Petal-like Microstructures Formed from Sterically Crowded Chromophores

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A sterically crowded triangular molecule (3PhA) was synthesized with three terminal triphenylamine (TPA) wings connected to the central ring structure via a diethylphenyl group. In contrast to the tendency of conventional triangular molecules to assemble into one-dimensional fibrous structures, the nonplanar distorted 3PhA formed micrometer-sized petal-like aggregates. When excited with ultraviolet (UV, 340-360 nm) and green (510 nm) light, 3PhA in organic solutions exhibited two fluorescence bands maximized at ~380-400 and ≥650 nm, respectively. The fluorescence properties did not change significantly even after the formation of flat petal-like structures. These experimental results are likely due to the distorted molecular structure of sterically crowded 3PhA, which can cause suppression of intramolecular rotation and weakening of intermolecular interactions.

Keywords: Fluorescence, petal-like structure, self-assembly, sterically crowded chromophore

1. Introduction

Fluorescent organic materials have attracted much attention because of their intriguing functions and potential applications in sensors, switches, and optical information storage [1-8]. Self-assembled structures have a variety of unexpected functions that are different from component molecules. Because external stimuli such as light, pressure, and heat may induce changes in intermolecular interactions, spatial arrangements and morphology, and/or conformational changes in the individual component molecules, such nano/microstructured materials serve a variety of functions. Many studies have reported on fluorescent materials with different shapes, sizes and functions [2-14]. Nevertheless, it is still challenging to understand the rational molecular design of component molecules and to investigate the absorption and fluorescence properties of their assembled structures.

Azobenzene is a representative photochromic compound, but is generally known to not fluoresce at ambient temperature [15-18]. This is because the energy in the excited state is highly consumed through non-radiative conformational changes, thus causing a significant reduction in the fluorescence intensity. To address this issue and to obtain fluorescent azo-containing chromophore, we designed sterically crowded 2,4,6-tris{(E)-(4'-(diphenylamino)-3,5-diethyl-[1,1'-biphenyl]-4-yl)diazenyl}benzene-1,3,5-triol (3PhA, Scheme 1) which has an azo-containing aromatic core and three nonplanar triphenylamine (TPA) wings [19-20]. Such o-hydroxy compounds can show fluorescence due to the presence of the tautomeric hydrazone form [21-25]. Due to the steric effect and substantial distortion of 3PhA chromophore, we expected that intramolecular rotation and intermolecular interactions would be considerably limited in an aggregated state. Absorption and fluorescence characteristics in organic solutions as well as in assembled states were investigated.

2. Experimental

2.1. Synthesis

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2,4,6-tris{(E)-(4’-(diphenylamino)-3,5-diethyl-1,1’-biphenyl]-4-yl)diazenyl}benzene-1,3,5-triol (3PhA)

3PhA was synthesized from the Suzuki-Miyaura coupling reaction of the 2,4,6-tris{(E)-(4-bromo-2,6-diethylphenyl)diazenyl}benzene-1,3,5-triol (1) in the presence of tetrakis(triphenylphosphine)palladium(0) \([Pd(PPh₃)₄]\) catalyst \([24,25]\). In a 200 mL three-neck round-bottom flask, the precursor (1, 0.50 g, 0.59 mmol) and a catalytic amount of Pd(PPh₃)₄, 4-(diphenylamino)phenylboronic Acid (Tokyo Chemical Industry Co., LTD, 0.69 g, 2.38 mmol) were dissolved in toluene (20 mL) under nitrogen atmosphere. A water solution of NaHCO₃ (1N, 60 mL) were added to the reaction mixture. The reaction mixture was stirred vigorously under refluxing condition for 18 hours. After cooling the mixture to room temperature, water and chloroform were added and stirred at room temperature for 30 minutes. The organic portion was washed several times with water and then dried over anhydrous MgSO₄. The crude compound was purified by repeated column chromatography (chloroform:n-hexane = 3:1, v/v) and recrystallization to obtain dark purple solid (0.35 g, yield 45%).

\[\text{Anal. Calcd: } C, 80.87\%; \text{ H, } 6.11\%; \text{ N, } 9.43\%. \text{ Found C, } 80.37\%; \text{ H, } 6.16\%; \text{ N, } 9.37\%. \text{ HR-ESI-MS (m/z): } \text{Found, 1336.6510 (= M+H), Calcd for } C_{90}H_{82}N_{9}O_{3} = 1336.6541.\]

2.2. Materials and Characterization

Spectroscopic grade tetrahydrofuran (THF), \(n\)-hexane (hexane) dichloromethane (DCM), methanol (MeOH) and ethanol (EtOH), which were purchased from KANTO chemical Co., Inc., Japan, were used to dissolve 3PhA molecule. Ultrapure water (which was purified to reach a minimum resistivity of 18.0 MΩ-cm (25°C) using a μPure HIQ water purification system, Romax, South Korea) was used for all experiments. After a 20-sec nitrogen purge, a screw-cap quartz cuvette containing 3PhA solution was sealed with Parafilm. \(^1\)H NMR, ultraviolet-visible (UV-vis) absorption and fluorescence spectra were obtained using a JEOL JNM-ECP500 (500 MHz), Shimadzu UV-2600 UV-vis spectrophotometer and a Horiba FluoroMax-4 spectrofluorometer, respectively.

X-ray diffraction (XRD) data were collected using a Rigaku MiniFlex 600 diffractometer with Cu radiation. Optical microscopy (OM) and fluorescence optical microscopy (FOM, \(\lambda_{ex} = 520–550 \text{ nm} \)) images were obtained using an Olympus BX53 microscope after placing ~3 drops of the 3PhA sample onto a clean glass substrate. FE-SEM (field-emission scanning electron microscopy, TESKAN-MIRA3-LM) samples were coated with approximately 5-10 nm thick platinum layer using a Cressington 108 auto sputter coater, Ted Pella, Inc.

3. Results and discussion

Whereas many triangular molecules have a tendency to form long fibrous structures, 3PhA with three terminal TPA wings at the periphery tends to assemble into micrometer-sized flat petal-like...
structures. For instance, when hexane was added dropwise as a poor solvent to a 3PhA THF solution, the resulting well-dispersed suspension [4 × 10⁻⁵ M THF-hexane (1:1, v/v) mixture] contained flat petal-like aggregates with the length and width of 2-5 μm and 0.5-2 μm, respectively (Fig. 1a). If MeOH was added instead of hexane, thin petals less than ~8 μm long were frequently observed from a 4 × 10⁻⁵ M THF-MeOH (1:1, v/v) mixed suspension (Fig. 1b).

By comparison, as MeOH (or EtOH as a poor solvent) was added to a 3PhA DCM solution, the mixed solution became opaque in the early stage, and then precipitation occurred slowly. Scanning electron microscopy (SEM) and optical microscopy (OM) images taken from such opaque samples display relatively larger, curved petal-like structures that are approximately 10 micrometers long (Fig. 1c). Such flat microstructures sometimes got tangled together to form more complex structures, as the assembly progressed sufficiently.

The self-assembly of 3PhA into flat petal-like structures instead of long fibrous structures appears to be associated with the highly distorted molecular structure containing three terminal TPAs and their stacking modes. We next employed absorption and fluorescence spectroscopic and XRD measurements to obtain such information.

Fig. 2a shows that 3PhA has three intense absorption bands at around 310, 390, and 530 nm. Considering that the short axis φ-φ* transition [26] of conventional azobenzene unit emerges at approximately 250-270 nm, the strong absorption band appearing in the shortest wavelength region seems to arise from TPA being linked to the central ring structure via a phenyl ring. The absorption band at around 530 nm is likely due to the energetic proximity of the (π,π*) and (n,π*) states and intramolecular proton-transfer reactions (keto-
Interestingly, the positions of the maximum absorption bands were not significantly affected by the solvents used in this study (THF and DCM) and aggregation (Fig. 2a). For example, as MeOH was added to 3PhA THF solution, self-assembly proceeded and the mixed solution became opaque. As a result, its turbidity (shown by the absorbance at >700 nm) increased prominently, but the obtained maximum absorption positions were hardly changed. In addition, the XRD pattern exhibited a strong peak at 2θ = 4.2° (d = 21.0 Å), which roughly corresponds to the molecular size. Two peaks appearing at 2θ = 21.6° and 23.3° (d = ~4.1 and 3.8 Å, respectively) are longer than frequently observed π−π stacking interaction distances [27,28]. These results can be interpreted as follows. The introduction of three propeller-shaped TPA wings into the distorted triangular structure appears to cause serious distortion of all phenyl rings in the molecule, consequently weakening π−π stacking interactions. For this reason, it appears that small and thin petal-like aggregates are formed preferentially.

When excited with UV (340-360 nm) and green (510 nm) light (Figs 2b and 4), 3PhA in organic (THF and DCM) solutions showed two fluorescence bands at ~380-400 nm and ≥650 nm, respectively. The two bands may be due to TPA being linked to the central ring structure via a diethylphenyl group and keto-hydrazone form [21-23], respectively.

Notably, regardless of the solvent nature, the assembly into micrometer-sized flat petal-like aggregates rarely resulted in a reduction in fluorescence intensity, but rather increased it slightly. The red fluorescence from a bunch of petals was thus confirmed with FOM (Fig. 5). The fluorescence quantum yield was found to be ~10⁻³. The restriction of free intramolecular rotation in the sterically crowded 3PhA molecule is likely responsible for maintaining fluorescence intensity even after the formation of aggregates.

4. Conclusion

We designed a highly distorted triangular chromophore with three nonplanar TPA wings being connected to the central ring structure via a phenyl ring. The triangular molecule have a tendency to assemble into fluorescent petal-like structures rather than long fibers. Compared to the corresponding solution, the assembly did not significantly change the maximum absorption bands and fluorescence properties. That is, the introduction of three TPA wings leads to serious distortion of all phenyl rings in the molecule, resulting in weakening of free intramolecular rotation and π−π stacking interactions. These results

Fig. 3. X-ray diffraction pattern of 3PhA aggregates

Fig. 4. Fluorescence spectra when excited at (a) 360 nm and (b) 510 nm.

Fig. 5. (a) OM and corresponding (b) FOM images of 3PhA aggregates obtained from 6.7×10⁻⁵ M DCM-MeOH (1:2, v/v) mixed solution.
may provide an efficient way to produce various fluorescent nano- and microstructures.

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