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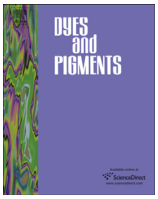

Thermally activated delayed fluorescence of *N*-phenylcarbazole and triphenylamine functionalised tris(aryl)triazines

Bin Huang [a, b], Zhihui Yin [b], Xinxin Ban [a], Wei Jiang [a, *], Yu Dai [b], Junya Zhang [b], Yuanyuan Liu [b], Yaping Yang [b], Yueming Sun [a, *]

[a] *School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu 211189, PR China*
[b] *Department of Chemical and Pharmaceutical Engineering of Southeast University Chengxian College, Nanjing, Jiangsu 210088, PR China*

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ABSTRACT

N–phenyl carbazole and triphenylamine functionalized tris(aryl)triazines, as well as the corresponding mononers, have been synthesized by Suzuki cross–coupling reactions. The electronic, photophysical and electrochemical properties of these materials can be effectively tuned by manipulation of the constitution of acceptor and donor units. *N*–phenyl carbazole and triphenylamine functionalized 2,4,6–trisphenyl–1,3,5–triazines exhibit small energy gaps between the singlet and triplet (0.24 eV and 0.18 eV), and offer potential for application as thermally activated delayed fluorescence materials. The results are supported by time–dependent density functional theory calculations, delayed and time-resolved fluorescence data.

1. Introduction

In recent years, tremendous efforts have been made in the development of materials for phosphorescent organic light emitting diodes (PHOLEDs) due to 100% theoretical internal efficiency [1–6]. Phosphorescent host materials and phosphors are indispensable to obtain high–efficiency PHOLEDs. However, traditional phosphors based on precious transition metals such as Ir(?), Pt(?), or Os(?) are rather expensive. The development of cheaper alternatives has attracted more and more attention [7,8]. One promising solution for this issue is the use of thermally activated delayed fluorescence (TADF) materials because they have the potential to substitute the phosphors for cost–effective and high–efficiency environmentally OLEDs [9–13].

For a TADF molecule, a small energy gap between the singlet and triplet (ΔE_{ST}) is required to promote reverse intersystem crossing (ISC) [9]. To achieve efficient TADF, the most probable way is via bipolar compounds based on intramolecular charge transfer (ICT) within systems containing donor and acceptor moieties. In an ICT based compound, the highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO) would be localized at the donor and acceptor moieties, respectively. Thus, effective separation of HOMO and LUMO leads to a small ΔE_{ST}. Enormous attempts have been made in the development of materials with small ΔE_{ST} values. Various TADF materials based on donor substituted cyanobenzene [9,14,15], triazine [16–25], sulfone [26–28], benzophenone [29], spirofluorene [30], oxadiazole and triazole [31] have been designed and applied to realize high–performance OLEDs.

Recently, our group reported a bipolar host composed of electron–transporting 2,4,6–trisphenyltriazine and hole–transporting *N*–phenylcarbazole, namely 2,4,6–tris(3–((9–phenyl)carbazol–3–yl)phenyl)triazine (**3a**) [32]. Utilizing **3a** as host material, highly efficient solution–processed single layer green PhOLED has been achieved. Density functional theory (DFT) has revealed that the LUMO level of **3a** is localized predominantly on the 2,4,6–trisphenyl–1,3,5–triazine unit while the HOMO level is distributed over the outer layer *N*–phenylcarbazole unit with a limited HOMO–LUMO overlap. The low HOMO–LUMO overlap leads to a small ΔE_{ST} of 0.24 eV. Inspired by the results, we have designed triphenylamine substituted 2,4,6–trisphenyl–1,3,5–triazine (**3b**) and decreased the ΔE_{ST} to 0.18 eV. To verify the TADF behavior of **3a**

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* Corresponding authors. Tel./fax: +86 25 52090621.
E-mail address: 101011462@seu.edu.cn (W. Jiang).

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and **3b**, we present a detailed study of photophysical characteristics including fluorescence solvatochromical effects, time-resolved fluorescence and phosphorescence, delayed fluorescence lifetime, and time−dependent density functional theory (TD−DFT). To reveal the importance of molecular configuration for giving effective TADF, *N*−phenylcarbazole and triphenylamine substituted benzonitriles (**2a**, **2b**) as the corresponding monomers of **3a** and **3b** have been prepared for comparison in this paper.

2. Experimental

2.1. General

DFT calculations of these compounds were performed using the Gaussian 09 program package [33]. The calculations were optimized at the B3LYP/6−31G(d) level of theory. The molecular orbitals were visualized using Gaussview. To investigate the properties of the excited states of these compounds, we performed quantum chemical calculations of the low−lying excited states of these compounds using TD−DFT. The ten lowest singlet and triplet excited states were calculated by the TD−DFT method at their optimized ground−state geometries using the same functional and basis set [12].

All materials and reagents were purchased from commercial sources and used without further purification. IR spectra were recorded on a 5DX-FT-2 spectrophotometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX300 NMR spectrometer at room temperature. Elemental analyses were performed on an Elementar Vario EL CHN elemental analyzer. UV−vis absorption spectra and fluorescence spectra were recorded on a spectrophotometer (Agilent 8453) and a fluorospectrophotometer (Jobin Yvon, Fluoromax−3), respectively. The transient photoluminescence decay characteristics and time-resolved fluorescence were recorded using a spectrofluorometer (Floromax-4, Horiba). The fast decay component was recorded with a 350 nm LED excitation source, while the slow decay component was recorded with a flash lamp source. Cyclic voltammetry (CV) measurements was carried out on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in CH_2Cl_2 solutions (10^{-3} M) at a scan rate of 100 mV s^{-1} with a conventional three−electrode configuration consisting of platinum plate working electrode, a silver wire pseudo−reference electrode, and a platinum wire counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) and ferrocene was selected as the internal standard. The solutions were bubbled with a constant nitrogen flow for 10 min before measurements.

2.1.1. X-ray crystallography

X-ray crystallographic analysis of **2b** was performed on a Nonius CAD-4 single-crystal diffractometer by using MoK_α radiation ($\lambda = 0.71073$ Å) with an $\omega/2\theta$ scan mode at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at calculated positions. The isotropic temperature factors were fixed to 1.2 times (1.5 times for CH_3 groups) the equivalent isotropic displacement parameters of the C-atom which the H-atom was attached to. Drawings were produced using Diamond 3.0 and Mercury 1.4.1 software. Crystallographic data for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplemental publications.

CCDC 994818 for **2b**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

2.2. Synthesis

2.2.1. Synthesis of 3−((9−phenyl)carbazol−3−yl)−benzonitrile (*2a*)

To a solution of 3−bromobenzonitrile (0.546 g, 3.0 mmol) and *N*−phenyl−3−(4,4,5,5− tetramethyl−1,3,2−dioxaborolane−2−yl)−6*H*−carbazole (**1a**, 1.107 g, 3.0 mmol) in toluene (20 mL) and ethanol (4 mL) was added aqueous K_2CO_3 solution (2.0 M, 2 mL). The reaction mixture was then purged with nitrogen for 10 min before adding tetrakis(triphenylphosphine)palladium(0) (0.055 g, 0.048 mmol). The reaction mixture was heated under reflux for 24 h under nitrogen. The resulting mixture was cooled to room temperature and then poured into water and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with saturated aqueous NaCl solution (2 × 10 mL) and dried with anhydrous Na_2SO_4. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography to afford **2a** as a white solid. Yield: 73.6%. Mp: 117−119 °C. IR (KBr, cm^{-1}):3057, 2225, 1626, 1597, 1501, 1472, 1455, 1402, 1361, 1232. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.35 (s, 1H), 8.24−8.21 (d, J = 7.5 Hz, 1H), 8.02 (s, 1H), 7.98−7.93 (d, J = 7.5 Hz, 1H), 7.69−7.36 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm):110.46, 110.74, 113.25, 119.24, 119.48, 120.75, 120.79, 123.57, 124.44, 125.44, 126.88, 127.39, 128.10, 129.92, 130.25, 130.37, 131.06, 131.22, 131.91, 137.73, 141.19, 141.82, 143.50. Anal. Calcd. for $C_{25}H_{16}N_2$ (%): C, 87.18; H, 4.68; N, 8.13. Found: C, 87.28; H, 4.72; N, 8.19. MS (MALDI-TOF) [m/z]:Calcd for $C_{25}H_{16}N_2$, 344.41; found, 344.3834.

2.2.2. Synthesis of N,N−diphenyl−(1,1′−biphenyl)−3′−cyano-4−amine (*2b*)

A procedure similar to that used for **2a** was followed but with *N,N*−diphenyl−4−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−-yl)aniline (**1b**) instead of **1a**. Yield: 62.5%. Mp: 122−124 °C. IR (KBr, cm^{-1}): 3005, 2229, 1588, 1514, 1482, 1432, 1401, 1330, 1276. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.83 (s, 1H), 7.79−7.77 (d, J = 7.8 Hz, 1H), 7.59−7.48 (m, 2H), 7.44−7.41 (d, J = 8.7 Hz, 2H), 7.32−7.26 (m, 4H), 7.16−7.04 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm):113.29, 119.33, 123.26, 123.70, 123.85, 124.75, 125.19, 128.11, 129.45, 129.82, 129.96, 130.45, 130.37, 131.21, 132.45, 142.25, 147.73, 148.66. Anal. Calcd. for $C_{25}H_{18}N_2$ (%): C, 86.68; H, 5.24; N, 8.09. Found: C, 86.74; H, 5.22; N, 8.13. MS (MALDI-TOF)[m/z]:Calcd for $C_{25}H_{18}N_2$, 346.42; found, 346.2814.

2.2.3. Synthesis of 3′,3′′′,3′′′′′−(1,3,5−triazine−2,4,6−triyl) tris(N,N−diphenyl−(1,1′−biphenyl)−4−amine) (*3b*)

To a solution of 2,4,6−tris(3−bromophenyl)triazine (**1c**, 0.546 g, 1.0 mmol) and **1b** (1.113 g, 3.0 mmol) in toluene (20 mL) and ethanol (4 mL) was added 2 mL of 2.0 M aqueous Na_2CO_3 solution. The reaction mixture was then purged with nitrogen for ten minutes before adding tetrakis(triphenylphosphine)palladium(0) (0.055 g, 0.048 mmol). The reaction mixture was heated under reflux for 24 h under nitrogen. The resulting mixture was cooled to room temperature and then poured into water and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with saturated aqueous NaCl solution (2 × 10 mL) and dried with anhydrous Na_2SO_4. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography to afford **3b** as a yellow solid. Yield: 42.4%. Mp: 209−211 °C. IR (KBr, cm^{-1}): 3060, 3032, 1591, 1527, 1510, 1492, 1436, 1406, 1358, 1328, 1276. ^{1}H NMR(300 MHz, $CDCl_3$) δ(ppm): 9.00 (s, 3H), 8.77−8.74 (d, J = 7.5 Hz, 3H), 7.86−7.83 (d, J = 7.5 Hz, 3H), 7.67−7.64 (d, J = 8.1 Hz, 9H), 7.31−7.06 (m, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm):123.44, 124.33, 124.88, 127.42, 127.92, 128.34, 129.48, 129.73, 131.12, 134.96, 137.12, 141.40, 147.90, 148.05, 172.03. Anal. Calcd. for $C_{75}H_{54}N_6$ (%): C, 86.68; H, 5.24; N, 8.09. Found: C, 86.74;