



A novel D-A-D-A-D type molecule based on substituted dihydroindolo [3, 2-b] carbazole with large two-photon absorption cross section and excellent aggregation-induced enhanced emission property



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ABSTRACT

Two novel D-A-D-A-D type molecules **T1** and **T2** based on substituted dihydroindolo [3, 2-b] carbazole with large two-photon absorption (2PA) cross section and excellent aggregation-induced enhanced emission (AIEE) property have been synthesized and characterized. Both compounds emit weakly fluorescent in THF, while a significant AIEE property is observed in water/THF (v/v 50%/50%) for **T1** and water/THF (v/v 90%/10%) for **T2** with a sharp increase in fluorescence intensity. The solid fluorescence of **T1** and **T2** is located at 575 nm and 588 nm, and their quantum efficiencies are determined to be 3.2% and 5.8%, respectively. The corresponding 2PA cross section values for **T1** and **T2** at 800 nm are 867 GM and 1300 GM by the open-aperture Z-scan technique. These excellent performances of both compounds make them as attractive alternatives for biophotonic and optoelectronic applications.

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1. Introduction

The two-photon absorption (2PA) materials have attracted scientists to research the progressive field such as two-photon dynamic therapy, up-converted lasing,¹ optical power limiting materials, two-photon microscopy and bioimaging.² Recently, a series of novel organic fluorophores with large 2PA cross section (σ) and good processability have been investigated.³ Its structure include asymmetrical donor- π -bridge-acceptor (D- π -A), symmetrical donor- π -bridge-donor (D- π -D), and donor- π -bridge-acceptor- π -bridge-acceptor- π -bridge-donor (D- π -A- π -A- π -D). The intramolecular charge transfer from the donor to the acceptor determines the 2PA cross section. Moreover, the solvent polarity, molecular coplanarity, and hydrogen-bonding can also fortify the 2PA cross section.⁴

Most 2PA dyes can be dissolved in organic solvent, while their fluorescence will become weak in aqueous media, the reason is its self-aggregation driven by limited solubility as well as π - π interactions.⁵ The biophotonic application in aqueous media for those

highly efficient 2PA materials is restricted. So it is considerable to investigate the 2PA dyes that can be soluble or dispersible in water and remain highly fluorescent in aqueous media.⁶ Recently, Tang and co-workers observed a phenomenon that some fluorophores have enhanced emission in aggregation, namely aggregation-induced emission (AIE). The inferential mechanism of AIE was restricted intramolecular vibrational and rotational motions (RIR) in the aggregated solid. This phenomenon had opened up a new avenue for the materials with large 2PA cross section.⁷ Prasad and co-workers investigated some dyes with aggregation-enhanced fluorescence and two-photon absorption properties.⁸ Tang and co-workers also investigated some organic molecules and polymers displaying 2PA and AIE properties. Our group also researched some dyes with significant AIE and 2PA features.⁹

The triphenylamine and carbazole have been widely used in optical and electroactive materials for their excellent electron-donating and transporting capabilities.¹⁰ Due to their special molecular structure, the triphenylamine and carbazole have aroused great interest and become the focus of progressive research in the 2PA field. Furthermore, cyano-substituted materials exhibit excellent optical and electrical properties due to their favorable electron affinities.¹¹ In this work, taking it into consideration that extending π -conjugation length largely and facilitating the effect of

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intramolecular charge transfer efficiently would enlarge the 2PA cross section, we introduce the substituted dihydroindolo [3, 2-b] carbazole as the central donor to a novel D-A-D-A-D type molecule. Combining the strong donating ability of the central donor and the peripheral donor, the 2PA cross section will be enlarged largely. Thus, these two compounds **T1** and **T2** (Fig. 1) with the substituted dihydroindolo [3, 2-b] carbazole as the central donor, the diphenylamine and carbazole as the peripheral donor and the cyano group as the acceptor have been synthesized. In view of the effective intramolecular charge transfer (ICT) effect and the strong electron-donating ability of these two dyes, excellent 2PA values and favorable AIEE properties can be anticipated.

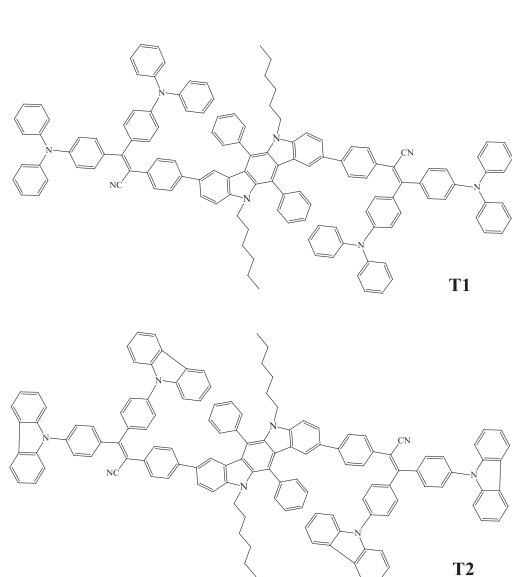


Fig. 1. The molecular structures of **T1** and **T2**.

2. Results and discussion

2.1. Synthesis

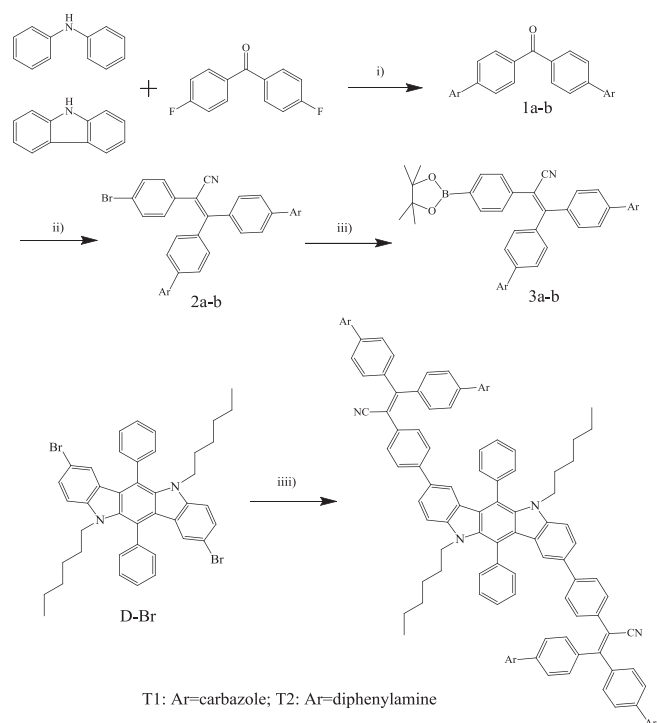
The synthetic routes of two compounds **T1** and **T2** are depicted in Scheme 1. Both two molecules were prepared via Knoevenagel condensation and Suzuki coupling reaction. The key intermediate compound D-Br was synthesized according to the previous literature¹² (ESI[†]). Both the final compounds were confirmed by proton and carbon nuclear magnetic resonance spectroscopy (¹H NMR, ¹³C NMR) and MALDI-TOF mass spectroscopy (MS).

2.2. One-photon absorption

The one-photon absorption of **T1** and **T2** in THF was shown in Fig. 2, the absorption maxima (λ_{\max}) of which were located at 398 nm, 397 nm, respectively. The λ_{\max} of both compounds was similar, which can be reasoned that the electron-donating ability of the central donor was stronger than that of the peripheral donor. So the whole electron-donating ability of both compounds was similar.

2.3. AIEE properties

The compounds **T1** and **T2** could dissolve in common organic solvents such as dichloromethane and THF, except water. Anhydrous THF and water were used to compose the mixture solution and to explore the AIEE attributes of **T1** and **T2**. The method to



Reagents and conditions: i) *t*-BuONa, DMF; ii) 4-Bromophenylacetonitrile, NaH, toluene; iii) bis(pinacolato)diboron, KAc, Pd(dppf)Cl₂, dioxane; iii) 3a-b, NaHCO₃, Pd(dppf)Cl₂, THF

Scheme 1. The synthetic route of compounds **T1** and **T2**.

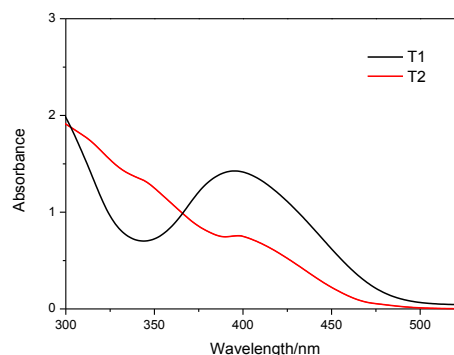


Fig. 2. One-photon absorption of **T1** and **T2** in THF at a concentration of 1.0×10^{-5} M.

disperse **T1** and **T2** in the primary way with adding different amounts of water to the anhydrous THF solution and making the water fraction (f_w) at 0–90%. Fig. 3a showed the corresponding emission spectra of **T1** at a concentration of 1.0×10^{-5} M. When $f_w < 40\%$, the PL intensity of **T1** was little changed, but, which became dramatically increased from $f_w = 40\%$ to $f_w = 50\%$ and its maximum was located at $f_w = 50\%$. When $f_w > 50\%$, the PL intensity became obviously quenched at the stage from $f_w = 50\%$ to $f_w = 70\%$, while which become increased from $f_w = 70\%$ to $f_w = 90\%$. Apparently, the emission of **T1** was induced by aggregation, thus verifying its AIEE attribute. The rotation of diphenylamine units against the dihydroindolo [3, 2-b] carbazole core may effectively deactivate its excited state to non-radiative, so the dye exhibited weak emission. From $f_w = 40\%$ to $f_w = 70\%$, the intramolecular rotation of the dye in the aggregate condition was restricted, so the non-radiative decay path was blocked, while the radiative decay path was activated, thus making the dye to be a strong emitter.⁹

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