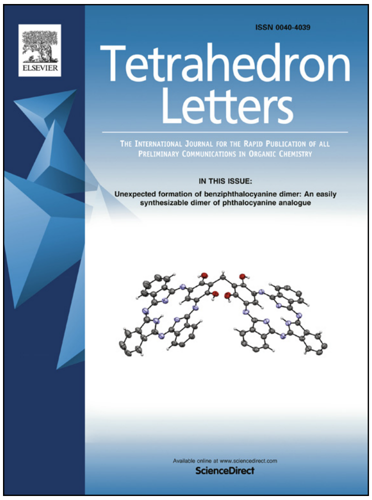

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Synthesis and properties of a new AIE macrocyclic emitter with triarylamine backbone

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ABSTRACT

A new macrocyclic AIE emitter composed of triarylamine backbone was successfully synthesized through convenient homocoupling procedure and easily purified by silica gel column chromatography, and recrystallization. The optical and electrochemical properties of the compound have been investigated. Intriguingly, the compound shows dual emission both 423 nm and 505 nm. This result implied that the violet emission was originated from an isolated component of the emitter, whereas the yellowish-green emission simultaneously exhibited AIE nature. The compound exhibits enough thermal stability and high glass transition temperature to be applied for organic devices.

Introduction

Much kind of studies have been done on organic light-emitting diodes (OLEDs), because they have a great potential to be applied to large full-color displays.[1-3] Traditional organic luminophores are mainly composed of planar aromatic rings. They emit efficiently in dilute solutions while being weakened or even totally quenched due to the formation of detrimental aggregates, which facilitate exciton interactions and nonradiative pathways.[4] In 2001, the group of B. Z. Tang reported aggregation-induced emission (AIE), which is the phenomenon making contrast with the aggregation-caused quenching (ACQ) effect.[5] Since the AIE effect is also observed in a film state, a lot of AIE molecules have been synthesized, and the optical properties of them have been investigated.[6] In various fluorophores, molecules having tetraphenylethene (TPE) unit show a strong emission by AIE effect.[7] Nowadays, many researchers have developed a lot of efficient solid-state emitters using TPE as the key building block because almost all TPEs are easily synthesized and show distinguished AIE effect.[8-10]

Organic electroluminescent materials with multifunctional properties, such as light-emitting and carrier-transporting abilities are ideal for high-technological and practical applications because they can simplify the device structure and reduce fabrication cost. Triphenylamine (TPA) has been utilized widely as an essential moiety as a building block of hole-transporting materials since it affords high hole mobility in an amorphous state.[11-14] However, TPA derivatives also suffer from the ACQ effect in the film state, which makes the device performance poor.[15] The ACQ problem can be solved easily by incorporation of the TPE unit. A variety of TPE–TPA derivatives have been developed and showed both good hole-transporting property and high PL efficiency.[16-19] Owing to the TPE unit, all the TPE–TPA adducts show AIE features and emit intense sky blue to green lights in solid films with high Φ_F values up to unity. As the orbital distributions of the HOMO and LUMO energy levels are close to those of *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB), one of the most famous hole-transporting materials, their hole-injection and transporting abilities are preserved.

In the preparation of macrocyclic compounds, low isolated yields often become crucial drawbacks in the practical view point. Our research group reported the synthesis of cyclic oligomers composed of triphenylamine via Pd catalyzed C-N coupling reaction of A-B type monomer [20], where the cyclic pentamer was isolated in an acceptable yield (11%) from the products containing liner and cyclic (hexa- and heptamer) oligomers as byproducts. However, it is generally difficult to remove cyclic byproducts with different degree of oligomerization from the crude products, and a time-consuming and complicated operation such as gel permeation chromatography (GPC) is required. Recently, Tohama et al. have developed an effective synthetic method for macrocyclic arylethenes via McMurry coupling. [21] In this report, we designed a cyclic oligotriphenylamine having TPE unit. It is expected that the rigid cyclic structure of the compound shows strong fluorescence emission preventing nonradiative decay as well as high thermal stability. Hitherto, there is no report on a macrocycle with TPA and TPE backbone.

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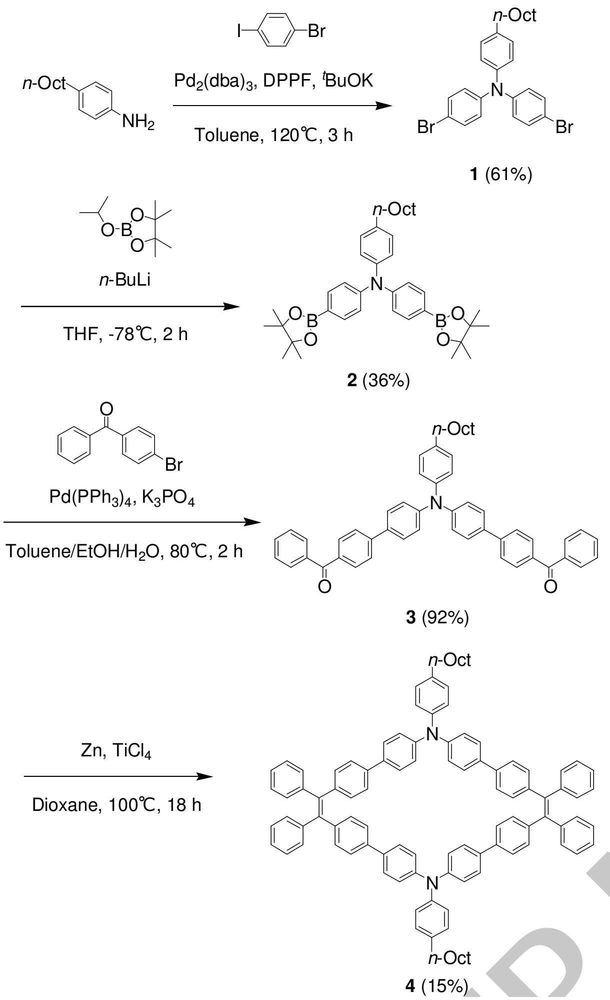
Results and discussion



Scheme 1. Synthetic routes to compound **4**.

The synthetic route for the target compound is depicted in Scheme 1. In this process, an amine intermediate **1** was synthesized from 4-*n*-octylaniline and 1-bromo-4-iodobenzene using palladium catalyst. Compound **1** was subsequently reacted with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to afford a pinacol ester **2**. A ketone intermediate **3** was synthesized from compound **2** and 4-bromobenzophenone using Suzuki-Miyaura cross coupling. The cyclic oligomer was synthesized from **3** via McMurry reaction in 1,4-dioxane in diluted conditions to prevent forming liner polymeric byproducts.[13] The final reaction, homocoupling of the dog-leg shaped ketone precursor **3** facilitates the formation of cyclic compound **4** without any cyclic byproduct. Actually, the yield of the final step was 15% where compound **4** is purified only by column chromatography and recrystallization. This result is a little bit better than that via C-N coupling reaction using Buchwald-Hartwig reaction reported by our group.[20]

Figure 1a shows UV-vis absorption spectrum for compound 4. Compared with cyclic pentamer of 4-butyltriphenylamine, the wavelength at absorption maximum (356 nm) is slightly blue-shifted (8 nm). As shown in Figures 1b, the emission peak of compound **4** is located at 505 nm in the film state. The absolute quantum yield measured by an integrating sphere is 34.6% for compound **4**. However, the emission peak of compound **4** is located at 423 nm for a dilute solution in THF. To investigate the features of the compound, we measured PL spectra in THF/water mixtures with different water fraction (f_w). As expected, the compound shows dual emission. Figure 2 shows the change of PL spectra (a) and PL intensity dependence on water content together with fluorescent images. When the water content is less than 30%, compound **4** shows peaks at around 423 nm. At 50% water content, the emission around 423 nm almost extincted, and that around 505 nm appeared. As the water fraction (f_w) increases, the aggregates form step by step. At 70% of f_w, the PL intensity at around 505 nm is over 19.8 times that in pure THF. On the other hand, at 10% of f_w, the PL intensity at around 423 nm is over 23.8 times higher than that at 90%. This result implied that the violet emission was from a single component of compound **4**, which was converted to an aggregation form with the increase of f_w, whereas the yellowish-green emission simultaneously exhibited typical AIE nature.

In case of most TPE emitters, the restriction of the intramolecular rotation (RIM) mechanism can be employed to explain the enormous difference of fluorescence behavior between solution state and solid state: the strong intermolecular interactions in solid state can restrict the rotation of the phenyl rings, which blocks the nonradiative channel, extends the conjugation, and enhances the emission. However, in the THF solution state of compound **4**, the rigid conformation of the cyclic structure, immobilizing the two phenyl groups in each of the TPE units, has partially hampered the RIM process and hence makes it emissive. Recently Zeng et al. reported a TPE based emissive molecule in which two diacetylenes are induced to restrict the rotation of phenyl rings in TPE, and consequently preserves the fluorescence in the diluted solution.[22] In the solid state, the RIM

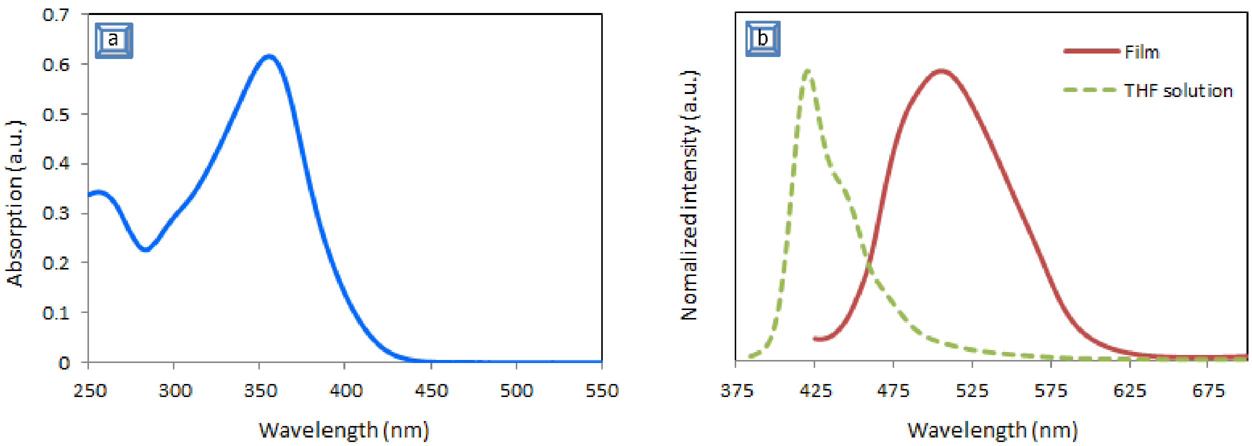


Figure 1. (a) UV–vis spectrum of compound **4** in THF solution (2.0 × 10^{-6} M). (b) Photoluminescence spectra of compounds **4** in solid film and THF solution (2.0 × 10^{-6} M). Excitation wavelength: 365 nm.

Table 1 Optical and electrochemical properties of compound **4**

Compound	λ_{abs} (nm)		Φ_F (%)[b]	T_g/T_d (°C)	HOMO (eV)[c]	LUMO (eV)	E_g (eV)[d]
	Solution[a]	Film[b]					
4	356	505	34.6	134/434	-5.55	-2.60	2.95

[a] 2×10^{-6} M in THF solution.

[b] Film drop-casted on quartz plate.

[c] HOMO levels were investigated by cyclic voltammetry with a reference electrode of Ag/AgCl:
HOMO $= - (V_{ox}+V_{(Ag/AgCl\ vs\ SHE)}+V_{(SHE\ vs\ vacuum)}) = - (V_{ox}+0.198+4.45)$.

[d] Estimated from the onset of the absorption spectra: $1240/\lambda_{onest}$.

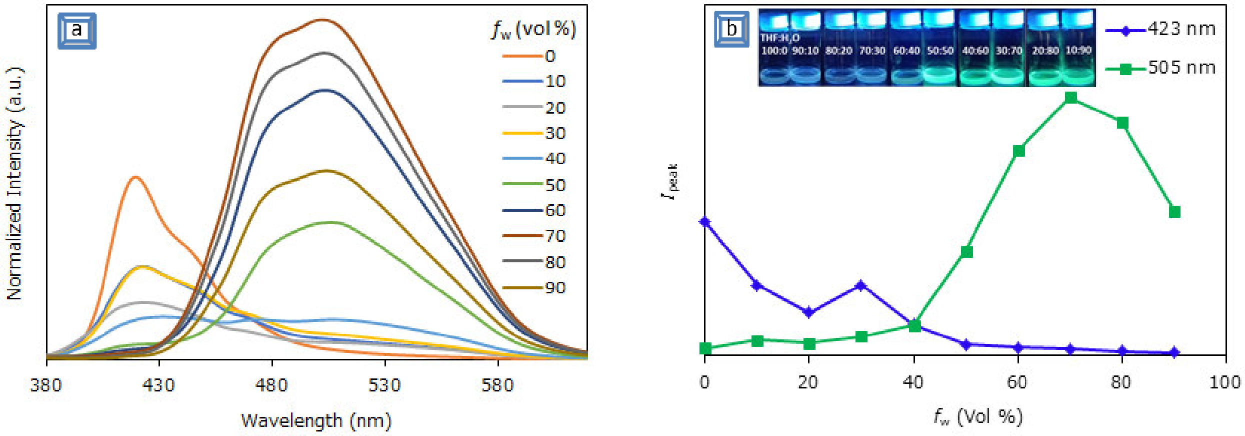
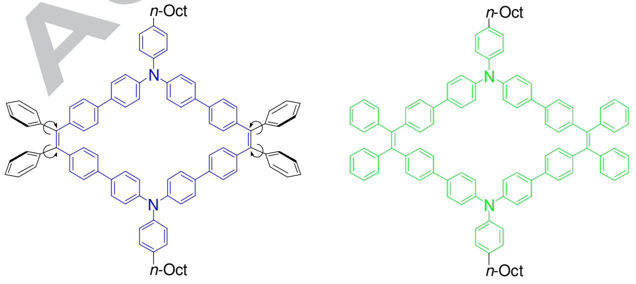


Figure 2. (a) PL spectra of compound **4** in THF/water mixtures with different water fractions (f_w). Inset: photo of compound **4** in THF/water mixtures (f_w = 0 and 90%) under UV lamp illumination. Excitation wavelength: 365 nm. (b) Emission peak intensity (I_{peak}) of compound **4** in THF and THF/water at varying f_ws at 423 nm and 505 nm. Concentration = 1.0×10^{-4} M.

process is further restricted, which shows red-shifted emission because of the π-extension caused by the other two phenyl groups in the TPE units (Figure3). The high planarity of **4** by the cyclization causes π–π interaction to form excimer, and also contributes to the red-shifted broad spectrum.[23] In previous studies, it's already found that the RIM process can be activated by many external factors, such as solvent viscosity, temperature, pressure, *etc.*[24-30] Rigidification of the conformation of TPE can also effectively promote the RIM process leading to change its emission behavior.

The thermal properties of compound **4** was investigated by thermo-gravimetric (TG) and differential scanning calorimetry (DSC) analyses as shown in Figures S4 and S5. The compound shows high thermal decomposition temperature (T_d; 434ºC). Compound **4** shows glass transition at 156ºC. Due to the cyclic rigid structure, compound **4** has higher glass transition temperature (T_g) than other TPE compounds suitable for wet processable electroluminescent devices, although the fluorescence quantum yield of **4** in the film state was moderate.[16] In DSC thermogram, there is no other thermal transitions such as a cold crystallization and a melting, indicative of amorphous nature of **4**. Indeed it is found that the thin film of 4 keeps the optical quality after 2 months. The electrochemical properties were revealed by cyclic voltammetry (CV) measurements (Figure S9). The measured data are summarized in Table 1. The energy levels of the highest occupied molecular orbital (HOMO) of the compound **4** was estimated from its oxidation potential according to an empirical formula, $E_{HOMO} = - (V_{ox}+0.198+4.45)$, whereas the LUMO energy level was obtained from the optical band gap energy (estimated from the onset wavelengths of the UV absorption) and the HOMO level. The HOMO level for compound **4** is −5.55 eV, suggesting that **4** has hole-transporting ability due to the introduction of the triphenylamine unit. The band gap was derived from the absorption edge in the absorption spectrum with the value of 2.95 eV for **4**. The LUMO value of sample can be estimated by subtraction of the optical band gap energy from the HOMO energy level with the value of −2.60 eV for **4**.

In conclusion, a macrocyclic compound **4** which bears triphenylamine and tetraphenylethylene backbones has been synthesized. The key preparation method for the macrocyclization using McMurry reaction has been developed, which gives a good conversion yield. The compound shows dual emission because of AIE and the rigidness of **4**. The compound also exhibits a high thermal stability and glass transition temperature, and the HOMO and LUMO values show suitable for hole-transporting materials. This work provides an effective method for preparation of the macrocyclic AIE material, which has great potential for OLED applications, even in non-doped emissive layer.



λ_{em} = 423 nm
(in solution state)

λ_{em} = 505 nm
(in solid state)

Figure 3. Structure images of compound **4** in solution and solid state.

A. Supplementary data

Supplementary data (spectroscopic methods, such as ^{1}H-, ^{13}C-NMR, mass spectroscopy and thermal properties with satisfactory results obtained) associated with this article can be found, in the online version, at http://.

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