Solid-state fluorescence changes of naphthooxazole-type fluorophores upon inclusion of organic solvent molecules

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Abstract

Naphthooxazole-type fluorophores (2) did not exhibit fluorescence in solution, but exhibited strong fluorescence in the solid state. Interestingly, a large red shift in colour and drastic decrease in fluorescence intensity were observed upon inclusion of guest molecules in the crystalline state. To elucidate the enclathrated guest-effects on the solid-state photophysical properties, the X-ray crystal structures of the guest-free and several guest-inclusion crystals have been determined. Furthermore, we have performed the semi-empirical molecular orbital calculations (PM3 and INDO/S) to investigate the effects of the molecular structures on the crystal packing structure. It was confirmed that the reasons for the red-shift of the absorption and fluorescence wavelength maxima and a drastic fluorescence quenching behaviour
upon formation of host-guest inclusion compounds of 2 are attributable to strong intermolecular π-π interactions and to the formation of continuous molecular linking by intermolecular hydrogen bonds.

Keywords: Fluorescence; Dyes; Inclusion compounds; Crystal structures; Heterocycles

1. Introduction

Solid-state fluorescence property of organic fluorescent dyes has recently received considerable attention because of their potential use in the construction of optoelectronic devices [1—10]. To design of strong solid-state emissive materials, it is very important to obtain information about the relationship between the photophysical properties and the chemical and crystal structures of fluorophores. Organic fluorescent host which can exhibit sensitive colour and fluorescence changes upon formation of host-guest inclusion complexes are a good candidate for elucidation of the solid-state photophysical properties. Recently, Stalke et al. have reported that disubstituted anthracene 9,10-(Ph₂P=S)₂C₁₄H₈ exhibits a dramatic fluorescence enhancement upon inclusion of toluene molecules in the crystalline state [11]. On the other hand, we have previously developed novel benzofurano[3,2-b]naphthoquinol-type [12—14], imidazo[5,4-a]-anthraquinol-type [15, 16] and phenanthro[9,10-d]imidazole-type [17] fluorescent hosts whose crystals exhibit a dramatic fluorescence enhancement upon inclusion of various gaseous amines, various organic solvents, and various carboxylic acids, respectively.
In contrast, we have quite recently developed novel naphthoxazole-type fluorophores (2) that exhibit a red shift in colour and a drastic fluorescence decrease upon inclusion of guest molecules in the crystalline state, to the best of our knowledge there are no such fluorescent hosts. In this paper, the enclathrated guest-effects on the solid-state photophysical properties and the crystal packing structures of the fluorophores 2 are discussed on the basis of the results of the semi-empirical molecular orbital calculations (PM3 and INDO/S) and the X-ray crystal structures.

2. Experimental

IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer for samples in KBr pellet form. Absorption spectra were observed with a JASCO U-best30 spectrophotometer. For the measurement of the solid-state fluorescence excitation and emission spectra of the crystals, a JASCO FP-777 spectrometer equipped with a JASCO FP-1060 attachment was used. Single-crystal X-ray diffraction was performed on Rigaku AFC7S diffractometer. Elemental analyses were recorded on a Perkin Elmer 2400 II CHN analyzer. 1H NMR spectra were recorded on a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral) or alumina (WAKO, about 300 mesh). Semi-empirical molecular orbital (MO) calculations were performed on FUJITSU FMV-ME4/657 by using the WinMOPAC Ver. 3 package (Fujitsu, Chiba, Japan).
2.1. *Synthesis of 4-[(4-diethylamino)phenylamino]-[1,2]naphthoquinone (1a)*

To a solution of 1,2-naphthoquinone-4-sulfonic acid sodium salt (9.48 g, 36.4 mmol), sodium acetate (9.91 g, 72.8 mmol), and NiCl₂ (4.72 g, 36.4 mmol) in acetic acid (25 ml) was added dropwise a solution of N,N-diethyl-1,4-phenylenediamine dihydrochloride (8.64 g, 36.4 mmol) in acetic acid (25 ml) with stirring at room temperature. After further stirring for 3 h, the reaction mixture was poured into water. The solution was neutralized with aq. Na₂CO₃ and the resulting precipitate was filtered, washed with water and dried to yield 9.10 g (78 %) of 1a as a blue solid: 229-231 °C (decomposition); ¹H NMR (400 MHz, [D₆]DMSO, TMS): δ = 1.11 (t, 6H), 3.42 (q, 4H), 5.63 (s, 1H), 6.75 (d, J = 8.05 Hz, 2H), 7.14 (d, J = 8.05 Hz, 2H), 7.70-7.72 (m, 1H), 7.83-7.85 (m, 1H), 8.02 (d, 1H), 8.29 (d, 1H), 9.77 (s, 1H); IR (KBr): ν = 3219, 1593, 1568 cm⁻¹; elemental analysis calcd (%) for C₂₀H₂₀N₂O₂: C 74.98, H 6.29, N, 8.74; found: C 74.77, H 6.11, N 8.87.

2.2. *Synthesis of 4-[(4-diethylamino)-2-(methyl)phenylamino]-[1,2]naphthoquinone (1b)*

To a solution of 1,2-naphthoquinone-4-sulfonic acid sodium salt (2.0 g, 7.68 mmol), sodium acetate (2.09 g, 7.68 mmol), and NiCl₂ (1.00 g, 7.68 mmol) in acetic acid (25 ml) was added dropwise a solution of N,N-diethyl-2-methyl-p-phenylenediamine monohydrochloride (1.65 g, 7.68 mmol) in acetic acid (25 ml) with stirring at room temperature. After further stirring for 7 h, the reaction mixture was poured into water. The solution was neutralized with aq. Na₂CO₃ and the resulting precipitate was filtered, washed with water and dried to yield 1.44 g (56 %) of 1b as a blue solid: ¹H NMR (400 MHz, [D₆]DMSO, TMS):
2.3. 4-[5-(4-diethylamino-phenylamino)-naphtho[1,2-d]oxazol-2-yl]benzonitrile (2a)

To a solution of the compound 1a (5.00 g, 15.6 mmol) and ammonium acetate (24.05 g, 0.31 mol) in acetic acid (170 ml) was add dropwise a solution of p-cyanobenzaldehyde (2.05 g, 15.6 mmol) in acetic acid (100 ml) with stirring at 90 °C. After further stirring for 3 h, the reaction mixture was neutralized with aq. Na2CO3 and the product was extracted with CH2Cl2. The organic extract was washed with water and evaporated. Then the residue was chromatographed on silica gel (CH2Cl2 : ethyl acetate = 10 : 1 as eluent) to give 2a (4.86 g, yield 72 %) as an yellow powder: m.p. 205-206 °C; 1H NMR (400 MHz, [D6]DMSO, TMS): δ = 1.11 (t, 6H), 3.35 (q, 4H), 6.76 (d, J = 9.03 Hz, 2H), 6.99 (s, 1H), 7.16 (d, 2H), 7.76 (t, 1H), 7.74 (t, 1H), 8.02 (d, 2H), 8.26-8.28 (m, 2H), 8.31 (s, 1H), 8.39 (d, J = 8.29 Hz, 1H), 8.48 (d, J = 8.29 Hz, 1H); IR (KBr): ̇ν = 3404, 2224 cm⁻¹; elemental analysis calcd (%) for C28H24N4O: C 77.75, H 5.59, N, 12.95; found: C 77.74, H 5.59, N 12.98.

2.4. 4-[5-(4-diethylamino-2-methyl-phenylamino)-naphtho[1,2-d]oxazol-2-yl]benzonitrile (2b)
To a solution of the compound 1b (1.00 g, 2.99 mmol) and ammonium acetate (3.69 g, 47.8 mmol) in acetic acid (25 ml) was added dropwise a solution of \textit{p}-cyanobenzaldehyde (0.39 g, 2.99 mmol) in acetic acid (25 ml) with stirring at 90 °C. After further stirring for 3 h, the reaction mixture was neutralized with aq. Na$_2$CO$_3$ and the product was extracted with CH$_2$Cl$_2$. The organic extract was washed with water and evaporated. Then the residue was chromatographed on silica gel (CH$_2$Cl$_2$ : ethyl acetate = 3 : 1 as eluent) to give 2b (4.86 g, yield 52 %) as an yellow powder: $^1$H NMR (400 MHz, [D$_6$]DMSO, TMS): $\delta$ = 1.12 (t, 6H), 2.11 (s, 3H), 3.35 (q, 4H), 6.32 (s, 1H), 6.61 (dd, 1H), 6.68 (d, 1H), 7.03 (d, 1H), 7.59 (t, 1H), 7.73 (t, 1H), 7.98 (d, 2H), 8.10 (s, 1H), 8.22 (d, 2H), 8.37 (d, 1H,), 8.52 (d, 1H); IR (KBr): $\tilde{\nu}$ = 3387, 2230 cm$^{-1}$; elemental analysis calc. (%) for C$_{29}$H$_{26}$N$_4$O: C 78.00, H 5.87, N 12.55; found: C 77.70, H 5.86, N 12.31.

2.5. Computational methods

All calculations were performed on FUJITSU FMV-ME4/657. The semi-empirical calculations were carried out with the WinMOPAC Ver. 3 package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were carried out using the PM3 method [18]. All geometries were completely optimized (keyword PRECISE). Experimental absorption spectra of the seven quinol derivatives were studied with the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic) [19—21]. All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which includes the configuration with one electron excited from any occupied orbital to any
unoccupied orbital, 225 configurations were considered for the configuration interaction [keyword CI (15 15)].

2.6. Preparation of guest-inclusion crystals

The host compound 2a or 2b was dissolved with heating in respective guest-solvent. The solution was filtered and kept for a few days at room temperature. The crystals that formed were collected by filtration. The host : guest stoichiometric ratio of the inclusion compounds was determined by means of $^1$H NMR integration and CHN analysis.

2.7. X-ray crystallographic studies

The reflection data were collected at 23 ± 1°C on a Rigaku AFC7S four-circle diffractometer by 2θ–ω scan technique, and using graphite-monochromated Mo$_{K\alpha}$ ($\lambda = 0.71069$ Å) radiation at 50 kV and 30 mA. In all case, the data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The reflection intensities were monitored by three standard reflections for every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. All calculations were performed using the teXsan [22] crystallographic software package of Molecular Structure Corporation. CCDC-630058 (2a) and CCDC-630059 (2a-acetone) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
**Compound 2a**

Crystals of 2a were recrystallized from ethanol as yellow needle, air stable. The one selected had approximate dimensions 0.60×0.20×0.40 mm. The transmission factors ranged from 0.96 to 0.99. The crystal structure was solved by direct methods using SIR 92 [23]. The structures were expanded using Fourier techniques [24]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. **Crystal data.**

C_{28}H_{24}N_{4}O, \( M = 432.52 \), triclinic, \( a = 10.530(1) \), \( b = 15.062(1) \), \( c = 7.425(1) \) Å, \( \alpha = 96.555(8)^{\circ} \), \( \beta = 105.994(9)^{\circ} \), \( \gamma = 86.429(8)^{\circ} \), \( U = 1124.0(2) \) Å³, \( T = 296.2 \) K, space group P1- (no.2), \( Z = 2 \), \( \mu(\text{Mo-K}_\alpha) = 0.80 \) cm⁻¹, 4195 reflections measured, 4191 unique (\( R_{int} = 0.018 \)) which were used in all calculations. The final R indices were \( R_1 = 0.069, \ wR(F^2) = 0.190 \) (all data).

**Compound 2a·acetone**

Crystals of 2a were recrystallized from acetone as red prism, air stable. The one selected had approximate dimensions 0.65×0.40×0.28 mm. The transmission factors ranged from 0.91 to 1.00. The crystal structure was solved by direct methods using SIR 92 [23]. The structures were expanded using Fourier techniques [24]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. **Crystal data.**

C_{30}H_{27}N_{4}O_{2}, \( M = 475.57 \), monoclinic, \( a = 15.282(8) \), \( b = 6.885(1) \), \( c = 23.807(4) \) Å, \( \beta = 92.44(2) \), \( U = 2502(1) \) Å³, \( T = 296.2 \) K, space group P2/n (no.13), \( Z = 4 \), \( \mu(\text{Mo-K}_\alpha) = 0.80 \) cm⁻¹, 4195 reflections measured, 4191 unique (\( R_{int} = 0.018 \)) which were used in all calculations. The final R indices were \( R_1 = 0.069, \ wR(F^2) = 0.190 \) (all data).
\(\mu(\text{Mo-K}_\alpha) = 0.81 \text{ cm}^{-1}\), 4591 reflections measured, 4412 unique \((R_{int} = 0.028)\) which were used in all calculations. The final R indices were \(R1 = 0.080\), \(wR(F^2)\) was 0.232 (all data).

### 3. Results and discussion

#### 3.1. Synthesis of naphthooxazole-type fluorophores

Naphthooxazole-type fluorophores 2a and 2b are conveniently synthesized as shown in Scheme 1. We first prepared the 4-aminated-1,2-naphthoquinones 1a and 1b in 78 and 56 % yield by refluxing sodium 1,2-naphthoquinone-4-sulphonate with the corresponding 1,4-phenylenediamine in acetic acid in the presence of nickel (II) chloride, respectively. Next, the compounds 1a and 1b were reacted with \(p\)-cyano-benzaldehyde in the presence of an excess amount of ammonium acetate in acetic acid gave 2a and 2b in 72 and 52 % yield, respectively.

#### 3.2. Spectroscopic properties of the naphthooxazole-type fluorophores in solution

The absorption spectra of the naphthooxazole-type fluorophores 2a and 2b in solution are summarized in Table 1. The visible absorption spectrum of 2a was measured in various solvents, such as benzene, 1,4-dioxane, dichloromethane, and acetone. The fluorophore 2a exhibits an intense absorption band at around 420 nm \((\varepsilon_{\text{max}}; 23700-31700 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1})\) in all solvents. Interestingly, the fluorophores 2a and 2b did not exhibit fluorescence in solution, but exhibited strong fluorescence in the solid state. Non-radiative decay would be accelerated by free rotation of the 4-diethylaminophenyl ring part of 2 in solution [25, 26].
3.3. Semi-empirical MO calculations (PM3, INDO/S)

The photophysical spectra of the compounds 2a and 2b were analyzed by using semi-empirical molecular orbital (MO) calculations. The molecular structures were optimized by using MOPAC/PM3 method [18], and then the INDO/S method [19–21] was used for spectroscopic calculations. The calculated absorption wavelengths and the transition character of the first absorption bands are collected in Table 2. As shown in Fig. 1, the calculated torsion angles between naphthooxazole ring and \( p \)-cyanophenyl group are 0.2° for 2a and 1.6° for 2b, respectively, which shows two rings are coplanar. Also, \( p \)-diethylaminophenyl groups are twisted from the plane of the naphthooxazole ring by about 45° for 2a and 47° for 2b, respectively.

The calculated absorption wavelengths and the oscillator strength values are relatively good compatible with the observed spectra in 1,4-dioxane, although the calculated absorption spectra are blue shifted. This deviation of the INDO/S calculations, giving high transition energies compared with the experimental values, has been generally observed [27, 28]. The calculations show that the longest excitation bands for 2a and 2b are mainly assigned to the transition from the HOMO to the LUMO, where HOMO is mostly localized on the aminonaphtho[1,2-d]oxazo moieties, and the LUMO is mostly localized on \( p \)-cyanophenyl moiety. The changes in the calculated electron density accompanying the first electron excitation are shown in Fig. 2, which show a strong migration of intramolecular charge-transfer character of 2a and 2b.

3.4. Inclusion ability in the crystalline state

In order to investigate their inclusion ability, we recrystallized the compounds
and 2b from various organic solvents. We have found that the compound 2a yields various host-guest inclusion compounds in stoichiometric ratios with guest molecules such as DMSO, piperidine, morpholine, and acetone in the crystalline state. The compound 2b also gave a host-guest inclusion compounds with 1,4-dioxane, DMSO, piperidine and morpholine. The characteristics of the guest-free and various guest-inclusion crystals obtained by recrystallization of the compounds 2a and 2b are summarized in Table 3. In both cases of 2a and 2b, compared to the guest-free crystals, the guest-inclusion crystals varied from yellow to red in colour and a drastic fluorescence quenching was observed (Fig. 3).

3.5. Solid-state fluorescence quenching behaviour upon formation of guest-inclusion crystals

In order to investigate the guest-effects on the solid-state photophysical properties, the fluorescence excitation and emission spectra of the guest-free and the guest-inclusion crystals of 2a and 2b were measured. The spectra recorded at the corresponding excitation and emission maxima of the guest-free and the guest-inclusion crystals are shown in Figs. 4 and 5. We have found that the fluorophores 2a and 2b exhibit a large red-shift in colour and a drastic fluorescence decrease upon inclusion of guest molecules in the crystalline state. In the case of 2a, the longest excitation band of the guest-free crystal was observed at 452 nm, however, that of the guest-inclusion crystals was observed at 507-580 nm. In addition, the guest-free crystal exhibited a strong fluorescence band with an emission maximum at 530 nm, whereas the guest-inclusion crystals exhibited weak fluorescence band with an emission maximum red shifted to around 558-610 nm. For example, the fluorescence intensity of the guest-free crystal is ca 100-fold compared
to that of acetone-inclusion crystal. In the case of 2b, similar spectral changes were also observed upon formation of guest-inclusion crystals.

3.6. Relation between the solid-state fluorescence properties and X-ray crystal structures

In order to investigate the enclathrated guest effects on the fluorescence properties of the crystal, we have determined the X-ray crystal structures of the guest-free and acetone-inclusion compound of 2a. The experimental details and crystal data are listed in Table S1. The crystal systems were a triclinic space group P\textit{\textbar} with \( Z = 2 \) for guest-free 2a, a monoclinic space group P2/n with \( Z = 4 \) for 2a·acetone.

The X-ray crystal structures of the guest-free and acetone-inclusion compound are shown in Figs. 6 and 7. In the guest-free host crystal, face-to-edge and edge-to-edge overlappings are observed between the naphthooxazole and the \( p \)-cyanophenyl moieties (Figs. 6-(b) and (c)). Also, there is a face-to-face overlapping between diethylaminophenyl groups of host molecules (Fig. 6-(d)). There are 18 short interatomic contacts of less than 3.6 Å between the host compounds, however, the contacts are almost face-to-edge type of overlap. On the other hand, in the acetone-inclusion crystal as shown in Fig. 7-(a), the formation of molecular linking by intermolecular hydrogen bonds between the cyano group of one molecule and the amino group of the next one is observed (NH···N angle = 159.0°, N···N distance = 3.11Å). In the molecular chain, the host molecules are arranged in the same direction in a given layer and in the opposite direction in the successive layers, which are not observed in the guest-free host crystal. There are two distinct types of face-to-face overlapping, which are covering the whole host molecule
through the donor unit of naphthooxazole moiety containing amino group and the acceptor unit of \( p \)-cyanophenyl group (Fig. 7-(b)). The interplanar distances between the naphthooxazole rings are ca. 3.48Å and 3.51Å, and there are 14 and 28 short interatomic contacts of less than 3.6 Å as shown in Figs. 7-(c) and (d), respectively, which suggest that much stronger donor-acceptor type \( \pi-\pi \) interaction exists in the acetone-inclusion crystal than in the guest-free crystal. A large red-shift of the absorption and fluorescence maxima and the solid-state fluorescence quenching by strong donor-acceptor type \( \pi-\pi \) interactions [12—17, 25, 26, 29-31] and continuous molecular linking by intermolecular hydrogen bonds [16, 17] between neigh-boring fluorophores are known. Consequently, in the acetone-inclusion crystal, it was confirmed that the formation of molecular linking by intermolecular hydrogen bonds and the strong \( \pi-\pi \) interactions between the fluorophores cause strong fluorescence quenching and a large red shift of excitation and emission maxima.

Furthermore, from the standpoint of the stereostructure of 2a, we investigated the effects of the geometric arrangement on the intermolecular interactions. The torsion angle between naphthooxazole ring and \( p \)-cyanophenyl moiety of 2a in the guest-free crystal is 21.9°, and \( p \)-diethylaminophenyl moiety is twisted from the plane of the naphthooxazole ring by 80.7° (Fig. 6-(b)). These torsion angles are large compared to those of the optimized geometries by MOPAC/PM3 calculations (0.2° and 44.9° in Fig. 1). On the other hand, as shown in Fig. 7-(b), these torsion angles of the molecule in acetone-inclusion crystal are very small compared to those of the molecules in the guest-free crystal. The torsion angles are close to those of the optimized geometries obtained by MOPAC/PM3 calculations. Consequently, the dye 2a in acetone-inclusion crystal is more planar than in guest-free crystal. It is clear that the small torsion angles of 2a in acetone-inclusion crystal are attributable to
stronger π–π intermolecular interactions than in the guest-free crystal.

4. Conclusions

We have developed novel naphthooxazole-type fluorophores that exhibit a large red shift in colour and a dramatic fluorescence decrease upon inclusion of guest molecules in the crystalline state. From the comparison of the X-ray crystal structures of the guest-free and guest-inclusion compounds, it can be confirmed that the reasons for the red-shift of the absorption and fluorescence wavelength maxima and a drastic fluorescence quenching behaviour upon formation of host-guest inclusion compound of fluorophores 2 are attributable to strong intermolecular π–π interactions and to continuous molecular linking formed by intermolecular hydrogen bonds.

Acknowledgments

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Reference


2004;69;6455


Figure and Scheme captions

Scheme 1. (i) **1a**: \(N,N\)-diethyl-1,4-phenylenediamine dihydrochloride, CH\(_3\)COONa, NiCl\(_2\), CH\(_3\)COOH, 3 h, RT, 78%; **1b**: \(N,N\)-diethyl-2-methyl-1,4-phenylenediamine, CH\(_3\)COONa, NiCl\(_2\), CH\(_3\)COOH, 7 h, RT, 56%; (ii) \(p\)-cyanobenzaldehyde, CH\(_3\)COONH\(_4\), CH\(_3\)COOH, 3 h, 90 °C, 72% for **2a**, 52% for **2b**.

Fig. 1. The optimized geometries of **2a** and **2b** by using MOPAC/PM3 method (a) a side view, and (b) a top view.

Fig. 2. Calculated electron density changes accompanying the first electronic excitation of **2a** and **2b**. The black and white lobes signify decreases and increase in electron density accompanying the electronic transition. Their areas indicate the magnitude of the electron density change.

Fig. 3. Crystals of the guest-free and guest-inclusion compounds of the naphtho[2a: (a) **2a** (guest-free), (b) **2a**·DMSO (1:1), (c) **2a**·piperidine (3:1), (d) **2a**·morpholine (1:1), (e) **2a**·acetone (2:1).

Fig. 4. Excitation (···) and emission (−) spectra of the guest-free and guest-inclusion crystals of **2a**: (a) **2a** (guest-free), \(\lambda_{\text{ex}} = 452\) nm, \(\lambda_{\text{em}} = 530\) nm, (b) **2a**·DMSO (1:1), \(\lambda_{\text{ex}} = 507\) nm, \(\lambda_{\text{em}} = 558\) nm, (c) **2a**·piperidine (3:1), \(\lambda_{\text{ex}} = 515\) nm, \(\lambda_{\text{em}} = 578\) nm, (d) **2a**·morpholine (1:1), \(\lambda_{\text{ex}} = 538\) nm, \(\lambda_{\text{em}} = 593\) nm, (e) **2a**·acetone (2:1), \(\lambda_{\text{ex}} = 580\) nm, \(\lambda_{\text{em}} = 610\) nm.

Fig. 5. Excitation (···) and emission (−) spectra of the guest-free and guest-inclusion crystals of **2b**: (a) **2b** (guest-free), \(\lambda_{\text{ex}} = 452\) nm, \(\lambda_{\text{em}} = 511\) nm, (b) **2b**·1,4-dioxane (1:1), \(\lambda_{\text{ex}} = 550\) nm, \(\lambda_{\text{em}} = 584\) nm, (c) **2b**·DMSO (1:2), \(\lambda_{\text{ex}} = 552\) nm, \(\lambda_{\text{em}} = 585\) nm,
(d) **2b-morpholine (1:1)**, $\lambda_{ex} = 569$ nm, $\lambda_{em} = 592$ nm.

Fig. 6. Crystal packing structure of **2a**: (a) a stereoview of the molecular packing structure, and (b) an edge-to-edge overlap, (c) a face-to-edge overlap, and (d) a face-to-face overlap between the fluorophores.

Fig. 7. Crystal packing and hydrogen bonding pattern of **2a-acetone**: (a) a stereoview of the molecular packing structure, (b) a side view, and (c) and (d) a top view of a face-to-face overlaps between the fluorophores. The interplanar distance between the naphthoxazole rings is ca. 3.48Å for (c) and 3.51Å for (d), respectively.

Table 1  Absorption spectral data of **2a** and **2b** in solution

Table 2  Calculated absorption spectra for the compounds **2a** and **2b**

Table 3  Host-guest molar ratios, crystal form, and colour of the guest-free and guest-inclusion crystals of **2a** and **2b**
Table 1
Absorption spectral data of 2a and 2b in solution

<table>
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<th>Compound</th>
<th>Solvent</th>
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<td>2a</td>
<td>benzene</td>
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<td></td>
<td>1,4-dioxane</td>
<td>420(25300)</td>
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<td></td>
<td>dichloromethane</td>
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<tr>
<td></td>
<td>Acetone</td>
<td>420(23700)</td>
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<td>415(25100)</td>
</tr>
<tr>
<td>Compound</td>
<td>$\mu$ / D$^a$</td>
<td>$\lambda_{\text{max}}$ / nm</td>
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$^a$The values of the dipole moment in the ground state.

$^b$Oscillator strength.

$^c$The transition is shown by an arrow from one orbital to another, followed by its percentage CI (configuration interaction) component.
Table 3  
Host-guest molar ratios, crystal form, and colour of the guest-free and guest-inclusion crystals of \(2a\) and \(2b\)

<table>
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<th>Host</th>
<th>Guest</th>
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<th>Crystal colour</th>
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<td>Prism</td>
<td>Red</td>
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Scheme 1. Ooyama et al.
Fig. 1. Ooyama et al.
Fig. 2. Ooyama et al.
Fig. 3. Ooyama et al.
Fig. 4. Ooyama et al.
Fig. 5. Ooyama et al.
Fig. 6. Ooyama et al.
Fig. 7. Ooyama et al.