.

The total integrated intensities as a function of temperature and excitation density are shown in Figure 4 of all samples. As seen from the Figure 4 (a) although the total integrated intensities remain almost constant for sample S1, S3 and S4, it increases steadily for sample S2 as the temperature rises. As seen from Figure 4(b), the total integrated PL intensities increase almost linearly for samples S2, S3 and S4 and the power of  $x^{0.7}$  for sample S4 as the excitation density increase.

To resolve these broad spectra that are composed of various emission bands, they were fitted using multiple Gaussian fittings. The best fits are obtained by assigning 5 Gaussian peaks as shown in the insets of Figure 3. The decomposed peaks and their relative integrated intensities normalized to total integrated intensity for the spectra taken at room temperature are shown in Figure 5. The decomposed peaks are realized at 1.58, 1.78, 2.04, 2.28 and 2.74 eV with varied peak and hence integrated intensities contribute to total integrated intensities depending on samples. From these peak positions the spectra can be divided into three spectral regions as near infrared (785-690 nm), red-orange-yellow (620-540 nm) and blue (450 nm). As clearly seen from the Figure 5, whereas the relative integrated intensity of one of the dominant emission band centered at about 2.28 eV decreases, the other dominant emission band peaked at 2.04 eV increases from sample S1 to sample S4.



Figure 4. The total integrated intensity versus excitation power density (a) and temperature (b) for all samples.

The normalized integrated intensity of the second most dominant emission band observed at 1.78 eV also depend on samples, hence the functional group connected to carbazole. The other lower intensity emission bands 1.58 and 2.74 have relatively lesser dependence on samples. From this observation, it could be argued that this newly synthesized Shift bases could be optimized and investigated further to obtain an emission with different white light color temperature or single emission bands from blue to near infrared region of the spectrum. By introducing different transition metals or rare-earth materials to main matrix structure, the studies could be extended more for further investigations.



**Figure 5**. The relative integrated intensities of decomposed emission peaks deduced by Gaussian fittings for sample S1, S2, S3 and S4. The peaks for each sample are placed vertically. The dashed line is drawn for eye-guide.

### CONCLUSIONS

Four novel substituted carbazole derivatives referred as S1, S2, S3 and S4 were successfully synthesized using condensation reaction between carbazole amines and aromatic aldehydes. All synthesized carbazole Schiff bases were purified by crystallizing from chloroform. They were characterized structurally by means of FT-IR, NMR and microanalysis and confirmed their formations. The temperature and excitation power density dependent PL measurements were also carried out for optical characterization. The broad and complex bands centered at about ~2.16 and ~1.76 eV are observed in PL spectra for all samples compared to reference carbazole host material, which indicate an efficient charge transfer to  $\pi$ -conjugated systems. Their relative intensities depend on functional groups associated with the carbazole. These newly synthesized Schiff bases could be considered as an active emissive or electron/hole transport layer for organic light emitting diodes. Further systematic investigations are needed to identify the origin of emission bands and optimize the structure for designated purposes.

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# SUPPLEMENTARY MATERIAL

All FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, LC-MS spectra (Figure 1-4) for S1-S4 are given in supportive/supplementary material.

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# Synthesis and Optical Characterization of Novel Carbazole Schiff Bases

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Abstract: In this study, newly substituted carbazole derivatives of S1; (Z)-4-((9-isobutyl-9H-carbazol-3ylimino)methyl)phenol, S2; (Z)-9-butyl- N-(2,3,4-trimethoxybenzylidine)-9H-carbazol-3-amine, S3; (Z)-4-((9-octyl-9Hcarbazol-3-ylimino)methyl)benzene-1,2-diol and S4; (Z)-3-((9-octyl-9H-carbazol-3-ylimino)methyl)benzene-1,2-diol compounds are synthesized by using condensation reaction between carbazole amines and aromatic aldehydes. All synthesized carbazole Schiff bases are purified by crystallizing from chloroform. The structural and optical characterizations of synthesized compounds are investigated by FT-IR (Fourier Transform-Infrared Spectroscopy), <sup>1</sup>H-NMR (Proton Nuclear Magnetic Resonance), <sup>13</sup>C-NMR (Carbon Nuclear Magnetic Resonance), LC-MS (Liquid Chromatography-Mass Spectrometry) and temperature dependent PL (Photoluminescence) measurements. The formations of synthesized Schiff bases were confirmed by FT-IR, NMR and microanalysis. Due to stronger  $\pi$ -conjugation and efficient charge transfer from host material, the broad and complex bands centered at about ~2.16 and ~1.76 eV are observed in PL spectra for all samples. Their relative intensities depend on functional groups associated with the carbazole. These newly synthesized Schiff bases could be considered as an active emissive layer for organic light emitting diodes.

Keywords: Carbazole, Carbazole Schiff Base, Synthesis, Optical Characterization, Photoluminescence, OLED.

# **1. INTRODUCTION**

Carbazoles and its derivatives have been received a great deal of interest due to their specific optical and electrochemical properties, which could potentially be explored to some device applications, such as organic lightemitting diodes (OLEDs) [1], organic photovoltaic devices (OPVs) [2], organic field-effect transistors (OFETs) [3], as wells as fundamental points of view [4,5]. Since the carbazole derivatives have high triplet energy and efficient energy transfer processes from hosts to doped triplet emitters, they can be used as host materials in highly efficient blue, green, or red electro-phosphorescent devices [6-10]. Numerous ways of functionalization of carbazoles or covalently linking to other molecules such as 3,6- or 2,7linking of carbazole molecules into dimers, trimers or oligomers [11,12], addition of enamine [13], and others [14-18] are reported for the enhancement of their conjugated  $\pi$ electron system and hence for the efficient light emitter.

Polycarbazoles and their nanocomposite films (polycarbazole/nanoZn and polycarbazole/nanoclayfilms) show protection of anodic corrosion on modified electrodes to form metal conserved region [19].

Carbazole Schiff bases demonstrate that they have superior fluorescence emission and also their  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  complexes show extra fluorescence emission [20-23].

For the synthesis of carbazole Schiff bases, a solvent free method were used and showed luminescence properties [24].

In current work, since Schiff bases containing carbazolyl groups are expected to have stronger conjugated system, higher intramolecular electron transfer efficiency and more stable structure than the general Schiff bases, four novel carbazole based Schiff bases referred as S1, S2, S3 and S4 were synthesized by condensation reaction between carbazole amines and aromatic aldehydes, and characterized by FT-IR, NMR, LC-MS, elemental analysis and temperature dependent PL spectroscopy.

# 2. MATERIALS AND METHODS

# 2.1. General

In this study, all starting materials were purchased from Merck, Sigma-Aldrich and Fluka Co., and used after further analytical purifications of solvents and chemical materials. A silica gel with column chromatography was used for chromatographic purifications. FT-IR spectra were taken using Perkin Elmer BX 2 FTIR spectrometer. Both <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) spectra were obtained from CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>OD solvents. LC-MS spectra were recorded on Agilent Technologies-1260 Infinity (LC) 6130 Quadropole (MS) Mass Spectrometry using acetonitrile as a solvent. Microanalyses were performed with a Thermo

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Scientific Flash 2000 elemental analyzer. Finally, temperature dependent photoluminescence measurements were carried out on powders placed in a close-cycled cryostat in the temperature range of 10–300 K and excitation densities between 0.01 and 1.04 W/cm<sup>2</sup>. A frequency tripled Nd:YLFQ-switched pulse laser at 349 nm were used for the

excitation. The luminescence was collected by suitable lenses and then dispersed with a 500 mm spectrometer using 1200 line/mm grating and detected by Intensified Charge Coupled Device (ICCD) camera.



Figure 1: Synthesis of the original carbazole Schiff bases (S1, S2, S3 and S4)

### 2.2. Experimental

General Procedure for Synthesis of Precursor Compounds: The N-substituted carbazoles were prepared according to the procedure reported in the literature [25]. Carbazole, alkyl halide, tetra butyl ammonium iodide and 50 % sodium hydroxide are refluxed at 77 °C. After a general work-up, the crude products are obtained and then purified over a silica gel column chromatography (1-3). The N-substituted mononitrocarbazoles (4-6) were prepared according to the procedure described in the literature [26]. The N-substituted carbazolyl is nitrated with concentrated nitric acid below 10 °C. The N-substituted monoamine carbazoles (7-9) were synthesized by using Pd/C and hydrazine hydrate [27]. The original carbazole Schiff bases were synthesized using Nsubstituted monoamine carbazoles with aromatic aldehydes by condensation reaction, Figure 1 (S1-S4).

General Procedure for Synthesis of Carbazole Schiff Bases: The original carbazole Schiff bases were synthesized using N-substituted monoamine carbazoles (7-9) with aromatic aldehydes by condensation reaction. N-substituted monoaminocarbazoles (7-9) (1.398 mmol) and aromatic aldehyde (1.398 mmol) were dissolved in 10 ml THF (Tetrahydrofuran) and refluxed in a 100 ml reaction flask for 24 hours. After that, one drop of acetic acid was added to solvent as a catalyst. As a result of condensation reaction reddish color was observed. The target compound was separated by precipitation with the addition of water. The crude product was filtered and washed with aqueous 5% of NaHCO<sub>3</sub>. The product was washed out with water and then dried. The final product was purified by recrystallization with chloroform, Figure 1.

3-(imine-p-hydroxybenzen)-N-isobutylcarbazole (S1).

S1 was obtained from p-hydroxybenzaldehyde and Nisobutyl-3-amine carbazole (7) following the general procedure for 5-6 h and then purified by recrystallization with chloroform (80%. m.p.: 223-224 °C). FT-IR ( $\gamma$  cm<sup>-1</sup>): 1619 (conjugated) -CH=N- stretch, 1545 aromatic -C=Cstretch, 743 1,2-disubstituted carbazolyl ring's bend, 822 and 858 1,2,4-trisubstituted carbazolyl ring's bend. <sup>1</sup>H-NMR (400 *MHz*, *CD*<sub>3</sub>*OD*): δ (Chemical Shift) 0.92 (t, 6H), 1.83 (m, H), 4.30 (t, 2H), 5.33 (s, H), 6.91 (d, 2H), 7.18 (m, 2H), 7.20 (m, H), 7.40 (m, 2H), 7.77 (m, 3H), 7.95 (s, H), 8.07 (d, H), 8.53 (s, H). <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD):δ 20.33, 30.98, 53.20, 108.87, 109.07, 111.76, 115.62, 118.61, 119.61, 120.16, 122.68, 123.21, 125.73, 130.48, 139.05, 143.63, 153.8, 159.34, 160.38. Anal. Calc. for  $C_{23}H_{22}N_2O$  (MW=342.43): C, 80.67; H, 6.48; N, 8.18. Found: C, 80.10; H, 6.60; N, 8.10%. LC-MS (m/z): 342.9 (M<sup>+</sup> "Molecular Ion Peak", CH<sub>3</sub>CN, Error % = 0.1834).

### 3-(imine-2,3,4-trimethoxybenzene)-N-butylcarbazole (S2).

S2 was obtained from 2,3,4-trimethoxybenzaldehyde and Nbutyl-3-amine carbazole (8) following the *general procedure* 5-6 h and then purified by recrystallization with chloroform (71%, m.p.: 44-45 °C). *FT-IR* ( $\gamma$  cm<sup>-1</sup>): 1627 (conjugated) – CH=N- stretch, 1601 aromatic –C=C- stretch, 745 1,2disubstituted carbazolyl ring's bend, <sup>8</sup>34 and 894 1,2,4trisubstituted carbazolyl ring's bend. <sup>1</sup>*H-NMR* (400 *MHz*, *CDCl<sub>3</sub>*): δ 0.96 (t, 3H), 1.42 (m, 2H), 1.87 (m, 2H), 3.94 (s, 9H), 4.30 (t, 2H), 6.82 (d, H), 7.24 (m, 2H), 7.41 (d, H), 7.46 (m, 2H), 7.48 (m, H), 8.02 (m, H), 8.14 (d, H), 8.95 (s, H). <sup>13</sup>*C-NMR* (100 *MHz*, *CDCl<sub>3</sub>*): δ 13.92, 20.58, 31.18, 53.48, 56.11, 60.99, 62.13, 108.0, 109.0, 112.4 (d), 118.8, 120.5, 122.5, 123.0, 123.5, 126.0, 139.1, 141.0, 142.0, 144.6, 153.8, 155.5, 156.1. Anal. Calc. for C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub> (MW=416.51): C, 74.97; H, 6.78; N, 6.73. Found: C, 75.00; H, 6.75; N, 6.70%. *LC-MS* (*m*/*z*): 415.0 (M<sup>+</sup>, CH<sub>3</sub>CN, Error % = 0.3625).

### 3-(imine-3,4-dihydroxybenzene)-N-octylcarbazole (S3).

S3 was obtained from 3,4-dihydroxybenzaldehyde and Noctyl-3-amine carbazole (9) following the general procedure for 5-6 h and then purified by recrystallization with chloroform (53%, m.p.: 126-127 °Č). FT-IR (y cm<sup>-1</sup>): 1625 (conjugated) -CH=N- stretch, 1594 aromatic -C=C- stretch, 743 1,2-disubstituted carbazolyl ring's bend, 867 and 900 1,2,4-trisubstituted carbazolyl ring's bend. <sup>1</sup>H-NMR (400 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>): δ 0.87 (t, 3H), 1.28 (m, 10H), 1.84 (m, 2H), 4.24 (t, 2H), 5.32 (s, 2H), 6.92 (d, H), 7.14 (t, H), 7.24 (m, 2H), 7.42 (m, 2H), 7.67 (d, 2H), 8.38 (d, H), 8.75 (s, H). <sup>13</sup>*C*-*NMR* (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 13.78, 22.56, 27.21, 28.93, 29.13, 29.32, 31.75, 43.20, 108.57, 109.26, 115.38 (2C), 117.80, 120.09, 125.30, 125.35, 125.78, 125.92, 126.06, 126.21, 135.0, 136.0, 139.0, 141.0, 145.0, 150.0, 163.0. Anal. Calc. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> (MW=414.54): C, 78.23; H, 7.29; N, 6.76. Found: C, 78.10; H, 7.15; N, 6.60%. LC-MS (m/z): 414.23 (M<sup>+</sup>, CH<sub>3</sub>CN, Error % = 0.0748).

### 3-(imine-2,3-dihydroxybenzene)-N-octylcarbazole (S4).

S4 was obtained from 2,3-dihydroxybenzaldehyde and Noctyl-3-amine carbazole (9) following the general procedure for 5-6 h and then purified by recrystallization with chloroform (78 %, m.p.: 105-106 °C). FT-IR ( $\gamma \ cm^{-1}$ ): 1619 (conjugated) -CH=N- stretch, 1600 aromatic -C=Cstretch, 740 1,2-disubstituted carbazolyl ring's bend, 822 and 982 1,2,4-trisubstituted carbazolyl ring's bend. <sup>1</sup>H-NMR (400 *MHz*,  $CD_2Cl_2$ ):  $\delta$  0.88 (t, 3H), 1.30 (m, 10H), 1.90 (m, 2H), 4.33 (t, 2H), 5.33 (s, 2H), 6.85 (m, 2H), 7.03 (d, H), 7.26 (t, 3H), 7.50 (m, 3H), 8.12 (d, H), 8.14 (s, H), 8.81 (s, H). <sup>13</sup>C-NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):δ 13.78, 22.57, 27.21, 28.91, 29.14, 29.31, 31.74, 43.27, 109.15, 109.43, 112.46, 116.64, 118.55, 118.71, 119.09, 119.29, 120.40, 122.60, 123.36, 126.18, 138.0, 139.0, 141.0, 145.0, 150.0, 159.0. Anal. Calc. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> (MW=414.54): C, 78.23; H, 7.29; N, 6.76. Found: C, 78.12; H, 7.16; N, 6.80%. LC-MS (m/z): 414.23 (M<sup>+</sup>, CH<sub>3</sub>CN, Error % = 0.0748).

### 4. RESULTS

The synthesized novel substituted carbazole derivatives (S1, S2, S3 and S4) by condensation reaction as described above are characterized by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, LC-MS and temperature dependent PL measurements.

In FT-IR spectra, while the N-H stretch of Alkylated carbazolyl amine and aromatic aldehite carbonyl C=O expected at 3355 cm<sup>-1</sup> and 1800 cm<sup>-1</sup>, respectively were disappeared, typical azomethine -CH=N- bond stretch at 1625±10 cm associated with carbazole Schiff base were clearly observed indicating their formation (see Figure 1g-h, Figure 2f-g, Figure 3d-e, Figure 4d-e in supporting information for S1, S2, S3 and S4, respectively). In addition, aldehyde's carbonyl stretch (1723 cm<sup>-1</sup>) and amine's  $-NH_2$  stretch (3300 cm<sup>-1</sup>) which seems a double band disappeared.

These compounds showed 'H-NMR peaks for different kinds of protons on their spectral data. In <sup>1</sup>H-NMR spectra, –CHO proton band of aldehyde and -NH<sub>2</sub> proton band of amine peaks expected at 9.88 ppm and 6.58 ppm were vanished. The formation of syntheses Schiff bases were confirmed by observing –CH=N- proton band at ~8.5-8.9 ppm (singlet) for azomethine proton. Similarly, in <sup>13</sup>C-NMR spectra, –CHO

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carbonyl band of aldehyde peak expected at 191 ppm was vanished. The formation of the syntheses Schiff bases were confirmed by observing –CH=N- carbon band at ~155.5-163.0 ppm for azomethine (see Figure 1a-f, Figure 2a-e, Figure 3a-c, Figure 4a-c of the supporting information for S1, S2, S3 and S4, respectively).

Furthermore, in LC-MS spectra the molecular ion band were observed at  $(M^+)$  342.17, 416.21, 414.23 and 414.23 g/mol for S1, S2, S3, and S4, respectively. Finally, elemental analysis data verify the molecular structures of novel carbazoly shift bases. Synthesized and characterized all of the original carbazole Schiff bases have an uninterrupted electron delocalization.

The pure powders placed in closed cycle cryostat were examined by PL over the temperature range of 10 to 300 K and excitation power density of 0.01 and 1.04 W/cm<sup>2</sup>. The PL spectra at 300K are shown in Figure 2 along with reference sample containing only carbazole for comparison. The reference sample has several relatively narrow peaks over the spectral range between 2.5 and 3.3eV with the most intense peak situated at 2.95 eV. The PL spectra of S1, S2, S3 and S4 show completely different character compared to reference carbazole. Due to stronger  $\pi$ -conjugation and efficient charge transfer from host material to conjugated part of compounds, broad and complex bands centered at about ~2.16 and ~1.76 eV are observed in PL spectra for all samples.



Figure 2: PL spectra of S1-S4 compared to carbazole taken at room temparature.

The temperature and excitation density dependency of PL spectra were examined for all four samples, and the results are shown in Figure 3. As seen from the figures, the overall emission characters such as peak positions and shape of spectra do not significantly change with temperature. The peak intensities of two broad bands of samples S1, S3 remain almost constant over the entire temperature ranges. On the other hand, they increase very slightly as the temperature increases for sample S2. For sample S4, the peak intensity of the first broad peak centered at about  $\sim 2.16$ eV decreases, whereas that of second broad peak centered at about  $\sim 1.76$  eV increases slightly initially from 10 K to 60 K.

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Figure 3. Temperature dependent PL spectra for S1 (a), S2 (b), S3 (c) and S4 (d). The inset shows an example of Gauss fitting used for peak identification.

The total integrated intensities as a function of temperature and excitation density are shown in Figure 4 of all samples. As seen from the Figure 4 (a) although the total integrated intensities remain almost constant for sample S1, S3 and S4, it increases steadily for sample S2 as the temperature rises. As seen from Figure 4(b), the total integrated PL intensities increase almost linearly for samples S2, S3 and S4 and the power of  $x^{0.7}$  for sample S4 as the excitation density increase.

To resolve these broad spectra that are composed of various emission bands, they were fitted using multiple Gaussian fittings. The best fits are obtained by assigning 5 Gaussian peaks as shown in the insets of Figure 3. The decomposed peaks and their relative integrated intensities normalized to total integrated intensity for the spectra taken at room temperature are shown in Figure 5. The decomposed peaks are realized at 1.58, 1.78, 2.04, 2.28 and 2.74 eV with varied peak and hence integrated intensities contribute to total integrated intensities depending on samples. From these peak positions the spectra can be divided into three spectral regions as near infrared (785-690 nm), red-orange-yellow (620-540 nm) and blue (450 nm). As clearly seen from the Figure 5, whereas the relative integrated intensity of one of the dominant emission band centered at about 2.28 eV decreases, the other dominant emission band peaked at 2.04 eV increases from sample S1 to sample S4.



Figure 4. The total integrated intensity versus excitation power density (a) and temperature (b) for all samples.

The normalized integrated intensity of the second most dominant emission band observed at 1.78 eV also depend on samples, hence the functional group connected to carbazole. The other lower intensity emission bands 1.58 and 2.74 have relatively lesser dependence on samples. From this observation, it could be argued that this newly synthesized Shift bases could be optimized and investigated further to obtain an emission with different white light color temperature or single emission bands from blue to near infrared region of the spectrum. By introducing different transition metals or rare-earth materials to main matrix structure, the studies could be extended more for further investigations.



**Figure 5**. The relative integrated intensities of decomposed emission peaks deduced by Gaussian fittings for sample S1, S2, S3 and S4. The peaks for each sample are placed vertically. The dashed line is drawn for eye-guide.

### CONCLUSIONS

Four novel substituted carbazole derivatives referred as S1, S2, S3 and S4 were successfully synthesized using condensation reaction between carbazole amines and aromatic aldehydes. All synthesized carbazole Schiff bases were purified by crystallizing from chloroform. They were characterized structurally by means of FT-IR, NMR and microanalysis and confirmed their formations. The temperature and excitation power density dependent PL measurements were also carried out for optical characterization. The broad and complex bands centered at about ~2.16 and ~1.76 eV are observed in PL spectra for all samples compared to reference carbazole host material, which indicate an efficient charge transfer to  $\pi$ -conjugated systems. Their relative intensities depend on functional groups associated with the carbazole. These newly synthesized Schiff bases could be considered as an active emissive or electron/hole transport layer for organic light emitting diodes. Further systematic investigations are needed to identify the origin of emission bands and optimize the structure for designated purposes.

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# SUPPLEMENTARY MATERIAL

All FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, LC-MS spectra (Figure 1-4) for S1-S4 are given in supportive/supplementary material.

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# **Highlights**

- New carbazole Schiff bases were synthesized successfully and characterized
- The formations of the compounds were confirmed using various techniques
- All compounds were examined with excitation power density dependent PL measurements
- The peak emission wavelengths can be altered by further optimization
- These could be considered as an active emissive-hole transport layers for OLEDs