Tetraphenylethynyl-Modified 1,8-Naphthalimide Dye with Efficient Aggregation-Enhanced Emission, Solvatochromism and Intramolecular Charge Transfer Characteristics

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Abstract. 1,8-naphthalimide (NI) dyes are one class of important organic luminophores with good photo-stability, high fluorescent quantum yields and broad emission color-tunability, which are widely used in biological and chemical fields. However, they exhibit bad ACQ property, which heavily limits their application in real word. Contrary to ACQ, tetraphenylethene (TPE) is an AIE luminogen. To eliminate the ACQ effect of NI, TPE was used as core and NI chromophores was used as peripheries to obtain a new dye TPEDNI. TPEDNI dye demonstrates typical aggregation-enhanced emission (AEE) characteristic with high fluorescence $\Phi_F$ solid up to 100% in the film state, which is 24 times of that for its THF solution. Besides, TPEDNI exhibits marked solvatochromism, and the emission peak red-shifts from 505 nm in hexane to 610 nm in acetonitrile. TPENI also displays evident intramolecular charge transfer property in THF/water mixtures.

1. Introduction
1,8-Naphthalimide dyes are one class of organic luminophores, which exhibit good photo-stability, high fluorescent quantum yields, and strong solvatochromic properties. The emission color of these dyes can be well tuned from blue to green, yellow and even to red through rational structure design. They can be readily modified with amino-, alkoxy-groups and varieties of functional groups at the N-imide position, or at the aromatic naphthalene moiety[1]. 1,8-Naphthalimides are widely used as fluorescence switcher, fluorescent cell markers in biology, n-type materials in electroluminescent devices and supermolecular moieties in photo-induced electron transfer (PET) system for sensing ions chemical sensors or biomolecules, anticancer and DNA-cleaving agents[2,3]. However, NI dyes display bad aggregation-caused emission quenching (ACQ) property[4]. They emit strongly in dilute solution, but in aggregate or in solid state, they become faintly emissive or even non-emissive because of aggregation between the planar chromophores. Like other planar aromatics, their rigid and planar chemical structure result in the formation of π-aggregates or excimers. The ACQ effect is very tough when they are used in bio-imaging and organic light emitting diodes (OLEDs) fields, owing to intrinsic aggregation under these conditions.

Contrary to the ACQ effect, Tang and colleagues found that a series of silole derivates and tetraphenylethene (TPE) derivates are not emissive in dilute solutions but become strongly emissive in aggregate and solid state. These compounds demonstrate aggregation-induced emission (AIE)[5] feature. Thanks to this unique property of AIE materials, they have been broadly applied in the high-tech field of optoelectronic devices, chemical sensors and biomedical probes and imaging. TPE
derivatives are very popular, which are easy to be synthesized and modified. It has been found that using TPE modified traditional fluorogens such as naphthalene, carbazole, perylene bisimides (PBI) and pyrene can turn these dyes into AIE-active emitters[5].

However, the TPE modified naphthalimide in the reported paper show low fluorescence quantum yields, which is 20.4% in H₂O/THF mixture with 90 vol% H₂O, which is 2.87 times of the Φ for its THF solution[6]. Here, TPE is used as core and two NI chromophores are used as peripheries, with hexyl as alkyl side chain at N atom, obtaining a new dye TPEDNI. TPEDNI show high fluorescence quantum yields, which is 40.3% in 90 vol% H₂O/THF mixture, which is which is 9.8 times higher than that in pure THF. Besides, TPEDNI shows typical aggregation-enhanced emission (AEE) activity, pronounced solvatochromism effect, and evident ICT property.

2. Experimental

2.1. Chemicals and materials
All the reagents here were supported by Aladdin, unless particularly illustrated. THF was purified and dried by using sodium as desiccant and benzophenone as chromogenic agent under 80°C and nitrogen.

2.2. Instrumentations
1H and 13C NMR data were tested on a Bruker AV 400 instrument. UV data were tested on a Milton Roy Spectronic 3000 Array instrument. Fluorescence data were tested on a Perkin-Elmer LS 55 instrument. ΦF were evaluated when quinine sulfate in 0.1 N H₂SO₄ (ΦF = 54%) was used as standard. The absorbance was remained between 0.04 and 0.06, which can keep away from the internal filter influence. Elemental analysis data were measured on a ThermoFinnigan Flash EA1112.

2.3. Synthesis

The synthetic routes to TPEDNI are displayed in Figure 1. The compounds 2, 4 and 6 were synthesized according to the reported literature[6]. Briefly, McMurry coupling of 4-bromo-benzophenone (1) in the presence of TiCl₄ and Zn powder in tetrahydrofuran (THF) afford 2, which then reacted with 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxa borolane (3) by metathesis of the bromine using n-BuLi in THF to yield 4. The imidization of 4-bromo-1,8-naphthalene dicarboxylic anhydride (5) with n-hexylamine in 2-methoxyethanol to yield 6. Suzuki coupling 4 with 6 catalyzed by Pd(PPh₃)₄ in basic media gave rise to TPEDNI in a yield of 76%.

The synthetic steps of TPEDNI are as follows. In a 250 mL two-necked flask, compound 6 (0.6g, 1.3mmol), 4 (0.64g, 1.1mmol), and Pd(PPh₃)₄ (144 mg) were added. The flask was first evacuated and then flushed with nitrogen, repeating three times. Then, THF (80 mL) and 2 M Na₂CO₃ (8mL) were added into the flask by syringe. The mixture were refluxed for 48 h. After cooled to 25°C, the mixture were poured into 80 mL H₂O and extracted with DCM. The DCM layer was dried by using anhydrous magnesium sulfate. After DCM was evaporated, the solid was purified by a silica gel column using ether/ethyl acetate (30:1 by volume) as eluent. A yellow solid was obtained in 84.5% yield (0.98 g). ¹H
NMR (400MHz, CDCl₃, δ): 8.61-8.63 (m, 4H), 8.18-8.20 (m, 2H), 7.66-7.71 (m, 4H), 7.18-7.32 (m, 18H), 4.17-4.21 (m, 4H), 1.72-1.76 (m, 4H), 1.25-1.44 (m, 12H), 0.86-0.89 (m, 6H); Anal. Calcd for C₆₂H₅₄N₂O₄: C 83.57, H 6.11, N 3.14; found: C 83.62, H 6.10, N 3.15.

3. Results and discussion

3.1 AEE and ICT

Figure 2. (A) Emission spectra of TPEDNI in THF/H₂O mixtures. (B) Plots of FL peak location and quantum yield of compound TPEDNI in THF/H₂O mixtures. (C) Images of TPEDNI in THF/H₂O mixtures under UV 365 nm. [TPEDNI] = 10⁻⁵ M.

NI derivatives always emit intense fluorescence in good solvents, while the light become faintly in aggregate or solid state. It has been proven that combination classical fluorogens with TPE moieties can turn these conventional materials into powerful emitters in aggregate or solid state[16-18]. Therefore, the emission behaviors of TPEDNI in THF/water mixtures and in solid state were investigated. When quinine sulfate was used as standard, the fluorescence quantum efficiencies (Φₚ) of TPEDNI in solutions was evaluated. In dilute THF solution, the Φₚ, solut of TPEDNI is 4.1%. While in solid film, the Φₚ, solid boosts up to 100%, indicating an amplification factor (Φₚ, solid/Φₚ, solut) of 24. Therefore, TPEDNI is expected to display aggregation-enhanced emission (AEE) feature. With common method, the fluorescence behaviors of TPEDNI were tested in THF/H₂O solvents. TPEDNI is insoluble in H₂O, so the molecules will aggregate in THF/H₂O solvents when H₂O fraction is high. The spectra and Φₚ, solute values are displayed in Figure 2A and 2B. TPEDNI emits weak green light in pure THF with a maximum at 534 nm. When H₂O is added, the fluorescence intensity decreased strongly due to the increased solvent polarity. When fₜₐₜ = 40%, the Φₚ, solute dropped to 1.9%. And then, with water further added, the FL intensity is further enhanced. This is because that the solvating powers of the mixtures decreased when fₜₐₜ > 40%, so the TPEDNI molecules start to aggregate. With fₜₐₜ = 90%, the Φₚ, solute increased to 40.3%, which is 9.8 times greater than that in pure THF, indicating the AEE property of
TPEDNI. Modification NI by AIE-active TPE successfully changed its emission behavior from ACQ to AIE, creating high efficiency solid emitter.

Combination NI and TPE groups can offer ICT process because that NI group is electron-accepting, while TPE group is electron-accepting. The emission peaks varies in the mixtures with different $f_w$ values. With water added, the emission spectra of TPEDNI red-shifted from 532 to 583 nm until $f_w$ reaches 40%; and then the emission spectra blue-shifted from 583 to 510 nm when $f_w$ varies from 40% to 90% (Figure 2B). Upon excitation by 365 nm UV light, TPEDNI in pure THF emits weak green luminescence (Figure 2C). When water is added, TPEDNI in mixed solutions emit weaker and weaker yellow to orange luminescence with $f_w$ increased. And when $f_w$ is further increased, the solutions of TPEDNI emit stronger and stronger yellowish-green to blue luminescence. It is because that when $f_w \leq 40\%$, the TPEDNI molecules still can dissolve in the mixtures, so with $f_w$ increased, the polarity of the mixture is enhanced, resulting the red-shift of the emission due to ICT process; and with $f_w$ further increased, owing to the mixtures solvating power decreased, the TPEDNI molecules start to aggregate, and then the molecules are wrapped in the nanoaggregates leading to a less polar environment for the luminogens, resulting the blue-shift.

### 3.2 Solvatochromism

![Figure 3](image_url)

**Figure 3.** (A) UV spectra and (B) normalized emission spectra of TPEDNI in different solvents. (C) Light emissions from TPEDNI solutions (10 µm) in (A) hexane, (B) cyclohexane, (C) toluene, (D) chloroform, (E) EA, (F) THF, (G) DCM, (H) DMF and (I) acetonitrile.

TPEDNI can dissolve well in normal organic solvents, which makes us investigate its optical properties easily. The spectroscopic properties of TPEDNI were investigated in different solvents. As shown in Figure 3A, the absorption spectra change little in different solvents. The absorption peaks appear at 363-379 nm (Table 1). In contrast, the fluorescence spectra of TPEDNI varied dramatically in different dissolvants. As shown in Figure 3B, when the dissolvent polarity was increased, from nonpolar dissolvants, for example, hexane, cyclohexane and toluene, to moderately polar dissolvants, for example, chloroform, ethyl acetate, THF and DCM, and to highly polar dissolvants, for example, DMF and acetonitrile, the fluorescence peaks are red-shifted from 505 to 610 nm (Table 1) bit by bit.
The emission colors changed from blue in nonpolar solvents to yellowish green in moderately polar solvents and to orange in highly polar solvents when TPEDNI solutions are excited by a UV 365 nm light (Figure 3C). The quantum efficiencies of TPEDNI in different solvents are estimated against quinine sulfate. As summarized in Table 1, the quantum efficiencies of TPEDNI in solutions are lower compared with that of traditional NI derivatives\[9\], which has no relation to solvent polarity. The reason is that the active rotations of phenyl groups in TPE moiety in TPEDNI molecular, which results in fast nonradiative relaxations and weaker emission. Besides, in highly polar acetonitrile, the emission of TPEDNI is so weak that the $\Phi_F$ for this solution is 1.6%.

### Table 1. Optical features of TPEDNI in various dissolvants$^a$

| solvent  | $\Delta f$ | $\lambda_{ab}$ (nm) | $\lambda_{em}$ (nm) | $\Delta \nu$ (cm$^{-1}$) | $\Phi_F$ (%) |
|----------|------------|----------------------|----------------------|---------------------------|-------------|
| hexane   | 0          | 363                  | 505                  | 8016                      | 4.9         |
| cyclohexane | 0.014     | 370                  | 502                  | 7671                      | 7.0         |
| toluene  | 0.149      | 370                  | 505                  | 7333                      | 2.7         |
| chloroform | 0.194     | 379                  | 542                  | 8007                      | 9.9         |
| EA       | 0.201      | 367                  | 531                  | 8494                      | 3.9         |
| THF      | 0.210      | 371                  | 535                  | 8447                      | 4.1         |
| DCM      | 0.218      | 370                  | 558                  | 9262                      | 9.5         |
| DMF      | 0.275      | 370                  | 602                  | 10534                     | 3.0         |
| acetonitrile | 0.306   | 365                  | 610                  | 11101                     | 1.6         |

$^a$ Abbreviations: $\Delta f$ = solvent polarity parameter, $\Delta \nu$ = Stokes shift.

### 4. Conclusion

In summary, we have successfully synthesized and characterized the new dye TPEDNI by readily available reactions. This dye demonstrates AEE property. The $\Phi_F$ of the TPEDNI solid ($\Phi_F$,$\text{solid} = 100\%$) is 23 times of that of TPEDNI in THF ($\Phi_F$,$\text{solut} = 4.1\%$). Because NI is an electron acceptor and TPE is an electron donor, TPEDNI is sensitive to solvents of varying polarities, with emission color being tuned from blue to orange by changing solvents from non-polar hexane to polar acetonitrile. In THF/water mixtures, TPEDNI exhibits ICT and AEE properties. In THF solution, TPEDNI emits weak green light. When H$_2$O was put into, the emission intensity became weak and the emission peak red shifted due to ICT process. With a large amount of water, TPEDNI start to aggregate, resulting its emission stronger through AEE process.

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