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Invited paper

## Synthesis and aggregation-induced emission enhancement of naphthalimide-rhodamine dye



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## ABSTRACT

A series of naphthalimide-rhodamine dye  $L_{1-4}$  with the different terminal structures were designed and synthesized. The rhodamine was used as bulky rigid substituent of naphthalimide to enhance the AIE property. All the naphthalimide-rhodamine dye exhibited the significant aggregation-induced emission enhancement. The strong fluorescence emissions in solid state were observed with emission peaks ranging from 549 to 608 nm. In high  $f_w$  mixture solution, the fluorescence intensity enhanced with the increase of water content, which can be attributed to two types of aggregation-induced morphology. The AIE dye-doped silica nanoparticles (Si-NPs) were prepared and exhibited good solubility in pure water. In addition, dye  $L_1$  and  $L_2$  exhibited the selective recognition toward  $Hg^{2+}$  ions and were successfully applied to the bioimages in living cells. The intramolecular fluorescence resonance energy transfer mechanism from the naphthalimide moiety to the rhodamine moiety was investigated.

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### 1. Introduction

The unique aggregation-induced emission (AIE) phenomenon discovered by Tang indicated the AIE fluorogen was virtually nonemissive as an isolated molecule, but became highly emissive in the aggregation state [1]. The restriction of intramolecular rotations (RIR) was proposed as the main cause of AIE effect [2,3]. The propeller-shaped molecule was found to be archetypical AIE fluorogen, such as tetraphenylsilole (TPS), tetraphenylethene (TPE), triphenylamine and so on [4–7]. Moreover, several groups (including our group) have reported the naphthalimide derivatives with AIE behavior [8–11].

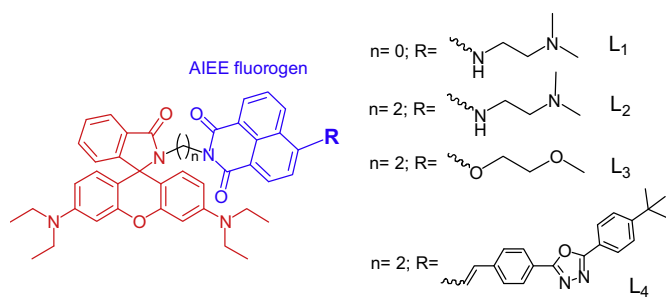
However, a review of previous investigations about AIE naphthalimide derivatives revealed that most derivatives were functionally modified by using bulky substituents and other pendant units in the 4-position of the naphthalimide ring to strengthen the restriction of intramolecular rotations. P. Thilagar [12] synthesized novel naphthalimide-BODIPY dyads and the bichromophoric dyads only differed structurally with respect to methyl substituents on the BODIPY fluorophore. The dyads showed dual emission and aggregation-induced emission switching. But, to the best of our knowledge, the AIE bichromophoric dye based

naphthalimide-rhodamine was barely reported [13]. Considerable attention about naphthalimide-rhodamine chemosensor has been paid to ions recognition based fluorescence resonance energy transfer mechanism [14–19].

Herein, we used rhodamine as bulky rigid substituent of naphthalimide and focussed on developing a series of naphthalimide-rhodamine dye  $L_{1-4}$  with the AIE phenomenon. Hydrazine hydrate or ethylenediamine was selected as the linker for adjusting the space between naphthalimide and rhodamine. The chemical structures were given in Scheme 1. The 4-(*N,N*-dimethylamino) ethylamino-1, 8-naphthalimides was well known PET-probes [20,21]. In this paper, *N,N*-dimethylethylenediamine, 2-methoxyethanol and 2-(4-tertbutyl phenyl)-5-(4-vinyl phenyl)-1,3,4-oxadiazole were respectively selected as the 4-position terminal structures of naphthalimide to regulate spectral properties. The photophysical properties in solid state and in the ethanol/water mixture solution were investigated. The AIE dye-doped Si-NPs were prepared to explore potential applications. In addition, dye  $L_1$  and  $L_2$  exhibited the selective recognition toward  $Hg^{2+}$  ions. The intramolecular fluorescence resonance energy transfer mechanism from the naphthalimide moiety to the rhodamine moiety was investigated by  $Hg^{2+}$ -induced or  $H^+$ -induced. And the naphthalimide-rhodamine dye was successfully applied to the bioimages in living cells.

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**Scheme 1.** The chemical structures of the naphthalimide-rhodamine dye  $L_{1-4}$ .

## 2. Experimental section

### 2.1. Materials and methods

The melting points were measured on the Microscopic Melting Point Meter X-4.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were determined using Bruker DMX 300 MHz spectrometer with TMS (tetramethyl silane) as internal standard. Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. HRMS were performed by a Bruker Ultraflex II MALDI-TOF mass spectrometer. Absorption spectra were recorded by using Shimadzu UV-3600 spectrophotometer and fluorescence spectra were acquired on HORIBA FL-4 Max spectrometer. Cell images were measured on the high resolution confocal microscope Leica TCS-SP8. TEM pictures were measured by the Tecnai G2-20 transmission electron microscope of FEI company (200 kV). Silica gel column chromatography was performed over Merck Silica gel 60. All the chemicals and reagents of analytical-reagent grade were purchased from commercial suppliers and used without further purification.

### 2.2. Synthesis

Compounds  $M_{1-3}$  were synthesized according to the literature recently reported [22–24].

#### 2.2.1. Compound $M_4$

A mixture of compound  $M_1$  (0.76 g, 1.66 mmol) and 4-bromo-1, 8-naphthalic anhydride (0.50 g, 1.80 mmol) in 20 mL glacial acetic acid was refluxed at  $100^\circ\text{C}$  for 12 h. After the reaction, 100 mL purified water was poured into the mixture. Then 1 mol/L NaOH solution is added dropwise to adjust the pH to 8–10. The precipitate was filtered and further purified by silica gel column chromatography (petroleum ether/ethyl acetate=2:1, V/V) to afford 0.89 g violet solid (Yield 74.7%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 8.52 (d,  $J=8.49$  Hz, 1H), 8.33 (d,  $J=7.05$  Hz, 1H), 8.09–8.11 (m, 2H), 7.93 (d,  $J=7.83$  Hz, 1H), 7.62–7.75 (m, 3H), 7.40 (d,  $J=7.11$  Hz, 1H), 6.79 (d,  $J=8.67$  Hz, 2H), 6.44 (d,  $J=8.31$  Hz, 2H), 6.13 (s, 2H), 3.25–3.40 (q,  $J=7.41$  Hz, 8H), 1.13 (t,  $J_1=5.94$  Hz,  $J_2=6.09$  Hz, 12H).

#### 2.2.2. Compound $L_1$

Compound  $M_4$  (0.50 g, 0.67 mmol) were dissolved in 10 mL *N,N*-dimethylethylenediamine under the nitrogen atmosphere. The reaction mixture was refluxed at  $100^\circ\text{C}$  for 24 h. A brown precipitate appeared after 100 mL purified water was poured into the mixture. The precipitate was filtered and further purified by silica gel column chromatography (dichloromethane as eluent) to afford yellow solid (Yield 81.2%). m.p.:  $298\text{--}299^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 8.33 (d,  $J=7.26$  Hz, 1H), 8.12 (d,  $J=6.84$  Hz, 1H), 7.90 (d,  $J=7.59$  Hz, 2H), 7.67–7.77 (m, 2H), 7.45 (d,  $J=7.11$  Hz, 1H), 6.73 (t,  $J_1=7.80$  Hz,  $J_2=7.53$  Hz, 3H), 6.35–6.42

(m, 3H), 6.13 (d,  $J=9.48$  Hz, 2H), 3.50–3.56 (m, 2H), 3.23–3.40 (m, 8H), 3.11–3.14 (m, 2H), 2.66 (s, 6H), 1.13 (t,  $J_1=J_2=6.48$  Hz, 12H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 163.83, 160.90, 153.97, 150.49, 149.26, 148.40, 133.70, 132.57, 130.45, 130.30, 128.79, 128.03, 126.43, 124.31, 123.87, 122.91, 121.91, 121.45, 119.83, 115.01, 114.10, 103.39, 97.12, 56.32, 44.36, 43.81, 39.88, 30.37, 29.20, 12.01; MS ( $m/z$ ): calcd. for  $\text{C}_{44}\text{H}_{47}\text{N}_6\text{O}_4^+$  723.4, found 723.4 ( $\text{M}+\text{H}^+$ ).

#### 2.2.3. Compound $M_5$

A mixture of compound  $M_2$  (2.66 g, 5.49 mmol) and 4-bromo-1, 8-naphthalic anhydride (1.67 g, 6.03 mmol) in 50 mL ethanol solution was stirred and refluxed for 12 h. After the removal of ethanol solvent, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate=3:2, V/V) to give 3.47 g yellow solid (Yield 85.0%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 8.44 (dd,  $J_1=7.53$  Hz,  $J_2=9.90$  Hz, 2H), 8.22 (d,  $J=7.83$  Hz, 1H), 7.84–7.91 (m, 2H), 7.71 (t,  $J_1=7.83$  Hz,  $J_2=7.95$  Hz, 1H), 7.30–7.37 (m, 2H), 6.91–6.93 (m, 1H), 6.34 (d,  $J=8.76$  Hz, 2H), 6.19 (s, 2H), 5.80 (d,  $J=7.38$  Hz, 2H), 4.24 (t,  $J_1=J_2=5.19$  Hz, 2H), 3.43 (t,  $J_1=5.43$  Hz,  $J_2=5.40$  Hz, 2H), 3.00–3.08 (q,  $J=7.21$  Hz, 8H), 1.00 (t,  $J_1=J_2=6.96$  Hz, 12H).

#### 2.2.4. Compound $L_2$

Compound  $L_2$  was synthesized according the similar synthetic procedure of  $L_1$  using  $M_5$  instead of  $M_4$ . A yellowish brown precipitate was purified further by silica gel column chromatography (dichloromethane as eluent) to afford 0.35 g yellow solid (Yield 69.3%). m.p.:  $142\text{--}143^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 8.48 (d,  $J=7.20$  Hz, 1H), 8.35 (d,  $J=8.28$  Hz, 1H), 8.22 (d,  $J=8.22$  Hz, 1H), 7.90–7.93 (m, 1H), 7.56 (t,  $J_1=7.71$  Hz,  $J_2=7.98$  Hz, 1H), 7.37–7.44 (m, 2H), 7.02–7.05 (m, 1H), 6.61 (d,  $J=8.43$  Hz, 1H), 6.49 (d,  $J=8.85$  Hz, 2H), 6.35 (d,  $J=2.28$  Hz, 2H), 6.02 (dd,  $J_1=8.88$  Hz,  $J_2=2.34$  Hz, 2H), 4.19 (t,  $J_1=6.06$  Hz,  $J_2=6.09$  Hz, 2H), 3.52 (t,  $J_1=6.00$  Hz,  $J_2=6.09$  Hz, 2H), 3.44 (s, 2H), 3.19 (q,  $J=7.02$  Hz, 8H), 2.88 (s, 2H), 2.46 (s, 6H), 1.10 (t,  $J_1=J_2=6.99$  Hz, 12H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 168.07, 163.44, 153.31, 152.88, 148.67, 147.97, 133.54, 131.58, 130.95, 130.29, 129.31, 128.35, 127.25, 125.62, 124.02, 123.27, 122.81, 122.37, 119.93, 110.28, 107.43, 105.32, 103.64, 97.36, 64.70, 56.46, 44.36, 43.68, 39.54, 38.73, 38.26, 29.18, 12.15; HRMS ( $m/z$ ): calcd. for  $\text{C}_{46}\text{H}_{51}\text{N}_6\text{O}_4^+$  751.3966, found 751.39668 ( $\text{M}+\text{H}^+$ ).

#### 2.2.5. Compound $L_3$

The same synthesis method was adopted for the preparation of dye  $L_3$  by using 2-methoxyethanol. A yellowish solid was afforded by silica gel column chromatography (petroleum ether/ethyl acetate=1:1, V/V). Yield: 62.7%; m. p.  $234\text{--}235^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 8.43 (dd,  $J_1=8.37$  Hz,  $J_2=13.77$  Hz, 2H), 8.36 (d,  $J=8.22$  Hz, 1H), 7.85 (t,  $J_1=2.19$  Hz,  $J_2=5.82$  Hz, 1H), 7.55 (t,  $J_1=7.89$  Hz,  $J_2=7.74$  Hz, 1H), 7.32–7.36 (m, 2H), 6.89–6.95 (m, 2H), 6.39 (d,  $J=8.82$  Hz, 2H), 6.26 (s, 2H), 5.91 (d,  $J=7.05$  Hz, 2H), 4.32 (t,  $J_1=4.17$  Hz,  $J_2=4.44$  Hz, 2H), 4.14 (t,  $J_1=5.79$  Hz,  $J_2=5.73$  Hz, 2H), 3.85 (t,  $J_1=4.47$  Hz,  $J_2=4.17$  Hz, 2H), 3.41–3.44 (m, 5H), 3.05–3.12 (m, 8H), 1.01 (t,  $J_1=6.87$  Hz,  $J_2=6.96$  Hz, 12H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 168.16 163.78 163.17 159.06 153.19 152.19 147.92 132.32 131.60 131.01 130.70 128.99 128.35 127.70 127.29 125.21 123.28 122.93 122.40 122.28 115.21 107.40 105.31 105.20 97.30 76.96 76.53 76.11 70.20 67.81 64.70 58.84 43.66 38.78 12.13; HRMS ( $m/z$ ): calcd. for  $\text{C}_{45}\text{H}_{47}\text{N}_4\text{O}_6^+$  739.3490, found 739.34898 ( $\text{M}+\text{H}^+$ ).

#### 2.2.6. Compound $M_6$

Under the nitrogen atmosphere, a mixture of compound  $M_3$  (2.52 g, 8.28 mmol), 4-bromo-1, 8-naphthalic anhydride (2.02 g, 7.29 mmol), tri(*o*-tolyl)Phosphine (48.1 mg, 0.158 mmol),  $\text{Pd}(\text{OAc})_2$  (18.0 mg, 0.0802 mmol),  $\text{K}_3\text{PO}_4$  (1.96 g, 9.25 mmol) in 20 mL *N,N*-dimethylformamide was refluxed for 24 h at  $125^\circ\text{C}$ . After cooled to room temperature, 100 mL methanol was added to the

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