Aggregation-induced bathochromic fluorescent enhancement for fluorenone dyes

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ARTICLE INFO

ABSTRACT

Organic solid-state luminescence materials with aggregation-induced emission enhancement have attracted considerable interest in recent years. In this work, we develop a class of 2,7-diphenylfluorenone derivatives that exhibit prominent aggregation-induced emission properties with high solid-state quantum yields. Their solid-state powders show a ~160 nm bathochromically shifted fluorescence and longer lifetime compared to their emission in dilute THF solution. The X-ray single structures and photophysical properties reveal that the mechanism of aggregation-induced emission in this class of fluorenone compounds is due to the formation of static excimers through hydrogen bonds in the solid state. The emission of their THF solution peaked at 380 nm and originates from the single molecule and the emission of their solid-state powder peaked at 550 nm originates from the excimers. The aggregation-induced emission properties and luminescence mechanism are further verified by the design of 2,7-diphenylfluorenone-diboronic acid adduct, which exhibited weak luminescence in high pH buffer and red-shifted strong luminescence in acidic buffer.

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1. Introduction

Organic luminescent materials have attracted numerous interest not only in the fundamental research field of photochemistry but also in the applied field of optoelectronic devices [1]. Having sufficient high solid-state luminescent efficiency is a fundamental issue for luminescent materials, because most organic devices are only able to function in either a film or crystalline state [2]. However, general organic fluorophores are highly emissive only in dilute solution and tend to show a decrease of luminescent efficiency in the solid state due to the aggregation-induced quenching (AIQ) effect [3].

Great effort has been exerted to enhance the solid-state efficiency of organic luminescent materials by using chemical, physical, and engineering approaches [4]. However, these attempts have achieved limited success. In 2001, an anti-AIQ phenomenon that a non-emissive compound in organic solution that exhibits an obviously enhanced fluorescence in its aggregated state, which is

referred to as aggregation induced emission (AIE) enhancement, was first reported by the Tang group [5]. This phenomenon offers a new path to obtain ideal organic solid-state luminescent materials. Consequently, a number of AIE molecules with different structures were developed by various research groups in the past decade [1c,6—16]. However, current studies of the AIE materials are primarily limited to several classes, such as silole, tetraphenylethene (TPE), tetraphenylpyrazine, cyano-stilbene and difluoroboron avobenzone compounds. For discoveries of new organic AIE systems, the design and synthesis of new AIE materials with high luminescent efficiency still remain important.

In addition, deciphering the AIE working principle is also of great significance. A correct mechanistic understanding of the AIE process may help to obtain new photophysical insights and develop new AIE luminogens. For the reported AIE processes, several possible mechanisms have been proposed to cater to the respective spectral phenomena [17], including restriction of intramolecular rotation (**RIR**) [17c], intramolecular planarization [6], the formation of J-aggregates [8], inhibition of photoisomerisation and the blockage of non-radiative relaxation pathways of the excited species [17d]. At present, the **RIR** mechanism has been widely explored

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and becomes the well accepted one in some AIE systems [17a]. However, the other proposed mechanisms have not been completely confirmed and approved until now, because of the lack of the in-depth verified experimental data. Elaborately designing experiments and strategies to verify the AIE mechanisms still remain a challenge and are of academic interest.

With this concept in mind, we have embarked on the development of new AIE compounds to enlarge the AIE library. Fluorene, with perfect rigidity planarity and π-conjugation, has been widely used as an optoelectronic material due to its excellent luminescent properties. However, in contrast to fluorene, fluorenone compounds have seldom been studied because they are almost non-emissive in solution [18]. Their AIE property was firstly found and reported by the Tao group [18a]. To carry out more extensive investigations and ascertain the AIE mechanisms, we synthesized two aryl substituted fluorenone derivatives: 2,7-diphenyl-9*H*-fluoren-9-one (**DPF**) and 2,7-bis(2-methylphenyl)-9*H*-fluoren-9-one (**MDPF**) in this paper. Their molecular structures are shown in Scheme 1; both of these compounds exhibit typical AIE properties and possess high solid-state fluorescence quantum yields. In addition, they exhibit a considerably different spectral character with those reported character to classic AIE compounds, which generally keep an almost identical emission peak position regardless of whether they are in the solid state or in solution. However, the solid-state fluorescence of the two fluorenone compounds shows a ~160 nm red-shift in comparison with their dilute THF solution. The abnormal spectra characteristics indicate their abnormal AIE procedure. To reveal the mechanism and have an insight into the optical process, we cultured single crystals of each compound and determined the X-ray crystal structures. Furthermore, enlightened from the reference reported by the Tang group [19], we designed and synthesized a **DPF**-diboronic acid adduct, ((9*H*-fluorene-2,7-diyl)bis(4,1-phenylene))diboronic acid (**BDPF**), through functionalising the terminal positions of **DPF** with two boronic acid units. The AIE mechanism was further verified by the spectral characteristics of **BDPF** in various pH buffers.

Scheme 1. Molecular structures of compounds **DPF** and **MDPF**, and the synthesis of compound **BDPF**. (a) Bromine, H$_2$O, reflux, 10 h; (b) Bis(pinacolato)diboron, [(C$_6$H$_5$)$_3$P]$_2$PdCl$_2$, potassium acetate, DMSO, 80 °C, 20 h; (c) Sodium periodate, hydrochloric acid, room temperature, 24 h.

2. Experimental section

2.1. Synthesis and characterizations of the subject compounds

Solvents for reactions and spectral measurements were dried and distilled before use. The reagents used for reactions were purchased from J&K Scientific Ltd. ^{1}H NMR spectra were recorded at 25 °C on Bruker Avance 500 MHz spectrometer using CDCl$_3$ as solvent. ^{13}C NMR spectra were recorded at 25 °C on Bruker Avance 125 MHz spectrometer using CDCl$_3$ as solvent. Element analyses (C, H) were performed using a PE 2400 autoanalyser. Mass spectrometry analyses were performed by a Bruker Biflex III matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometer.

Compound **DPF** was synthesized according to literature method reported by us [17b].

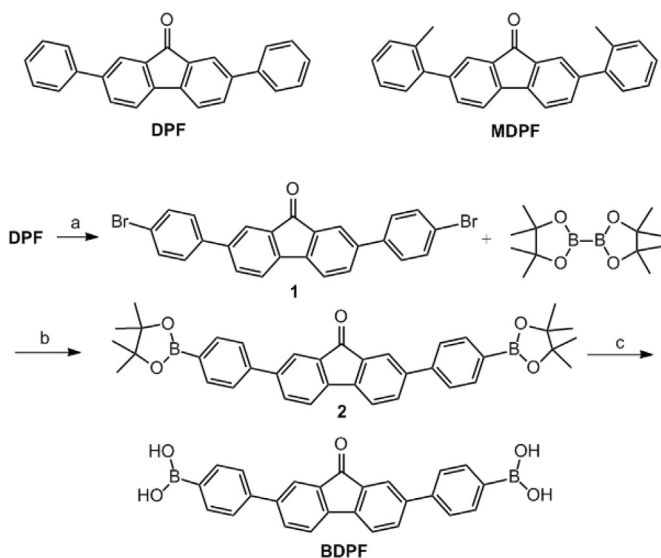#### 2.1.1. Synthesis of 2,7-bis(2-methylphenyl)-9H-fluoren-9-one (MDPF)

A mixture of 2,7-dibromo-9*H*-fluoren-9-one (0.60 g, 1.77 mmol), 2-methylphenylboronic acid (0.60 g, 4.41 mmol), Pd(PPh$_3$)$_4$ (20 mg, 0.02 mmol), toluene (20 mL), ethanol (5 mL) and 2 M K$_2$CO$_3$ aqueous solution (2 mL) was heated to 80 °C with stirring under an argon atmosphere. The yellowish-green crystals directly precipitated from the reaction system after the mixture reacted for approximately 3 h at 80 °C. The crude crystals were recrystallized from tetrahydrofuran (THF)/ethanol (3:7, v/v) to yield compound **MDPF** (0.49 g, 78%). Melting point (m.p.): 138 °C–140 °C. IR (KBr, cm^{-1}): 3414, 3051, 2952, 1925, 1710, 1605, 1463, 1381, 1111, 840, 758,735. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 2.31 (s, 6H), 7.25–7.30 (m, 8H), 7.45–7.47 (d, *J* = 7.5 Hz, 2H), 7.58–7.60 (d, *J* = 7.6 Hz, 2H) and 7.65 (s, 2H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 193.9, 143.1, 142.9, 140.6, 135.6, 135.3, 134.5, 130.6, 129.5, 127.9, 126.1, 125.2, 120.2 and 20.5. TOF-MS-EI: *m/z* 360.1 [M]$^+$. Elemental anal. calcd. for C$_{27}$H$_{20}$O: C, 89.97 and H, 5.59. Found: C, 89.68 and H, 5.72.

2.1.2. Synthesis of 2,7-bis(4-bromophenyl)-9H-fluoren-9-one (1)

A mixture of compound **DPF** (0.30 g, 0.90 mmol), Br$_2$ (0.20 mL, 3.9 mmol) and H$_2$O (10 mL) were heated to reflux and stirred for 10 h. Afterwards, the mixture was cooled to room temperature and filtered off under suction, washed with water. The residue was recrystallized from THF to yield 2,7-bis(4-bromophenyl)-9*H*-fluoren-9-one **1** (0.25 g, 57%) as an orange crystal. Melting point (m.p.): 283 °C–284 °C. IR (KBr, cm^{-1}): 3414, 3048, 1714, 1605, 1582, 1458, 1296, 1177, 1070, 1003, 815, 782, 744. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.51–7.53 (m, 4H), 7.61–7.65 (m, 6H), 7.72–7.74 (d, *J* = 7.7 Hz, 2H) and 7.90 (s, 2H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 193.5, 143.3, 141.1, 138.7, 135.3, 133.2, 132.1, 128.4, 122.9, 122.3 and 121.0. TOF-MS-EI: *m/z* 488.3 [M]$^+$.

2.1.3. Synthesis of 2,7-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-9-one (2)

A mixture of compound **1** (0.20 g, 0.40 mmol), bis(pinacolato)diboron (0.26 g, 1.0 mmol), potassium acetate (0.20 g, 2.0 mmol) and bis(triphenylphosphine)palladium(II) chloride (10.2 mg) in dimethylsulfoxide (DMSO, 10 mL) was stirred under Argon at 80 °C for 20 h. After completion, solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel and elution with dichloromethane-petroleum ether (1:1, v/v) yielded compound **2** (0.20 g, 87%) as yellow crystals. Melting point (m.p.): >300 °C. IR (KBr, cm^{-1}): 3419, 2976, 1714, 1608, 1520, 1465, 1361, 1144, 1091, 857, 824, 656. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.38 (s, 24H), 7.59–7.65 (q, *J* = 7.6 Hz, 6H), 7.75–7.78 (d, *J* = 7.7 Hz, 2H) and 7.90–7.95 (t, *J* = 7.9 Hz, 6H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 193.7, 143.3, 142.4, 142.1, 135.5, 135.2, 133.5, 126.1, 123.2,