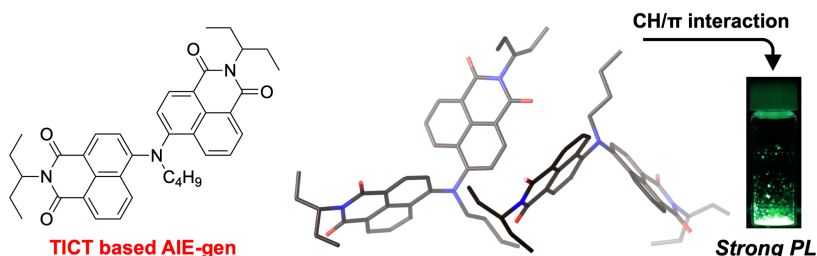


Aggregation-Induced Emission of Nitrogen-Bridged Naphthalene Monoimide Dimers

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Supporting Information Placeholder



ABSTRACT: We have prepared four 4-aminonaphthalene monoimide derivatives and examined the aggregation-induced emission (AIE) properties. A nitrogen-bridged dimer is AIE-active and exhibits bright green emission with a high quantum yield in the solid state. The X-ray diffraction analysis suggests that the key of the bright luminescence is the favorable crystal packing dominated by CH/ π interaction. The late-stage cyanation of the dimer tuned its AIE color from green to orange.

Aggregation-induced emission (AIE) is a phenomenon in which a non-emissive or weakly emissive chromophore in solution exhibits enhanced luminescence in the aggregated states.^{1,2} Creating new AIE-active molecules, so-called AIE-gens, offers fundamental insight to connect solution-phase molecular photophysics with bulk material science. Furthermore, the manipulation of AIE has enabled various practical applications such as optoelectronic devices,³ luminescent sensors,⁴ and bioimaging markers.⁵

The suppression of twisted intramolecular charge transfer (TICT)⁶ is a representative guideline for the design of AIE-gens.^{1,7} The selected examples are shown in Figure 1. These molecules consist of donor and acceptor units, which are connected with rotationally flexible single bonds. In solution, photoexcitation of these molecules initially provides a relatively coplanar locally excited (LE) state, and the subsequent rotation around the single bonds affords a twisted charge transfer (CT) state, which is non-emissive or weakly emissive in many cases. The formation of aggregates restricts this bond rotation to allow emission from the LE state. These TICT-based AIE-gens are attractive because they mostly exhibit bathochromically shifted luminescence relative to those of other AIE-gens, which should be beneficial to the biological applications.⁸

4-Aminonaphthalene monoimide is a fluorescent donor-acceptor dye emitting bright yellow fluorescence.⁹ Its photophysical processes including photoexcited charge transfer have been actively explored.¹⁰ Furthermore, these unique properties enabled practical applications including DNA photocleavage and sugar-detection.¹¹ Nevertheless, studies on the AIE behavior of 4-aminonaphthalene

monoimide derivatives have been still limited.^{12,13} Xu, Lu, and co-workers reported that 4-dihydropyrazolynaphthalene monoimide exhibited AIE-behavior and integrated it into AIE-polymers.¹² However, the fundamental insight on the structure-property relationship remains immature. Here we demonstrate that a nitrogen-bridged naphthalene monoimide dimer act as an AIE-gen exhibiting green emission. This dimer exhibits bright emission in the solid state at 521 nm with a quantum yield of 50%, which is 10 times higher than that of the corresponding monomeric analogue, 4-diphenylaminonaphthalene monoimide. Furthermore, the late-stage peripheral C-H functionalization of the dimer enabled fine-tuning of its emission color, realizing orange emission at 582 nm.

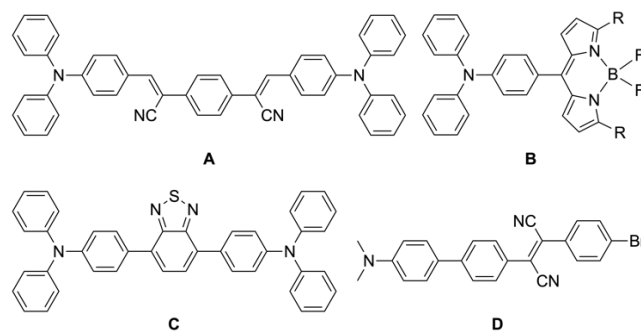


FIGURE 1. TICT-based AIE-active molecules.

The synthesis of 4-aminonaphthalene monoimide derivatives **2–5** is shown in Scheme 1. A Buchwald–Hartwig amination¹⁴ of 4-

bromonaphthalene monoimide **1** with butylamine under the Pd-PEPPSI-IPr¹⁵ catalysis provided 4-(butylamino)naphthalene monoimides **2** in 87% yield. The product was further subjected to the cross-coupling reaction with **1**, affording nitrogen-bridged naphthalene monoimide dimer **3** in 83% yield. The coupling reaction with diphenylamine also provided 4-(diphenylamino)naphthalene monoimide **4** in 49% yield. A similar transformation of **1** with 4-butylaminoaceneaphthene furnished the corresponding aminated product **5** in 63% yield, which structurally resembles (A-D-A)-type dimer **3**. **SCHEME 1**. Synthesis of 4-aminonaphthalene monoimide derivatives **2–5**.

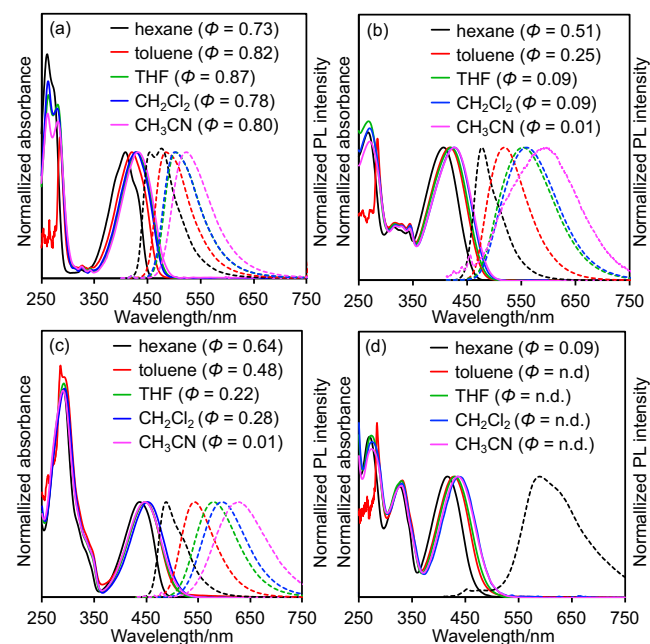
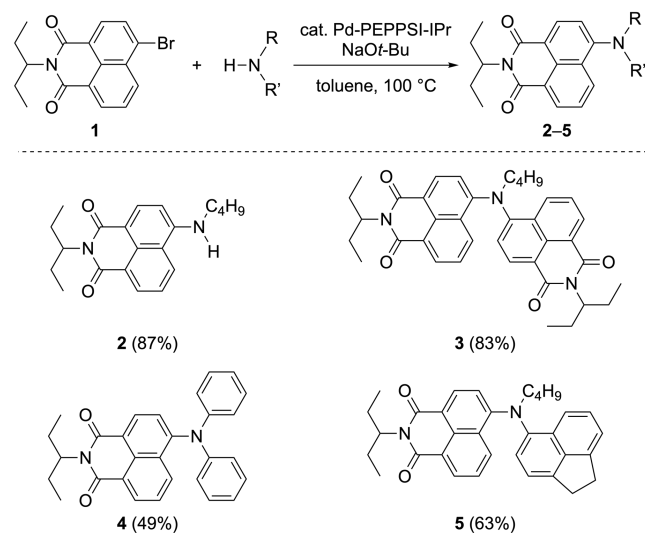


FIGURE 2. UV/Vis absorption (solid lines) and emission (dashed lines) spectra of (a) **2**, (b) **3**, (c) **4**, and (d) **5** in hexane, toluene, THF, CH₂Cl₂, and CH₃CN.

Figure 2 shows the UV/Vis absorption and emission spectra of **2–5** in hexane, toluene, CH₂Cl₂, THF, and CH₃CN. Whereas the ground state absorption spectra of these molecules displayed similar solvent-dependency, their emission properties were markedly

different. As the solvent polarity increased, the emission spectra of 4-(butylamino)naphthalene monoimide **2** shifted to the long wavelength region (Figure 2a). The Stokes shifts were plotted *versus* solvent polarity parameters Δf given by the Lippert–Mataga equation (1) (Supporting Information (SI), Figure S18a).¹⁶ The linear correlation suggests that the observed red-shift is attributable to the stabilization of the excited state in polar solvents. Nitrogen-bridged naphthalene monoimide dimer **3** exhibited similar solvent-dependency in light of the Lippert–Mataga plot (SI, Figure S18b). However, the quantum yields drastically dropped down to 1% as increasing Δf values (Figure 2b), which is contrasting to the intense emission of **2** in polar CH₃CN ($\Phi_F = 80\%$). 4-Diphenylaminonaphthalene monoimide **4** also exhibited the polarity-dependent decrease of quantum yields (Figure 2c). The decrease of quantum yields in polar solvents is characteristic of TICT dyes, which can be ascribed to the conformational change from the emissive LE state to the non-emissive CT state.^{6,7}

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

Acenaphthene-attached derivative **5** is almost non-emissive in all the solvents. Even in apolar hexane, the emission is barely detectable with a small quantum yield of 9% (Figure 2d). Importantly, the peak top at 589 nm is red-shifted by ca. 100 nm relative to those of **2–4**. A similar trend was observed for an analogous 4-aminonaphthalene monoimide having an electron-donating 1-(4-methoxyphenyl)piperazine group around the nitrogen atom.^{10b} Its excited state dynamics were examined by Wasielewski and co-workers with employing the pump-probe spectroscopy. They concluded that the origin of weak emission in apolar toluene was the transiently generated charge-separated state. Our theoretical calculations suggest that the HOMO level of acenaphthene is higher than that of 1-(4-methoxyphenyl)piperazine (SI, Figure S25). Thus, we assume that the relatively electron-rich acenaphthene unit of **5** transferred the electron to the photoexcited 4-aminonaphthalene moiety, affording a charge separated state showing red-shifted emission in hexane.

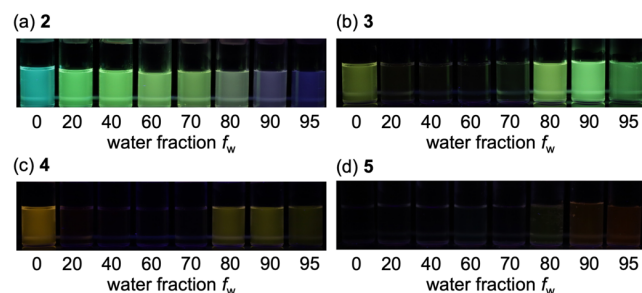


FIGURE 3. Photographs of THF/water solutions of (a) **2**, (b) **3**, (c) **4**, and (d) **5** under photoirradiation at 365 nm. f_w = water fraction (vol %).

The AIE behaviors of **2–5** were examined by monitoring the emission in THF/water mixtures (Figure 3,4 and SI, Figure S19). The concentration was kept at $1.0 \times 10^{-5} \text{ M}^{-1}$ with different water fraction f_w (vol %) from 0% to 95%. The emission of 4-(butylamino)naphthalene monoimide **2** becomes gradually weakened as increasing the water fraction, indicating that **2** is not AIE-active. Although dimer **3** and 4-diphenylaminonaphthalene monoimide **4** are moderately emissive in THF, their emissions are virtually undetectable in the moderate water fractions ($f_w = 20\text{--}70$ vol %). These results can be accounted for by the facilitated conformational change to a dark TICT-state under the polar conditions. The further increase of water fractions resulted in the formation of aggregates exhibiting green

emissions at 531 and 569 nm, respectively. Notably, the emission intensity of the aggregates of dimer **3** is stronger than that of THF solution, which clearly indicates that **3** is AIE-active (Figure 4a). Acenaphthene-attached derivative **5** is almost non-emissive regardless of the water fractions, which can be explained by the generation of non-emissive charge separated state.

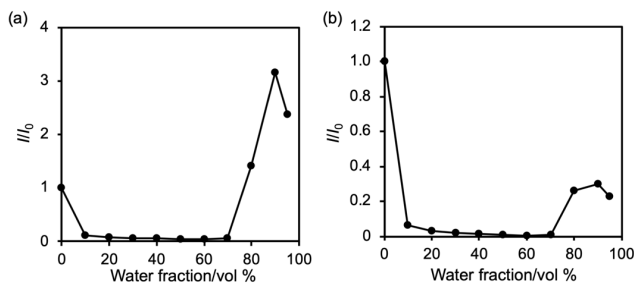


FIGURE 4. I/I_0 plots of (a) **3** and (b) **4** for the water-dilution experiments. I = emission intensity at the peak top. I_0 = emission intensity at the peak top in THF.

The above-described studies have shown that both **3** and **4** form emissive aggregates. However, the emission of dimer **3** in the aggregates is substantially more intense than that of **4** (Figures 3 and S19). To gain further insights, we carried out X-ray diffraction analyses. The single crystals of **3** and **4** were obtained by slow vapor diffusion of hexane to the CH_2Cl_2 solutions. The molecular structures and packing patterns are shown in Figure 5. The dimer **3** adopted a non-symmetric structure in light of the torsion angles between the central nitrogen and naphthalene monoimide units (22° and 71°), suggesting that one of two naphthalene monoimide units is well-conjugated with the central nitrogen atom. In the crystal packing, the component molecules interacted with each other through CH/π interaction without forming π - π stacking. Contrastingly, 4-(diphenylamino)naphthalene monoimide **4** formed an antiparallel π -stacked dimer with the interplanar spacing of 3.46 Å.

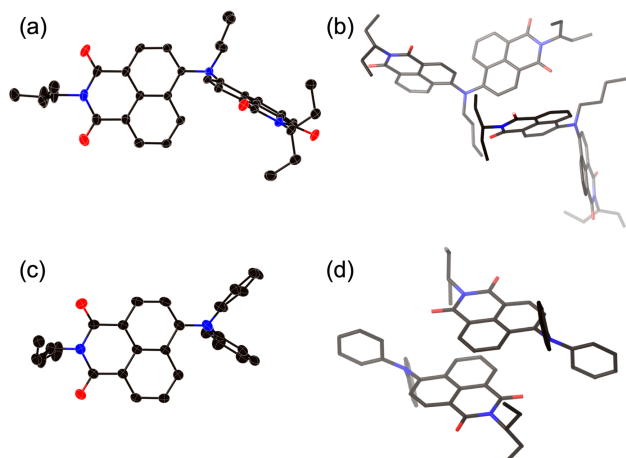


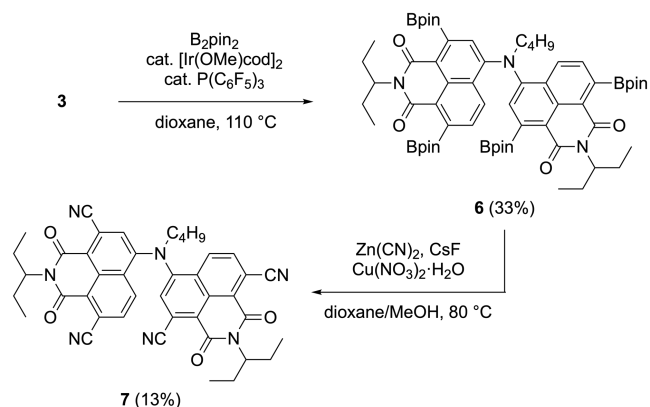
FIGURE 5. X-ray crystal structures of **3** and **4**. (a) Top view of **3**. (b) Selected packing pattern of **3**. (c) Top view of **4**. (d) Selected packing pattern of **4**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

The solid samples of **3** and **4** were prepared by recrystallization from CH_2Cl_2 /hexane. The experimental X-ray powder diffraction patterns were matched with the simulated one on the basis of the corresponding single crystal structures (SI, Figure S15,16). The diffraction reflection spectrum of **4** is red-shifted relative to that of **3** (SI,

Figure S21), which can be explained by the term of exciton coupling¹⁷ in the face-to-face stacking. Furthermore, the quantum yield of **3** ($\Phi_F = 0.50$) is almost 10 times higher than that of **4** ($\Phi_F = 0.05$). The weak solid-state emission of **4** should originate from its packing arrangement because π - π stacking potentially promotes various undesirable deactivation pathways such as excimer formation.¹⁸

The aggregates of **4** generated in THF/water were collected by filtration. The X-ray powder diffraction measurement gave an ill-defined spectrum with weak signals similar to that of the crystal structure (SI, Figure S16). Namely, although these aggregates mainly lack well-ordered molecular arrangement, they contain a small amount of π -stacked dimer. The emission spectrum of these aggregates is substantially blue-shifted relative to that of crystalline solids (SI, Figure S22). Hence, we assume that the observed emission is attributed to the sterically constrained monomeric molecule with the suppression of TICT and the partial formation of nearly non-emissive π -stacked dimer decreased the overall emission intensity. It is worth noting that we also tried to check the X-ray powder diffraction pattern of aggregates of dimer **3**. However, the aggregates of dimer **3** were too small to be collected by filtration. Considering that the emission of aggregates resembles that of crystalline solids (SI, Figure S23), π - π stacking should not be formed even in the aggregates.

SCHEME 2. Synthesis of cyanated dimer **7**.



Finally, the peripheral functionalization of dimer **3** was examined in order to tune the emission color (Scheme 2). The Ir-catalyzed borylation¹⁹ of **3** with bis(pinacolato)diboron selectively proceeded at the C–H bonds neighboring to the carbonyl groups to afford the borylated product **6**. The yield of **6** was determined to be 78% on the basis of the ^1H NMR analysis. However, more than half of the product was decomposed during the purification step, affording **6** in an isolated yield of 33%. The regioselectivity can be explained by the function of the carbonyl unit as a directing group.²⁰ The boryl groups were converted to cyano groups to provide **7** in 13% yield by treatment of **6** with $\text{Zn}(\text{CN})_2$, CsF, and $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.²¹ The structure of **7** was unambiguously determined by the X-ray diffraction analysis (Figure 6a). The cyanated dimer **7** adopted a slipped stacked packing with aligning the dipole moments. The absence of CH/π interaction could be due to the steric hinderance of the cyano groups. The solid sample was prepared by recrystallization from CH_2Cl_2 /hexane, which emitted orange luminescence at 582 nm with the quantum yield of 6%. The emission of **7** in THF/water was monitored by changing the water fraction f_w (vol %) (Figure 6b,c). While the solutions are virtually non-emissive in the range of low water fractions ($f_w = 0$ –60%), the further increase of the water fraction generated aggregates exhibiting orange emission at 595 nm. Namely, the cyano-

substituted dimer **7** is a red-emissive AIE-gen. The relatively weak emission intensity of the aggregates could be explained by the facilitated non-radiative deactivation due to the decreased S_0 – S_1 energy gap as well as its slipped stacked packing in the solid state.

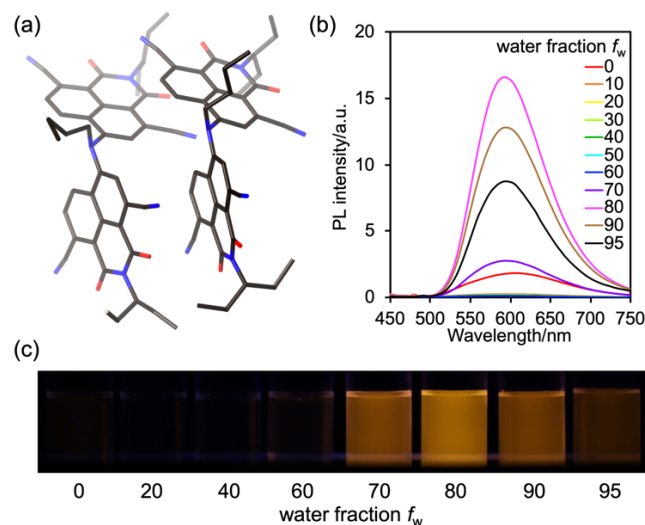


FIGURE 6. (a) Selected packing pattern in the crystal structure of **7**. All hydrogen atoms are omitted for clarity. (b) Emission spectra of THF/water solutions of **7** ($1.0 \times 10^{-5} \text{ M}^{-1}$, $\lambda_{\text{ex}} = 420 \text{ nm}$). (c) Photograph of THF/water solutions of **7** under photoirradiation at 365 nm. f_w = water fraction (vol %).

In summary, we synthesized a series of 4-aminonaphthalene monoimide derivatives **2**–**5** and examined their AIE-behaviors. Among them, nitrogen-bridged naphthalene monoimide dimer **3** and 4-(diphenylamino)naphthalene monoimide **4** formed emissive aggregates, which can be attributed to the suppression of TICT in the conformationally restricted aggregated states. Although their TICT-behaviors in solution are quite similar, the emission intensities in the solid samples are markedly different. Namely, the emission quantum yield of dimer **3** (50%) is 10 times higher than that of monomer **4** (5%). The X-ray diffraction analyses suggest that the intense emission of **3** can be attributed to the favorable packing pattern dominated by CH/ π interaction. We also achieved the late-stage functionalization of dimer **3** to afford an orange-emissive AIE-gen **7**.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and spectral data for all new compounds. Crystallographic data (CIF files) for **3** (93 K, 293 K), **4** (93 K, 293 K), and **7** (93 K).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have approved of the final version of the manuscript.

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The authors declare the absence of any potentially competing financial interests.

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