Dyes and Pigments 132 (2016) 1–6

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Tuning the singlet-triplet energy splitting by fluorination at 3,6 positions of the 1,4-biscarbazoylbenzene

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ARTICLE INFO

Article history:
Received 18 March 2016
Received in revised form
13 April 2016
Accepted 17 April 2016
Available online 24 April 2016

Keywords:
Fluorinated carbazole
Mesomeric effect
Triplet energy

ABSTRACT

While it has been known in the past decades that fluorination induces stability and electron transporting ability, less is known is the effect of fluorination on singlet-triplet energy splitting. A series of carbazole derivatives with fluorination at the 3 and/or 6 positions are synthesized using oxidative biaryl coupling method. It was found that fluorine at the 3 and/or 6 positions of 1,4-biscarbazoylbenzene (CCP) reduces the singlet energies and lowers the Lowest Unoccupied Molecular (LUMO) level compared to the non-substituted molecules The triplet energies are almost unaffected by the fluorination. This is in contrast with *tert*-butyl substituents where the triplet energies are reduced. Density functional theory is used to examine the frontier molecular orbitals. It was found that fluorination of carbazole at 3 and/or 6 positions increase the effective conjugation as a result of mesometric effect while *tert*-butyl substituents lower the bandgap through hyperconjugation. Fluorination of carbazole at 3 and 6 positions strongly depleted the connecting benzene of electrons at the LUMO levels. This gives rise to partial spatial separation of the highest occupied molecular orbital (HOMO) and the LUMO levels in fluorinated CCP which reduces the singlet-triplet energy splitting.

1. Introduction

High efficiency deep blue organic phosphorescent light emitting diodes (PhOLEDs) require high triplet hosts in order to effectively confine the triplet excitons formed on the blue phosphorescent emitters [1,2]. However, blue phosphorescent emitters tend to have a significantly shorter lifetime compared to other phosphorescent emitters of different colors. In order to harvest 75% of the triplet excitons, thermally activated delayed fluorescence (TADF) offers a possible solution and a better stability [3–5]. For an efficient TADF facilitated by the fast reverse intersystem crossing, a small singlet-triplet energy splitting (ΔE_{ST}) is required. Often the singlet energy, S_1, is considerably higher than the triplet energy,T_1, by 0.5–1.0 eV in most light-emitting chromophores [6]. In order to obtain low ΔE_{ST}, spatially separated Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) are often used [7]. This is often easily achieved by introducing a large steric hindrance structure or a donor-acceptor system with twist/spiro/bulky connection [8]. It would be interesting to see whether ΔE_{ST} can be tuned by using non-chromophoric substituents. Two of the possible substituents considered here are fluorine and *tert*-butyl groups.

Halogenations can be an effective strategy for lowering the LUMO levels and converting organic semiconducting materials into n-type and even ambipolar [9,10]. Halogenations tend to decrease the bandgap of the organic semiconducting materials with the exception of fluorine [11]. Carbazole molecules are among the most stable wide bandgap semiconducting molecules that were extensively studied for the design of low molecular weight and polymeric hosts [12–14]. The facile modification by coupling reaction with various functional groups and the high triplet energy of the carbazole moiety can be maintained by introducing chromophoric substituents at the 3,6 positions or 9 position of carbazole to

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http://dx.doi.org/10.1016/j.dyepig.2016.04.030
0143-7208/

minimize the extension of conjugation [15]. Fluorination has been used to widen the bandgap of the carbazole such as poly(*N*-vinyl-2,7-difluoro-carbazole) [16]. Alkyl groups are used to facilitate its solubility [17].

In order to study the effect of ΔE_{ST} by fluorination as non-chromophoric substituents, we use 1,4-biscarbazoylbenzene as a reference molecule. Fluorine as a substituent on an aromatic ring can act as a both σ-electron withdrawing and π electron donating side group [18,19]. It would be interesting to see how such behavior can modulate the properties of semiconducting materials in particularly the ΔE_{ST}. Here, we show that by fluorinating at the 3,6 positions of the 1,4-biscarbazoylbenzene (CCP), we can reduce ΔE_{ST} while maintaining the high T_1. This is in contrast with *tert*-butyl groups where such substituents reduce the T_1 significantly.

2. Experimental

2.1. Molecular orbital calculation

Quantum chemical calculations of the fluorinated carbazoles at different substituent positions were carried out using density functional theory (DFT) as implemented in Gaussian 09 software package. The ground state molecular structures were optimized using Becke three parameter hybrid exchange-correlation functional (B3LYP) with 6-311G (d,p) basis set and the triplet excited states were obtained using time-dependent DFT at the same basis set. All the Gaussian 09 files are submitted to Symmetric Multi-Processing (SGiAltix4700, 64x Dual Core Intel Itanium 2 64 bits processors) at University of Malaya High Performance Computing (UMHPC) and Academic GRID (2x Quad Core Intel® Xeon® CPU E5450 @ 300 GHz) for calculations. Higher accuracy of triplet energies can be obtained by using correction factor as described in the paper [20].

2.2. Synthesis of the fluorinated carbazole derivatives

Unlike other halogen atom (Cl, Br or I), there is no report in the literature on direct fluorination of the carbazole. Most methods that have been used either involved the conventional method of Sandmayer reaction [21] or halogen exchange method [22]. The novel fluorinated carbazole derivatives are synthesized using oxidative biaryl coupling method. The novel/new compound **4**, **5**, and **6** were synthesized in three steps. The first step involved the *N*-arylation of the aniline **7** with boronic acid **8** by a copper-catalyzed cross-coupling reaction to produce diarylamines in good yields.[32] The resulting diarylamines were then subjected to intramolecular oxidative biaryl coupling in the presence of one equivalence of Pd(II) acetate to give the respective fluorinated carbazoles in very good yields, Scheme 1 [23].

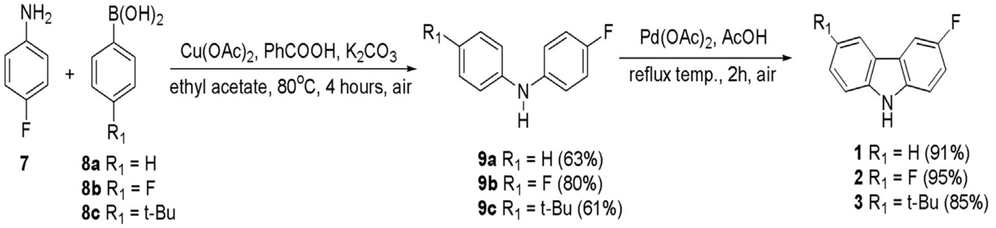
The fluorinated carbazole **1**, **2**, and **3** and carbazole itself were then reacted with 1,4-diiodobenzene under Ullman coupling reaction as shown in Scheme 2 to produce new fluorinated carbazole derivatives in moderate yields [24].

2.3. Characterization of fluorinated carbazole derivatives

All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a Bruker AVANCE III 400 NMR Spectrometer with tetramethylsilane as the internal standard. Mass was determined by Microflex MALDI-TOF instrument using CH_2Cl_2 as solvent without any matrix added. Thermal decomposition temperature, T_d was measured using Perkin Elmer (TGA4000) with a compact ceramic furnace under a dry nitrogen gas flow at a heating rate of 10 °C min^{-1}. The data can be found in supporting information. Absorption spectra were recorded with a SHIMADZU UV–Vis Spectrophotometer (UV-2600) and photoluminescence spectra were recorded with a Fluorescence Spectrophotometer (Gary, Eclipse). Cyclic voltammetry was performed on the Autolab Potentiostat/Galvanostat model using CH_2Cl_2 solutions as solvent (10^{-3} M) at a scan rate of 100 mV^{-1} with glassy carbon as the working electrode, a silver wire as the reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium hexafluoroborate 99% (0.01 M) and ferrocene was selected as the internal standard. TA Differential Scanning Calorimeter (DSCQ20) was used to determine the phase transition temperatures of the compound heating at a rate of 10 °C min^{-1} under dry nitrogen environment. The fluorinated carbazoles are dissolved in tetrahydrofuran at concentration of 1 mg/mL. The samples were attached to the sample holder in a nitrogen cryostat (Janis). The samples were excited at 350 nm by a 150 fs pulsed Ti:sapphire laser (Spectra-Physics Hurricane) at 1 kHz repetition rate in conjunction with an ultrafast optical parametric amplifer (Quantronix TOPAS). A monochromator (Princeton Instruments Acton SP 2150) and then to a gated intensified CCD camera (Andor ICCD 334T) are used to capture the phosphorescence.

3. Results and discussion

We synthesized 3-fluorocarbazole (3-F-Cz) 3,6-difluorocarbazole (3,6-F-Cz) and 3-*tert*-butyl-6-fluorocarbazole (3-ter-6-Cz) with carbazole as a comparison. Fig. 1(a) shows the absorption spectra of non-substituted carbazole (Cz) and fluorinated carbazoles while Fig. 1(b) shows the absorption spectra of non-substituted CCP and fluorinated CCPs in dichloromethane solution. All the fluorinated carbazoles and CCPs at 3 and/or 6 positions are red-shifted into lower energies. The band-gap can be estimated from the edge of the wavelength of each absorption curve. The bandgaps for nonsubstituted Cz, 3 F-Cz, 3-ter-6-Cz and 3,6-F-Cz are 3.59 eV, 3.52 eV, 3.44 eV and 3.39 eV respectively. Similar trends are observed for CCP and fluorinated CCPs as shown in Fig. 1(b). For non-fluorinated CCP, the bandgap is 3.46 eV while for 1,4-bis(3-fluorocarbazoyl)benzene (3,3-F-CCP), 1,4-bis(3-*tert*-butyl-6-fluorocarbazoyl)benzene (3-*tert*-6-F-CCP) and 1,4-bis(3,6-difluorocarbazoyl)benzene (3,6-d-F-CCP) are 3.34 eV, 3.32 eV and 3.30 eV respectively. In both carbazoles and CCPs, functionalization



Scheme 1. Synthesis of fluorinated carbazole derivatives.