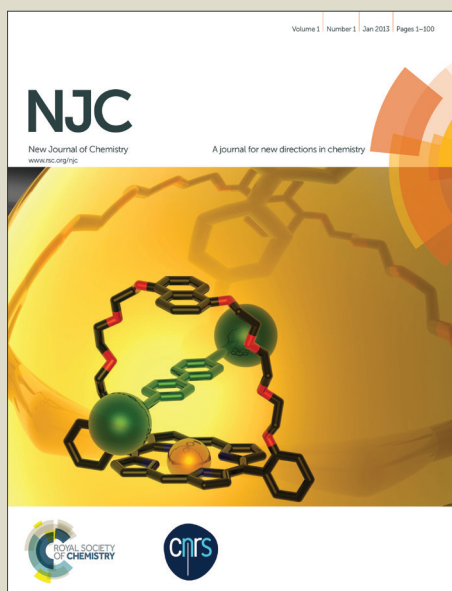


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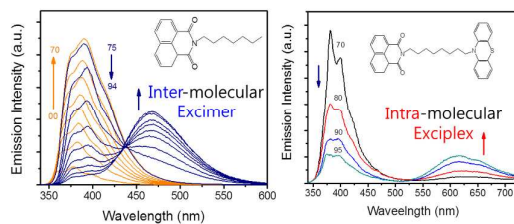
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Graphic abstract**Excimer and exciplex emissions of 1,8-naphthalimides caused by aggregation in extremely polar or nonpolar solvents**

Dae Won Cho and Dae Won Cho

1,8-naphthalimides showed the aggregation induced emission in both extremely polar or nonpolar solvents, which attributed to the intermolecular-excimer and intramolecular-exciplex formations



Excimer and exciplex emissions of 1,8-naphthalimides caused by aggregation in extremely polar or nonpolar solvents

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1,8-Naphthalimides (NI) aggregate in both extremely polar and nonpolar solvents. The aggregation induced emission of NIs is attributed to the intermolecular excimer and/or the intramolecular exciplex formations.

Aggregation, which occurs in the solid states of aromatic molecules, often leads to a lowering of fluorescence efficiencies or even total quenching of emission.¹ This quenching effect has greatly limited the scope of the organic light emitting diode device applications of these substances.² In contrast, aggregation induced emission (AIE)³ or aggregation induced emission enhancement (AIEE)⁴ is recognized to be intriguing phenomena that take place in aggregate or solid state states of some organic molecules that are employed in luminescence systems.^{5,6} It has been proposed that AIE is a consequence of a decrease in the nonradiative decay rate constant caused by restrictions of intramolecular rotation of groups. In cases where emission enhancements occur, the wavelength maxima for emission do not change because the restriction of molecular motion does not perturb the electronic nature of the fluorophore.

On the other hand, aggregation of some substances not only leads to fluorescence enhancement but also to a large shift of the emission wavelength.^{4,7} The shift is a result of changes in electronic properties of the excited-states that take place in proceeding from the solution to the dense phase. Some typical examples of these changes have been classified as intramolecular charge-transfer,^{8,9} excimer formation,¹⁰ and excited-state proton-transfer.¹¹

Usually, dispersions of aggregators were prepared by using the precipitation method, involving adding different fractions of water (poor solvent) to tetrahydrofuran (THF) (good solvent). In contrast, extremely nonpolar solvent serve as poor solvents

for moderately polar molecules. Hence, one of the main causes of aggregation of organic substances is their poor solubility in either extremely polar or nonpolar solvents, depending upon whether they themselves are nonpolar or polar (Chart 1).

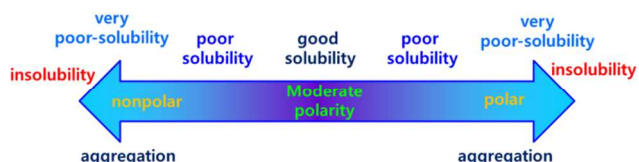
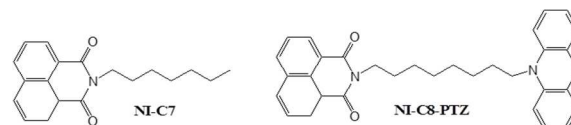


Chart 1 Schematic diagram for showing aggregation versus solubility trends.

In the investigation described below, we subjected two 1,8-naphthalimide (NI) derivatives to studies aimed at determining how their AIE properties vary with changes in solvent polarity. For this purpose, *N*-heptyl-1,8-naphthalimide (NI-C7) and *N*-(8-phenothiazinyloctyl)-1,8-naphthalimide (NI-C8-PTZ) (Scheme 1) were prepared using previously described methods.¹²⁻¹⁴ We determined the AIE for NI derivatives in the solvents between two extremes about polarity. NI derivatives in good soluble-solvents have fluorescence wavelength maxima at *ca.* 380 nm. However, NI-C7 displays an intense blue-emission, and red-emission occurs from NI-C8-PTZ in response to increases in the content of poor solvents in which the respective substances are less soluble.



Scheme 1 Molecular structures

To gain insight into the origin of the AIE phenomena, the effects of concentrations in H₂O/CH₃CN and *n*-hexane solutions on the emission properties of NI-C7 and NI-C8-PTZ

were explored. In CH₃CN solution and H₂O/CH₃CN mixtures, only a slight bathochromic shift and the presence of long wavelength tail absorption are observed in these spectra as the water fraction increases (Fig. 1). The long wavelength absorption is attributed to the Mie or light scattering effects suggesting the aggregation in solutions of higher water content.^{5,6,15-18} Both compounds exhibit an isosbestic point at 334 nm, which is the excitation wavelength to measure the emission spectra.

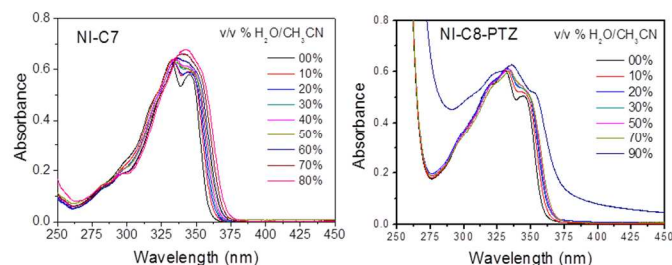


Fig. 1 Absorption spectra of 48 μM NI-C7 and 15 μM NI-C8-PTZ in H₂O/CH₃CN.

In contrast to the minor effects seen in the absorption spectra, addition of water to CH₃CN solutions of the NIs causes a dramatic change in their fluorescence spectra. For example, the emission spectrum of NI-C7 in CH₃CN contains a weak band at 380 nm ($\phi_f = 0.021$), which is attributed to the monomer species (Fig. 2a).¹² In direct response to an increase of the v/v fraction of water in the H₂O/CH₃CN solutions from 0 to 70%, the intensity of the emission band increases 10-fold in association with a shift in the wavelength maximum from 380 to 390 nm (deep-purple, inset of Fig. 2a).

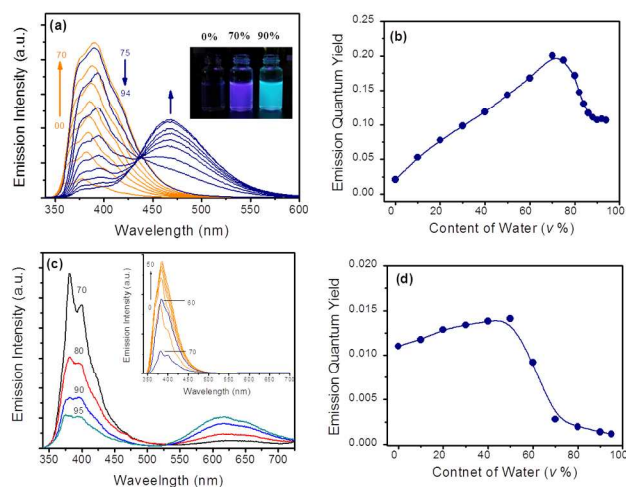


Fig. 2 Emission spectra of (a) 15 μM NI-C7 (fraction interval: 10 v/v% in range of 0-70%, then 5 v/v% interval in range of 75-90%), and (c) 25 μM NI-C8-PTZ in H₂O/CH₃CN. $\lambda_{\text{ex}} = 334$ nm. Inset in figure are photographs of vials under 365 nm light irradiation, and (c) emission spectra of NI-C8-PTZ in CH₃CN solutions containing water fractions (v/v) in the 0-70% ranges. (b and d) total emission quantum yields of NI-C7 and NI-C8-PTZ in CH₃CN solutions containing water fractions (v/v) in the 0-95% ranges.

It is well known that main deactivation route for singlet excited states of NI derivatives is intersystem crossing (ISC), a process that transforms a higher energy excited singlet state (π, π^* , S_1) to a lower energy excited triplet state (n, π^* , T_2).¹⁹ The relative ordering and energy spacing between these states is altered by changes in the polarity of a solvent and especially its protic nature. Specifically, as the solvent polarity increases, the S_1 state shifts to lower energies while the T_2 state shifts to higher energies. Therefore, the efficiency of the ISC process decreases, and the fluorescence efficiency increases. These phenomena are responsible for the observed fluorescence changes seen with NI-C7, whose emission is enhanced markedly and slightly red shifted when the water content of H₂O/CH₃CN solutions increases. Further addition of water to H₂O/CH₃CN solutions of NI-C7 (70-95 v/v%) initiates aggregation in conjunction with a large decrease in blue emission centered at 390 nm and simultaneous growth of a cyan emission band at 470 nm (Fig. 2a). The presence of an isoemissive point at 440 nm indicates that the photophysical change, promoted by water addition and caused by aggregation, corresponds to a stoichiometric (equilibrium) change between two excited state species.

The results of further studies revealed that the emission characteristics of NI-C8-PTZ are also governed by solvent polarity/proticity. The emission intensity at 380 nm for NI-C8-PTZ in CH₃CN, attributed to the NI fluorophore (Fig. c), increases as the water content of the solution increases from 0-50 v/v%. Moreover, when the water content of the solution exceeds 50%, the purple emission band at short wavelength (380 nm) disappears in concert with the rise of a red emission band at 600 nm. Also, an isoemissive point is present at ca. 525 nm.

The findings described above show that water promotes dramatic changes in the fluorescence properties of NI-C7 and NI-C8-PTZ. The fluorescence emission bands at 380 nm for both NIs undergo red-shifts and dramatic increases in intensity as the water contents of CH₃CN solutions increase. However, when the water contents of solutions are very high, aggregation formation takes place, leading to decreases in the intensities of the absorption band at 380 nm along with simultaneous increases in the intensities of long wavelength bands in the visible region. However, the greatly different wavelengths of the maxima of the new visible emission bands suggest that differences exist between the natures of aggregation formation, which in the case of NI-C7 likely involves interaction between only NI moieties. Accordingly, we propose that the emission band at 470 nm for NI-C7 arises from an excimer, an excited intermolecular complex, in which π - π interactions occur between the respective NI chromophores.²¹

As shown in Fig 2b and 2d, the emission quantum yields are enhanced in a regular manner by addition of water to the CH₃CN solution. However, the emission quantum yields decrease when the water fraction is above 70% for NI-C7 and 50% for NI-C8-PTZ, respectively. This phenomenon might be caused by different aggregation formation and the excimer or exciplex species have lower quantum yields.

Table 1. Emission lifetimes (ns) of NI derivatives in CH₃CN, H₂O/CH₃CN (v/v = 1:1), and *n*-hexane

	CH ₃ CN ^a	H ₂ O/CH ₃ CN ^c	<i>n</i> -hexane ^b
NI-C7	0.14	1.8 (30)	< 0.05 (1.70)
NI-C8-PTZ	0.085	0.62 (1.8)	< 0.05 (5.35)

^a Data from ref. 12). ^b Data from ref. 20). Monitoring wavelength is 380 nm. ^c Parenthesis values measured at 480 nm for NI-C7 and 600 nm for NI-C8-PTZ, respectively.

On the other hand, the 600 nm band for NI-C8-PTZ likely corresponds to emission from an intramolecular exciplex, in which interactions take place between the PTZ and NI chromophores. The unique behavior of NI-C8-PTZ that contains a strong electron donating PTZ group tethered to a strong electron accepting NI group suggests that excited state stabilization in extremely polar or nonpolar solvents takes place by charge transfer interactions in an intramolecular complex.

The emission lifetimes of NI derivatives were measured in CH₃CN, H₂O/CH₃CN (v/v = 1:1), and *n*-hexane (Table 1). The lifetimes for monomeric NI-C8-PTZ are shorter than those of NI-C7 in all solvents, because the photoinduced electron transfer (PET) process between acceptor NI and donor PTZ occurred. The emission lifetimes are increased according to increasing of solvent polarity, which is consistent with quantum yield changes. The lifetimes of excimer and exciplex measured in *n*-hexane or H₂O/CH₃CN mixtures are quite long compared to those of the monomeric species.

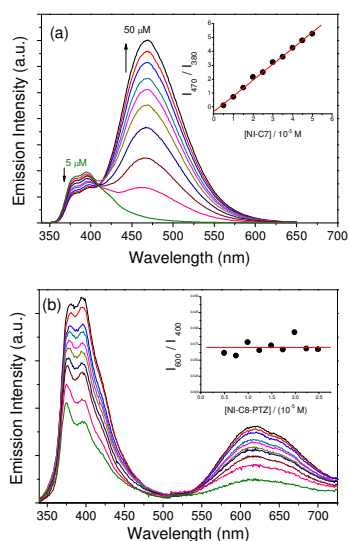


Fig. 3 NI concentration dependence of concentration on emission spectra of (a) NI-C7 (5 – 50 μM, interval is 5 μM) and (b) NI-C8-PTZ (5 – 25 μM, interval is 2.5 μM) in H₂O/CH₃CN (v/v = 90%). λ_{ex} = 334 nm. Inset figures indicate the ratio of the emission intensities; (a) $I_{470\text{ nm}}/I_{380\text{ nm}}$, (b) $I_{600\text{ nm}}/I_{400\text{ nm}}$.

In order to gain clear experimental support for the bases of the respective decreases and increases in the intensities of the short and long wavelength bands, the effects of concentrations of NI-C7 and NI-C8-PTZ in 90% H₂O/CH₃CN solutions to were evaluated (Fig. 3). As can be seen by viewing the spectra displayed in Fig. 3a, a change in the concentration of NI-C7

from 5 μM to 50 μM brings about a marked decrease in the intensity of 370 nm band and increase in the 470 nm band. A plot (inset Fig. 3a) of the ratios of the intensities at 380 and 470 nm ($I_{470\text{ nm}}/I_{380\text{ nm}}$) versus NI-C7 concentration is linear, demonstrating that the long wavelength emission takes place from an intermolecular excimer.

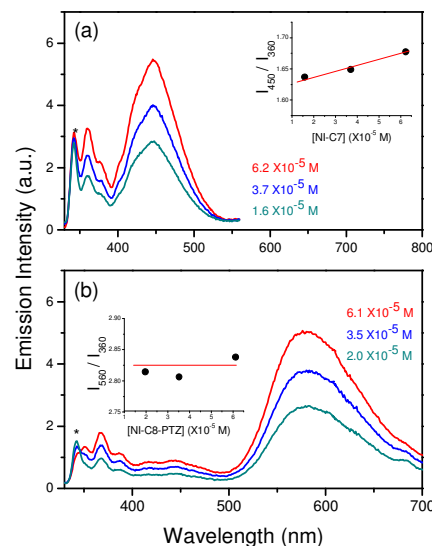


Fig. 4 Emission spectra of (a) NI-C7 and (b) NI-C8-PTZ with different concentrations measured in *n*-hexane. λ_{ex} = 310 nm. Inset plots indicate the ratio of the emission intensities; (a) $I_{450\text{ nm}}/I_{360\text{ nm}}$, (b) $I_{560\text{ nm}}/I_{360\text{ nm}}$. Asterisk denotes the Raman peak of solvent.

In contrast, analysis of the spectral changes, displayed in Fig. 3b, shows that the ratio of the intensities of the 370 and 600 nm emission bands of NI-C8-PTZ are not dependent of the concentration. Specifically, in the course of increasing concentration of NI-C8-PTZ, the intensities of both emission bands gradually increase in a parallel manner. Clearly, concentration has no effect on the ratio of the intensities of these bands (inset in Fig 3b) as would be expected if the 600 nm band is associated with emission from the excited state of an intramolecular complex, which is generated by interaction between NI and PTZ moieties.²¹

Since their solubility in nonpolar solvents is typically low, NI derivatives are expected to undergo aggregation in *n*-hexane. Inspection of the spectra in Fig. 4 shows that emission bands of the NI derivatives in *n*-hexane are similar to those water-CH₃CN mixtures containing high water contents.

Importantly, NI-C7 and NI-C8-PTZ display dual emissions in *n*-hexane with 360 nm bands associated with emission from the monomeric species and the longer wavelength bands assigned to emission from the respective intermolecular excimer of NI-C7 (450 nm) and intramolecular exciplex of NI-C8-PTZ (580 nm). Emission maxima in the spectra of *n*-hexane solutions are observed at shorter wavelengths compared to those of the NIs in more polar solvents, as expected based on the typical effects of solvent polarity. In addition, like in the case of water-CH₃CN mixtures, the intensities of emission at 360 and 450 nm vary with the concentration of NI-C7 in *n*-

hexane in the manner expected for formation of exciplex (inset in Fig. 4a). However, no concentration dependence is observed for the ratio of the intensities of the 360 and 580 nm emission bands for NI-C8-PTZ in *n*-hexane, an observation that is consistent with long wavelength emission originating from the excited state of an intramolecular complex between the NI and PTZ moieties.

It is interesting that the excimer and exciplex of these NIs in *n*-hexane emit at shorter wavelengths compared to those in more polar water/CH₃CN mixtures. This phenomenon suggests that the singlet excited state energies of both complexes are influenced by solvent polarity. In addition, the fluorescence quantum yields (ϕ_f) of NI-C7 and NI-C8-PTZ in *n*-hexane are smaller by a factor of nearly 100 than those in CH₃CN. As mentioned above, this is a consequence of the fact that the energies of S₁ and T₂ states of NIs are so close in nonpolar solvents that ISC process occurs efficiently. For this reason, AIEs for NIs in nonpolar solvents are much smaller than they are in polar solvent.

In summary, although a large number of substances have been observed to display AIE, in most cases the origins of the effect have not been fully explored. The investigation described above has successfully uncovered the reason why AIE takes place in different types of NI derivatives. As shown in figure 5, in nonpolar solvents, the T₂ state lie in lower compared to the S₁ state. Thus the intersystem crossing process is efficient. On the other hand, the fluorescence intensity increase caused by increasing solvent polarity (or the fraction of protic polar solvent) is attributed to the energy ordering between S₁ and T₂ states. In the case of the simple NI derivative (NI-C7), the AIE at long wavelength in extremely polar or nonpolar solvents is associated with formation of an excited state dimer (excimer) arising by π - π interactions between the respective NI chromophores. However, in the case of NI-C8-PTZ, which contains a strong electron donating PTZ group tethered to a strong electron accepting NI group, AIE in extremely polar or nonpolar solvents is a consequence of the generation of an intramolecular complex (exciplex) that is likely stabilized by charge transfer interactions.

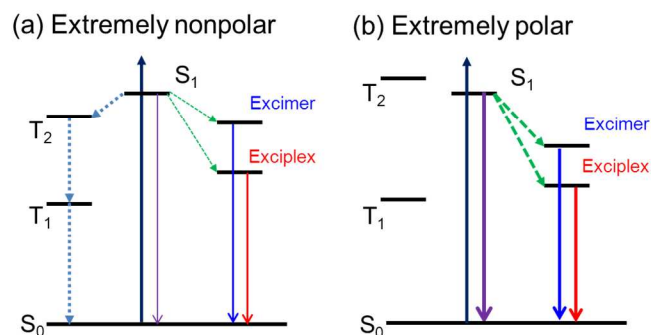


Fig. 5 Schematic energy diagram for NI derivatives in (a) extremely nonpolar and (b) extremely polar solvent.

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Notes and references

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