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Self-assembling of cholesterol-appended benzothiadiazoletriphenylamine two-photon absorption dye



PIĞMĔNTS

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ABSTRACT

Cholesterol-appended benzothiadiazole—triphenylamine two-photon absorption dye was prepared and its self-assembling nature was investigated. The dye gave viscous fluid organogels in aliphatic hydrocarbon solutions such as cyclohexane, in which one-dimensional supramolecular aggregates are formed through the van der Waals interactions among the cholesterol moieties and the intermolecular hydrogen-bonding interactions among the carbamate spacer moieties. The supramolecular self-assembling was confirmed by the line-broadening effect in the ¹H NMR spectra, and by the bathochromic shifts of the absorption and emission bands. The bathochromic shift of the absorption band suggested that the benzothiadiazole—triphenylamine moieties take a *J*-like aggregation mode. Under the self-assembled conditions, the dye showed a negative exciton splitting pattern in the CD spectrum, suggesting the one-dimensional stacking with a left-handed twisting mode. The two-photon absorption nature in the parent benzothiadiazole—triphenylamine chromophore is maintained in the self-assembled system.

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1. Introduction

Supramolecular self-assembly composed of organic π -conjugated molecules has been of much interest in view of their potential application to material sciences [1-8]. Benzothiadiazole dyes and their derivatives are attractive candidates of the organic π -conjugated molecules, because of their strongly electron-accepting nature [9,10]. In addition, the dyes provide another character of strong light-emitting ability both in solution and solid state [11,12]. On the other hands, two-photon absorption dyes can be created by simple strategy on the basis of a connection between donor and acceptor moieties, by which the intramolecular charge-transfer character is enhanced to generate two-photon absorption nature [13,14]. Recently, we have created benzothiadiazole-based two-photon absorption dyes with light-emitting ability on the basis of a combination of the electron-withdrawing benzothiadiazole core and electron-donating triphenylamine moieties [15]. Then, the twophoton absorption dyes were developed to functional systems such as two-photon-excited red fluorescence emitting system [16],

two-photon-induced single oxygen sensitizing system [17], and two-photon-triggered emitting OFF–ON system [18]. In the application to the functional two-photon absorption materials, an ordered arrangement of the two-photon absorption dyes is important to enhance the functionalities as well as to generate a new functionality. In this paper, we report the first finding of an arrangement of the benzothiadiazole—triphenylamine dye via supramolecular self-assembling. The strategy is based on the introduction of the four self-assembling cholesterol moieties [19,20], which are appended to a benzothiadiazole core through hydrogen-bonding carbamate moieties.

2. Experimental

2.1. General

All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus Fourier transform infrared spectrometer and measured as KBr pellets. ¹H NMR spectra were determined in CDCl₃, CD₂Cl₂, and cyclohexane- d_{12} with a JEOL JNM-AL 400 spectrometer. Residual solvent protons were used as internal standard and chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (*J*) are reported in hertz (Hz).



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Scheme 1. Preparation of 4.

Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. Fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a BRUKER Auto FLEX spectrometer using delayed extraction mode and with an acceleration voltage of 20 keV. Samples were prepared from a solution of dichloromethane using dithranol as the matrix.

Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F_{254}). Column chromatography was carried out on

Table 1

Organic solvents tested for gelation by 4.^a

Solvent	20 °C (5 °C)
Hexane	Ι
Cyclohexane	S (G)
Methylcyclohexane	S (pG)
Benzene	S
Toluene	S
Methanol	I
Ethanol	I
Dichloromethane	S
Chloroform	S
1,2-Dichloroethane	S (R)
1,1,2,2-Tetrachloroethane	S
Acetone	I
Ethyl acetate	R
Acetonitrile	I
DMSO	pG
1,4-Dioxane	S (R)
1-Butanol	R
2-Propanol	R
NMP	tpG

^a [**4**] = 10.0 mM; G = gel, pG = partial gel, tG = turbid gel, tpG = turbid partial gel, R = recrystallization, S = solution, I = insoluble.

silica gel (WAKO C300). DMF was distilled from calcium hydride under reduced pressure, and stored under an argon atmosphere. 1,1,2,2-Tetrachloroethane was distilled from calcium hydride under an argon atmosphere just before use. THF was distilled from sodium and benzophenone under an argon atmosphere just before use. Methanol was dried over 4A molecular sieves. Preparation of **1** [16] and **3** [21] was reported previously.

2.2. Spectroscopic measurement

UV-vis spectra were measured on a JASCO V-570 spectrophotometer in 0.01 cm width quarts cell (1.0 mM), 0.1 cm cell (0.1 mM), and 1.0 cm cell (0.01 mM). Fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer. Film samples for the measurements of UV-vis and fluorescence spectroscopy were prepared by drop casting and the subsequent spin-coating (2000 rpm, 30 s) from cyclohexane solutions (100 µL) on quartz cell (12.5 \times 12.5 \times 45 mm). CD spectra were measured on a JASCO J-715 spectropolarimeter in 0.1 cm width quarts cell (1.0 mM). Atomic force microscopy (AFM) images were obtained on an SII SPA400 DFM (tapping mode). SI-DF20 type tips were used. Samples were prepared by drop casting from 0.001 mM cyclohexane solution on freshly cleaved mica. Two-photon absorption cross-sections were measured by using an open aperture Z-scan method with femtosecond pulses from an optical parametric amplifier (Quantronix TOPAS) excited by an 1 kHz repetition Ti:sapphire regenerative amplifier system (Quantronix Integra). The pulse width is 120 fs and the spatial profiles were characterized by knife-edge method and can be a Gaussian profile [16]. The two-photon absorption cross-sections were estimated on the basis of AF-50 (45 GM) used as a two-photon absorption benchmark [22].

2.3. 4,7-Bis{4-[N,N-bis(4-formylphenyl)amino]phenyl}-2,1,3-benzothia diazole (2)

To a solution of 1 (873 mg, 1.40 mmol) and dry DMF (4.34 mL, 56.0 mmol) in dry 1,1,2,2-tetrachloroethane (6 mL) was added dropwise POCl₃ (2.61 mL, 28.0 mmol) at 0 °C, and the mixture was heated at 90 °C for 4 days. During the heating, a mixture of dry DMF (1.30 mL, 16.8 mmol) and POCl₃ (0.80 mL, 8.4 mmol) in dry tetrachloroethane (0.9 mL) was added three times after 1, 2, and 3 days. The reaction mixture was poured into ice water, neutralized with aqueous 1 N NaOH solution, and extracted with chloroform. The combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue including tetrachloroethane was passed through a short pad of silica eluting with chloroform and the filtrate was evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography eluting with chloroform to give 2 in 46% yield (473 mg, 0.64 mmol): Pale orange powder; mp 226-228 °C; IR (KBr, cm⁻¹) 3032, 1693 (v_{C=0}), 1588, 1505, 1480, 1321, 1283, 1215, 1163, 825; ¹H NMR (CDCl₃) δ 7.23–7.38 (m, 12 H, ArH), 7.83 (d, *J* = 8.6 Hz, 8 H, ArH), 7.85 (s, 2 H, ArH), 8.04 (d, *J* = 8.6 Hz, 4 H, ArH), 9.93 (s, 4 H, CHO); FAB-MS (NBA, positive) *m*/*z* 734 (M⁺). Anal. Calcd for C₄₆H₃₀N₄O₄S: C, 75.19; H, 4.12; N, 7.62; Found: C, 75.00; H, 4.03; N, 7.65.

2.4. 4,7-Bis{4-[2-(3β -cholest-5-en-3-ylcarbamate-N-yl)ethylamino methyl]phenyl}-2,1,3-benzothiadiazole (**4**)

To a suspension of **2** (147 mg, 0.20 mmol) in dry THF (4 mL) and dry methanol (4 mL) was added **3** (416 mg, 0.88 mmol) at room temperature under an argon atmosphere, then the mixture was heated at 50 °C for 4 h. The imination reaction was monitored by the measurement of ¹H NMR (CDCl₃), which indicated the disappearance of



Fig. 1. ¹H NMR spectra of **4** in dichloromethane- d_2 (top) and cyclohexane- d_{12} (bottom) at 1.0 mM.

CHO proton signal (9.93 ppm) and the appearance of N=CH proton signal (8.26 ppm). Then the reaction mixture was cooled to 0 °C, sodium borohydride (38 mg, 1.0 mmol) was added and the mixture was stirred at room temperature for 13 h. The reaction mixture was quenched by the addition of water. The formed precipitate was collected by filtration, and washed with water, and methanol. The crude product was purified by silica gel column chromatography eluting with dichloromethane/methanol/NH₄OH (190:9:1, v/v/v) to give 4 in 20% (105 mg, 0.041 mmol): Red solid: mp 175–176 °C, IR (KBr, cm⁻¹) 3420 (v_{NH}), 3345 (v_{NH}), 3031, 2937, 2903, 2867, 1718 (v_{C=0}), 1700 (v_{C=0}), 1600, 1508, 1478, 1320, 1267, 1136, 1031, 1015, 823; ¹H NMR (CDCl₃) δ 0.66, 1.00 (s, each 12 H, Me), 0.86 (d, J = 6.6 Hz, 24 H, Me), 0.91 (d, J = 6.6 Hz, 12 H, Me), 0.94–1.63 (m, 88 H, CH and NH), $1.76-2.04(m, 20 H), 2.21-2.43(m, 8 H), 2.81(t, J = 5.6 Hz, 8 H, NHCH_2),$ 3.26-3.36 (m, 8 H, CONHCH₂), 3.76 (s, 8 H, ArCH₂NH), 4.44-4.56 (m, 4 H, OCH), 5.00–5.10 (m, 4 H, NHCOO), 5.36 (d, J = 4.9 Hz, 4 H, CH=C), 7.14 (d, J = 8.3 Hz, 8 H, ArH), 7.19 (d, J = 8.6 Hz, 4 H, ArH), 7.23 (d, *J* = 8.3 Hz, 8 H, ArH), 7.74 (s, 2 H, ArH), 7.88 (d, *J* = 8.6 Hz, 4 H, ArH); MALDI-TOF-MS (positive, dithranol) m/z 2559.80 (M⁺, calcd for C₁₆₆H₂₃₈N₁₂O₈S 2559.83). Anal. Calcd for C₁₆₆H₂₃₈N₁₂O₈S · 0.8CH₂Cl₂:C, 76.18; H, 9.18; N, 6.39: Found: C, 76.08; H, 9.24; N, 6.45.

3. Results and discussion

3.1. Synthesis

Cholesterol-appended benzothiadiazole dye **4** was prepared from the condensation reaction between tetraformyl derivative **2** and cholesterol carbamate with terminal amino group **3** [21], followed by treatment with sodium borohydride (Scheme 1). The synthetic intermediate **2** was obtained from **1** [16] by treatment with DMF/POCl₃. The new compounds were characterized by spectroscopic methods and elemental analysis.

3.2. Aggregation properties

The self-assembling of **4** was checked easily by gelation aggregate test (Table 1). In aromatic hydrocarbon solvents such as benzene and toluene, and in chlorinated solvents such as dichloromethane and chloroform, 4 dissolved as monomer. In contrast 4 formed viscous fluid organogels at 10 mM in aliphatic hydrocarbon solvents such as cyclohexane and methylcyclohexane, and in DMSO and NMP solvents. In the organogels, the self-assembling of the **4** molecules proceeds to form one-dimensional supramolecular aggregates mainly through the van der Waals interactions among the cholesterol moieties, as widely found in cholesterol-based organogels (see, the Supporting Information, Fig. 1) [19]. In the ¹H NMR spectrum, linebroadening effect arising from the self-assembling was observed in cyclohexane- d_{12} (1.0 mM) at 20 °C (Fig. 1). Such broadening was not observed in dichloromethane- d_2 . Thus, we decided to study the selfassembling nature in cyclohexane as an effective solvent and in dichloromethane as ineffective one.

The aggregate can be visualized by atomic force microscopy (AFM). The aggregated cyclohexane solution (0.001 mM) was casted on freshly cleaved mica. The AFM image indicates a hierarchical tree-like structure with a height of ca. 15 nm (Fig. 2). The aggregate seems to be created by the self-assembling of the **4** molecules and the subsequent hierarchical self-organization.



Fig. 2. AFM image and the height profile of 4.

3.3. UV-vis absorption and fluorescence spectral properties

In the UV–vis spectra of 1 and 4, the two absorption maxima were observable around 310 nm and 460-470 nm. The former can be assigned to $\pi - \pi^*$ transition and the later to charge-transfer arising from donor-acceptor (CT)transition the triphenylamine-benzothiadiazole chromophore [16]. In 4, the CT band (474 nm) in the cyclohexane solution is observed at longer wavelength than that (466 nm) in the dichloromethane solution; nevertheless, the polarity of cyclohexane is lower than that of dichloromethane (Fig. 3a). On the other hand, such solventdependent change was not observed in 1 without the cholesterol moieties: the CT bands appeared at 455 nm both in cyclohexane and dichloromethane [16]. The bathochromic shift in the cyclohexane solution of 4 would be attributed to the selfassembling of the 4 molecules, in which the benzothiadiazoletriphenylamine moieties take a *I*-like aggregation mode [23]. The CT band (472 nm) in the film aggregate state coincides with that (474 nm) in the cyclohexane solution but not with that (466 nm) in the dichloromethane solution (Fig. 3a).

The self-assembling in cyclohexane is facilitated with increasing concentration (from 0.001 to 1.0 mM): the intensity of the longer wavelength region of the CT band increased (Fig. 3b, and the Supporting Information, Fig. S4). The concentration-dependent self-assembling in **4** is reflected also in steady-state fluorescence spectra. The emission band shifts bathochromically from 594 nm to 620 nm with the increase of concentration (from 0.001 to 1.0 mM), according to facilitated self-assembling (Fig. 4b). The emission band (620 nm) at the high concentration of 1.0 mM is similar to that (621 nm) in the film aggregate state (Fig. 4a). The bathochromic shift would be attributed to a stabilization effect on the excited state in the self-assembled aggregates [24]. In contrast, in dichloromethane, the CT absorption band at 466 nm and the emission band at 648 nm in **4**



Fig. 3. (a) UV-vis spectra of **4** in dichloromethane and cyclohexane (1.0 mM), and in film. (b) UV-vis spectra of **4** in cyclohexane at 0.001, 0.01, 0.1, and 1.0 mM.

changed scarcely depending on concentration (see, the Supporting Information, Figs. S2 and S3).

3.4. CD spectral properties

Under the self-assembled conditions, the cyclohexane solution of **4** is CD-active even at the lower concentration ($\sim 0.01 \text{ mM}$) (Fig. 5, and the Supporting Information, Figs. S5). The CD spectrum showed a negative exciton splitting with the first negative Cotton effect at 507 nm and the second positive Cotton effect at 444 nm. The intersection at 475 nm was in accordance with the CT absorption band at 474 nm. Probably, the negative exciton splitting observed around the triphenylamine—benzothiadiazole chromophore is due to the one-dimensional stacking of the **4** molecules with a left-handed twisting mode [25], as widely found in cholesterol-appended dyes [19]. In contrast, the strong Cotton effect around at 270–350 nm would include the chiroptical contribution arising from macroscopic alignment of fibrous large aggregates (see, the Supporting Information, Figs. S5 and S6) [26].

3.5. Infrared spectral properties

In addition to the van der Waals interactions among the cholesterol moieties, the intermolecular hydrogen-bonding interactions among the carbamate moieties work most effectively to stabilize the self-assembled



Fig. 4. (a) Fluorescence spectra of **4** in dichloromethane and cyclohexane (1.0 mM), and in film. (b) Fluorescence spectra of **4** in cyclohexane at 0.001, 0.01, 0.1, and 1.0 mM (excited at 475 nm).



Fig. 5. CD spectrum of 4 in cyclohexane at 1.0 mM (0.1 cm width cell).



Fig. 6. C=O stretching vibration region in the IR spectra of **4** in dichloromethane and cyclohexane (1.0 mM), and in KBr.

aggregate structure. In the cyclohexane solution (1 mM), the hydrogenbonded C=O stretching band at 1700 cm⁻¹ was observed in addition to the non-hydrogen-bonded one at 1720 cm⁻¹, as found in the KBr solid state showing the C=O bands at 1700 and 1718 cm⁻¹. In contrast, only the non-hydrogen-bonded C=O stretching band at 1714 cm⁻¹ was detected in the dichloromethane solution (Fig. 6). Similar trends were observed for the NH stretching bands. The hydrogen-bonded NH stretching band was appeared around 3350 cm⁻¹, whereas the nonhydrogen-bonded one around 3450 cm⁻¹.

3.6. Two-photon absorption spectral properties

The two-photon absorption cross-sections (δ) were estimated by using an open aperture Z-scan method with a femtosecond Ti:sapphire laser source [16]. The cholesterol-appended dye **4** is TPA-active both in the self-assembled and in the non-selfassembled conditions (1.0 mM): the δ values of 110 GM in cyclohexane and 147 GM in dichloromethane at 800 nm. The results indicate that two-photon absorption nature is maintained even in the self-assembled system where the benzothiadiazole two-photon absorption chromophores are arranged with *J*-like aggregate mode.

4. Conclusions

In conclusion, we have demonstrated that benzothiadiazole two-photon absorption dye is self-assembled to form an aggregate by introducing the four cholesterol moieties. In the aggregate, the benzothiadiazole moieties are arranged with *J*-like helical stacking mode. The two-photon absorption nature in the parent benzothiadiazole—triphenylamine chromophore is maintained in the self-assembled system. We believe that the present selfassembled two-photon absorption system will be developed to material sciences such as optical power limitation, microfabrication, three-dimensional optical data storage.

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Appendix A. Supplementary Information

Supplementary Information related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.04.019.

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