



Efficient blue-emitting molecules by incorporating sulfur-containing moieties into triarylcyclopentadiene: Synthesis, crystal structures and photophysical properties



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ABSTRACT

Three highly fluorescent blue-emitting molecules, namely 1,2-diphenyl-4-(4-thiophenyl)-1,3-cyclopentadiene (**DPCP 1**), 1,2-diphenyl-4-(4-thiophenyl)phenyl)-1,3-cyclopentadiene (**DPCP 2**) and 1,2-diphenyl-4-(4-dibenzothiophenyl)phenyl)-1,3-cyclopentadiene (**DPCP 3**), have been synthesized by using aryl-substituted cyclopentadiene and thiophene or dibenzothiophene as ingredients. The single crystal structure analysis reveals that **DPCP 1–3** are non-coplanar structures and bulky substituents on cyclopentadiene core imposed a significant reduction on intermolecular interactions, hence leading to their intense blue emission in both solution and solid state. **DPCP 1** and **DPCP 3** also showed a typical aggregation-induced emission enhancement in mixed water/acetone solution. These compounds exhibited good thermal stability with decomposition temperatures between 239 and 383 °C. The non-doped organic light-emitting diodes using **DPCP 3** as the emitting layer displayed a very low turn-on voltage at 3.2 V and pure blue emission with the Commission Internationale de l'Éclairage (CIE_{x,y}) coordinates of (0.16, 0.16) and a maximum luminance of 2277 cd m⁻².

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1. Introduction

The development of high efficient organic optoelectronic materials has attracted tremendous attention from both the academic and industrial research communities because of their promising applications in the fields of organic light-emitting diodes (OLEDs) [1], illumination [2], photovoltaic cells [3], molecular probes [4], bio-labeling [5] and photonic devices [6]. Most of organic fluorophores are highly emissive in their dilute solutions, but it becomes weakly luminescent when fabricated into thin films. In the solid state, the molecules aggregate to form less emissive species such as excimers, leading to a reduction in the luminescence efficiency [7]. Such aggregation-caused quenching (ACQ) effect has become a drawback to the development of high efficient and stable OLEDs [8]. Since the anti-ACQ compounds 1-methyl-1,2,3,4,5-

pentaphenylsilole and 1-cyano-*trans*-1,2-bis-(4'-methylbiphenyl) ethylene having strong emission in the aggregated state than that in dilute solution were reported by Tang et al. [9] and Park et al. [10], respectively, different type of materials with aggregation-induced emission (AIE) or aggregation induced emission enhancement (AIEE) characteristics have been discovered [11]. The restriction of intermolecular rotations (RIR), molecular planarization, prevention of exciton diffusion and *J*-aggregates formation effects are accepted to understand enhanced emission phenomena [12]. However, the efficient AIE or AIEE materials systems for blue-emitting molecules are still quite limited.

In order to decrease the aggregation quenching of aromatic hydrocarbons possessing extended π -conjugation and planar skeleton, some efforts have been spent to modify the fluorophore backbone by attaching bulky substituents to the molecular core [13]. For examples, a series of aryl-functionalized blue emitting pyrene derivatives were synthesized by steric hindrance introduced through bulky substituents in its 1-, 3-, 5-, 6-, 8- and 9H position of pyrene core [14], respectively. Several quinacridone derivatives with high-emission property in both solution and solid

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state were synthesized based on the introduction of two propeller-like pentaphenyl groups to a quinacridone core [15]. Furthermore, cyclopentadiene derivatives (CPs) are known for versatile organic molecules due to their good electrical and optical properties [16,17], as well as multicolor emission in nano-aggregation [18]. Huang et al. [19] reported two CPs named 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (TPCP) and 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (PPCP) which were used in blue light-emitting OLEDs. Yoshino et al. [20] reported multicolor OLEDs based on PPCP or PPCP-doped poly(3-alkylthiophene) as emissive layer. Recently, our researches are mainly focused on the molecule design and understanding relationship between molecular structures and optoelectronic properties of the polyphenyl substituted CPs, and a new class of triarylsubstituted CPs with good thermal stability and strong fluorescence in solid state were synthesized [21]. It has been demonstrated that the introduction of rich electron-donor moieties into the molecular backbone of CPs would improve the emission efficiency and color purity of the target molecules.

In this work, we would like to introduce thiophene and dibenzothienophene segments with the good amorphous film forming ability and the electron-transporting ability [22] into the 4-position of the 1,2-diphenyl or 1, 2, 4-triphenyl cyclopentadienyl core to obtain a series of novel blue emission materials, namely 1,2-diphenyl-4-thiophenyl-1,3-cyclopentadiene (**DPCP 1**), 1,2-diphenyl-4-(4-thiophenyl)phenyl-1,3-cyclopentadiene (**DPCP 2**) and 1,2-diphenyl-4-(4-dibenzothienophenyl)phenyl-1,3-cyclopentadiene (**DPCP 3**). We present a comprehensive investigation on these three CPs compounds, which not only encompasses their thermal, photophysical and electrochemical properties, but also the emphatically studies on their single-crystal structures and DFT calculation have been investigated to understand the relationship between chemical structures and luminescent properties. The resulting non-coplanar structures due to the steric hindrance of bulky phenyl ring and sulfur-containing moieties could suppress the intermolecular π - π interactions and reduce the aggregation formation. It is worth mentioning that an efficient pure blue OLEDs based on **DPCP 3** as the neat emitting layer was achieved.

2. Experimental section

2.1. Materials and methods

All reagents were analytical reagent grade and used as received. The solvents were purified with standard methods and dried as needed. All ^1H and ^{13}C NMR spectra were referenced to a Bruker AVANCE-400 MHz magnetic resonance spectrometer. HRMS were acquired on Micromass-GTC spectrometer. Differential scanning calorimetry (DSC) curves were obtained with a TA Instruments thermal analyzer (910S) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Thermogravimetric analyses (TGA) were performed with a METTLER TOLEDO (TGA/SDTA 851^e) under nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. UV absorption measurements were conducted on HITACHI U-4100 UV-vis Spectrophotometer. The photoluminescence (PL) studies were confirmed with a JASCO FP-6300 spectrofluorometer with a 150 W Xe lamp. The relative fluorescence quantum yields were estimated relative to solutions of $5 \times 10^{-5}\text{ M}$ quinine sulfate with $\Phi_{\text{F}} = 0.55$ in 0.1 M sulfuric acid solution as a standard sample [23]. Cyclic voltammetry (CV) measurement was carried out on a Shanghai Chenhua electrochemical workstation CHI660C in a three-electrode cell with a Pt disk working electrode, an Ag/AgCl reference electrode, and a glassy carbon counter electrode. All spectra were carried out at room temperature.

2.2. Synthesis

2.2.1. 1,2-Diphenyl-4-thiophenyl-1,3-cyclopentadiene (**DPCP 1**)

A solution of thiophene-2-carboxaldehyde (2.50 g, 22.29 mmol) and acetophenone (6.70 g, 55.83 mmol) in ethanol was heated to $65\text{ }^\circ\text{C}$, and aqueous sodium hydroxide (2.23 g, 55.83 mmol) was added to the solution. The mixture was heated to reflux for 1 h and then cooled to room temperature. The intermediate product was cyclized in Zn/CH₃COOH system for 5 h, in which zinc dusts were added per hour. The solution layer was poured into 600 mL water to get white precipitate. The solid was collected by filtration and then dried under vacuum, and it was dehydrated in the presence of concentrated hydrochloric acid for 3 h and then cooled to room temperature [19]. Light yellow solid precipitate was obtained by filtration. The obtained solid was purified by column chromatography on silica gel using dichloromethane/petroleum ether as eluent to obtain the product in yield 78%. ^1H NMR (400 MHz, CDCl₃) δ (ppm): 7.39–7.38 (m, 2H), 7.36–7.34 (m, 1H), 7.33–7.30 (m, 4H), 7.28–7.25 (m, 2H), 7.24–7.22 (m, 2H), 7.10–7.17 (m, 1H), 7.16–7.02 (m, 1H), 7.01–6.86 (m, 1H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ (ppm): 144.4, 144.3, 142.2, 139.5, 137.1, 136.8, 134.9, 132.9, 132.1, 128.5, 128.4, 128.3, 128.1, 127.8, 127.2, 126.6, 126.1, 125.3, 124.7, 122.9, 44.87. MS (API-ES): calcd for C₂₁H₁₆S, M: 300.1. Elem. Anal.: C, 83.98%; H, 5.42%; S, 10.71%. Found: C, 83.96%; H, 5.37%; S, 10.67%.

2.2.2. 1,2-Diphenyl-4-(4-thiophenyl)phenyl-1,3-cyclopentadiene (**DPCP 2**)

1,2-Diphenyl-4-(4-bromophenyl)-1,3-diene was synthesized according to our previously work [21] in essentially similar procedures. 1,2-diphenyl-4-(4-bromophenyl)-1,3-diene (0.78 g, 2.10 mmol) and the 2-thiopheneboronic acid (0.31 g, 2.40 mmol) in toluene (15 mL), 2 M aqueous K₂CO₃ solution (10 mL) and ethanol (5 mL) were added. The mixture was stirred for 30 min under an argon atmosphere at room temperature. Then the Pd(PPh₃)₄ catalyst was added and the reaction mixture was stirred at $80\text{ }^\circ\text{C}$ for 24 h allowing the temperature to decrease gradually to room temperature [14a,24]. The crude product was concentrated and purified by silica gel column chromatography using petroleum ether/dichloromethane (v:v, 10:1, yield 76%). ^1H NMR (400 MHz, CDCl₃) δ (ppm): 7.61–7.55 (m, 4H), 7.41–7.39 (m, 2H), 7.35–7.28 (m, 6H), 7.26–7.21 (m, 3H), 7.19–7.17 (m, 1H), 7.09–7.06 (m, 2H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ (ppm): 142.0, 140.4, 139.1, 138.1, 136.9, 136.6, 131.5, 128.5, 128.4, 128.3, 128.2, 127.7, 127.2, 126.6, 123.7, 122.8, 45.84. MS (API-ES): calcd for C₂₇H₂₀S, M: 376.1. Elem. Anal.: C, 86.21%; H, 5.39%; S, 8.63%. Found: C, 86.13%; H, 5.35%; S, 8.52%.

2.2.3. 1,2-Diphenyl-4-(4-dibenzothienophenyl)phenyl-1,3-cyclopentadiene (**DPCP 3**)

The synthesis of **DPCP 3** was similar to the above description for **DPCP 2** except that 2-thiopheneboronic acid was replaced by 4-dibenzothiopheneboronic acid. The light yellow powder was obtained with the yield of 85%. ^1H NMR (400 MHz, CDCl₃) δ (ppm): 8.23–8.21 (m, 1H), 8.19–8.17 (m, 1H), 7.88–7.86 (m, 1H), 7.79–7.74 (m, 4H), 7.59–7.57 (d, 1H), 7.56–7.54 (m, 1H), 7.51–7.49 (m, 2H), 7.46–7.44 (m, 2H), 7.39–7.34 (m, 5H), 7.32–7.29 (d, 1H), 7.27–7.25 (d, 1H), 7.22–7.21 (d, 1H), 7.16 (s, 1H), 4.04 (s, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ (ppm): 144.5, 142.2, 139.7, 139.6, 139.1, 138.5, 137.2, 136.8, 136.7, 136.3, 135.8, 135.4, 132.4, 128.7, 128.6, 128.5, 128.3, 127.8, 127.3, 126.9, 126.8, 126.7, 125.3, 125.2, 124.4, 122.7, 121.8, 120.5, 45.0. MS (API-ES): calcd for C₃₅H₂₄S, M: 476.2. Elem. Anal.: C, 88.29%; H, 5.16%; S, 6.78%. Found: C, 88.20%; H, 5.08%; S, 6.73%.

2.2.4. Single-crystal X-ray crystallography

The single crystals of three compounds were grown from a mixture of CH₂Cl₂ and CH₃OH. X-ray crystal structure

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