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A combined experimental and theoretical investigation of imidazole–carbazole fluorophores

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ABSTRACT

Two different tri and tetra substituted imidazole derivatives connected with carbazole moiety were synthesized by using Vilsmeier–Haack formylation followed by multicomponent cyclisation reaction. Results obtained from spectroscopic (^1H NMR, ^{13}C NMR, Mass) and single crystal X-ray diffraction analysis of synthesized compound revealed its chemical structure. UV–vis and photoluminescence studies in various solvents with different polarity demonstrated that these compounds were sensitive to the polarity of the microenvironment in the excited state. Results of TGA and AFM analysis demonstrated that the compounds exhibited good thermal and morphological stabilities over very harsh conditions. DFT calculations were performed to elucidate the structural and electrochemical properties of these compounds. The computed result revealed the ground state of the molecules was majorly stabilized by $\sigma \rightarrow \sigma^*$ interaction and the natural hybrid orbital compositions and occupancies predict that the bonding interactions between C and N centers possess pure σ bond with sp^2 hybridization.

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1. Introduction

In recent years vast number of organic heterocyclic compounds, particularly carbazole and imidazole have received immense attention owing to their potential use in molecular designs targeting biological and electronic applications [1,2]. Historically, carbazole has shown great potential in applications, such as solar cells [3–5], electrophotography [6], organic light-emitting diodes (OLEDs) [7–9] and as photorefractive materials [10,11]. The strong emission and absorption properties of carbazole and their derivatives have been exploited as electroluminescent and hole transporting layers of OLEDs as wide band gap energy transfer materials to lower band gap emitters [1,12,13]. Its efficient use in organic semiconductor devices is primarily due to the formation of stable radical cations and its efficient hole-mobility properties. In fact, the first polymeric electroluminescent device, fabricated by Partridge, incorporated polyvinylcarbazole (PVK) as the active emitting layer [14]. More recently, carbazole based materials have shown great potential as host materials in phosphorescent OLED devices, due to their high triplet energy levels and low oxidation potentials [15,16]. Although carbazole-based small molecules and polymeric materials have both been applied, small molecules have improved chemical purity compared to the latter because they can be purified by chromatography, recrystallisation or train sublimation. Moreover, the molecular and optical properties of carbazole can be tuned by modifying its 2-, 3-, 6-, 7-, and 9-positions [17–19].

Imidazole is quite attractive due to their biological activities [20,21] and their use in fabrication of light-emitting devices [22,23], employing them as electron-transporting layer and as sensitizers in dye-sensitized solar cells [24,25], applications in metal sensors [26,27] and non linear optics (NLO) [28,29]. Functional imidazoles have been mainly developed due to their broad optical absorption, bright photoluminescence and bipolar transport characteristics. There is a growing interest in the design and synthesis of imidazoles enriched with functional chromophores to enhance their optical and charge transport properties. Imidazole containing carbazole hybrids are interesting due to their excellent emission and thermal properties. The combination of electron transport properties of imidazole and hole transporting properties of carbazole displayed excellent ambipolar host materials for electroluminescent devices [1,2]. In view of this, the work presents synthesis of tri and tetra substituted imidazole conjugated with carbazole moiety by simple Vilsmeier–Haack reaction and multicomponent cyclisation. Further, synthesized compounds were characterized using NMR, Mass and single crystal XRD techniques. Moreover, the photophysical, electrochemical, thermal and morphological properties of the compounds were explored.

2. Experimental section

2.1. Reagents and instruments

All the chemicals were commercially available and they were used without further purification. ^1H NMR and ^{13}C NMR were recorded on a Bruker Avance 400 (400 MHz) NMR spectrometer.

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Dimethylsulfoxide (DMSO-d₆) and CDCl₃ were used as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a FDMS, VG Instruments ZAB-2 mass spectrometer. X-ray crystallographic diffraction data were collected on a Bruker SMART APEX-II CCD diffractometer at room temperature using graphite-monochromated Mo K α radiation ($\lambda=0.71073$ Å). Integration and cell refinement were carried out using Bruker SAINT. The structures were solved by direct methods (SHELXS 86/SHELXS 97) and refined by full-matrix least squares on F^2 using SHELXL 97. All non-hydrogen atoms were refined anisotropically. MERCURY was used for all graphical representation of the results. Steady state spectroscopic measurements were conducted both in solution and thin films prepared by vacuum (2×10^{-6} mbar) deposition on a quartz plate. Absorption spectra of solution and thin film were obtained using UV–vis spectrophotometer (JASCO V360). Photoluminescence emission spectra of solution and thin film were obtained using fluorescence spectrophotometer (Perkin Elmer–LS55 & Horiba Jobin Yvon FluoroLog 3 Spectrofluorometer). Photoluminescence quantum efficiencies (Φ_{PL} values) of thin films on quartz plates were measured using a 6 in. integrating sphere (Labsphere) attached with Horiba Jobin Yvon FluoroLog 3 Spectrofluorometer through optical fiber and a PMT detector (Hamamatsu). Quantum yield of the compounds in solution were calculated by following standard procedure using 9,10-diphenylanthracene ($\Phi_f=0.95$ in ethanol) [30] as reference by the following equation.

$$\Phi_f = \Phi_R \frac{I_S \times OD_R \times n_R^2}{I_R \times OD_S \times n_S^2} \quad (1)$$

where Φ_R is the fluorescence quantum yield of reference, I_S and I_R are the area of the sample and reference under the emission spectrum, OD_R and OD_S are the optical density at the excitation wavelength of the reference and sample, n_S and n_R are refractive index of solvent of sample and reference. In all measurements, the optical density of solutions does not exceed 0.1. Effect of solvents on spectral behaviour of the compounds were analysed in cyclohexane (CyHex), chloroform (CHCl₃), ethylacetate (EtOAc), tetrahydrofuran (THF), dichloromethane (DCM), ethanol (EtOH), methanol (MeOH), acetonitrile (MeCN), *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solutions. Solvents of the highest available quality (Spectroscopic or HPLC grade) were used. Emission spectra were recorded by exciting the samples at their absorption maximum unless otherwise mentioned. All the experiments were performed at room temperature at a concentration of 4×10^{-6} M.

The electrochemical properties were investigated by cyclic voltammetry (CV) in DMF using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. The experiments were performed at room temperature (1 mM concentration) with a three-electrode cell consisting of a platinum wire as an auxiliary electrode, a saturated Ag/Ag⁺ reference electrode and a platinum working electrode. Thermogravimetric analyses (TGA) was performed under nitrogen atmosphere at heating rate of 10 °C min⁻¹. Melting points were determined by the open capillary tube method using a Toshniwal melting point apparatus and are uncorrected. The topography of the thin films were analyzed by Atomic Force Microscopy imaging (5×5 μ m and 2×2 μ m) using acoustic AC mode with a silicon nitride tip (resonance frequency of 295 kHz), in order to evaluate the effect of thermal stress on the thin film morphology.

2.2. Computational details

All calculations on the synthesized molecules have been performed using Gaussian 09W [31]. The ground-state geometries of the molecules were fully optimized at the DFT level using B3LYP

[32–35] functional with 6-31+G(d,p) basis set. The vibrational frequency analysis of the optimized geometries confirms that all the optimized geometries correspond to minima on the potential energy surface by exhibiting all real frequencies. The Mulliken and NPA charges were also calculated and used to show the basic nature of the nitrogen atom of the compounds. Natural bond orbital (NBO) [36] analysis have been performed on the molecule at the B3LYP/6-31+G(d,p) level in order to elucidate the intramolecular, hybridization and charge transfer within the molecule. The second order perturbation energy analysis was carried out to evaluate the donor–acceptor interactions in the ground state of the molecules.

2.3. Synthesis

General procedure for the synthesis of 9-ethyl-9*H*-carbazole-3-carbaldehyde (9-CA).

A mixture of DMF (2 mmol) and POCl₃ (1 mmol) in 5 ml of 1,2-dichloroethane (DCE) were allowed to cool for 0 °C and stirred for 30 min. To this, 9-ethylcarbazole (1 mmol) in DCE (5 ml) was added and the mixture was stirred at 100 °C for 8 h. The mixture was quenched with ice cooled water and filtered, washed with water, dried in vacuo and the compound was purified by column chromatography (silica gel 60–120 mesh, hexane/EtOAc) (5:1 v/v) as a eluent to afford the compound 9-CA as a yellow solid.

General procedure for the synthesis of target compounds (CBI and MCB).

A mixture of NH₄OAc (4 mmol), *p*-anisidine (2 mmol only for MCB) benzil (1 mmol), and 9-CA (1 mmol) in acetic acid (6 ml) were refluxed for 4 h. The mixture was poured into cooled water and filtered, washed with water, dried in vacuo and the compound was purified by column chromatography (silica gel 60–120 mesh, hexane/EtOAc) (4:1 v/v) as a eluent to afford the target compound CBI and MCB as a colorless solid.

The 3-(4,5-diphenyl-1*H*-imidazol-2-yl)-9-ethyl-9*H*-carbazole (CBI).

Yield: 85%, mp: 225–228 °C, ¹H NMR (400 MHz, DMSO-d₆): δ_H 1.21 (t, 3H, 7.2 Hz), 4.42 (q, 2H, 7.2 Hz), 7.17 (t, 2H, 7.6 Hz), 7.26 (t, 2H, 7.8 Hz), 7.31 (d, 1H, 7.2 Hz), 7.42–7.47 (m, 3H), 7.48 (d, 2H, 7.6 Hz), 7.55 (d, 2H, 7.6 Hz), 7.58 (d, 1H, 8 Hz), 7.65 (d, 1H, 8.8 Hz), 8.11 (d, 1H, 7.6 Hz), 8.16 (d, 1H, 8.4 Hz), 8.79 (s, 1H), 12.54 (s, 1H); ¹³C NMR: δ_C 13.72, 37.08, 109.20, 109.33, 117.28, 119.10, 120.25, 121.59, 122.25, 122.28, 123.64, 126.00, 126.40, 127.19, 128.22, 139.50, 140.02, 146.86; HRMS (*m/z*): calculated 413.1892, found 414.1978.

A 9-ethyl-3-(1-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazol-2-yl)-9*H*-carbazole (MCB).

Yield: 78%, mp: 235–237 °C, ¹H NMR (400 MHz, CDCl₃): δ_H 1.42 (t, 3H, 7.2 Hz), 3.74 (s, 3H), 4.30 (q, 2H, 7.2 Hz), 6.75 (d, 2H, 8.4 Hz), 7.01 (d, 2H, 8.4 Hz), 7.15–7.18 (m, 4H), 7.20–7.25 (m, 4H), 7.27 (s, 1H), 7.32–7.36 (t, 1H, 7.2 Hz), 7.38 (s, 1H), 7.43 (d, 1H, 7.2 Hz), 7.48 (d, 1H, 8.4 Hz), 7.63 (d, 2H, 7.2 Hz), 7.91 (d, 1H, 7.8 Hz), 8.22 (s, 1H); ¹³C NMR: δ_C 13.87, 37.63, 55.40, 108.05, 108.66, 114.25, 119.17, 120.60, 121.48, 121.58, 122.74, 123.11, 125.90, 126.55, 126.86, 127.61, 127.86, 128.10, 128.26, 128.33, 128.41, 129.74, 130.34, 130.74, 131.14, 131.29, 134.92, 138.05, 139.76, 140.35, 148.39; HRMS *m/z*: calculated 519.2311, found 520.2389.

3. Results and discussion

3.1. General synthesis

The synthetic procedures and structures of the compounds CBI and MCB are shown in Scheme 1. The first step of the synthesis was Vilsmeier–Haack reaction of 9-ethylcarbazole followed by condensation of benzil with aldehydes (9-CA) in presence of ammonium

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