Molecular design of novel non-planar heteropolycyclic fluorophores with bulky substituents: convenient synthesis and solid-state fluorescence characterization†

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Novel indeno[1,2-*b*]benzo[4,5-*e*]pyran-11-one-type fluorophores exhibiting intense solid-state fluorescence were conveniently synthesized and the relation between their solid-state photophysical properties and the X-ray crystal structures were investigated, which demonstrates that non-planar structures with sterical hindered substituents prevent the fluorophores from forming short π–π contacts causing fluorescence quenching in the solid state.

Strong solid-emissive fluorophores have attracted increasing attention in materials science due to their uses in basic research[1–10] and in the construction of optoelectronic devices.[11] However, organic fluorophores with strong solid-emissive properties are rare, because most organic fluorophores undergo fluorescence quenching in aggregation states. Many efforts have been carried out to avoid the concentration quenching. For example, the construction of guest–host-doped emitter systems,[2] the introduction of bulky substituents to the original fluorophores,[3,4] and the formation of fluorescent clathrates[5,6] or fluorescent salts[7] are known to be useful methods towards solving the problem of fluorescence quenching by aggregation. Strong intermolecular π–π interaction[3c,4,6,8] or continuous intermolecular hydrogen bonding[4b,10] between neighboring fluorophores have been suggested as the main factors of fluorescence quenching. However, the key point in the design of new strong solid-emissive fluorophores is to remove the factors inducing concentration quenching in molecular aggregation states.

In this paper, we report a molecular design of the novel indeno[1,2-*b*]benzo[4,5-*e*]pyran-11-one-type fluorophore (**3**), constructed by a non-planar structure with sterical hindered substituents: the convenient synthesis, solid-state fluorescence properties, and the X-ray crystal structures of **3a**–**3c** are reported. The synthetic pathway is shown in Scheme 1. We used 3-(dibutylamino)-6-hydroxy-6-phenylnaphtho[2,3-*b*]benzofuran-11(6*H*)-one **1** [4a] as a starting material. The reaction of **1** with organolithium reagents gave **2a**–**2c** in 60–70% yield. The structures of **2a**–**2c** were confirmed by X-ray diffraction analysis.† Next, the conversion of **2a**–**2c** to novel heteropolycyclic fluorophores (**3a**–**3c**) was performed in 90–100% yield by a photochemical rearrangement reaction, which is a new photoreaction we have found in this research. As a typical example, Fig. 1 shows (a) the absorption and (b) fluorescence spectral changes obtained by irradiation of **2b** in 1,4-dioxane at 365 nm with a black light. Upon irradiation, a new, intense absorption band appeared at around 455 nm together with isosbestic points at 325 and 363 nm, and the corresponding fluorescence band appeared at 520 nm.

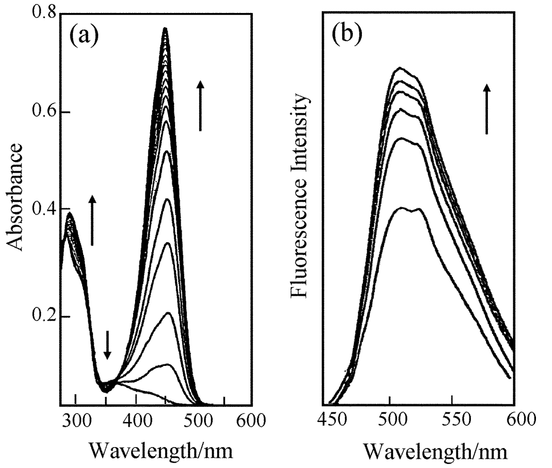
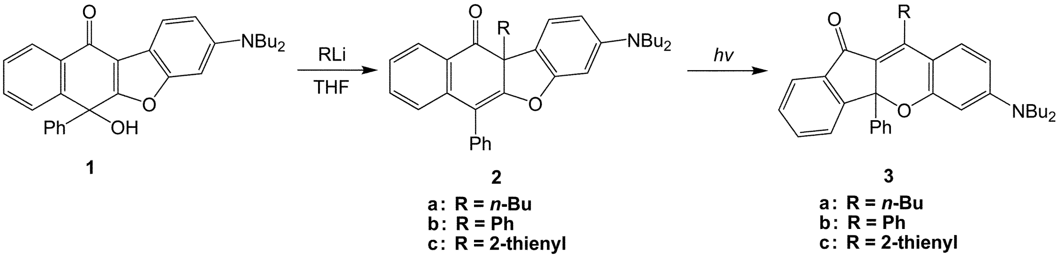


Fig. 1 (a) Absorption and (b) fluorescence spectral changes upon photoirradiation of **2b** in benzene. [**2b**] = 2.5 × 10^{-5} M.



a: R = *n*-Bu
b: R = Ph
c: R = 2-thienyl

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Scheme 1

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Table 1 Spectroscopic properties of **3a**–**3c** in 1,4-dioxane and in the crystalline state

	In 1,4-dioxane			In the crystalline state		
	λ_{max}^{abs}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	λ_{max}^{fl}/nm	Φ	λ_{max}^{ex}/nm	λ_{max}^{fl}/nm	Φ
3a	447 (32 300)	497	0.053	485	522	0.39
3b	455 (30 500)	519	0.013	495	531	0.15
3c	460 (28 600)	532	0.003	537	567	0.06

Table 1 summarizes the absorption and fluorescence spectral data of the products, **3a**–**3c** in 1,4-dioxane and in the crystalline states. In 1,4-dioxane, the absorption maxima at around 447–460 nm and the fluorescence maxima at around 497–532 nm are both red-shifted by conjugation with the substituent (R) in the order of **3a** < **3b** < **3c**. On the other hand, the fluorescence intensity decreases dramatically in the order of **3a** ($\Phi = 0.053$) ≫ **3b** ($\Phi = 0.013$) > **3c** ($\Phi = 0.003$). The low fluorescence quantum yields suggest that non-radiative decay is accelerated by free rotation of the phenyl ring and thienyl ring in solution.[12]

Of particular interest are the solid-state phtophysical properties. The fluorescence emission intensities of **3a**–**3c** are in the order of **3a** ($\Phi = 0.39$) > **3b** ($\Phi = 0.15$) > **3c** ($\Phi = 0.06$) in the crystalline state, which is quite different from the results obtained in 1,4-dioxane. Since the rotation of the substituents is restricted in the solid state, the fluorescence quantum yields are higher in the solid states than in solution. The longest wavelengths of the absorption and fluorescence maxima of **3a**–**3c** are red-shifted in the order of **3a** ≈ **3b** < **3c** in comparison with those of fluorescence maxima of **3a**–**3c** in 1,4-dioxane. From the lower quantum yields of **3c** in both solution and the solid state, it was considered that a strong electron-donating effect of the thienyl group caused not only red-shift of the absorption and fluorescence maxima but also significant fluorescence quenching.

To gain more detailed information, the X-ray crystal structures have been determined.‡ The molecular packing structures are shown in Figs. 2–4 which demonstrate that the three crystals are built up by a centrosymmetric pair unit of two enantiomers. Fig. 5 shows the schematic structure of one of the enantiomers. The heteropolycyclic skeleton is non-planar because of the existence of the central sp^3 carbon where the phenyl group is attached. We expected that such non-planar structures with sterically hindered substituents (the phenyl, R, and 7-dibutylamino groups) prevent the fluorophores from forming short π–π contacts causing fluorescence quenching in the solid state. In fact, the dihedral angles between the indenone skeleton and the benzopyran skeleton of **3a**–**3c** are near 150.2, 150.1, and 153.1°, respectively. The compounds **3a** and **3b** which exhibit strong solid-state fluorescence have only one or two interatomic contacts of less than 3.60 Å between the neighboring fluorophores in the crystal structure (Figs. 2 and 3). On the other hand, the compound **3c** which exhibits unexpected weak solid-state fluorescence has 15 interatomic contacts of less than 3.60 Å between the neighboring fluorophores

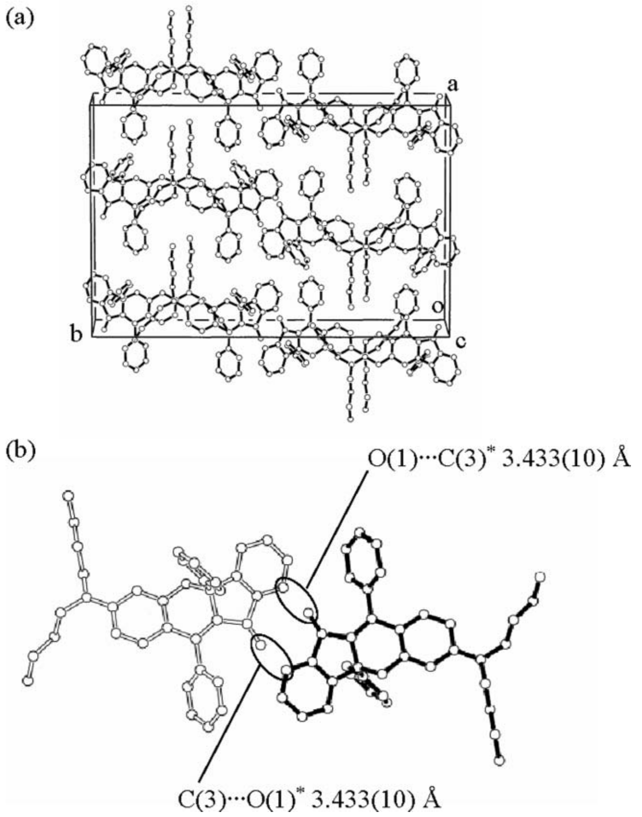

Fig. 2 Crystal packing of **3a**: (a) a view of the molecular packing structure and (b) nearest contact between enantiomers.

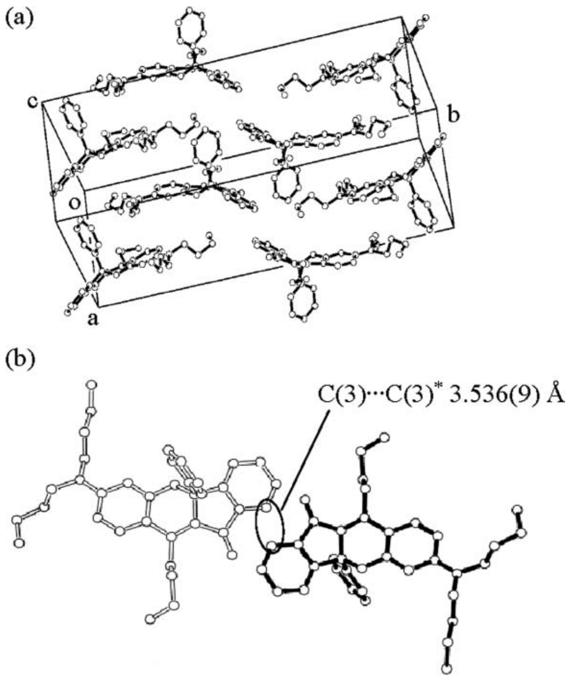

Fig. 3 Crystal packing of **3b**: (a) a view of the molecular packing structure and (b) nearest contact between enantiomers.

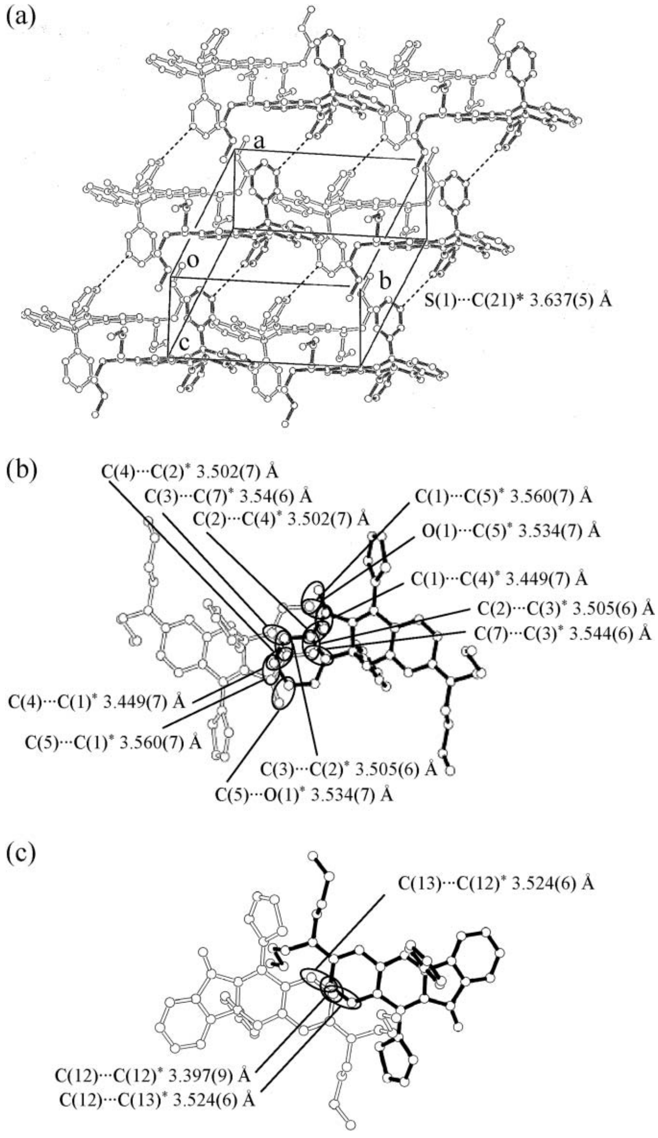

Fig. 4 Crystal packing of **3c**: (a) a view of the molecular packing structure and (b) and (c) nearest contact between enantiomers.

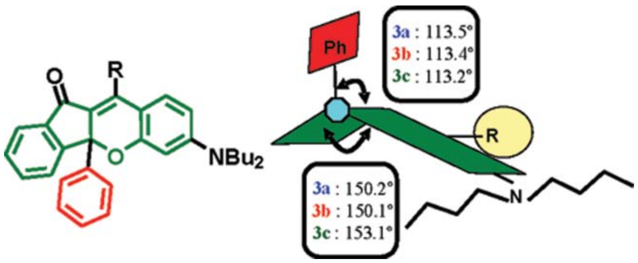

Fig. 5 Schematic representation of the molecular structure of **3a**–**3c**.

[Fig. 4(b) and (c)]. As shown in Fig. 4(a), the fluorophores are linked continuously by intermolecular CH ··· S bonds between the adjoining benzene and thienyl rings of neighboring fluorophores. Thus, the formation of the continuous molecular linking by CH ··· S bonds allows the fluorophore **3c** to form such a massed molecular packing structure.

In conclusion, novel heteropolycyclic fluorophores (**3a**–**3c**) have been designed and conveniently synthesized by using a novel photoreaction that we have found. The X-ray crystal analysis has demonstrated that, in the crystals of **3a** and **3b**, the non-planar structure with sterically hindered substituents prevents the fluorophores from forming short intermolecular contacts and produces intense solid-state fluorescence emission. In the crystal of **3c**, the formation of CH ··· S bonding between adjoining benzene and thienyl rings of neighboring fluorophores increases intermolecular interactions and reduces the fluorescence intensity compared with the crystals of **3a** and **3b**. Thus, new useful information concerning the solid-state fluorescence has been obtained.

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Notes and references

‡ Crystal data for **2a**: $C_{34}H_{39}NO_2$, $M = 493.69$, monoclinic, $a = 14.321(2)$, $b = 11.583(3)$, $c = 17.877(2)$ Å, $\beta = 104.490(8)^\circ$, $U = 2871.3(9)$ Å^3, $T = 296.2$ K, space group $P2_1/n$ (no. 14), $Z = 4$, μ(Mo-K$_\alpha$) = 0.70 cm^{-1}, 5552 reflections measured, 5047 unique ($R_{int} = 0.042$) which were used in all calculations. The final R indices were $R_1 = 0.074$, wR $(F^2) = 0.183$ (all data). Crystal data for **2b**: $C_{36}H_{35}NO_2$, $M = 513.68$, monoclinic, $a = 9.081(2)$, $b = 20.626(4)$, $c = 15.600(3)$ Å, $\beta = 98.69(2)^\circ$, $U = 2888(1)$ Å^3, $T = 296.2$ K, space group $P2_1/c$ (no. 14), $Z = 4$, μ(Mo-K$_\alpha$) = 0.72 cm^{-1}, 5427 reflections measured, 5087 unique ($R_{int} = 0.059$) which were used in all calculations. The final R indices were $R_1 = 0.055$, wR $(F^2) = 0.174$ (all data). Crystal data for **2c**: $C_{34}H_{33}NO_2S$, $M = 519.70$, triclinic, $a = 10.088(8)$, $b = 16.317(6)$, $c = 9.031(6)$ Å, $\alpha = 91.18(4)$, $\beta = 97.28(6)$, $\gamma = 72.73(4)^\circ$, $U = 1407(1)$ Å^3, $T = 296.2$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-K$_\alpha$) = 1.46 cm^{-1}, 6872 reflections measured, 6463 unique ($R_{int} = 0.084$) which were used in all calculations. The final R indices were $R_1 = 0.094$, wR $(F^2) = 0.194$ (all data). Crystal data for **3a**: $C_{34}H_{39}NO_2$, $M = 493.69$, monoclinic, $a = 9.471(5)$, $b = 30.489(6)$, $c = 10.734(5)$ Å, $\beta = 114.03(3)^\circ$, $U = 2830(2)$ Å^3, $T = 296.2$ K, space group $P2_1/a$ (no. 14), $Z = 4$, μ(Mo-K$_\alpha$) = 0.71 cm^{-1}, 5417 reflections measured, 4981 unique ($R_{int} = 0.050$) which were used in all calculations. The final R indices were $R_1 = 0.053$, wR $(F^2) = 0.117$ (all data). Crystal data for **3b**: $C_{36}H_{35}NO_2$, $M = 513.68$, orthorhombic, $a = 20.947(7)$, $b = 31.759(7)$, $c = 8.758(7)$ Å, $U = 5826(4)$ Å^3, $T = 296.2$ K, space group $Pbca$ (no. 61), $Z = 8$, μ(Mo-K$_\alpha$) = 0.71 cm^{-1}, 5385 reflections measured, 4786 unique ($R_{int} = 0.000$) which were used in all calculations. The final R indices were $R_1 = 0.055$, wR $(F^2) = 0.108$ (all data). Crystal data for **3c**: $C_{34}H_{33}NO_2S$, $M = 519.70$, triclinic, $a = 11.009(2)$, $b = 13.949(5)$, $c = 9.752(2)$ Å, $\alpha = 97.99(2)$, $\beta = 101.46(2)$, $\gamma = 72.82(2)^\circ$, $U = 1397.1(6)$ Å^3, $T = 296.2$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-K$_\alpha$) = 1.47 cm^{-1}, 6801 reflections measured, 6426 unique ($R_{int} = 0.040$) which were used in all calculations. The final R indices were $R_1 = 0.079$, wR $(F^2) = 0.184$ (all data). CCDC reference numbers 605725–605730. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607891e.

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