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1 Introduction

Fluorometric probes responding to various stimuli have been extensively investigated because of their significance in analytical tools,¹ bioprobes,²⁻⁴ chemical sensors,⁵⁻¹¹ molecular logic operators^{12,13} and molecular switches.¹⁴ In particular, fluorophores, which display changes in fluorescence colour and intensity depending on the microenvironments of a medium, attracted broad interest because they are potentially useful as the signalling moiety in various fluorescent sensors and probes. Additionally, the elucidation of the effects of specific media or solvents on the fluorescence behaviour of microenvironment-sensitive fluorophores is one of the central issues to understand the detailed mechanism of fluorophore-solvent interactions, such as hydrogen bonding effects.¹⁵⁻¹⁹

Conventional fluorophores responding to the microenvironments of a medium have been constructed on the basis of the concept of the intramolecular charge-transfer (ICT) electronic character of the fluorescent state. The pioneering ICT fluorophores showing marked solvatofluorochromism are 2-(dimethylamino)-6-propionylnaphthalene (PRODAN) and the related compounds.²⁰ 4-Aminophthalimide is a representative ICT fluorophore sensitive not only to solvent polarity but also to intermolecular hydrogen bonding with a protic solvent.^{21,22} Hydrogen bonding between 4-aminophthalimides and alcohol molecules results in the quenching of the fluorescence *via* the promoted non-radiative pathways through internal conversion and/or intersystem crossing.^{21,22}

Molecular structures in the fluorescent state of ICT fluorophores are additional factors to control their fluorescence efficiency. A twisted intramolecular charge-transfer (TICT) mechanism has been proposed as one of the major non-radiative decay processes.^{23–27} The replacement of a dialkylamino functionality in 4-alkylamino-1,8-naphthalimide and the related compounds with an aziridinyl functionality effectively suppressed the deactivation process through the TICT state, resulting in the enhancement of the fluorescence quantum yields.²⁴

6-Dimethylamino-2,3-naphthalimide (6-DMN) has been reported as an efficient ICT fluorophore displaying positive sol-

Fluorescence behaviour of 2-, 3- and 4-amino-1,8-naphthalimides: effects of the substitution positions of the amino functionality on the photophysical properties[†]

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The absorption and fluorescence spectra of a series of 1,8-naphthalimide derivatives incorporating the amino functionality at the 2-, 3- and 4-positions of the naphthalene ring (**2APNI**, **3APNI** and **4APNI**, respectively) were systematically investigated in various solvents and in the solid state. The fluorescence spectra of **2APNI** were insensitive to solvent polarity and intermolecular hydrogen-bonding even in a protic medium such as methanol. Thus, **2APNI** displayed blue fluorescence with a moderate fluorescence quantum yield ($\lambda_{max}^{F} = 420-445$ nm, $\Phi_{F} 0.2-0.3$) in the solvents investigated. In contrast, the fluorescence spectra of **3APNI** and **4APNI** were strongly solvent dependent showing positive solvatofluorochromism with large Stokes shifts. Upon increasing the solvent polarity, the fluorescence colours changed from blue in hexane ($\lambda_{max}^{F} = 429$ nm) to orange-yellow in methanol ($\lambda_{max}^{F} = 564$ nm) for **3APNI**, and from blue in hexane ($\lambda_{max}^{F} = 460$ nm) to yellow in methanol ($\lambda_{max}^{F} = 538$ nm) for **4APNI**. The fluorescence quantum yields of **3APNI** and **4APNI** decreased with increasing solvent polarity. In the solid state, **APNIs** displayed red-shifted fluorescence emission compared to that in solution ($\lambda_{max}^{F} = 541$ nm for **2APNI**, 575 nm for **3APNI**, and 561 nm for **4APNI**) and the fluorescence quantum yields in the solid state were lower than those in solution.



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vatofluorochromism.^{28,29} Imperiali and co-workers applied the fluorophore to bioprobes for monitoring protein binding interactions.^{28,29} We have demonstrated that 5- and 6-amino-2,3naphthalimides (**5ANI** and **6ANI**, see Fig. 1 for the molecular structures) respond to solvent polarity to show solvent-dependent fluorescence colour changes covering the entire visible region.³⁰ The fluorescence of **5ANI** and **6ANI** was quenched by methanol through internal conversion of the fluorescent state to the ground state. In contrast, the fluorescence behaviour of 1-amino-2,3-naphthalimides (**1ANI**) was not affected by the microenvironment of the media presumably because of tight intramolecular hydrogen bonding between the amino and imide carbonyl functionalities.³⁰ It was revealed that the amino substitution positions appreciably affected the fluorescence features of **ANIs**.

Due to the efficient fluorescence abilities, amino-1,8naphthalimides have been used as fluorescence emitting moieties. 4-Amino-1,8-naphthalimide is one of the most popular fluorophores and has been applied to various fluorescent chemical and biological probes.31-34 Conventionally, 3- and 4-amino-1,8-naphthalimides have been extensively studied whereas few reports are available on the fluorescence properties of the 2-amino derivative. Only the absorption and fluorescence spectral data for N-ethyl-2-amino-1,8-naphthalimide in ethanol were stated in the literature.³⁵ By considering the molecular structure of 2-amino-1,8-naphthalimide, intramolecular hydrogen bonding is possible, and its photophysical features are expected to be different from those of the 3- and 4-amino derivatives. These anticipations prompted us to prepare the 2-amino-1,8-naphthalimide fluorophore and to compare its photophysical behaviour with those of the corresponding 3- and 4-amino derivatives. In the present study, a series of amino-substituted N-propyl-1,8-naphthalimides incorporating the amino functionality at the 2-, 3- and 4-positions of the naphthalene ring (2APNI, 3APNI and 4APNI, see Fig. 1 for the molecular structures) were prepared, and their steadystate and time-resolved fluorescence spectra as well as the



Fig. 1 Chemical structures and abbreviations of the amino-substituted 2,3-naphthalimide (ANI) and 1,8-naphthalimide (APNI) series.

absorption spectra were systematically observed to reveal the effect of the amino-substitution positions on the electronic features of the amino-1,8-naphthalimide fluorophores.

2 Results and discussion

2.1 Preparation of APNIs

The synthetic routes to APNIs are shown in Scheme 1. N,N'-Diphenyloxalimidoyl dichloride 2, which was prepared by the reaction between aniline and oxalyl chloride in the presence of PCl₅, was reacted with 2-methoxynaphthalene 2 in benzene affording acenaphthylenedione 3.36,37 Compound 3 was oxidized with hydrogen peroxide under alkaline conditions to form 1,8-naphthalic anhydride 4.³⁸ Anhydride 4 was reacted with propylamine (PrNH₂) in acetic acid to give 2-methoxy-Npropyl-1,8-naphthalimide 5. The methoxy functionality of compound 5 was converted into triflate 7 by a reaction with BBr₃ followed by treatment with Tf2O. The Buchwald-Hartwig reaction³⁹ of compound 7 with *t*-butyl carbamate effectively produced compound 8. The tert-butoxycarbonyl (Boc) group in compound 8 was removed under acidic conditions affording the desired 2APNI. 3APNI was synthesized through a two-step reaction sequence: 3-nitro-1,8-naphthalic anhydride 9 was reacted with PrNH₂ to yield 3-nitro-N-propyl-1,8-naphthalimide 10; subsequently, the nitro group of compound 10 was reduced under a hydrogen stream in the presence of Pd/C to give 3APNI. 4APNI was obtained by N-alkylation of 4-amino-1,8-naphthalimide 11. All new compounds were characterized by NMR and IR spectroscopy as well as elemental analysis.

2.2 Ground-state geometries of APNIs

To understand the structural and electronic features of **APNIs** in the ground state, theoretical calculations were performed by using density functional theory (DFT).⁴⁰ The PBE0 functional⁴¹ and 6-311+G(d,p) basis sets⁴² were used for geometry optimization. The obtained geometries are presented in the ESI.[†] In Table 1, the structural parameters around the amino functionality of **APNIs** are summarized: bond lengths between the amino nitrogen and the aromatic carbon atom $[d(C^{Ar}-NH_2)]$ and for the imide C=O bonds $[d(C=O^{\alpha})]$, the folding angle between the mean planes of the aromatic ring and the amino moiety (φ , see Table 1 for definition), atomic charges of the amino nitrogen and one of the imide oxygen (O^{α}) atoms and the calculated ground-state dipole moment. The atomic charges were estimated by natural orbital analysis.⁴³

The calculation results predict that **2APNI** shows structural features different from those of **3APNI** and **4APNI**. The $d(C^{Ar}-NH_2)$ value of **2APNI** (1.345 Å) was smaller than those of **3ANPI** (1.383 Å) and **4ANIP** (1.373 Å) whereas the $d(C=O^{\alpha})$ value of **2APNI** (1.231 Å) was larger than those of **3APNI** (1.215 Å) and **4APNI** (1.217 Å). The amino moiety in **2APNI** is coplanar with the napthalimide ring ($\varphi = 0.30^{\circ}$) whereas that in **3APNI** and **4APNI** is pyramidalized ($\varphi = 33.8^{\circ}$ for **3APNI** and 32.4° for **4APNI**). One of the amino hydrogen atoms seems to form

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Scheme 1 Synthetic routes to APNIs. Reagents and conditions: (i) AlCl₃, benzene, 49%. (ii) H₂O₂, NaOH, EtOH, 94%. (iii) PrNH₂, AcOH, 99% for 5, 93% for 10. (iv) BBr₃, CH₂Cl₂, 93%. (v) Tf₂O, TEA, CH₂Cl₂, 88%. (vi) *t*-Butyl carbamate, Pd₂dba₃, XantPhos, Cs₂CO₃, dioxane, 64%. (vii) CF₃COOH, CH₂Cl₂, 61%. (viii) H₂, Pd/C, DMF, 64%. (ix) MeONa, MeOH, PrBr, DMF, 61%.

Table 1 Calculated molecular structures and structural parameters of APNIs (PBE0/6-311+G(d,p) under vacuum)



	J(CAT NILL)	$d(C - O^{\alpha})$		Atomic charge ^{<i>a</i>}		b
Compound	$\begin{pmatrix} a(C - NH_2) \\ (Å) \end{pmatrix}$	a(C=O) (Å)	$\left(^{\circ} ight)$	NH ₂	Ο ^α	(D)
2APNI	1.345	1.231	0.30	-0.751	-0.659	4.89
3APNI 4APNI	1.383 1.373	$1.215 \\ 1.217$	33.8 32.4	-0.798 -0.775	-0.598 -0.606	4.92 6.28

 a Estimated by the natural bond analysis method. b Calculated dipole moment in the ground state.

intramolecular hydrogen bonding with the O^{α} atom as the NH···O^{α} distance was calculated to be 1.851 Å. The features of the conjugation and hydrogen bonding are illustrated in Fig. 2.³¹

The hydrogen-bonding effects were studied by FT-IR spectroscopy (Fig. S1 in the ESI[†]) and by calculating the atomic charges of the amino nitrogen and O^{α} atoms. The N–H stretching bands ($\nu_{\rm N-H}$) of **2APNI** were observed at 3404 (asymmetrical, *as*) and 3292 (symmetrical, *sym*) cm⁻¹ which appeared in the lower wavenumber region compared to those observed for **3APNI** and **4APNI**; 3471 (*as*) and 3365 (*sym*) cm⁻¹ for **3APNI**, 3433 (*as*) and 3350 (*sym*) cm⁻¹ for **4APNI**. It has been stated that the N–H stretching band tends to shift to a lower fre-



Fig. 2 Intramolecular hydrogen bonding and conjugation features in 2APNI and 4APNI.

quency region upon intramolecular hydrogen bond formation.⁴⁵ The IR spectral features of **2APNI** are considered to be due to effective hydrogen bonding.

The atomic charge of the amino nitrogen and O^{α} atoms of **2APNI** was respectively calculated to be -0.751 and -0.659. The amino nitrogen atom of **2APNI** was predicted to be more positive than those of **3APNI** (-0.798) and **4APNI** (-0.775). The O^{α} atom of **2APNI** was predicted to be more negative than that of **3APNI** (-0.598) and **4APNI** (-0.606). The calculated dipole moment in the ground state (μ_g) is larger for **4APNI** (6.28 D) than for **3APNI** (4.92 D) because of the more effective separation of the nitrogen donor and the imide acceptor moieties. These results indicate that the amino group in **2APNI** effectively conjugated with the naphthalimide moiety in the ground state which was consistent with the features illustrated in Fig. 2.

2.3 Electronic absorption spectra of APNIs

The electronic absorption spectra of **APNI**s were obtained in various solvents to understand their electronic characteristics in the ground state. The electronic absorption spectra of **APNI**s (normalized) are illustrated in Fig. 3. The absorption maximum wavelengths (λ_{max}^{Abs}) and the molar absorption coefficients (ε) are listed in Table 2.

2APNI showed a structured absorption band in the 405–420 nm wavelength region. The large ε values of the band (log ε = 4.05–4.10, Table 2) indicate that the character of the band is of an allowed π , π^* transition. The absorption band is almost insensitive to solvent polarity showing only a slight redshift from 405 nm in hexane to 420 nm in DMSO ($\Delta \lambda_{max}^{Abs}$ = 15 nm). The absorption spectral behaviour of 3APNI and 4APNI was different from that of 2APNI. Both 3APNI and 4APNI displayed broad absorption bands in the wavelength region of 394-438 nm for 3APNI and 389-538 nm for 4APNI, which appreciably red-shifted depending on the solvent polarity. The solvatochromic shifts upon changing the solvent from hexane to DMSO ($\Delta \lambda_{max}^{Abs}$) were 44 nm for 3APNI and 48 nm for 4APNI (Fig. 3 and Table 2). These results indicated that 3APNI and 4APNI have a polar character in the ground state due to the conjugation between the electron donating amino part and the electron accepting imide moiety.

To gain an insight into the excited state electronic properties of **APNIs**, the electronic transitions were analysed by theoretical calculations by using time-dependent density-functional theory (TD–DFT)⁴⁶ at the TD-PBE0/6-311+G(d,p) level. The ground-state geometries optimized at the PBE0/6-311+G(d,p) level were used for the TD-DFT calculations. The solvent effects of toluene were studied by using a polarizable continuum model⁴⁷ to compare the calculated transitions with the experimental spectra. The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), calculated transition wavelengths (λ_{TR}) and oscillator strengths (f) are listed in Table 3. The HOMO and LUMO images of **APNIs** are illustrated in Fig. 4. The calculated electronic transition wavelengths and the oscillator Photochemical & Photobiological Sciences



Fig. 3 Electronic absorption spectra of **2APNI** (a), **3APNI** (b) and **4APNI** (c) in various solvents. The vertical bars display the calculated wavelengths and oscillator strengths for the electronic transition of **ANPIs** in toluene.

strengths of **ANPIs** in toluene are denoted with vertical bars in Fig. 3.

The calculated electronic transitions for APNIs well reproduced the experimental absorption bands although the calculated transition energies for 2APNI were slightly overestimated. The electronic transitions were also calculated at the TD-B3LYP/6-31+G(d,p) level and the results were similar to those obtained at the TD-PBE0/6-311+G(d,p) level (Fig. S3 in the ESI[†]). The $S_0 \rightarrow S_1$ transition of the three APNI isomers solely consists of a HOMO \rightarrow LUMO transition. Both the HOMO and LUMO of 2APNI were distributed over the naphthalimide π system and the amino moiety. As expected from its ground-state geometry ($\varphi = 0.3^\circ$, Table 1), the amino functionality appreciably conjugates with the naphthalimide moiety. The HOMO \rightarrow LUMO transition of 2APNI is, thus, assigned to a π , π^* transition. In the case of **3APNI**, the HOMO and LUMO were located on the aminonaphthalene and 1,8naphthalimide moieties, respectively. Thus, the nature of the S_1 state of **3APNI** is of an ICT. For **4APNI**, as the amino group effectively conjugates with the naphthalimide part in the ground state, the HOMO and LUMO extend over the entire

Table 2 Photophysical parameters of APNIs

Compound	Solvent	$\lambda_{\max}^{Abs a} (nm) (\log \varepsilon)$	$\lambda_{\max}^{Fa}(nm)$	Stokes shift (cm ⁻¹)	${\Phi_{ m F}}^b$	$\Phi_{ m NR}{}^c$	$\tau_{\mathrm{F}}\left(\mathrm{ns}\right)$	$k_{\rm F}^{\ \ d} \left(10^7 \ {\rm s}^{-1} \right)$	$k_{\rm NR}^{e} (1$
2APNI	Hexane	405 (— ^g)	420	880	f	f	f	f	f
	Toluene	414 (4.05)	433	1060	0.27	0.73	1.71	15.8	42.7
	CH_2Cl_2	413 (4.05)	427	790	0.25	0.75	g	g	g
	AcOEt	414 (4.05)	432	1000	0.20	0.80	g	g	g
	MeCN	413 (4.05)	435	1220	0.26	0.74	1.74	14.9	42.5
	DMSO	420 (4.11)	445	1340	0.30	0.70	g	g	g
	Methanol	418 (4.10)	442	1290	0.23	0.77	1.86	12.4	41.4
3APNI	Hexane	394 (— ^g)	429	2070	f	f	f	f	f
	Toluene	407 (3.69)	464	3020	0.72	0.28	11.7	6.2	2.4
	CH_2Cl_2	408 (3.71)	475	3460	0.73	0.27	g	g	g
AcC Mee DM	AcOEt	418 (3.43)	495	3720	0.53	0.47	g	g	g
	MeCN	417 (3.68)	510	4370	0.49	0.51	17.7	2.8	2.9
	DMSO	438 (3.70)	543	4410	0.68	0.32	g	g	g
	Methanol	425 (3.48)	564	5800	0.23	0.77	12.4	1.9	6.2
4APNI	Hexane	389 (— ^g)	460	3970	f	f	f	f	f
	Toluene	400 (4.09)	482	4250	0.98	0.02	8.7	11.2	0.2
	CH_2Cl_2	405 (4.09)	492	4370	0.94	0.06	g	g	g
	AcOEt	414 (4.04)	500	4150	0.70	0.30	g	g	g
	MeCN	416 (4.05)	517	4700	0.58	0.42	10.1	5.7	4.2
	DMSO	437 (4.07)	532	4090	0.72	0.28	g	g	g
	Methanol	433 (4.11)	538	4510	0.39	0.61	7.3	5.4	8.4

TD-DFT PBE0/6-311+G(d,p) level in toluene

Compound	HOMO (eV)	LUMO (eV)	$\lambda_{\mathrm{TR}}^{a}$ (nm)	ſ ^b	Configuration
2APNI 3APNI 4APNI	-6.32 -6.28 -6.25	-2.25 -2.52 -2.40	368 403 392	$0.2542 \\ 0.1452 \\ 0.2982$	$\begin{array}{l} \text{HOMO} \rightarrow \text{LUMO} \\ \text{HOMO} \rightarrow \text{LUMO} \\ \text{HOMO} \rightarrow \text{LUMO} \end{array}$

^{*a*} Calculated wavelength for the $S_0 \rightarrow S_1$ transition. ^{*b*} Calculated oscillator strength.



Fig. 4 Frontier orbital surfaces of APNIs.

molecule. The electronic transition of 4APNI is, thus, considered to be a π , π^* from the polarized S₀ state to the polarized S_1 state.

2.4 Fluorescence behaviour of APNIs

The fluorescence spectral features of N-ethyl-3-amino-1,8naphthalimide⁴⁸ and *N*-butyl-4-amino-1,8-naphthalimide⁴⁹ in various solvents have been reported. In the present study, the fluorescence behaviour of APNIs, incorporating the amino functionality at different positions, was systematically investigated to understand the effects of the amino-substitution positions on their fluorescence behaviour. The fluorescence emission spectra of APNIs are illustrated in Fig. 5, and the fluorescence maximum wavelength (λ_{max}^{F}) and the photophysical parameters are presented in Table 2. As the fluorescence excitation spectra were identical to the absorption profiles, the emission bands are unambiguously assigned to APNIs (Fig. S2 in the ESI⁺).

2APNI showed a structured emission band displaying a slight red-shift from 420 nm (in hexane) to 445 nm (in DMSO) upon increasing the solvent polarity ($\Delta \lambda_{\text{max}}^{\text{F}}$ = 25 nm, Fig. 5a and Table 2). The fluorescence quantum yield ($\Phi_{\rm F}$) of 2APNI varied in a narrow range of 0.20-0.30 irrespective of the solvent used. It has been found that the protic medium (MeOH) provided minimal effect on the fluorescence efficiency. These results are interpreted in terms of the intramolecular hydrogen bonding between the amino hydrogen and imide carbonyl oxygen atoms which was predominant over intermolecular hydrogen bonding with MeOH.

3APNI and 4APNI displayed broad fluorescence bands. Upon increasing the solvent polarity, the emission maximum of 3APNI appreciably red-shifted showing positive solvatofluorochromism from 429 nm in hexane to 564 nm in methanol $(\Delta \lambda_{\text{max}}^{\text{F}} = 135 \text{ nm}, \text{ Fig. 5b and Table 2})$. Accordingly, the fluo-



Fig. 5 Fluorescence spectra of 2APNI (a), 3APNI (b) and 4APNI (c) in various solvents.

rescence colour changed from blue to orange-red. The emission band of **4APNI** also red-shifted from 460 nm in hexane to 538 nm in methanol ($\Delta \lambda_{max}^{F} = 78$ nm, Fig. 5c and Table 2) displaying a fluorescence colour change from blue in hexane to yellow in methanol. The Lippert–Mataga equation (eqn (1))^{50,51} was adopted to further understand the effects of solvent polarity on the solvatofluorochromism of **APNIs**,

$$\Delta \tilde{\nu} = \tilde{\nu}_{\rm A} - \tilde{\nu}_{\rm F} = \frac{2\Delta\mu^2}{hca_0^3}\Delta f \tag{1}$$

$$\Delta \mu = \mu_{\rm e} - \mu_{\rm g} \tag{2}$$

$$\Delta f = \frac{\varepsilon_{\rm r} - 1}{2\varepsilon_{\rm r} + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{3}$$

where $\Delta \tilde{\nu}$ is the Stokes shift estimated by the experimentally observed difference of peak wavenumbers between the absorption and fluorescence emission spectra, *h* is the Planck constant, *c* is the velocity of light in vacuum (eqn (1)), $\Delta \mu$ is the difference of the dipole moments between the ground (μ_g) and excited (μ_e) states (eqn (2)), a_0 is the Onsager cavity radius,⁵² and Δf is the orientation polarizability of the solvents expressed by the dielectric constant (ε_r) and refractive index (*n*) of the solvents (eqn (3)). The a_0 values of **APNI**s were determined as the half of the mean distance between the amino nitrogen and the two carbonyl oxygen atoms which were estimated from the optimized geometries by theoretical calculations;⁵³ 3.159 Å for **2APNI**, 3.838 Å for **3APNI**, and 3.620 Å for **4APNI**.

The Lippert-Mataga plots for APNIs are displayed in Fig. 6. The plots displayed linear correlations and from the slopes of the lines, the $\Delta \mu$ values were estimated to be 1.7 D for **2APNI**, 5.9 D for **3APNI**, and 2.4 D for **4APNI**. The $\Delta \mu$ value of **4APNI** was similar to that estimated from the reported spectral data of N-butyl-4-amino-1,8-naphthalimide (2.4 D).48 From these results, we conclude the following three points concerning the effects of the amino-substituent positions of APNIs: (i) 2APNI displayed the smallest fluorescence spectral shift upon changing the solvent polarity among the ANPIs studied due to the small dipole moment change ($\Delta \mu = 1.7$ D) which originated from the π , π^* transition with little ICT character. (ii) **3APNI** displayed significant solvent-dependent Stokes shift and solvatofluorochromic shift ($\Delta \lambda_{max}^{F}$ = 135 nm) both of which were caused by a significant ICT property derived from the deviated distributions of the HOMO and LUMO. (iii) Although 4APNI showed appreciable positive solvatofluorochromism $(\Delta \lambda_{\text{max}}^{\text{F}} = 78 \text{ nm})$, the estimated $\Delta \mu$ value (2.4 D) was smaller than that for 3APNI (5.9 D). As both the S_0 and S_1 states possess a significantly polar character, the absorption and fluorescence bands red-shifted in a parallel manner depending on the solvent polarity, resulting in a small change in the Stokes shift compared to the case of 3APNI.

2.5 Photophysical parameters

To investigate in more detail the photophysical properties of **APNIs**, the fluorescence lifetimes ($\tau_{\rm F}$) of **APNIs** were measured in three representative solvents; toluene as a nonpolar aprotic solvent, acetonitrile as a polar aprotic solvent, and methanol as a polar protic solvent. The fluorescence decay profiles are presented in Fig. S5 in the ESI.[†] The quantum yield for non-



Fig. 6 Lippert–Mataga plots for **2APNI** (•), **3APNI** (•) and **4APNI** (•). The point observed for **3APNI** in MeOH was not used for the line fitting because it was obviously affected by the intermolecular hydrogenbonding with MeOH.^{25,30}

radiative processes (Φ_{NR}) and the fluorescence (k_F) and non-radiative (k_{NR}) rates were estimated by eqn (4)–(6), and are summarized in Table 2.

$$\Phi_{\rm NR} = 1 - \Phi_{\rm F} \tag{4}$$

$$k_{\rm F} = \Phi_{\rm F} \tau_{\rm F}^{-1} \tag{5}$$

$$k_{\rm NR} = \Phi_{\rm NR} \tau_{\rm F}^{-1} \tag{6}$$

The obtained $\Phi_{\rm F}$, $k_{\rm F}$, and $k_{\rm NR}$ values were plotted as a function of an empirical solvent-polarity parameter, $E_{\rm T}(30)$, to understand the relationships between these photophysical parameters and the solvent polarity (Fig. 7). The detailed fluorescence properties of the related 3- and 4-aminonaphthalimide derivatives (**3AENI** and **4ABNI**, see Fig. 7d for the molecular structures), in which only alkyl substituents at the imide nitrogen atom were different from those of **APNI**s, have been reported.^{35,48,49} The reported $\Phi_{\rm F}$, $k_{\rm F}$ and $k_{\rm NR}$ values for **3AENI** and **4ABNI** are complementarily plotted with those of **APNI**s in Fig. 7 in order to find trends in the solvent dependencies of the photophysical properties of the amino-substituted 1,8-naphthalimide systems.

It was found that the $\Phi_{\rm F}$, $k_{\rm F}$ and $k_{\rm NR}$ values of **2APNI** were independent of the solvent polarity (Fig. 7a and Table 2), which may be because of the intramolecular hydrogen bonding and effective conjugation between the amino and View Article Online Paper

imide functionalities in the ground state (Fig. 2). We have observed a similar fluorescence behaviour for the related compound 1ANI (see Fig. 1 for the structure) whose spectral features are insensitive to the solvent polarity and intermolecular hydrogen bonding in a protic medium due to efficient intramolecular hydrogen bonding.³⁰ In contrast, the photophysical properties of 3APNI and 4APNI were appreciably affected by the solvent properties. The $\Phi_{\rm F}$ values of **3APNI** and **4APNI** decreased with increasing solvent polarity (Fig. 7b and 7c). This trend may arise from a decrease in the $k_{\rm F}$ values with increasing solvent polarity (Fig. 7b and c). Accordingly, the $k_{\rm NR}$ values were enhanced with increasing solvent polarity. As the S₁ states of 3APNI and 4APNI possess an ICT character, the probability of non-radiative processes, *i.e.* intersystem crossing and/or internal conversion from the fluorescent states, could be increased. That the charge-transfer nature promotes nonradiative processes has been discussed for the deactivation processes of a charge-transfer complex between triplet benzophenone and anisol.⁵⁴ The $k_{\rm NR}$ values of **3APNI** and **4APNI** in MeOH are larger than those in aprotic solvents; indeed, the $k_{\rm NR}$ values of 3APNI and 4APNI respectively increased 2.6- and 42-fold in methanol compared to those observed in toluene. Intermolecular hydrogen bonding between these compounds and the hydroxy functionality of MeOH is considered to accelerate internal conversion from the fluorescent state to the ground state as in the cases of the related amino-substituted



Fig. 7 $\Phi_{\rm F}$ (\bullet), $k_{\rm F}$ (\bullet), and $k_{\rm NR}$ (\bullet) values for **2APNI** (a), **3APNI** (b), and **4APNI** (c) plotted as a function of $E_{\rm T}$ (30). The open circles in (b) and (c) are for the reported values of $\Phi_{\rm F}$ (\bigcirc), $k_{\rm F}$ (\bigcirc), and $k_{\rm NR}$ (\bigcirc) for **3AENI**⁴⁹ and **4ABNI**,⁴⁸ respectively. (d) Molecular structures of **3AENI** and **4ABNI**.

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aromatic imides.^{30,55} Photodegradation can be excluded as a major deactivation process in methanol because **3APNI** and **4APNI** were photochemically stable under the fluorescence measurement conditions (Fig. S4 in the ESI†).

2.6 Solid-state fluorescence of ANPIs

Solid-state fluorescence is gaining increasing interest from the viewpoint of potential application in emitting devices and elucidation of the aggregation-induced control of fluorescence properties. The solid-state fluorescence spectra of APNIs were obtained as displayed in Fig. 8. Their fluorescence maximum wavelengths $[\lambda_{\max}^{F}(\text{solid})]$ and quantum yields $(\Phi_{F}^{\text{Solid}})$ are listed in Table 4. The $\lambda_{max}^{\rm F}({\rm solid})$ values were observed at longer wavelengths compared to the λ_{max}^{F} values in solution (cf. Table 2 and Fig. 4). The difference between the fluorescence maximum wavelengths $(\Delta \lambda_{max}^{F})$ in the solid state and in hexane solution is listed in Table 4. The solid-state fluorescence spectra of APNIs appreciably red-shifted compared to those in hexane; $\Delta \lambda_{\text{max}}^{\text{F}}$ = 121 nm for **2APNI**, 146 nm for **3APNI** and 101 nm for 4APNI. Therefore, the molecules of APNIs are considered to tightly interact with each other in the solid state. The fluorescence quantum yields in the solid state were much smaller than those observed in solution ($\Phi_{\rm F}^{\rm Solid}$, 0.075 for 2APNI, 0.011 for 3APNI and 0.018 for 4APNI). These results suggest that the intermolecular interactions derived from tight molecular



Fig. 8 Solid-state fluorescence spectra of 2APNI (—), 3APNI (—) and 4APNI (—).

 Table 4
 Solid state fluorescence maximum wavelengths and quantum yields of APNIs

Compound	$\lambda_{\max}^{F}(\text{solid})(\text{nm})$	$\Delta\lambda_{\max}^{\mathrm{F}}{}^{a}\left(\mathrm{nm}\right)$	$arPhi_{ m F}^{ m Solid}$	
2APNI	541	121	0.075	
3APNI	575	146	0.011	
4APNI	561	101	0.018	

^{*a*} Difference of fluorescence maximum wavelengths between in solution (hexane) and in the solid state, $\Delta \lambda_{max}^{F} = \lambda_{max}^{F}(\text{solid}) - \lambda_{max}^{F}(\text{in hexane})$.

packing in the solid state are operating to self-quench the fluorescent state **APNI** molecules.²⁵ Currently, as single crystals suitable for X-ray crystallographic analysis were not obtained for **APNI**s, the exact mechanism for the fluorescence quenching is not clear and is under investigation.

3 Summary

The photophysical behaviour of the amino-substituted 1,8naphthalimides APNIs was systematically studied. In particular, the fluorescence behaviour of the 2-amino derivative, 2APNI, was investigated for the first time. Clear contrasts in the fluorescence features were observed among the three APNI derivatives. The absorption and fluorescence spectra of 2APNI were insensitive to the microenvironments of the solvent because of intramolecular hydrogen bonding and effective conjugation between the amino functionality and the imide part in the ground state. 3APNI showed an appreciable solvatochromic shift of the fluorescence, from blue (λ_{max}^{F} = 429 nm) in hexane to orange in MeOH (λ_{max}^{F} = 564 nm) along with polarity-induced enhancement of the Stokes shift. 3APNI serves as a microenvironment-sensing probe as stated previously.³¹ In the case of **4APNI**, both the absorption and fluorescence bands red-shifted depending on the solvent polarity. The $k_{\rm NR}$ values of **3APNI** and **4APNI** increased with increasing solvent polarity presumably because the polar character in the fluorescent state would promote the non-radiative process(es), e.g., intersystem crossing. The fluorescence quantum yields of APNIs were drastically reduced in the solid state compared to those in solution. In the solid state, the fluorescent states of APNIs were effectively quenched presumably by intermolecular interactions. The present results demonstrate the effects of the amino-substitution position on the photophysical features of amino-substituted ICT fluorophores and would provide a hint to designing a future environment-responding luminescent probe.

Conflicts of interest

There are no conflicts to declare.

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