Cyclic Emitter with Tetraphenylsilane and Tetraphenylethene Units Exhibiting Tunable Color Emissions

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A novel cyclic emitter composed of tetraphenylsilane and tetraphenylethene backbone was successfully synthesized through a convenient homocoupling procedure. The optical and thermal properties of the compound were revealed. Intriguingly, the compound showed different color emissions in solid film, THF solution, and THF/water mixtures. It is assumed that the violet emission was from an isolated component of the emitter, whereas the sky blue and the green emissions were from a crystalline state, and an amorphous state, respectively. The red-shifted emissions were caused by the change of nature of the excitonic coupling.

Keywords: McMurry reaction | Cyclic emitter | Mechanochromism

Intensive studies have been conducted on organic lightemitting diodes (OLEDs), as they have a great potential to be applied to large full-color displays.^{1–3} The range of applications of organic functional compounds has recently expanded rapidly, with especially innovative uses in optoelectronics.⁴ Most conjugated organic molecules have been reported to display red, green, and blue electroluminescence (EL).⁵ Emitters with high efficiency and long lifetime of red and green light have recently been developed. However, it seems very difficult to develop materials that emit violet or blue light with high efficiency since a wide band gap, with a large difference between the energy levels of adjacent hole and electron transporting layers, is an intrinsic property of blue-light emitters. Moreover, if the single emitter exhibits tunable color emission dependent on the aggregation state, it is possible to fabricate a multicolor device with the emitter.⁶

More than 80 years ago, unusual photophysical behaviors induced by the aggregation of pseudoisocyanine chloride (PIC chloride) were independently reported by Scheibe,⁷ and Jelley.⁸ The aggregates of PIC chloride (J-aggregate) in aqueous solutions exhibit a sharp, red-shifted absorption band, as well as a strong fluorescence. In 2001, Tang and co-workers found a similar phenomenon, designated aggregation-induced emission (AIE),⁹ which is a contrasting phenomenon of the aggregationcaused quenching (ACQ)¹⁰ effect. Aggregation enhances the intensity of fluorescence from the compound without quenching.¹¹ Among various fluorophores, molecules with tetraphenylethene (TPE) unit exhibit a strong AIE effect.¹² Nowadays, many researchers have developed a lot of efficient blue emitters using TPE as the key building block because TPE derivatives are easily synthesized and afford strong AIE effect.

Recently, aryl-substituted silanes have been considered as attractive OLED materials for blue electrophorescence devices.¹³ Current studies focus on the improvement of their morpholog-

ical stability. Their $\sigma^* - \pi^*$ conjugation endows them with lowlying lowest unoccupied molecular orbitals (LUMO)s and hence high electron affinity and high electron mobility.¹⁴ The combination of TPE with silane affords AIE-active blue materials with high Φ_F values (55–64%) in the solid state. Blue-emitting OLEDs fabricated utilizing these luminogens as emitters showed good performances.¹⁵

Our research group reported the synthesis of cyclic oligomers composed of triphenylamine via Pd-catalyzed C–N coupling reaction of A-B type monomer.¹⁶ It has been found that thermal and morphological stabilities are improved due to the absence of end groups in the applications to hole transporting materials. The rigid nature of cyclic molecules is also advantageous for fluorescent materials since it prevents nonradiative transition by hampering intramolecular motion.

In this report, we designed a novel cyclic emitter with tetraphenylsilane and alkylated TPE backbone which is appropriate for wet processes in device fabrication. Characteristic photophysical and thermal properties are presented. In addition, preliminary results for the mechanochromic nature of the synthesized emitter are also demonstrated.

Scheme 1 shows the synthetic route of a targeted cyclic compound. A ketone intermediate 1 was synthesized from 4-bromobenzoyl chloride and amylbenzene using aluminum chloride. A pinacol ester 2 was synthesized from bis(4bromophenyl)diphenylsilane and bis(pinacolato)diboron using a palladium catalyst. The compound 1 was reacted with compound 2 to afford a diketone 3. The cyclic compound 4 was synthesized from the homocoupling of 3 via McMurry reaction in 1,4-dioxane in diluted conditions to prevent formation of linear polymeric by-products.¹⁷ It is considered that the final reaction, the homocoupling of the dog-leg shaped ketone precursor 3 facilitates the formation of cyclic compound 4 without the contamination by larger cyclic by-products. Actually, 4 was isolated only by column chromatography and recrystallization (yield of the final step; 10.4%). The synthetic procedure for the cyclic compound 4 is as follows; To a solution of tetrachlorotitanium (1.60 mL, 14.6 mmol) in 1,4-dioxane (900 mL), zinc powder (1.91 g, 29.2 mmol) was added slowly with stirring at -10 °C under a nitrogen atmosphere, and then the mixture was heated at 100 °C for 2 h. To the suspension, a solution of compound 3 (1.12 g, 1.46 mmol) in 1,4-dioxane (100 mL) was added, and then the mixture was heated at reflux for 15 h. A solution of 10% K_2CO_3 in water was carefully added and the mixture was extracted with CH2Cl2. The organic layer was washed with brine and dried over anhydrous MgSO₄, and the solvents were evaporated to give a crude product, which was purified by silica gel column chromatography (eluent: CH₂Cl₂ and hexane) and recrystallized from toluene and EtOH to give

Table 1. Photophysical and thermal characteristics of compound 4

Compound	$\lambda_{ m abs}/ m nm$ in THF $^{ m a}$	$\lambda_{ m abs}/ m nm$ in film ^b	$\lambda_{ m em}/ m nm$ in THF $^{ m a}$	$\lambda_{ m em}/ m nm$ in THF/water $(10/90)^a$	$\lambda_{ m em}/ m nm$ in film ^b	$T_{\rm g}/^{\rm o}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$	$E_{\rm g}^{\rm c}/{\rm eV}$
4	352	343	417	470	509	167	458	2.96

 $^{a}1 \times 10^{-4}$ M. ^bFilm drop-casted on a quartz plate. ^cEstimated from the onset of the absorption spectrum in film: $1240/\lambda_{onest}$.



Scheme 1. Synthetic route of compound 4.

the compound **4**, which was characterized by ¹H- and ¹³C NMR. These spectra are presented in Supporting Information (SI) (Figures S1 and S2). The thermal properties of compound **4** was investigated by differential scanning calorimetry (DSC) and thermogravimetric (TGA) analyses as shown in Figures S3 and S4. As listed in Table 1, compound **4** shows high thermal decomposition temperature (T_d ; 458 °C), and a glass transition at 167 °C. Due to the cyclic rigid structure, compound **4** has higher glass-transition temperature (T_g) than other TPE substituted silane applicable to electroluminescent devices.¹⁵

Figure 1 shows photoluminescence (PL) spectra for **4** in THF, THF/water (10/90) solutions, and a drop-cast film together with UV-vis absorption spectrum in THF. Table 1 lists the optical properties for **4**. The band gap was determined from the absorption edge in the absorption spectrum with the value of 2.96 eV for **4**, which is close to other blue emissive layer materials.^{18,19} For the THF solution, a violet emission peak was observed at 417 nm with the shoulders around 440 and 470 nm. The Stokes shift was 65 nm, which was determined with PL and UV-vis absorption spectra. Width at half maximum of the PL spectrum of the THF solution was 42 nm, which appears to be



Figure 1. UV–vis absorption spectrum of compound **4** in pure THF, and PL spectra in pure THF, THF/water mixture ($f_w = 90\%$), and solid film. Excitation wavelength: 365 nm.

smaller than those of other OLED emitters partially ascribed to its conformationally rigid cyclic structure. As shown in Figure 1, in THF/water (10/90), the emission maximum was red-shifted to 470 nm affording a relatively broad peak with shoulder around 440 and 510 nm. In a film state, the emission around 510 nm became predominate, and appeared to be greenish to the naked eye. Since compound 4 includes TPE moieties, it is reasonably presumed that the increased intensity of red-shift emission in THF/water is related to the formation of nanoparticles similar to the observation in AIE luminogens. In order to confirm this assumption, its emission behaviors in THF and THF/water mixtures with varying water fractions (f_w s) were monitored.

Figure 2 shows the change of PL spectra (a), and the PL intensity, and fluorescent images (b) for the solution in THF and THF/water mixtures. When the water contents were less than 50%, compound 4 showed violet emission with the peak at 417 nm, and the intensity of the emission decreased with the increase of water content indicating that the weak aggregation of the fluorophore occurred. The mixture containing 60% water exhibited an emission peak at 470 nm with shoulders around 440 and 510 nm. Over water content of 60%, the intensities at 470 nm slightly decreased. Judging from the dependence of water content, it is suggested that the violet emission was from a single component of 4, and the sky blue emission arose from partially crystalline nanoparticles resulting from the precipitation. In the solution state, the intramolecular rotation of TPE units, which is known as the low-frequency modes of the reorganization energy, serves as a relaxation channel for the excited state to decay, while in the aggregated state, the rotation is strongly restricted to block the nonradiative decay pathway and produce the radiative excitons. The red-shifted emission in the nanoparticles is considered to be caused by the dipole-dipole interactions between neighboring molecules leading to the excitonic coupling. In the case of compound 4, even in THF



Figure 2. (a) PL spectra of compound 4 in THF/water mixtures with different water fractions (f_w). Excitation wavelength: 365 nm. (b) Emission peak intensity (I_{peak}) of compound 4 in THF and THF/water at varying f_w s at 417 and 470 nm. Concentration = 1.0×10^{-4} M. Inset: photographs of the solutions of compound 4 in THF/water mixtures ($f_w = 0-90\%$) under UV irradiation.



Figure 3. Photographs of solids for (a) as-prepared and (b) ground compound 4 taken under UV light ($\lambda_{ex} = 365$ nm).

solution the rigid conformation of the cyclic structure, immobilizing the two phenyl groups in each of the TPE units, has partially hampered the rotation of the phenyl rings, resulting in the relatively intense violet emission.

Remarkably, in the film state, the emission peak of compound 4 was located at 510 nm which is red-shifted to 93 nm compared with the THF solution, although the wavelength at the absorption maximum was 343 nm similar to that of the solution as shown in Figure S5. Figure 3 shows the photographs of as-prepared (a) and ground (b) compound 4 under UV-irradiation suggesting that compound 4 possesses mechanochromic nature as reported for other TPE-containing luminogens.12b,20 Judging from the colors, the natures of aggregates in THF/water (10/90), and the film are similar to that of as-prepared and that of ground samples, respectively. Indeed, PL spectrum for as-prepared sample (Figure S6) measured with an integrating sphere showed almost the same wavelength at absorption maximum (480 nm) as that in THF/ water (10/90). In order to understand the origin of mechanochromism, X-ray diffraction (XRD) powder patterns were obtained as shown in Figure S7. Since XRD pattern exhibits a number of sharp diffraction peaks and amorphous hallow around $2\theta = 20^\circ$, as-prepared sample (recovered after recrystallization) consisted of both crystalline and amorphous domains. In DSC thermogram (Figure S3), no thermal transition such as cold crystallization and melting was observed except glass transition. Inconsistency between XRD and DSC results can be explained

by the fact that the thermogram was recorded on the second scan experiment, and the stable amorphous nature of compound **4** due to the conformational versatility.

For the ground sample, the sharp diffractions observed in as-prepared sample vanished, and only amorphous hollow was observed indicative of amorphous nature of ground sample. Drop-cast solution afforded highly transparent film, suggesting that the obtained film was also amorphous. Consequently, the origin of mechanochromism is related to the crystalline and amorphous transition, and it is reasonable that the emissions at 470 and 510 nm originate from the crystalline and amorphous solids, respectively.

Red-shifted emissions from amorphous TPE-containing luminogens have been often reported.²⁰ It is generally recognized that in the crystalline state of TPE derivatives, the phenyl rings in TPE moiety are twisted to fit into crystalline lattices, and in the amorphous state, more planar conformation changing the nature of the excitonic coupling from the crystalline state, is adopted to afford the red-shifted emission. In order to validate our speculation, crystalline parameters should be elucidated. Fluorescent quantum yields (Φ_F 's) of as-prepared and film samples were determined to be 51 and 53%, respectively (excitation at 365 nm). These values are comparable to that of the solution (57%).

In conclusion, a cyclic emitter composed of tetraphenylsilane and TPE moieties was successfully synthesized. The key step for the macrocyclization is McMurry reaction in dilute conditions. The compound in THF solution, THF/water mixtures ($f_w = 90\%$), and the solid film showed violet, sky blue, and green emissions, respectively. Mechanochromism based on the crystalline–amorphous transition was also observed. The detailed emission mechanism and the OLED evaluation of compound **4** will be revealed in the near future. The tunable nature of the emission color with relatively high fluorescent quantum yields makes it possible to fabricate a multicolor device utilizing compound **4** as a single emitter.

Supporting Information is available on http://dx.doi.org/ 10.1246/cl.170636.

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