

Salicylaldehyde Azines as Fluorophores of Aggregation-Induced Emission Enhancement Characteristics

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A series of salicylaldehyde azine derivatives were found to exhibit interesting aggregation-induced emission enhancement (AIEE) characteristics. In good solvent, all these compounds displayed very weak fluorescence, while strong emission was observed when they were placed in poor solvent. Moreover, the AIEE color of these compounds varied from green to red depending on the substituents on azines. Their in situ formation also promises potential applications in fluorescence sensing of hydrazine.

Organic dyes that exhibit strong fluorescent emission in their aggregate or solid state have attracted increasing attention in recent years.¹ These fluorophores of aggregation-induced emis-

sion enhancement (AIEE)² characteristics not only promise great potential applications in optical sensors, light emitting diodes, photovoltaic cells, and photoemitters, but also challenge the current knowledge of the photoluminescence process and may help us extend our understanding on fluorescence mechanisms. However, most organic fluorescent dyes show fluorescence quenching in their aggregate or solid states owing to the formation of delocalized excitons or excimers, which may cause enhanced nonradiative deactivation of the excited state.³ Only a limited number of organic compounds have been reported to display AIEE characteristics, such as siloles,^{2c,d,4} 1-cyano-*trans*-1,2-bis(4'-methylbiphenyl)ethylene (CN-MBE),^{2b,5} thienylazulene,⁶ arylethene derivatives,⁷ *cis*-2,5-diphenyl-1,4-distyrylbenzene, and 1,4-di[(*E*)-2-phenyl-1-propenyl]benzene (PPB).⁸ Therefore, exploration in new AIEE fluorophores is still of great interest.

A design principle of AIEE molecules in published articles was the connection of two or more conjugated/aromatic moieties by rotatable C–C single bonds.^{2,4–8} Fluorophores of this type exhibit free intramolecular rotation in the single molecule state, but the rotation is inhibited in the aggregated state. Because intramolecular rotation could be an effective mechanism for fluorescence quenching,³ such fluorophores generally show AIEE characteristics. However, although it is quite simple in molecular design, the synthesis of these potential AIEE compounds is often complicated.

In this paper, a series of facilely synthesized salicylaldehyde azine derivatives⁹ were found to exhibit AIEE characteristics (Scheme 1). They are different in molecular design compared to most reported AIEE fluorophores: (1) two salicylaldehyde moieties are connected by rotatable N–N single bond rather than C–C bond and (2) intramolecular hydrogen bonds therein ensure intramolecular rotation allowed only for the N–N bond. More interestingly, the AIEE color is dependent on the substituents of these azine derivatives (from green ($\lambda_{\max} = 513$ nm) to red ($\lambda_{\max} = 570$ nm)). As one can monitor the color of AIEE fluorescence simply by varying a single chemical substitution, this research may help in developing multicolor AIEE dyes. In aqueous solution containing 4% acetic acid, in

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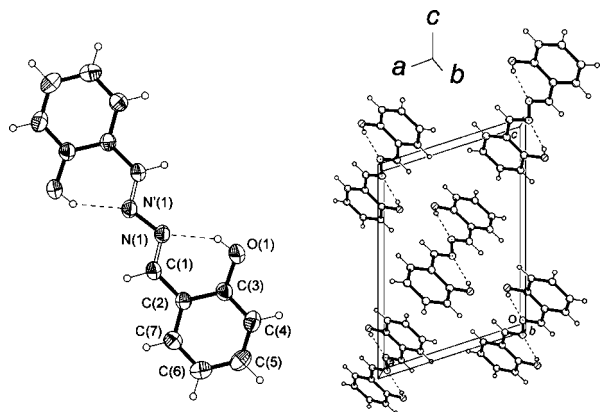
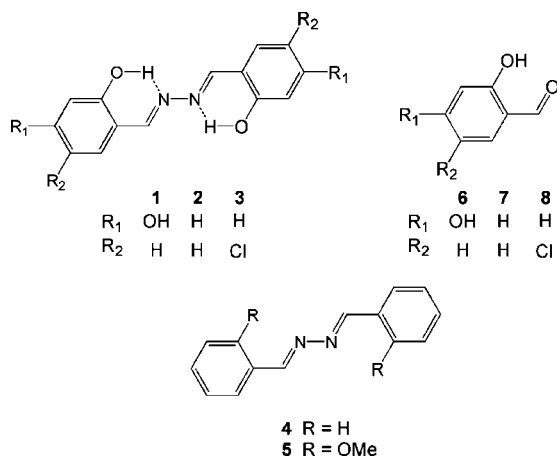


FIGURE 1. Crystal structure of compound **2**. Left: ORTEP drawing with 35% probability ellipsoids. Right: A packing view along the *b* direction.

SCHEME 1. Chemical Structures of Compounds 1–8



situ formation of these AIEE schiff bases is also successfully applied in the sensing of lower ppm levels of hydrazine,¹⁰ which is an energetic and hazardous compound.

Compounds **1–5** were synthesized by very simple procedures of condensing corresponding salicylaldehyde derivatives and hydrazine hydrate in ethanol or ethanol/dichloromethane. They were characterized by NMR, ESI-MS, and elemental analysis. The crystal structure of **2** is shown in Figure 1. Intramolecular hydrogen bonds of salicylaldehyde moieties and stacking of molecules could be clearly observed as expected, suggesting its potential as an AIEE fluorophore by inhibition of free intramolecular rotation when changed from solution to aggregate state.

The AIEE characteristics of **1–3** are investigated in ethanol/water (from 9:1 to 1:9, v/v) buffered by 10 mM HEPES at pH 7.0 and shown in Figure 2. In a good solvent of 9:1 ethanol/water, **1–3** were well dispersed and displayed structured absorption spectra and weak fluorescence emission of their “solution” state. However, when they were in a poor solvent of 1:9 ethanol/water, level-off tails in the visible region of their absorption spectra (commonly observed in nanoaggregates suspensions¹¹) clearly suggested the formation of “aggregate”

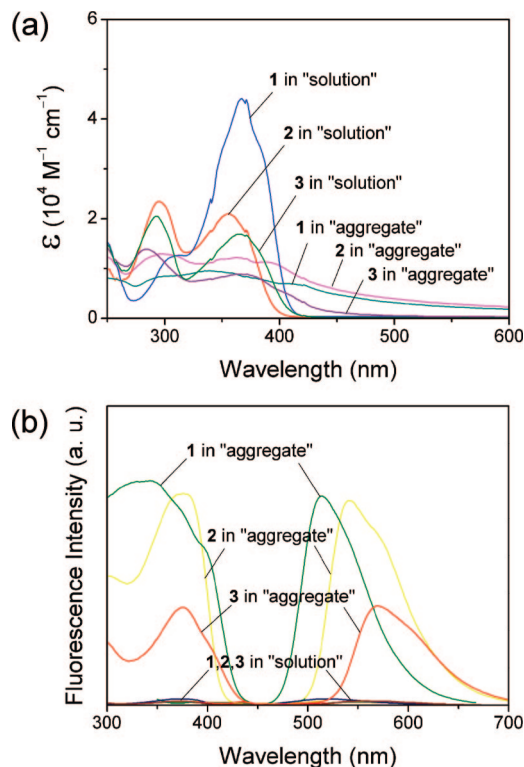


FIGURE 2. Absorption (a) and fluorescence excitation/emission spectra (b) of **1–3** (10 μ M) in “solution” (ethanol/water, 9:1, v/v) and “aggregate” (ethanol/water, 1:9, v/v) states.

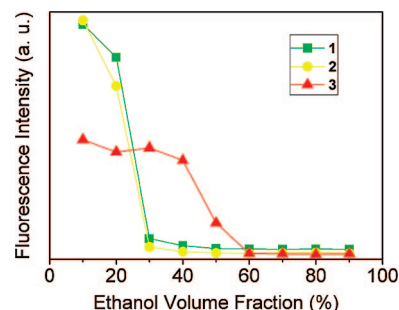


FIGURE 3. Effect of ethanol volume fraction on the AIEE fluorescence intensity (peaks in fluorescence spectra) of **1–3** (10 μ M) in ethanol/water containing 10 mM HEPES at pH 7.0. Excitation was performed at 400 nm.

state, and strong fluorescence emission was observed consequently. This AIEE effect could be explained by the blocking of the nonradiative intramolecular rotation decay of excited molecules through formation of J- or H-aggregates.^{2b,12} The explanation is supported by the fluorescence enhancement of **1–3** as the viscosity of solvent (glycol/glycerin) increased (Figure S1 in the Supporting Information), because high viscosity would inhibit intramolecular rotation and induce the AIEE effect. The quantum yields¹³ of **1–3** in their solution and aggregate states were determined as 0.002, 0.002, 0.001, 0.13 ($\tau = 3.09$ ns), 0.11 ($\tau = 3.05$ ns), and 0.05 ($\tau = 2.32$ ns), respectively. As illustrated in Figure 3, the AIEE effect occurs at 30% volume fraction of ethanol for **1** and **2**, and 60% for **3**.

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(13) Calculated by using quinine sulfate in 0.1 M H_2SO_4 (excitation at 366 nm) as a standard ($\Phi = 0.55$) for solution. For solid, an integral sphere was applied with $BaSO_4$ white plates as a standard ($\Phi = 1.0$).

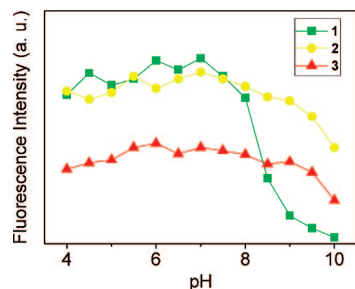


FIGURE 4. Effect of pH on the fluorescence intensity (peaks in fluorescence spectra) of **1–3** (10 μ M) in ethanol/water 1:9 (v/v) containing 10 mM HEPES at various pH. Excitation was performed at 400 nm.

Lower ethanol volume fraction was found to enhance the AIEE effect of **1–3**, which was in agreement with the fact that more aggregates should form in poorer solvents. Besides absorption/fluorescence spectra, the formation of fluorescent aggregates of **1–3** in poor solvent are also supported by the results of dynamic light scattering (DLS, Figure S2(a) in the Supporting Information), solid state fluorescence (Figure S3 in the Supporting Information), and SEM (Figure S4 in the Supporting Information): (1) no particle (>5 nm) could be observed for **2** in 30% ethanol (nonfluorescent), while particles of micro- or submicrometer sizes were detected when volume fraction of ethanol was decreased to 20% or 10% (fluorescent); (2) the solid state fluorescence of **1–3** (solids isolated by centrifugation from 100 μ M **1–3** in ethanol/water (1:9, v/v) buffered by 10 mM HEPES at pH 7.0) correlated well with their AIEE aggregate fluorescence in poor solvent; and (3) SEM images of the solids obtained in (2) also suggested the formation of particles with similar sizes revealed by DLS results.

The substituents of these aromatic azines play important roles in both the availability and emission color of AIEE. Although **1–3** showed the AIEE effect when dispersed in poor solvent compared to good solvent, no fluorescence or AIEE effect could be observed for benzaldehyde azine (**4**) or 2-methoxybenzaldehyde azine (**5**) whether in 9:1 or 1:9 ethanol/water. Absorption spectra of **4** and **5** showed no level-off tail in the visible region even in 9:1 to 1:99 ethanol/water, indicating no aggregate state was formed for these two compounds due to their good solubility. More interestingly, when the electron donating OH group is at the 4-position of azine **1**, the color of the AIEE was green ($\lambda_{\max} = 513$ nm), while with Cl substitution at the 5-position of azine **3**, the color shifted to red ($\lambda_{\max} = 570$ nm). Azine **2** without substitution showed a yellow ($\lambda_{\max} = 542$ nm) AIEE effect.

The effect of pH on AIEE fluorescence is investigated for **1–3** in ethanol/water (1:9, v/v) buffered by HEPES at pH 4.0–10.0 (Figure 4). Increasing pH resulted in a slight decrease in the AIEE effect of **2** and **3** but nearly eliminated that of **1** when pH reached 10.0. Actually, according to DLS result (Figure S2(b) in the Supporting Information), no particle (>5 nm) was found for **1** in ethanol/water (1:9, v/v) at pH 10.0, but micrometer-sized particles were detected when pH increased to 7.0. This suggested that **1** might undergo deprotonation at higher pH and negatively charged ions of **1** tended to release from fluorescent aggregates to form weakly fluorescent monomers.

Because the corresponding substituted salicylaldehydes are completely nonfluorescent and exhibit strong reactivity toward hydrazine to form azines of AIEE characteristics, one might apply these aldehydes as chemodosimeters for hydrazine detec-

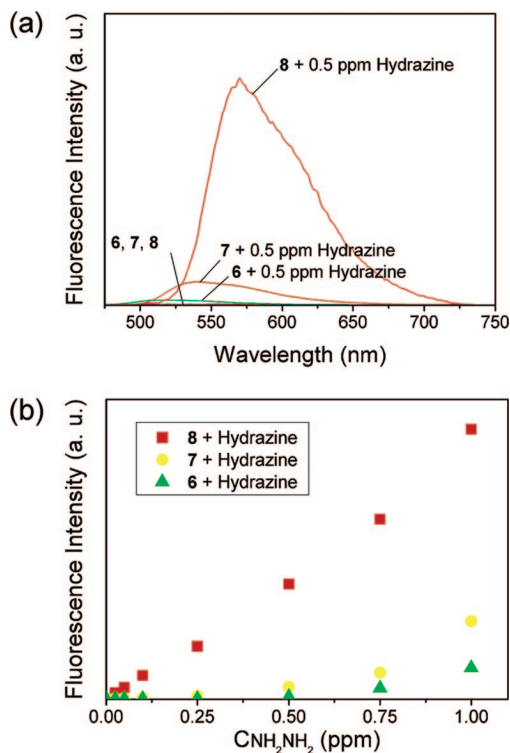


FIGURE 5. Fluorescence spectra (a) and titration curves (intensity of peaks in fluorescence spectra) (b) of **6–8** (2 mM) in the absence and presence of various amounts of hydrazine in water containing 4% (volume fraction) AcOH and 20% ethanol. Excitation was performed at 400 nm.

tion by fluorescence enhancement. As shown in Figure 5, 4-hydroxysalicylaldehyde (**6**), salicylaldehyde (**7**), and 5-chlorosalicylaldehyde (**8**) were utilized to detect hydrazine at lower ppm level in aqueous solution containing 4% AcOH and 20% ethanol, respectively. Among these three candidates, **8** showed the highest sensitivity, as could be seen from the time-dependent fluorescence experiment for reaction kinetics (Figure S5 in the Supporting Information). The high sensitivity of **8** is probably because of the strong reactivity of **8** to hydrazine due to the electron withdrawing effect of 5-chloro substitution. The reaction products of **6–8** with hydrazine were isolated and confirmed by ESI-MS and NMR to be **1–3** as expected, respectively. DLS experiment (Figure S2(c) in the Supporting Information) also revealed that the reaction of **8** and hydrazine yielded some submicrometer-sized particles of **3** in solution, which led to the fluorescence observed. Interestingly, hydroxylamine, 1,2-ethyldiamine, ammonia, methylamine, common metal ions, and anions of various inorganic acids showed nearly no interference to hydrazine sensing by **8**, suggesting its high selectivity.

In conclusion, we described the AIEE fluorescence properties of a series of salicylaldehyde azine derivatives **1–3** in this paper. It is very interesting to note that the AIEE fluorescence color of these azines could be monitored by the substituent on the phenyl ring. This AIEE effect suggests the great potential of sensing hydrazine in water by salicylaldehyde derivatives with high sensitivity and selectivity.

Experimental Section

Synthesis of Compounds 1–5. General Procedure: In a 100 mL flask 7.0 mmol of a certain aldehyde was dissolved in 50 mL of ethanol. Hydrazine hydrate (0.2 g, 3.4 mmol; 85%) was then

added dropwise with vigorous stirring at room temperature. After the addition, the stirred mixture was allowed to stand at room temperature overnight, and the resulting precipitation was filtered and washed by 30 mL of ethanol or ethanol/water (1:1, v/v) 3 times. After drying, azines were obtained in high yields (62–79%). Recrystallization of the products was carried out in DMSO/ethanol (1:1, v/v). If the aldehyde was not easily soluble in ethanol, ethanol/dichloromethane (1:2, v/v) was used as solvent. The addition of NaOH in DMSO-*d*₆ was for a sufficient solubility of each compound in ¹³C NMR measurement.

4-Hydroxysalicylaldehyde Azine (1). **1** was synthesized with 4-hydroxysalicylaldehyde as dark yellow solid (yield 65%). ESI mass spectrometry: *m/z* 271.2 ([M – H][–]); M[–] calcd 272.1. ¹H NMR (DMSO-*d*₆) δ (ppm) 6.34 (d, 2H), 6.41 (dd, 2H), 7.43 (d, 2H), 8.78 (s, 2H), 10.22 (br, 2H), 11.41 (br, 2H). ¹³C NMR (DMSO-*d*₆) δ (ppm) 103.0, 108.7, 110.8, 133.5, 161.2, 162.3, 162.6. Elemental Anal. Found: C 61.5, H 4.56, N 10.1. Calcd for C₁₄H₁₂N₂O₄: C 61.8, H 4.44, N 10.3.

Salicylaldehyde Azine (2). **2** was synthesized with salicylaldehyde as a yellow solid (yield 75%). ESI mass spectrometry: *m/z* 239.3 ([M – H][–]); M[–] calcd 240.1. ¹H NMR (DMSO-*d*₆, 2.5 equiv of NaOH) δ (ppm) 6.08 (dd, 2H), 6.34 (d, 2H), 6.89 (dd, 2H), 7.48 (d, 2H), 8.83 (s, 2H). ¹³C NMR (DMSO-*d*₆, 2.5 equiv of NaOH) δ (ppm) 109.7, 121.8, 122.6, 127.9, 132.0, 159.8, 172.6. Elemental Anal. Found: C 69.6, H 5.17, N 11.5. Calcd for C₁₄H₁₂N₂O₂: C 70.0, H 5.03, N 11.7.

5-Chloro-salicylaldehyde Azine (3). **3** was synthesized with 5-chloro-salicylaldehyde as a yellow solid (yield 79%). ESI mass spectrometry: *m/z* 307.3 ([M – H][–]); M[–] calcd 308.1. ¹H NMR (DMSO-*d*₆, 2.5 equiv of NaOH) δ (ppm) 6.32 (d, 2H), 6.84 (dd,

2H), 7.48 (d, 2H), 8.79 (s, 2H). ¹³C NMR (DMSO-*d*₆, 2.5 equiv of NaOH) δ (ppm) 112.6, 122.6, 124.2, 125.9, 131.5, 158.6, 171.4. Elemental Anal. Found: C 54.1, H 3.41, N 8.89. Calcd for C₁₄H₁₀Cl₂N₂O₂: C 54.4, H 3.26, N 9.06.

Benzoaldehyde Azine (4). **4** was synthesized with benzoaldehyde as a light yellow solid (yield 51%). ESI mass spectrometry: *m/z* 209.4 ([M + H]⁺); M⁺ calcd 208.1. ¹H NMR (CDCl₃) δ (ppm) 7.46 (m, 6H), 7.85 (dd, 4H), 8.68 (s, 2H). ¹³C NMR (CDCl₃) δ (ppm) 128.7, 128.9, 131.3, 134.2, 162.2. Elemental Anal. Found: C 80.2, H 5.96, N 13.1. Calcd for C₁₄H₁₂N₂: C 80.7, H 5.81, N 13.4.

2-Methoxybenzoaldehyde Azine (5). **5** was synthesized with 2-methoxybenzoaldehyde as a light yellow solid (yield 61%). ESI mass spectrometry: *m/z* 269.3 ([M + H]⁺); M⁺ calcd 268.1. ¹H NMR (DMSO-*d*₆) δ (ppm) 3.89 (s, 6H), 7.05 (dd, 2H), 7.15 (d, 2H), 7.51 (dd, 2H), 7.99 (d, 2H), 8.95 (s, 2H). ¹³C NMR (DMSO-*d*₆) δ (ppm) 56.3, 112.5, 121.2, 122.2, 127.1, 133.5, 157.1, 159.3. Elemental Anal. Found: C 71.5, H 6.23, N 10.2. Calcd for C₁₆H₁₆N₂O₂: C 71.6, H 6.01, N 10.4.

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Supporting Information Available: Experimental procedures, characterization data, and additional figures for the compounds described. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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