Self-assembling of Cholesterol-appended Benzothiadiazole Fluorescent Dyes

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Cholesterol-appended benzothiadiazole fluorescent dyes were self-assembled to form aggregates through van der Waals interactions among the cholesterol moieties, hydrogen-bonding interactions among the carbamate moieties, and π-stacking interactions among the benzothiadiazole moieties.

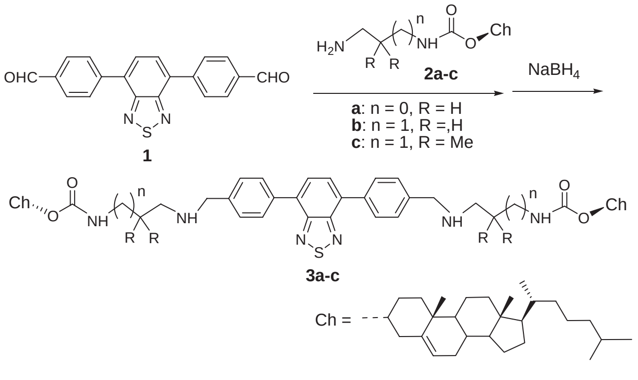
Aromatic molecules with material functionalities such as light-emitting and carrier-transporting abilities have been of much interest in recent years in view of their potential applications for electronics and optoelectronics. 4,7-Diaryl-2,1,3-benzothiadiazoles are known as strongly fluorescent dyes[1] and strong electron-acceptors.[2] Recently, we have developed benzothiadiazole-based dyes to functional materials such as dichroic fluorescent materials in liquid crystal displays,[3] light-harvesting antennas as well as energy-transfer reagents in fullerene-dyad systems,[4] and two-photon absorbing materials with red-light emitting ability[5] and singlet oxygen sensitizing ability.[6] On the other hand, recently, supramolecular structures composed of functional aromatic molecules have been applied as novel functional materials.[7] In this letter, we report the first finding of a benzothiadiazole-based supramolecular system. The strategy is based on the introduction of the two self-assembling cholesterol moieties,[8] which are appended to a benzothiadiazole core through hydrogen-bonding carbamate moieties.

Cholesterol-appended benzothiadiazole dyes **3a**–**3c** with various linker moieties (ethylene linker for **3a**, propane-1,3-diyl for **3b**, and 2,2-dimethylpropane-1,3-diyl for **3c**) were prepared from condensation reactions between diformyl derivative **1**[3a] and cholesterol carbamates with terminal amino group **2a**–**2c**,[9] followed by treatment with sodium borohydride (Scheme 1).

In aliphatic hydrocarbon solutions such as cyclohexane and methylcyclohexane (10 mM), **3a**–**3c** formed viscous fluid organogels. Probably, one-dimensional self-assembled supramolecular aggregates composed of **3a**, **3b**, and **3c** molecules are formed mainly by van der Waals interactions among cholesterol moieties, as widely found in cholesterol-based organogels.[8] In contrast, **3a**–**3c** dissolved molecularly in chlorinated solvents such as dichloromethane and chloroform. In the ^{1}H NMR spectrum, line-broadening effect arising from the self-assembling was observed in **3a** in cyclohexane-d_{12} (1.0 mM) at 20 °C.[10] Thus, we decided to study the self-assembling nature of **3a**–**3c** in cyclohexane as an effective solvent and in dichloromethane as an ineffective one.

In the UV–vis spectra of **3a**–**3c**, the absorption maxima were observable around 275 nm and around 390 nm in cyclohexane and dichloromethane. In cyclohexane, the UV–vis spectra of **3a** changed depending on the concentration (from 0.01 to 1.0 mM) (Figure 1a). At the higher concentration (1.0 mM), the absorption band at 388 nm was considerably broadened and the intensity of the longer wavelength region around 450 nm increased. The spectral change can be attributed to the π-stacking interaction among the benzothiadiazole moieties. A self-assembled stacking structure was found in the crystal state of 4,7-diphenylbenzothiadiazole.[5b] Similar spectral change was observable in **3b**. In contrast, **3c** provided only the broadening effect without the intensity change at the longer wavelength region. In dichloromethane, no concentration effects were observed in **3a**–**3c**.[10]

Under the self-assembled conditions, the cyclohexane solutions of **3a** (1.0 and 0.1 mM) and **3b** (1.0 mM) are CD-active (Figure 1b). In **3a** (1.0 mM), strongly negative, negative, and positive Cotton effects were given at 405 ($\Delta\varepsilon = -174$ cm^2 mmol^{-1}), 284 ($\Delta\varepsilon = -586$ cm^2 mmol^{-1}), and 262 nm ($\Delta\varepsilon = 354$ cm^2 mmol^{-1}). The first Cotton effect is corresponding to the absorption band around 388 nm. In the second and third



Scheme 1.

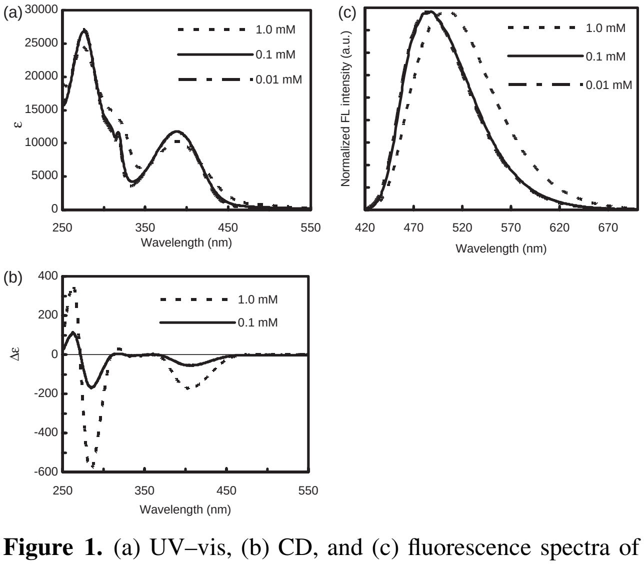


Figure 1. (a) UV–vis, (b) CD, and (c) fluorescence spectra of **3a** in cyclohexane (0.01, 0.1, and 1.0 mM).

Cotton effects with negative and positive signs, the intersection at $\lambda_{\Delta\varepsilon=0}$ of 272 nm was in accordance with the absorption band around 275 nm, suggesting appearance of negative exciton splitting.[11] The CD intensity in **3a** was reduced with decreasing concentration. In **3b**, only higher concentration sample at 1.0 mM is CD-active. Further, very weak Cotton effects were observed in **3c** even at the higher concentration of 1.0 mM. On the other hand, all the dichloromethane solutions of **3a**–**3c** are CD-silent, as expected.[10] The Cotton effects observed around the benzothiadiazole chromophore region would be due to chiroptical contribution from the chirally-ordered aggregates, as widely found in cholesterol-appended dyes.[8] One of the most plausible explanations of the negative exciton splitting is the one-dimensional stacking of the molecules with left-handed twisting mode.[8a]

The aggregation is reflected in steady-state fluorescence spectra. In dichloromethane, the emission band at 512 nm in **3a**–**3c** changed scarcely depending on concentration.[10] In contrast, in cyclohexane solutions of **3a**, the emission band was shifted bathochromically from 488 to 505 nm with increasing concentration (from 0.01 to 1.0 mM), according to facilitated aggregation (Figure 1c). The bathochromic shift observed in cyclohexane solutions would be attributed to a stabilization effect on the excited state in the aggregates.[12] The trend of the concentration-dependent fluorescence spectral change in **3a** ($\Delta\lambda$, 7 nm), **3b** ($\Delta\lambda$, 2 nm), and **3c** ($\Delta\lambda$, $\approx$0 nm) is in accordance with the trend of the UV–vis and CD spectra, indicating the order of aggregate stability to be **3a** > **3b** > **3c**. Thus, the replacement of ethylene linkers in **3a** with 1,3-propylene **3b** or 2,2-dimethyl-1,3-propylene **3c** decreases the aggregation ability. The short ethylene linkers are effective to arrange the benzothiadiazole moieties so that they can enjoy the π-stacking interactions, leading to the construction of one-dimensional aggregate.

The contribution of the hydrogen-bonding interactions in the carbamate moieties in **3a**–**3c** was checked by infrared spectroscopy. In dichloromethane (1.0 mM), **3a**–**3c** indicated the C=O stretching bands at 1716 cm^{-1}, which can be assigned to the non-hydrogen-bonded C=O groups, as expected. In contrast, the cyclohexane solution of **3a** (1.0 mM) indicated the two type C=O stretching bands, the strong intensity band at 1693 cm^{-1} and the medium intensity band 1730 cm^{-1}, as found in the KBr solid state (1700 and 1725 cm^{-1}). The former band can be assigned to the hydrogen-bonded C=O groups whereas the later band to the non-hydrogen-bonded groups. In **3b** and **3c**, the contribution of the hydrogen-bonding interaction decreased. Similar trends were observed for the NH stretching bands.[10] The foregoing results indicate that the intermolecular hydrogen-bonding interactions work most effectively in **3a** to stabilize the self-assembled supramolecular structure.

As a summary of the spectral results, one can conclude that van der Waals interactions among the cholesterol moieties mainly hold the self-assembled structure along with hydrogen-bonding interactions among the carbamate moieties and π-stacking interactions among the benzothiadiazole moieties. The molecules are stacked one-dimensionally through the non-bonded interactions to form elongated supramolecular aggregates, as found in cholesterol-appended dyes.[8]

In conclusion, we have demonstrated that self-assembling of the benzothiadiazole fluorescent dyes is actually achieved by introducing the cholesterol moieties via the carbamate spacers.

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