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Triphenylethylene-based fluorophores: Facile preparation and full-color emission in both solution and solid states

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ABSTRACT

A series of triphenylethylene-based luminophoric molecules were efficiently synthesized. The substituent effect of the fluorophores on their photophysical properties was then investigated. Consequently, it was found that longer conjugated system and larger molecular dipole of the donor–π–acceptor fluorophores could result in bathochromic shifts of UV–vis absorption and emission bands, so do the Stokes shifts. Especially, full-color fluorescent emissions in both solution and solid states could be achieved by changing conjugation length and substituents with different electron-donating or accepting abilities in the triphenylethylene skeleton. The density functional theory calculations further demonstrated that with the increase of the electron-donating or accepting abilities of the substituents, the energy gaps of the fluorophores gradually decreased, which elucidated the substituent effect of the organic fluorophores on their photophysical properties.

1. Introduction

Considerable interest about luminescent materials has been attracted to organic lighting-emitting diodes (OLEDs) because of their vast application in display and lighting in recent years [1–3]. However, many organic fluorophores with multiple aromatic rings suffer from the notorious aggregation-caused quenching (ACQ) effect in solid states [4–6]. In 2001, Tang's group discovered a novel and unusual phenomenon, termed aggregation-induced emission (AIE), which is an anti-ACQ effect [7]: Many molecules are weak or non-luminescent in the solution state but become highly emissive when in the aggregated states. It has technological implications to modulate solid-state optical properties of fluorophores due to their real world applications, which are commonly used as solid films in photonic and electronic devices [8–11]. Notably, motivated by the commercial potentials of full-color displays [12,13] and white-lighting emission [14–16], it has a urgent need to realize multicolor emission with molecular mixtures of similar chemical structures. However, a limited number of fluorophores was found to show admirable color-tunable AIE behaviors in the solid state. Most of the AIE-active molecules reported emit blue and green lights [17–20]. Triphenylethylene is also an AIE-type molecule [21–25]. It has a twisted structure, and is relatively easily prepared. It can be transformed into its derivatives with donor–π–acceptor (D–π–A) system due to the asymmetric nature of its structure, which could modulate emission to longer wavelength more easily. Remarkably, the D–π–A type molecules usually exhibit distinctive fluorescence properties owing to their intramolecular charge transfer (ICT) transitions, which endows them with tuned electronic states under various environments [26–29].

In this work, we designed and synthesized a series of triphenylethylene skeleton derivatives. Their max emission peaks could be tuned in full-color range both in solution and solid states by conjugation extension and introduction of the D–π–A structure, from 383 nm to 643 nm in THF solution and from 458 nm to 687 nm in solid, respectively.

2. Results and discussion

2.1. Synthesis

Herein, we report a series of fluorophores **3a**–**c**, **4a**–**c**, **5a**–**c**, and **7a**–**e** based on a triphenylethylene skeleton consisting of various combinations of different substituent (Scheme 1). In the design of these compounds, we take the following factors into account. (i) As an AIE-type molecule, triphenylethylene can make its derivatives exhibit AIE properties [21–25]. (ii) Conjugation length extension can generate a significant bathochromic shift of fluorescent

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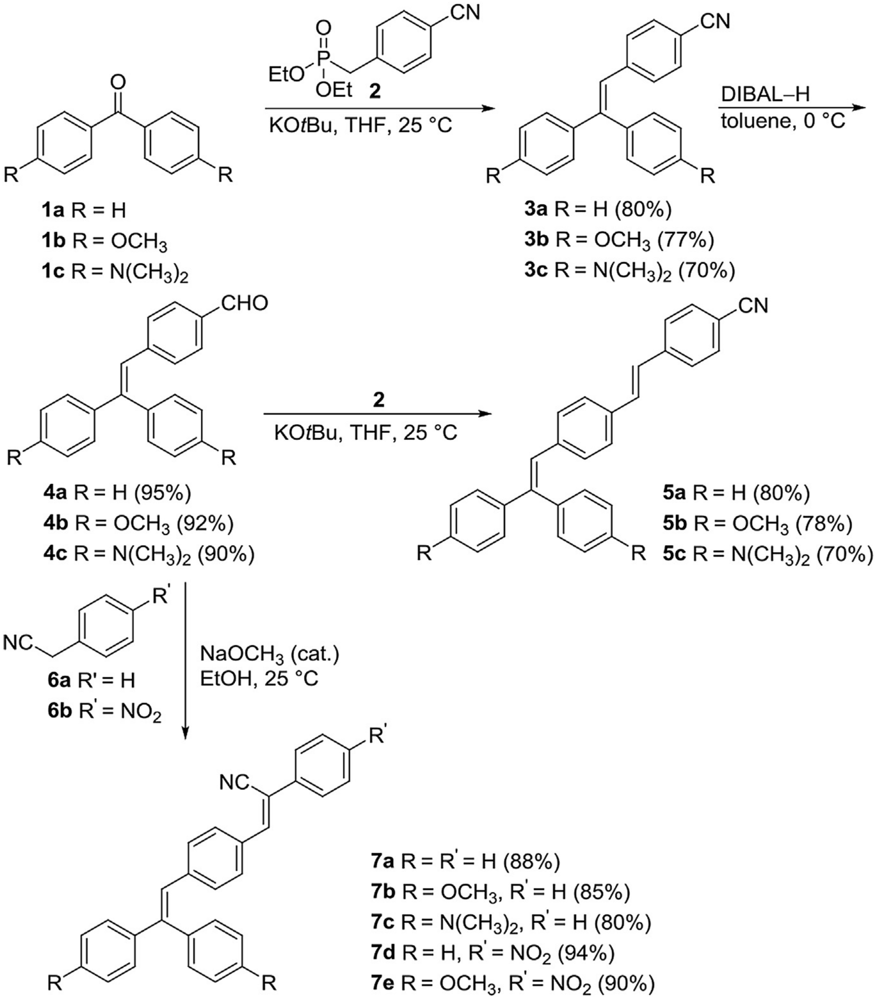

Scheme 1. Synthesis and structures of fluorophores **3a**–**c**, **4a**–**c**, **5a**–**c**, and **7a**–**e**.

emission [30]. (iii) Both electronic and steric effects of a cyano group affect the emission process of an AIE fluorophore [31–33]. (iv) The D–π–A system is an attractive electronic structure for organic light-emitting materials because the photophysical and redox properties can be fine-tuned by the judicious combination of a donor and an acceptor [34–36]. By the combination of the conjugative effect, strong intramolecular push–pull electronic effect, and twisted structure, these fluorophores show fluorescence and large Stokes shifts in both solution and solid states.

By combining all the considerations above, the triphenylethylene derivatives **3a**–**c** [37,38] were prepared through a Horner-Wadsworth-Emmons (HWE) olefination reaction from commercial substituted benzophenones **1a**–**c** and phosphite ester **2** [39] in 70–80% yields in the presence of potassium *tert*-butoxide at 25 °C. The methoxyl ($-OCH_3$) and dimethylamino [$-N(CH_3)_2$] groups were employed as the electron donor (D) groups, because they had the different strength of the electron-donating ability which could be reflected from the molecular dipole moments (Table 1) and the substrates could be obtained directly from the commercial reagents. At the same time, a cyano (–CN) group was introduced as an electron acceptor (A) group in order to facilitate subsequent functional group transformation. Then, reduction of the –CN groups in compounds **3a**–**c** by DIBAL-H afforded the aldehydes **4a**–**c** [11,40,41] in 90–95% yields (another type fluorophores). With the aldehydes **4a**–**c** in hand, on one hand, the π-extended derivatives **5a**–**c** were obtained in 70–80% yields by the HWE olefination reaction of aldehydes **4a**–**c** with phosphite ester **2** under the same conditions as described above. On the other hand, in order to make the conjugated system more twisted for increasing AIE effect of the molecules, compounds **7a**–**c** were synthesized in 80–88% yields through the Knoevenagel condensation of aldehydes **4a**–**c** with phenylacetonitrile **6a**. Another two compounds **7d** and **7e** were also synthesized from aldehydes **4a** and **4b** with *p*-nitrobenzeneacetonitrile **6b** in 90–94% yields for the increasing of molecular polarity by the introduction of nitro ($-NO_2$) group. The chemical structures of the new compounds were all characterized by ^1H and ^{13}C NMR, and high resolution mass spectra (see supporting information).

2.2. Photophysical properties

With all the synthetic compounds in hand, UV–vis absorption spectra was first investigated in diluted THF solution (Table 1 and Fig. S1). The spectra of the fluorophores **3a**, **4a**, **5a**, and **7a** show a single absorption band corresponding to a π–π* transition with λ_{max} at 321 nm (**3a**), 333 nm (**4a**), 366 nm (**5a**), and 366 nm (**7a**), respectively. The introduction of electron-donating (D) groups in the benzene ring of triphenylethylene skeleton produces the emergence of a new transition from 350 nm (**3b**) to 436 nm (**7c**) assigned to an intramolecular charge transfer (ICT) between the