

Contribution of Radiative Rate Constants to Crystallization-Induced Emission Enhancement in Boron-Fused Azobenzene Complexes

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Abstract

Analysis of emission enhancement in an aggregated state has been developed by focusing on suppression of nonradiative processes by intermolecular interactions. On the other hand, it is difficult to evaluate contribution of radiative processes despite its significant role in improving emission. Herein, the contribution of radiative processes to crystallization-induced emission enhancement (CIEE) is evaluated. By comparing optical properties between isolated and crystalline states at 77 K to minimize structural relaxation, acceleration phenomena of the radiative process originating from the intermolecular interactions in crystal are clarified. Consequently, it is experimentally proved that a large refractive index in an organic crystal mainly promotes the radiative processes in CIEE even without significant intermolecular electronic interactions.

Introduction

Crystallization-induced emission enhancement (CIEE) is the unique photophysical property known as luminescence, which is further enhanced by crystallization compared to the less ordered states such as amorphous or dispersion in polymer matrix.¹ Owing to the excellent luminescent property in solid, CIEE-active compounds have been regarded as crucial materials for real-world applications in organic (opto)electronics such as sensors,^{2,3} light-emitting diodes,⁴ optical waveguides,⁵ field effect transistors,⁶ and solid-state lasers.⁷ A variety of CIEE-active molecules have been developed including conventional dibenzofulvene,^{1,8–10} other π -conjugated molecules,^{11–15} cluster compounds,^{16,17} ionic compounds,¹⁸ and complexes with main group elements.^{19–31}

CIEE is considered to be closely related to aggregation-induced emission (AIE).³² The restriction of some factors accessible to a conical intersection (*e.g.*, intramolecular motion, rotation, and vibration) by aggregation has been considered as an origin of the AIE effect.^{33,34} In the conical intersection, the probability of nonradiative internal conversion is maximum.^{35–38} In most cases, the plausible mechanism of CIEE is similar to that of AIE because of the similar structural features such as high motility leading to emission quenching in solution and amorphous, and bulkiness enough to suppress aggregation-caused quenching (ACQ) by π - π stacking in crystal. From a computational survey, it is suggested that multiple intermolecular interactions in crystal restrict structural relaxation of the photoexcited molecule more tightly than in amorphous. Thus, stronger

emission with a smaller Stokes shift and a nonradiative rate constant (k_{nr}) were obtained.³⁹ However, it is still difficult to predict whether the CIEE property is obtained, and the structure–property relationship has not been fully understood.⁴⁰ Recently, the comprehensive study was conducted to examine the photoresponse in polymer matrix and crystal by separately discussing the effects of inter- and intramolecular contributions to the rate constants.⁴¹ Nevertheless, the change in radiative rate constant (k_r) has been still difficult to be evaluated precisely because the suppression of the structural relaxation by intermolecular interactions, related to k_{nr} , was dominant at an ambient condition in most cases.⁴² Additionally, there is still difficulty in the estimation for the contribution of crystallization to k_r especially for the compounds that are not sufficiently luminescent in the less ordered solid states. Thus, a design guideline of molecular aggregates to increase the k_r value will be a powerful strategy to improve the performance of molecular aggregates and overcome the energy gap law in near-infrared (NIR) solid-state luminescence.^{42,43}

Herein, we proposed an evaluation system for CIEE-active molecules to clarify the contribution of k_r using boron-fused azobenzene complexes (BAz).⁴⁴ BAz is one of the class of CIEE-active molecules that showed weak luminescence not only in solution but also in the less ordered solid states due to their intrinsic high motility, while exhibited bright luminescence in crystal. To minimize the structural relaxation, we compared optical properties in the vitrified solution (less ordered) and the crystal (highly ordered) at low temperature. As a result, around 1.5-

fold increase in k_r was observed even in the halogenated BAz crystals where there are few intermolecular electronic interactions. From these data, it was experimentally revealed that the increases in k_r mainly originate from the difference in the polarizability of the media. We herein show that to discuss the emission enhancement in the aggregated states, it is significant to evaluate not only the restriction of the molecular motion but also the polarizability of the media.

Results and discussion

Synthesis and characterization

The pristine BAz complex (**BAz-H**) and halogenated derivatives (**BAz-F**, **BAz-Cl**, and **BAz-Br**) were prepared by the reaction with the corresponding azobenzene tridentate ligands and boron trifluoride in the presence of triethylamine in toluene at 100 °C with moderate isolated yields (34% for **BAz-F** and 38% for **BAz-Cl**) according to Scheme 1 and the previous reports for **BAz-H** and **BAz-Br**.^{44–46} All compounds showed good solubility in common organic solvents and good stability in an ambient atmosphere. The chemical structures of the products were confirmed by ¹H, ¹³C{¹H} and ¹¹B{¹H} NMR spectroscopy, high-resolution mass spectrometry, and elemental analyses (see the Electronic Supplementary Information (ESI)).

Scheme 1

Crystal structures

Fortunately, single crystals of all BAz derivatives suitable for the single crystal X-ray diffraction (SCXRD) analysis at 143 K were obtained by slow evaporation from CH₂Cl₂ (for **BAz-H**) or hexane (for **BAz-Br**), and vapor diffusion under hexane atmosphere from CH₂Cl₂ (for **BAz-F** and **BAz-Cl**) (Figure 1a and Tables S1–S4). Static disorder was regarded in nitrogen for all

compounds and in oxygen and fluorine for **BAz-Cl**.⁴⁷ The torsion angles between the two planes consisting of C(1)–C(6) and C(7)–C(12) rings ranged from 160° to 164°, suggesting that the formation of flexural structures. Due to the nonplanar skeleton and steric hindrance of the boron substituent, slip-stacked dimers facing the π -plane were observed from all compounds (*e.g.*, the silver and gold molecular pairs in Figure 1b). The distances between these aromatic rings were from 3.13 to 3.61 Å, indicating the existence of π – π stacking interactions. As shown in Figures S1–S4, a variety of intermolecular hydrogen bonds such as C–H $\cdots$ F, C–H $\cdots$ O, and C–H $\cdots$ π , as well as halogen bonds such as X–X, C–X $\cdots$ π , B–F $\cdots$ π , B–F $\cdots$ B, and Cl $\cdots$ O (X = F, Cl, Br) should play a significant role in stabilization of the crystal packing structure and subsequently restriction of structural relaxation in the excited state, which are favorable for achieving emission enhancement in crystal as mentioned later.

Optical properties at an ambient condition

The crystals used for optical measurements were also prepared by recrystallization from their hexane solutions to clarify structural information. From the comparison with powder X-ray diffraction (PXRD) patterns, it is strongly suggested that the crystals used for optical measurements possessed the similar crystal structures to their corresponding single crystals (Figure S5). All crystals showed relatively intense fluorescence (FL) from the orange to deep-red region with

increased absolute FL quantum yields (Φ_{FL} , $\Phi_{\text{FL}} = 6.1\text{--}17\%$) in crystal although weak FL property was commonly exhibited not only in diluted solutions ($\Phi_{\text{FL}} \sim 0\%$) but also in poly(methylmethacrylate) (PMMA) films with 1 wt% dye concentration ($\Phi_{\text{FL}} = 0.8\text{--}2.3\%$) (Figures 2a and 2c and Table S5). These emission enhancements are a typical CIEE behavior. Detailed optical properties in chloroform and PMMA matrices were summarized in Figure S6 and Table S5. The Φ_{FL} value of **BAz-H** ($\Phi_{\text{FL}} = 6.1\%$) increased by fluorination ($\Phi_{\text{FL}} = 17\%$), whereas gradual decreases in Φ_{FL} values were observed by replacing halogens from F to Cl ($\Phi_{\text{FL}} = 12\%$) or Br ($\Phi_{\text{FL}} = 6.7\%$). According to the FL lifetime measurements, the k_{r} value of **BAz-H** ($k_{\text{r}} = 0.68 \times 10^8 \text{ s}^{-1}$) was approximately doubled by introducing halogen substitutions ($k_{\text{r}} = 1.1\text{--}1.3 \times 10^8 \text{ s}^{-1}$) (Figures 2d and S7), which was comparable with the tendency of the molar extinction coefficient (ϵ) value in chloroform solutions (Figure S6a and Table S5). On the other hand, the k_{nr} value of **BAz-H** ($k_{\text{nr}} = 1.0 \times 10^9 \text{ s}^{-1}$) was halved by fluorination ($k_{\text{nr}} = 5.4 \times 10^8 \text{ s}^{-1}$) and enhanced in steps by replacing from F to Cl ($k_{\text{nr}} = 1.0 \times 10^9 \text{ s}^{-1}$) or Br ($k_{\text{nr}} = 1.7 \times 10^9 \text{ s}^{-1}$) (Figure 2e). In **BAz-Cl** and **BAz-Br**, the heavy atom effect might also be involved.⁴⁸ In comparison of the rate constants in the crystals and PMMA matrices, it was revealed that both increases in the k_{r} values and decreases in the k_{nr} values contributed to the CIEE phenomena especially in **BAz-H**, **BAz-F** and **BAz-Cl**, similarly to previous CIEE-active molecules (Figure 2d and 2e).^{22,25,30,49} However, the Φ_{FL} values of BAZ derivatives in both before and after crystallization were still relatively low. It is probably due to

intrinsic high molecular motility, which might disturb the accurate evaluation of the effects from CIEE.^{28,44}

Figure 2

Optical properties at 77 K

We compared the optical properties of the complexes in vitrified 2-methyltetrahydrofuran (2MeTHF) solutions (1.0×10^{-5} M, *i.e.*, dispersed state) and crystal at the temperature of liquid N₂ (77 K) (Figures 3 and S8 and Table S6). Since the structural relaxation, which is one of the main reasons for the high k_{nr} of the BAz scaffolds, should be suppressed at 77 K, the impact of intermolecular interactions and molecular surroundings in crystal packings on the CIEE properties is able to be more accurately evaluated. Indeed, the blue-shifted FL spectra and significantly larger Φ_{FL} values were commonly observed in crystal at 77 K compared at room temperature. It is likely that non-radiation channels should be closed by freezing molecular motions. Interestingly, larger Φ_{FL} values in crystal than those in solution were detected from **BAz-H** and **BAz-F** at 77 K (Figure 3b). Remarkably, the k_r value of the crystalline sample of **BAz-F** was 1.7-fold larger than that in the solution (Figure 3c), while little change in the k_{nr} value was observed (Figure 3d). From the kinetic data, it was found that the larger k_r should be originated from an increase in the ratio of the

faster component of the FL decay curve (Table S6). **BAz-Cl** and **BAz-Br** also showed 1.5 times larger k_r values by crystallization, whereas the k_{nr} values increased simultaneously probably due to heavy atom effects. It should be noted that k_r is a function of the polarizability known as the Strickler–Berg (SB) equation (1),^{41,50,51}

$$k_{r,SB} = 0.667[\text{cm}^2\text{s}^{-1}]n^2\tilde{\nu}_{\text{FL}}^2f \quad (1)$$

where n is the refractive index of the environment, $\tilde{\nu}_{\text{FL}}$ is the wavenumber (cm^{-1}) of the fluorescence spectrum under the assumption that the band is sharp and the Stokes shift is negligible, and f is the oscillator strength. Details of the process for deriving the equation (1) are shown in ESI. Considering the higher refractive index in crystal compared to solution,⁵² increase in k_r by ~ 50% is generally expected simply because of the polarizability effect,⁴¹ as seen in halogenated BAZ derivatives at 77 K.

To exclude the effect of coordination and/or interaction between 2MeTHF and the boron moiety on the optical properties, the optical properties in another vitrified state using a mixed solvent of toluene (Tol) and 2-methylpentane (2MP) (1/9, v/v) at 77 K were also evaluated (Figure 3 and Table S6). Although there was little difference in the λ_{FL} values, the Φ_{FL} values were improved from that in 2MeTHF. It was indicated that fluorescence of the BAZ derivatives could be

weakened or enhanced by some interaction with 2MeTHF. For **BAz-H** and **BAz-F**, k_r values in the mixed solvent (Tol/2MP = 1/9 v/v) were higher than that in 2MeTHF. Meanwhile, k_r values of **BAz-Cl** and **BAz-Br** showed opposite tendency. From those results, it can be said that we are able to experimentally observe the clear increase in the k_r values by crystallization.

Figure 3

Theoretical calculation

To obtain further insights into the increase in k_r by crystallization, we also focused on two more factors generally mentioned in previous studies: increased molecular planarity and exciton interactions represented by J-aggregation.^{41,53} The calculation of the electronic transition was performed with time-dependent DFT (TD-DFT) at TD-M06-2X/6-311+G(d,p) level (Table S7). First, the torsion angle of the two planes consisting of C(1)–C(6) and C(7)–C(12) rings in the fully-relaxed single molecule (**Opt**) was larger than that in the single molecule in crystal (**Monomer**), suggesting the molecular planarization in crystal. Nevertheless, the oscillator strength (f) of the $S_0 \rightarrow S_1$ transition in **Monomer** was smaller than that in **Opt** (Figure S9). This result implies that the increased molecular planarity might hardly contributed to the increase in k_r . Second, the exciton coupling of the nearest neighbor dimer in crystal (**Dimer**) was evaluated with energy splitting

method (Figure S10).⁵⁴ For all compounds, the transition electronic dipole moment was parallel with the long molecular axis. Regardless of the pitch angle (θ) between the transition electronic dipole moment and the π -stack direction, H-aggregate formation with the forbidden S_1 state was implied for each **Dimer** (Table S8). This deviation should be attributed to the point dipole approximation, which is inapplicable for molecular crystals.^{55,56} Meanwhile, the calculated coupling strength ($\Delta\epsilon$) of the halogenated BAz derivatives were small ($\Delta\epsilon = 0.05\text{--}0.08$ eV). This should derive from the large intermolecular distance (R , $R = 5.20\text{--}6.49$ Å) likely due to the nonplanar structure as a steric hindrance.⁵⁷ These results suggest that the effect of the exciton coupling on the increase in k_r is also small. Therefore, the observed increase in k_r for halogenated BAz derivatives should mainly originate from the higher polarizability in the crystal surrounding compared to the dispersed states. On the other hand, the calculated coupling strength of **BAz-H** was relatively large ($\Delta\epsilon = 0.16$ eV). This indicates that the reduction of k_r of **BAz-H** should be induced by the electronic interaction caused by H-aggregation compared to those of the halogenated BAz derivatives.⁴¹

To obtain further information on the intermolecular interaction, an independent gradient model based on Hirshfeld partition of molecular density (IGMH) analysis⁵⁸ was performed for **Dimer**. From the IGMH analysis, it was suggested that **BAz-H** and **BAz-F** showed stronger intermolecular interactions derived from the van der Waals interaction than **BAz-Cl** and **BAz-Br**

(Figure S11). It is supported that the small k_r value of **BAz-H** should be caused by forming tight H-aggregation represented with the high calculated coupling strength ($\Delta\epsilon = 0.16$ eV). Although **BAz-F** also had strong intermolecular interaction involving H-aggregation, the enhancement of k_r was observed because of the weakest calculated coupling strength ($\Delta\epsilon = 0.05$ eV) among the halogenated BAz derivatives. In **BAz-Cl** and **BAz-Br**, there were few intermolecular interactions, which should cause the weak calculated coupling strength ($\Delta\epsilon = 0.08$).

Next, we simulated the radiative constant ($k_{r,SB}$) from the Strickler–Berg equation (1). The values of $\tilde{\nu}_{FL}$ and f are calculated from the TD-DFT calculation at TD-M06-2X/6-311+G(d,p) level with **Opt**, **Monomer**, and **Dimer** geometries. A refractive index (n) in a vitrified solution and crystal was simulated by using the Lorentz–Lorenz equation.⁵⁹ The details are shown in ESI. The refractive indices of the BAz derivatives were estimated to be 2.09 for **BAz-H**, 2.03 for **BAz-F**, 2.19 for **BAz-Cl**, and 2.30 for **BAz-Br** (Table S9), which are acceptable values as organic crystals.⁵² In addition, the refractive index of the vitrified solution (Tol/2MP = 1/9 v/v) was calculated to be 1.53 under the assumption that the vitrified solution forms the amorphous state (Table S10). As a result, it was revealed that the $k_{r,SB}$ value mainly depended on the n value because the $k_{r,SB}/n^2$ value was almost constant (Table S11). This means that the CIEE in the BAz derivatives can be dominantly affected not by the electronic intermolecular interaction but by the refractive index of the media. It is noted that the slight decrease in $k_{r,SB}$ in crystal was theoretically predicted due to

the effect of H-aggregation, especially in **BAz-H** and **BAz-F**, from the viewpoint of the decrease in the oscillator strength. The calculated $k_{r,SB}$ values are relatively higher than measured k_r values mainly because of the discrepancy between the calculated and observed $S_0 \rightarrow S_1$ transition energies.

We evaluated the experimental relationship among the experimentally-measured parameters, such as radiative constant (k_r) and energy of the fluorescence ($\tilde{\nu}_{FL}$) and the calculated values, such as refractive index (n) and oscillator strength (f) according to the Strickler–Berg equation (1). The $\tilde{\nu}_{FL}$ values were estimated as an approximated energy calculated from the maximum fluorescence intensity. To evaluate the contribution of each factor to k_r based the equation (1), the values of k_r/n^2 , k_r/f , and $k_r/\tilde{\nu}_{FL}^2$ were calculated (Table S12). As a result, in the halogenated BAZ derivatives, the smallest differences in k_r/n^2 between in the vitrified solution (Tol/2MP = 1/9 v/v) and in crystal were obtained. In addition, f and $\tilde{\nu}_{FL}$ in crystal were smaller than those in vitrified solutions, which reduced the k_r . This means that the refractive index dominantly contributes the increase in k_r . The large decrease in k_r/n^2 in the **BAz-H** crystal should be caused by the effect of H-aggregation. The gradual increase in k_r/n^2 of the halogenated BAZ derivatives in the vitrified solution (Tol/2MP = 1/9 v/v) was derived from the elevation of f . Consequently, the value of $k_r/n^2 f \tilde{\nu}_{FL}^2$ was nearly constant (0.22–0.26 cm² s⁻¹). This implies that it was experimentally confirmed that k_r follows the Strickler–Berg equation (1) in the isolated state. It is noted that the discrepancy of the value of $k_r/n^2 f \tilde{\nu}_{FL}^2$ between in the vitrified solution and crystal should be attributed to the fact that the value

of f in crystal was not accurately estimated. This is because that the electronic intermolecular interaction among the multiple molecules are analyzed under the approximation of only the interaction between two molecules (**Dimer**). Since the refractive index (n) can be modulated independently of k_{nr} , our findings are helpful for establishing design guidelines for highly efficient solid-state luminescence especially in the NIR region, where an exponential increase in k_{nr} is inevitable due to the energy gap law.^{42,43}

Finally, to evaluate the effect of intersystem crossing (ISC) on the nonradiative constant (k_{nr}), the magnitude of the spin-orbit coupling (SOC) from singlet (S_n) to triplet (T_n) states was estimated by using **Opt**, **Monomer**, and **Dimer** geometries. The details of the calculation methods are shown in ESI. As a result, almost the same SOC values about 10 cm^{-1} were obtained in the BAz derivatives regardless of their geometries (Figure S12 and Table S13). This fact suggests that the increases in k_{nr} observed in **BAz-Cl** and **BAz-Br** crystals should be at least not due to the internal heavy atom effect. Since there are few intermolecular electronic interactions in **BAz-Cl** and **BAz-Br**, ISC should be induced by the external heavy atom effect associated with the multiple molecules in crystal. Considering the fact that phosphorescence was not detected at 77 K, the excited energy accessed to the T_1 state should be consumed through the nonradiative process.

Conclusion

We proposed a strategy for evaluating the contribution of k_r to CIEE phenomena. Comparison of the optical properties of vitrified solution and crystal at 77 K highlighted the change in k_r by minimizing the structural relaxation. This method afforded the more accurate indication about the impact of the crystal surroundings on the optical property, especially for the CIEE dyes which are difficult to evaluate at an ambient condition due to low fluorescence in amorphous. As a result, around 1.5-fold increase in k_r of the halogenated BAz derivatives from vitrified solution to crystal was experimentally clarified. This should be mainly attributed to the higher polarizability of the crystal surrounding, and it was implied that the molecular planarization and exciton coupling might be minor contributions. In other words, the organic crystals with high density and refractive index have the potential to show bright solid-state luminescence. From our results, it is also expected that emission behaviors could be precisely controllable in vitrified solutions by modulating refractive indices. This methodology should be a powerful tool not only for precisely evaluating the relationship between crystal structures and optical properties with CIEE-active molecules but also for leading to novel designs for improving intrinsic luminescent properties of molecular aggregates. We also expect that the analysis of both k_r and k_{nr} will lead to creation of highly efficient solid-state emission. As accumulated information with molecular systems other than BAz accumulates, it is expected that scientific generality of our findings could be verified.

Conflicts of interest

There are no conflicts to declare.

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Electronic Supplementary Information.

Instrumentations, materials, synthetic procedures, characteristic data (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, HRMS, elemental analysis, single crystal X-ray structures), experimental data (powder X-ray diffraction, optical properties at room temperature and 77 K), theoretical calculation data.

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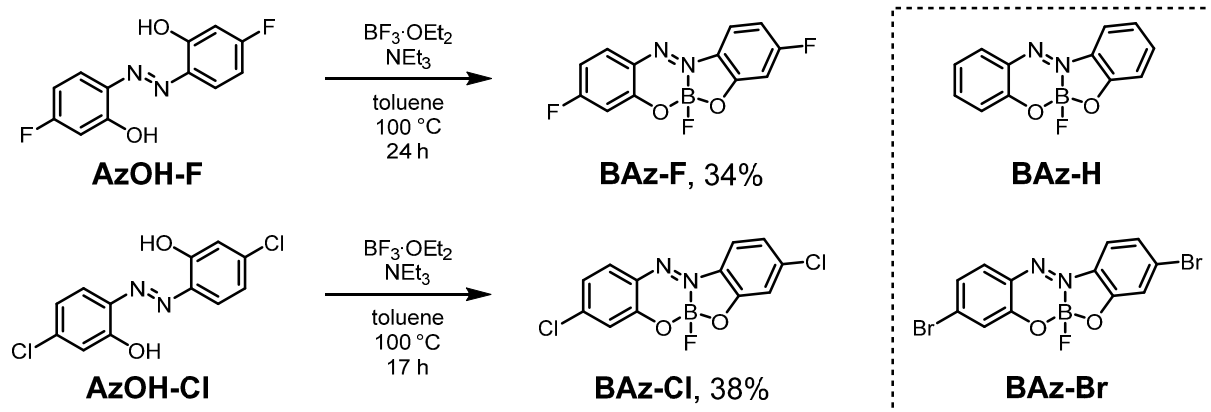
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Scheme 1. Synthetic schemes for **BAz-F** and **BAz-Cl**, and chemical structures of **BAz-H** and **BAz-Br** in the dotted box.

Figure 1: Crystal structures

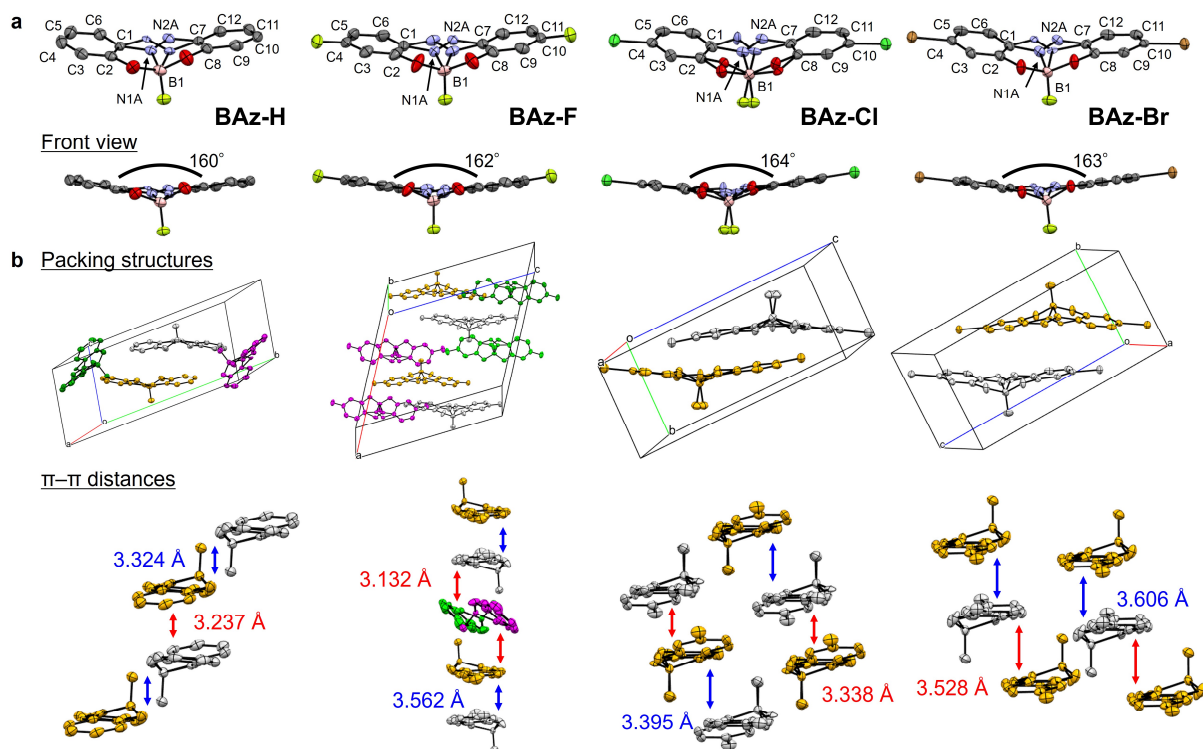


Figure 1. (a) ORTEP drawings and (b) packing diagrams (color: symmetry operation) with the distance of selected short contacts corresponding to π - π interactions for BAZ derivatives. Thermal ellipsoids are scaled to the 50% probability level.

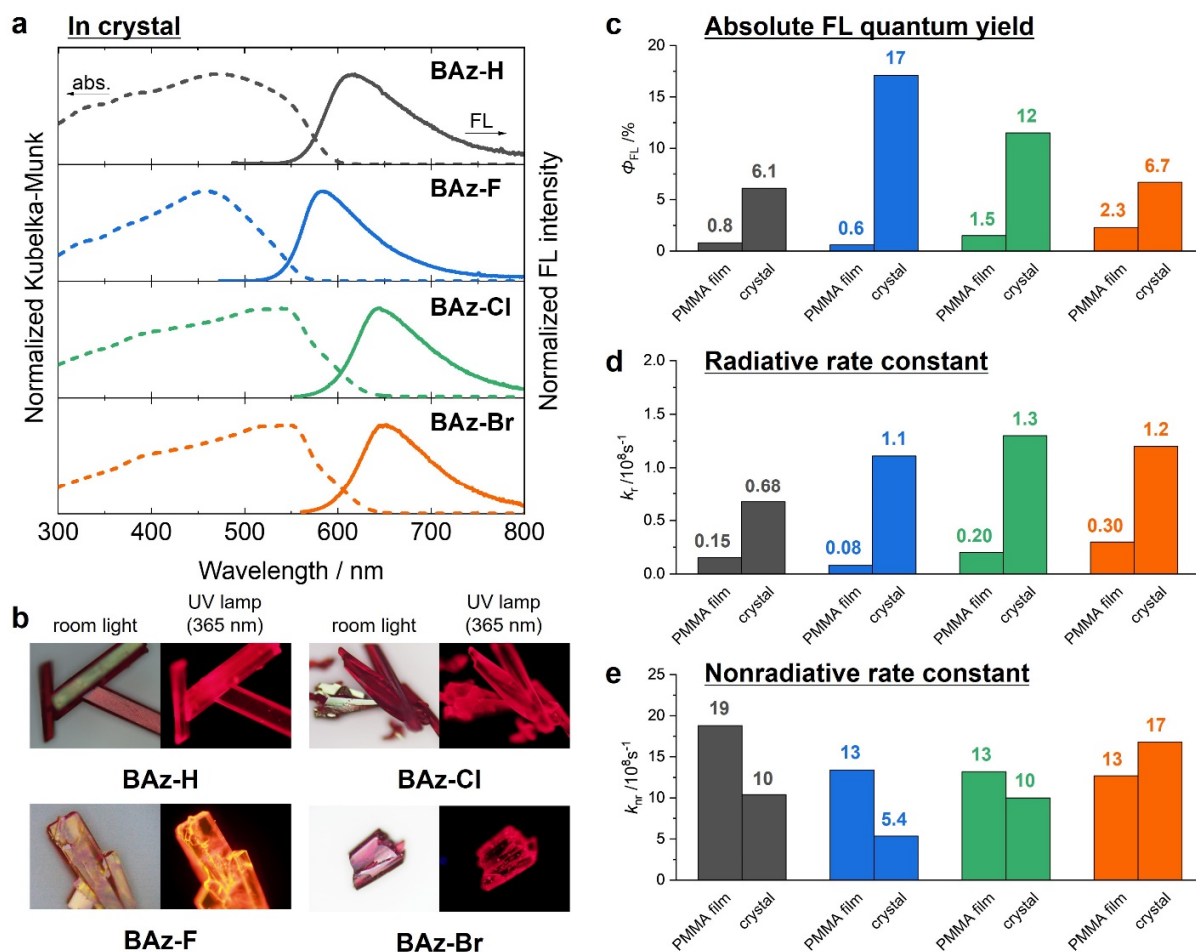


Figure 2. (a) Normalized diffuse reflection spectra and normalized FL spectra in crystal at room temperature. (b) Photos of crystals of BAz derivatives under room light and UV irradiation (365 nm). (c, d, e) Comparison of (c) absolute FL quantum yield, (d) radiative rate constant, and (e) nonradiative rate constant between 1 wt% PMMA films and crystals of BAz derivatives at room temperature.

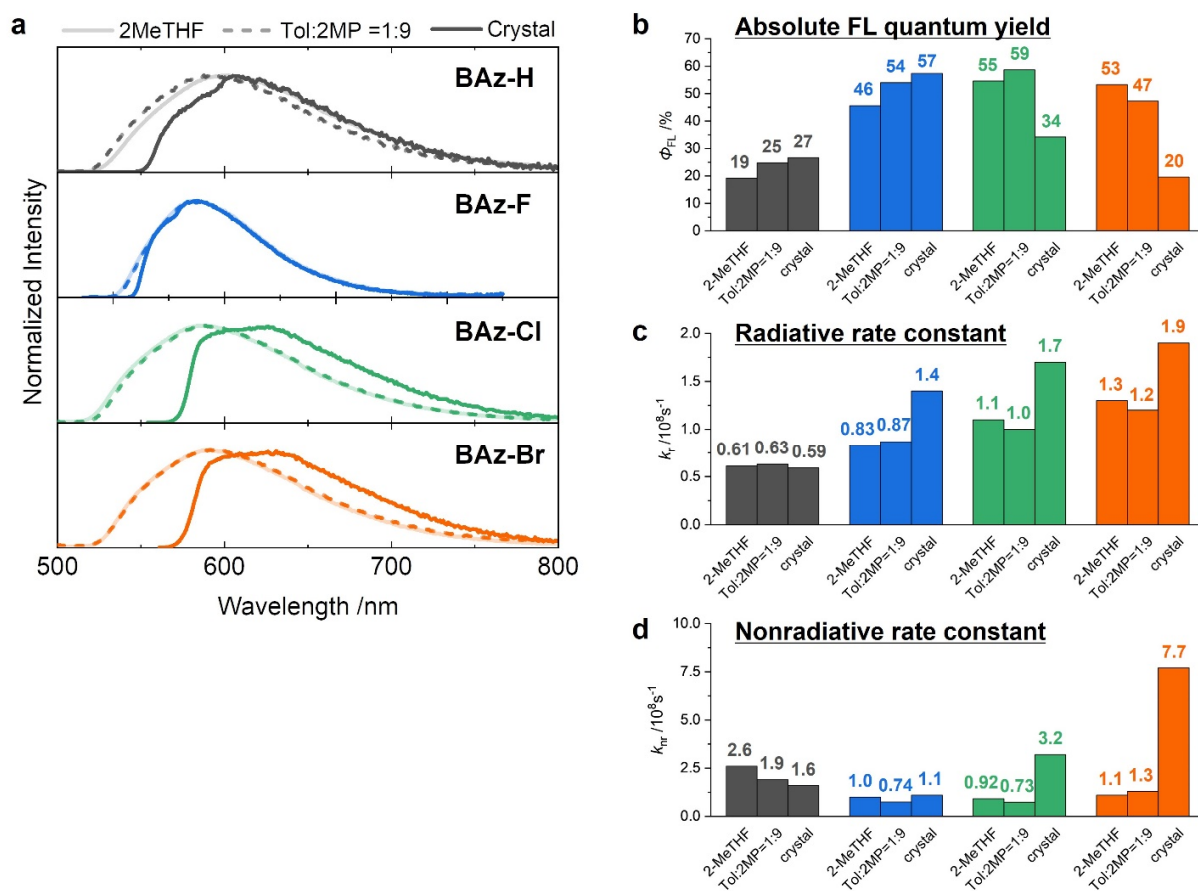


Figure 3. (a) Normalized FL spectra of BAZ derivatives in 2-methyltetrahydrofuran (2MeTHF) (1.0×10^{-5} M, pale solid lines), a mixed solvent of toluene (Tol) and 2-methylpentane (2MP) (1/9, v/v) (1.0×10^{-5} M, pale dotted lines), and crystal (thick solid lines) at 77 K. (b, c, d) Comparison of (b) absolute FL quantum yield, (c) radiative rate constant, and (d) nonradiative rate constant among 2MeTHF solution (1.0×10^{-5} M), Tol/2MP = 1/9 (v/v) solution (1.0×10^{-5} M), and crystal of BAZ derivatives at 77 K.