

# Multi-branch effect on aggregation-induced emission enhancement and tunable emission of triphenylamine fluorophores



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## HIGHLIGHTS

- AIEE and CIEE active fluorophores (MOTPA)s containing triphenylamine were synthesized.
- The single branch fluorophores (SMOTPA) presented a tunable emission.
- Fluorescence imaging experiments of TMOTPA in living A549 cells proved its potential for practical applications.

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## ABSTRACT

We designed and synthesized three triphenylamine-based compounds (MOTPA)s, namely 4-(((4-methoxyphenylimino)methyl)phenyl)-diphenylamine (SMOTPA), di(4-((4-methoxyphenylimino)methyl)phenyl)amine (DMOTPA), and tris(4-((4-methoxyphenylimino)methyl)phenyl)amine (TMOTPA). Initially, MOTPA)s possessed aggregation- and crystallization-induced emission enhancement (AIEE and CIEE) properties via the restrained intramolecular charge transfer (ICT) state, and by preventing  $\pi$ - $\pi$  stacking and restricted intramolecular rotation. It was also demonstrated that multi-branch effect of triphenylamine was benefit to enhance AIEE and CIEE. The phenomenon was explained by X-ray diffraction analysis and calculations. Interestingly, the single branch fluorophores (SMOTPA) presented a tunable emission. The green emission of SMOTPA originating from the twisted intramolecular charge transfer (TICT) state in the strong polar solvent (methanol) transformed into a strong blue fluorescence assigned to the local excited (LE) state in the aggregated and crystalline states due to the restraint of the TICT state. Fluorescence imaging experiments of TMOTPA in living A549 cells proved its potential for practical applications.

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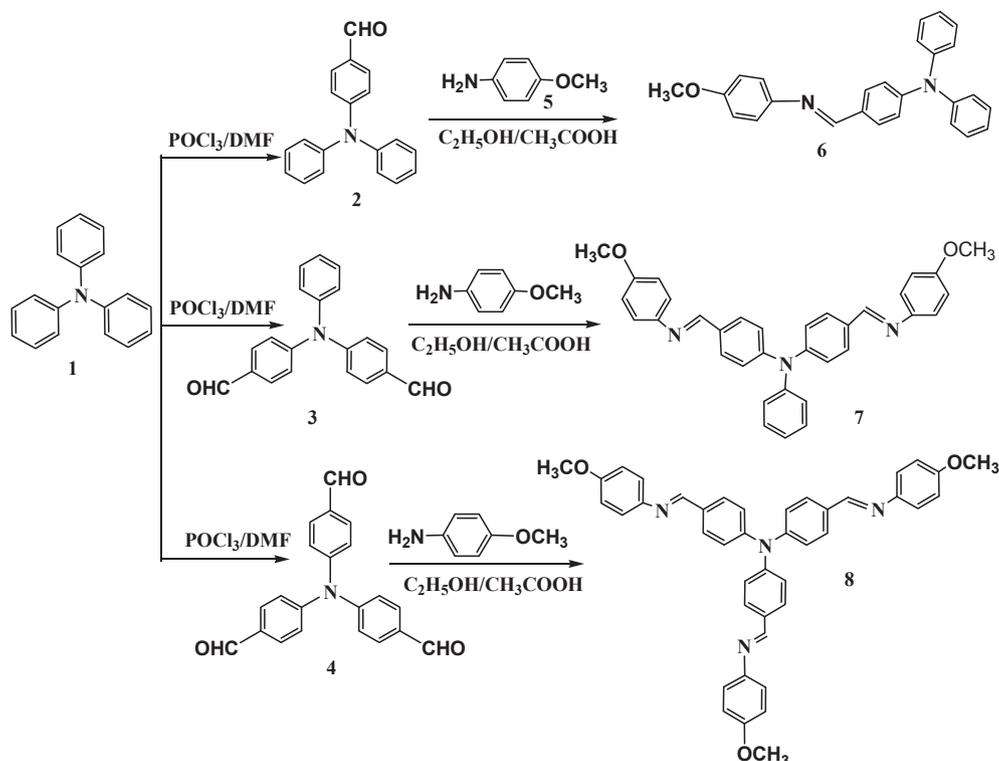
## 1. Introduction

Luminescent materials have attracted widespread interest in the past decade owing to a series of advantages in the fields of analytical, biological, medical sciences, particularly organic light-emitting diodes (OLEDs) [1–4]. Among the diverse classes of organic conjugated systems [4–8], the materials absorb electromagnetic radiation by virtue of an intramolecular charge transfer (ICT) and emit from the corresponding photo excited state. Such materials exhibit considerable potential in various applications, such as molecular electronics, integrated photonic devices, non-linear optics (NLO) [9–12]. Aggregation-induced emission (AIE)

or Aggregation-induced emission enhancement (AIEE) was first discovered by Tang et al., In 2001 [13,14]. This phenomenon overcame the aggregation-caused quenching (ACQ) effect of the traditional organic fluorophores at high concentration or aggregation state [15,16], thereby allowing their potential applications in various fields. Through experimental and theoretical investigations, the reasons of AIE characteristic include restriction of intramolecular rotations (RIR) and preventing  $\pi$ - $\pi$  stacking [17–21], restricted intramolecular charge transfer (ICT) [22] or twisted intramolecular charge transfer (TICT) [23,24], or *cis-trans* isomerization [25]. At the supramolecular level, some types of specific molecular packing, such as J-aggregation [26,27], dimer/excimer stacking [28,29], herringbone stacking [30], or even the weakly coupled H aggregation [31], can also help to maintain the emission in solid states, probably due to some specific emissive-favorable exciton coupling. Although these mechanisms have

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**Scheme 1.** The synthetic route of three MOTPAs.

been intensively investigated over the past decades, further studies on structure–property relationships are still required for the complete understanding of the condensed-state emission mechanism and eventually for the rational design of practical functional solid-state emitters [32,33].

Until now, the emission of the designed AIE-gens covers the whole range of visible light, from deep blue to near-IR. Like other emissive materials, because of their intrinsic wide band gap, efficient and stable blue AIE-gens are still scarce. Considerable effort has been devoted to exploring efficient fluorescent materials for OLEDs. Controlling the intramolecular conjugation is useful to achieve blue emission. The main strategies are crystallization-induced blueshifted emission, modification of the linkage mode, creation of a twisted conformation, interruption of the conjugation and reduction of the conjugation unit. Some good blue AIE luminogens have been designed. The crystal of hexaphenylsilole emitting blue light of a propeller shaped non-planar molecule [34] was the first unearthed silole derivative of AIE. Until now, some materials with ICT and AIE properties have been reported [34–36]. In our previous work, we have developed a series of D- $\pi$ -A AIE-active triphenylamine derivatives [37,38], wherein the mechanisms of solid-state emission enhancement include restriction of rotation [37], specific molecular packing, such as herringbone stacking and intermolecular hydrogen bond interactions [38]. In this paper, we reported another series of triphenylamine derivatives, MOTPAs. Here, the triphenylamine unit is a donor, and Schiff base is an acceptor. Furthermore, we studied the luminescence effect of them. Interestingly, SMOTPA displayed two different fluorescence colors in methanol solvent (green) and aggregate state or crystal state (blue). These new observations indicate that the previously verified mechanism of the restricted rotation in the aggregation state is incomplete in this case. Moreover, the investigation on the D- $\pi$ -A molecules may help to

reveal the intrinsic process of the fluorescence enhancement and spectral shifts in their molecular aggregates.

## 2. Experimental section

### 2.1. Materials and instruments

Triphenylamine, 4-Methoxyphenylamine, 4-Methylbenzenesulfonic acid, POCl<sub>3</sub>, DMF, NaOH, CH<sub>2</sub>Cl<sub>2</sub>, THF, MgSO<sub>4</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OH, CDCl<sub>3</sub> and DMSO were purchased from J&K (CHINA). Melting points were determined on a Kofler melting point apparatus and uncorrected. IR spectra were obtained in KBr discs using a Nicolet 170SX FT-IR spectrometer. Elemental analyses were performed on a Yancoo CHNSO Corder MT-3 analyzer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using an INOVA 400 at 400 and 100 MHz, respectively, with TMS as the internal standard, DMSO-D<sub>6</sub> as the deuterated solvent and chemical shifts reported in ppm. Mass spectra were recorded using a Finnigan MAT95 mass spectrometer. The absorption and fluorescence spectra were obtained on a CARY50 UV-VIS spectrophotometer and an FLS920 fluorescence spectrophotometer. The relative fluorescence quantum yields were calculated relative to the solutions of  $5 \times 10^{-5}$  mol L<sup>-1</sup> quinine sulfate ( $\Phi = 0.55$ ) in 0.1 mol L<sup>-1</sup> sulfuric acid solution as a reference sample [39,40], and the absolute solid fluorescence quantum yields were obtained on a Edinburgh Instruments FS920 integral sphere system. Single crystal XRD data were collected on a Bruker SMART APEX-II CCD area detector using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Powder X-ray diffraction (PXRD) was employed using a Panalytical X'Pert-Pro MPD X-ray diffraction with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) over the  $2\theta$  range of 10°–90°. Fluorescence microscopy imaging of the nano-aggregations was performed by a Leica DM2500 M. SEM images of the aggregations were obtained by Hitachi S4800. All the

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