



Synthesis, characterisation and electroluminescence behaviour of π -conjugated imidazole–isoquinoline derivatives



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ABSTRACT

A series of highly fluorescent, isoquinoline π -conjugated imidazole derivatives have been synthesized and fully characterized. Their photophysical, electrochemical and thermal properties have also been discussed. The interplay of amorphous and crystalline nature of the compounds in thin film and fine powder have been analysed by using X-ray diffraction and atomic force microscopic (AFM) techniques. An organic light emitting diode consisting of 4-(4-(1-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)phenyl)isoquinoline as the emitting layer doped with 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CPB) showed ideal blue emission (CIE: 0.16, 0.08). "Pure" white light (CIE: 0.34, 0.32) comprising of a blue light from excimers and an orange light from electromers at a high voltage has been achieved by using the compounds 2-(4-(isoquinolin-4-yl)phenyl)-1H-phenanthro[9,10-d]imidazole & 2-(4-(isoquinolin-4-yl)phenyl)-1-(4-methoxyphenyl)-1H-phenanthro[9,10-d]imidazole as single-emitting components. To elucidate the structural and optical properties, computational calculations have been performed. Computed results reveal all the electronic transitions are of $\pi \rightarrow \pi^*$ type and energy of the $S_0 \rightarrow S_1$ follows same variation trend with the band gap.

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1. Introduction

Since Tang and co-workers [1] report of an archetypical example of a modern Organic light emitting diodes (OLEDs), it has been a topic of great interest for many researchers due to their applications in lighting and flat panel displays. A wide variety of improvements to OLEDs have been made using novel materials and device structures to achieve improved efficiency at simple synthetic routes, easy device fabrication and low driving voltages [2–5]. The hunt for efficient blue and white electroluminescence is of particular interest because it is an essential component to realise OLEDs in display as well as lighting applications. Many research groups have successfully prepared efficient blue [6,7] and white fluorophores [8,9] for OLEDs, but efficient one, which can match the National Television System Committee (NSTC) and Commission Internationale d'Éclairage standard blue CIE (x,y) coordinates of (0.14, 0.08) and white (0.33, 0.33) has been achieved by very few

compounds. But most of them lack amorphous nature in thin films and OLEDs usually require formation of very thin organic layers with amorphous morphologies that provide pinhole free thin films.

Compared to the multi-emitting-component WOLEDs, a single-emitting-component WOLEDs could show many advantages, such as better stability, better reproducibility, and a simpler fabrication process. However, few materials are known to show white-light emission as a single-emitting component but synthesized by multistep process, among them very few have been reported to emit "pure" white light [10–12]. Therefore, the search for new organic light-emitting materials with new structures for use in single-emitting-component WOLEDs is of obvious interest and importance. Excluding the utilisation of mixture of three organic components emitting three colours (blue, green, and red) to get white light [13,14], a widely employed approach in recent years is the use of single chromophore that emits white light resulted from the combination of its monomeric (blue) and excimeric or electromeric (orange) emission [15–18]. The latter emission results from a stacking of molecules that is usually induced by π – π interactions.

Materials containing aromatic heterocyclic segments, e.g., quinoline [19,20], and oxidazole [21], had been reported to exhibit better electron injection and transport ability, but these materials

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were found to be undesirable as emitting layers in OLEDs due to their low luminance [22]. The typical heterocyclic molecule, imidazole with N1, C2, C4 and C5 positions substituted with different groups are used extensively in OLEDs for efficient blue [23–25] and white light applications [26]. Herein, we report the synthesis, crystal structure, film forming behaviour, photophysical, photo and electroluminescence properties of imidazole substituted isoquinoline derivatives. These new π -conjugated compounds, in particular, the phenanthrene based compounds, can serve as a single-emitting component for WOLEDs, emitting almost “pure” white light with stable CIE coordinates under different driving voltages.

2. Experimental section

2.1. General methods

The ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 400 (400 MHz) NMR spectrometer. Mass spectra were obtained on an FDMS, VG Instruments ZAB-2 mass spectrometer. Steady state spectroscopic measurements were conducted both in solution and thin films prepared by vacuum (2×10^{-6} mbar) deposition on a quartz plate. The thickness of films was measured using Alpha Step profilometer (KLA Tencor). Absorption spectra of solution and thin film were obtained using UV–vis spectrophotometers (JASCO V360). Photoluminescence emission spectra of solution and thin film were obtained using fluorescence spectrophotometer (PerkinElmer – LS55 & Horiba Jobin Yvon FluoroLog 3 Spectrofluorometer). Photoluminescence quantum efficiencies (Φ_{PL} values) for solutions were obtained using 9,10–diphenylanthracene as reference [27]. The Φ_{PL} values of thin films on quartz plates were measured using a 6 inch integrating sphere (Labsphere) attached with Horiba Jobin Yvon FluoroLog 3 Spectrofluorometer through optical fibre and a PMT detector (Hamamatsu). Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed under nitrogen atmosphere at heating rate of $10^\circ\text{C}/\text{min}$. 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 was analysed by Atomic Force Microscopy imaging ($5 \times 5 \mu\text{m}$ and $2 \times 2 \mu\text{m}$) 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. Fluorescence lifetime measurements were carried out in a picosecond time correlated single photon counting (TCSPC) spectrometer. The excitation source is the tunable Ti–sapphire laser (Tsunami, Spectra Physics, USA). The fluorescence decay was analysed by using the software provided by IBH (DAS-6).

2.2. Syntheses

2.2.1. Synthesis of 4-(isoquinolin-4-yl)benzaldehyde (2)

4-bromoisquinoline (1) (1 g, 4.7 mmol) was treated with 4-formylphenylboronic acid (0.77 g, 5.17 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.27 g, 0.235 mmol), K_2CO_3 (1.94 g, 14.1 mmol) in THF (50 ml) at 70°C under nitrogen atmosphere for 12 h and progress of the reaction was monitored by TLC. The reaction mixture was quenched with water, extracted with CH_2Cl_2 and washed with brine (2×10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/hexane) to afford pure 4-(isoquinolin-4-yl)benzaldehyde. The yields and important spectral data are given below.

^1H NMR (CDCl_3): 7.66 (4H, m), 7.83 (1H, d, 8.4 Hz), 8.02 (3H, m), 8.47 (1H, s), 9.26 (1H, s), 10.09 (1H, s); ^{13}C NMR: 53.5, 76.9, 77.3, 77.6, 124.1, 127.4, 128.0, 128.3, 129.3, 130.7, 131.0, 131.9, 133.5, 135.7, 142.7, 143.2, 152.7, 191.7.

2.2.2. Synthesis of compounds 1–4

A mixture of corresponding diketone (1 mmol), 4-(isoquinolin-4-yl)benzaldehyde (1 mmol), p-anisidine (4 mmol, in case of 2 & 4), ammonium acetate (4 mmol) and glacial acetic acid (8 mL) was refluxed for 4 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into distilled water with stirring. The separated solid was filtered off, washed with water and dried to give the expected product in good yields.

2.2.2.1. 4-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenyl)isoquinoline (1). ^1H NMR ($\text{DMSO}-d_6$): 7.24 (1H, d, 7.2 Hz), 7.31 (2H, t, 7.6 Hz), 7.39 (1H, d, 7.2 Hz), 7.45 (2H, t, 7.6 Hz), 7.53 (2H, d, 7.2 Hz), 7.58 (2H, d, 7.6 Hz), 7.67 (2H, d, 8.4 Hz), 7.75 (1H, m), 7.82 (1H, m), 7.93 (1H, d, 8 Hz), 8.23 (1H, d, 7.6 Hz), 8.28 (2H, m), 8.52 (1H, s), 9.36 (1H, s), 12.84 (1H, s); ^{13}C NMR: 123.9, 125.4, 126.5, 127.1, 127.5, 127.7, 128.0, 128.1, 128.2, 128.4, 128.6, 129.9, 130.2, 130.9, 131.1, 131.3, 132.0, 133.0, 135.1, 136.0, 137.3, 142.4, 145.1, 152.0; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{21}\text{N}_3$ ($\text{M} + \text{H}$) $^+$ 424.1813, found 424.1816.

2.2.2.2. 4-(4-(1-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)phenyl)isoquinoline (2). ^1H NMR (CDCl_3): 3.79 (3H, s), 6.85 (2H, d, 8.8 Hz), 7.07 (2H, d, 8.8 Hz), 7.19 (3H, m), 7.25 (6H, m), 7.42 (2H, d, 7.2 Hz), 7.63 (5H, m), 7.91 (1H, d, 8 Hz), 8.01 (1H, d, 7.6 Hz), 8.46 (1H, s), 9.24 (1H, s); ^{13}C NMR: 55.4, 114.3, 124.7, 126.6, 127.2, 127.3, 127.9, 128.0, 128.2, 128.4, 128.6, 128.9, 129.5, 129.8, 129.9, 130.4, 130.6, 130.7, 131.1, 131.4, 132.7, 134.0, 134.5, 136.7, 138.4, 142.8, 146.5, 152.1, 159.3; HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{27}\text{N}_3\text{O}$ ($\text{M} + \text{H}$) $^+$ 530.2232, found 530.2235.

2.2.2.3. 2-(4-(isoquinolin-4-yl)phenyl)-1H-phenanthro[9,10-d]imidazole (3). ^1H NMR ($\text{DMSO}-d_6$): 7.65 (2H, m), 7.81 (6H, m), 7.98 (1H, d, 8.8 Hz), 8.26 (1H, d, 8 Hz), 8.51 (2H, d, 8.4 Hz), 8.57 (2H, m), 8.63 (1H, d, 7.2 Hz), 8.87 (2H, m), 9.39 (1H, s), 13.60 (1H, s); ^{13}C NMR: 121.9, 123.9, 1254.3, 126.4, 127.1, 127.5, 128.0, 128.1, 129.9, 130.4, 131.2, 131.9, 133.0, 137.1, 142.4, 148.7, 152.2; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{19}\text{N}_3$ ($\text{M} + \text{H}$) $^+$ 422.1657, found 422.1655.

2.2.2.4. 2-(4-(isoquinolin-4-yl)phenyl)-1-(4-methoxyphenyl)-1H-phenanthro[9,10-d]imidazole (4). ^1H NMR (CDCl_3): 3.96 (3H, s), 7.14 (2H, d, 8.8 Hz), 7.27 (2H, m), 7.46 (5H, m), 7.65 (3H, m), 7.68 (1H, m), 7.78 (2H, m), 7.90 (1H, d, 8.4 Hz), 8.04 (1H, d, 7.6 Hz), 8.47 (1H, s), 8.71 (1H, d, 8.0 Hz), 8.78 (1H, d, 8.4 Hz), 8.90 (1H, d, 8.0 Hz), 9.25 (1H, s); ^{13}C NMR: 55.7, 115.3, 120.9, 122.7, 123.1, 124.1, 124.6, 124.9, 125.6, 126.3, 127.2, 127.9, 128.3, 128.4, 128.5, 129.3, 129.4, 130.0, 130.1, 130.3, 130.7, 131.2, 132.7, 134.0, 137.4, 142.6, 150.6, 152.1, 160.4; HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{25}\text{N}_3\text{O}$ ($\text{M} + \text{H}$) $^+$ 528.2075, found 528.2074.

2.3. Computational details

All calculations on the synthesized molecules have been performed using Gaussian 09 [28]. The ground-state geometries of the studied molecules were fully optimized at the DFT level using B3LYP [29–32] functional with 6-31G(d,p) basis set and the excited state geometries were optimized by the ab initio configuration interaction singles method (CIS) [33]. The vibrational frequency analysis of the optimized geometries confirms that all the optimized geometries are found to be of minimum energy on the potential energy surface by exhibiting all real frequencies. The electronic absorption and emission spectra, both in vacuum and in solvent, were systematically investigated by the time-dependent density functional theory (TD-DFT) [34–37] method at PBE0 [38–39]/6-31+G(d,p) level. The solvent

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