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# Fluorescence Aggregation-Caused Quenching versus Aggregation-Induced Emission: A Visual Teaching Technology for Undergraduate Chemistry Students

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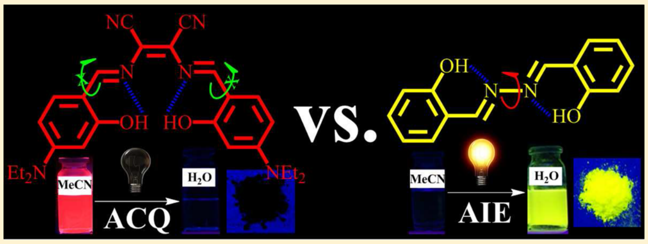
S *Supporting Information*



**ABSTRACT:** A laboratory experiment visually exploring two opposite basic principles of fluorescence of aggregation-caused quenching (ACQ) and aggregation-induced emission (AIE) is demonstrated. The students would prepared two salicylaldehyde-based Schiff bases through a simple one-pot condensation reaction of one equiv of 1,2-diamine with 2 equiv of salicylaldehyde. The resulting fluorescent dyes have similar chemical structures but possess ACQ and AIE properties, respectively. Their ACQ/AIE properties and pH sensing applications would then examined by visually qualitative analysis (UV lamp, light-emitting diode, and naked eye) and quantitative analysis (fluorometer). Finally, in a deeper level, X-ray single crystal structure analysis was utilized to reveal the inherent relationships between molecular structures/molecular arrangements and ACQ/AIE properties. This lesson is suitable for many areas of chemistry, especially for organic and analytical chemistry.

**KEYWORDS:** *Upper-Division Undergraduate, Analytical Chemistry, Organic Chemistry, Fluorescence Spectroscopy, X-ray Crystallography, Hands-On Learning/Manipulatives, Aldehydes/Ketones, pH, Solid State Chemistry, Solutions/Solvents*

## ■ INTRODUCTION

Luminescence (fluorescence or phosphorescence), which is spontaneous light emission coming from excited electronic states after absorption of UV/visible light, has received great attention in many disciplines, such as chemistry, physics, material science, medicine, and biology.[1−4] Among numerous works[2−13] demonstrating the basic principles of fluorescence or phosphorescence in this Journal, the photophysical properties including absorption and emission spectra,[2] luminescence decay lifetime[5] and quantum yield (Φ),[6] emission quenching,[7] and sensing applications[8−11] of organic luminescent materials are generally studied in dilute solution. In these conditions, it is thought that there are no intermolecular interactions between the isolated organic molecules in dilute solution. However, many organic materials in dilute solution exhibit very different photophysical properties compared with in concentrated solution. For example, it is a common phenomenon that luminescence is often weakened or quenched at high concentrations. This "concentration quenching" is mainly caused by the "formation of aggregates", which has frequently been referred to as "aggregation-caused quenching" (ACQ).[14] It should be noted that the ACQ effect is harmful to some practical applications. For example, the preferred work conditions for detection applications are water, but most organic luminescence probes are hydrophobic aromatics and cannot be dissolved in water. Therefore, they are liable to precipitate and aggregate in water, resulting in ACQ effect. Moreover, the ACQ effect might be more harmful and challenging for organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells applications,[15] where the luminophores are in solid state and might have a more severe ACQ effect.

Tang and co-workers recently discovered an exactly opposite phenomenon to the notorious ACQ effect. 1-Methyl-1,2,3,4,5-pentaphenylsilole molecule (Figure 1) had no fluorescence in a

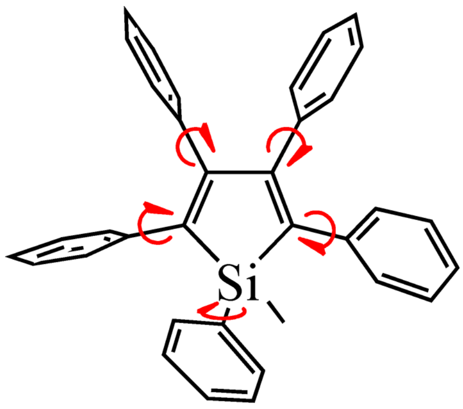


**Figure 1.** Chemical structure of AIE-active 1-methyl-1,2,3,4,5-pentaphenylsilole.

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dilute ethanol solution. In concentrated solutions or solid films, however, its fluorescence became very strong.[16] In dilute organic solution, its five phenyl rotors undergo dynamic intramolecular rotations (IRs), which provides a possible way to nonradiatively annihilate its excited states and results in the absence of luminescence. Nonetheless, in the aggregates, molecules are tightly packed, which would eliminate these IRs. Furthermore, silole molecules cannot pack through face-to-face $\pi-\pi$ interactions due to its propeller shape (Figure 1). This restriction of both IRs and $\pi-\pi$ interactions would help to turn off the nonradiative transitions and turn on the radiative pathways. Thereby, the silole molecules become emissive in the aggregate state. The authors termed the process "aggregation-induced emission" (AIE). After that, the AIE-active materials have been an area of topical interest in a number of research areas, including OLEDs, luminescence probes, and bioimaging.[17,18]

Although a lot of classroom experiments on fluorescence and phosphorescence have been present for decades,[2−13] to the best of our knowledge, none entails the synthesis and study of ACQ/AIE-active fluorophores. This classroom experiment describes a visual teaching lesson, ACQ vs AIE, in which undergraduate chemistry students are exposed to the magnificent world of luminescence. Students would prepare one ACQ-active (**SB1**)[19,20] and one AIE-active (**SB2**)[21,22] Schiff base (Figure 2) by a simple one-pot condensation of diamine with 2 equiv of salicylaldehyde and then try to examine their ACQ/AIE properties and pH sensing applications. Moreover, if students were interested in the inherent relationships between molecular structures/molecular arrangements and ACQ/AIE properties of these two similar Schiff bases, they could obtain more information from the X-ray single crystal structure analyses.

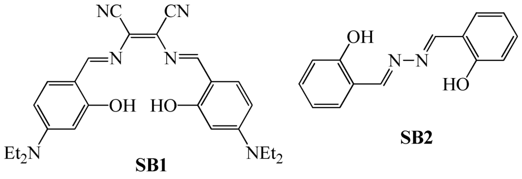

**Figure 2.** Chemical structures of **SB1** and **SB2**.

## ■ EXPERIMENTAL OVERVIEW

This experiment is 1 day (8 h) class. During the experiment, students would prepare, purify, and characterize ACQ/AIE properties of organic dye **SB1** and **SB2**. **SB1** and **SB2** can be synthesized in a straightforward way with high yields (Figure 3). The reactions can be done in air. Water-free and oxygen-free conditions are unnecessary. Purifications can be ready to accomplish by recrystallization and filtration. Students would use fluorescence spectroscopy and hand-held UV light to examine AIE/ACQ phenomenon. The experimental data would be processed by software, such as Microsoft Excel and Origin. Owing to the time limit of class, the parts of pH sensing application and molecular structures/molecular arrangements can be demonstrated by teacher.

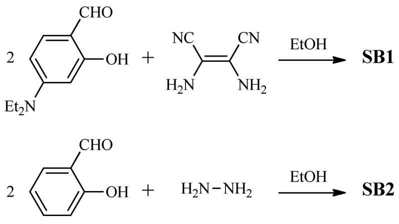

**Figure 3.** General methods for the preparation of **SB1** and **SB2**.

The experiment has been performed by two groups. One is a senior-class organic chemistry group (8 students), the other is a senior-class analytical chemistry group (10 students). For an 8-h 1 day experiment, during the morning, students would finish two reactions within 4 h and then purify the dyes by recrystallization from ethanol in the refrigerator during lunch time. The chemical reactions are very quick and complete. As determined by thin-layer chromatography, the reactions are complete within 1 h with almost 100% yields. During the afternoon, students use approximately half an hour to isolate and dry the dyes by filtration. Then, students examine their ACQ/AIE properties by visually qualitative analysis (UV lamp, LED, and naked eye) and quantitative analysis (fluorometer) within 3 h. In the remainder (half an hour) of the class period, the teacher demonstrates the pH sensing application and molecular structures/molecular arrangements and summarizes the experiment. After the experiment, students process data and write experimental reports. If laboratories are not going to have the opportunity for undergraduates to spend 8 h in 1 day in the laboratory, the experiment can be performed in two half days, just like morning and afternoon portions of the 8-h 1 day experiment.

## ■ EXPERIMENTAL DETAILS

### Materials and Instrumentation

All reagents and organic solvents were purchased from commercial suppliers and used without further purification. UV/visible absorption spectra were recorded using a UV 765 spectrophotometer (Shanghai Precision & Scientific Instrument). Fluorescence spectra were obtained using an F-7000 Fluorescence spectrophotometer (Hitachi). A hand-held UV lamp (360 nm) or UV LED (385 nm) was used as light source to excite fluorescence for visual demonstrations. The synthetic procedures and fluorescence analysis methods of **SB1** and **SB2** were described in the Supporting Information.

### Synthesis of SB1

4-(Diethylamino)salicylaldehyde (2.1 mmol, 0.41 g) was added 100 mL of absolute ethanol of diaminomaleonitrile (1.0 mmol, 0.11 g). After adding one drop of sulfuric acid as a catalyst, the mixture was stirred and refluxed for 2 h to give a dark green precipitate. The precipitate was filtered and then recrystallized from ethanol (∼50 mL) in the refrigerator to give a dark green solid. After suction filtering, ethanol washing (20 mL), and air drying, 0.34 g dark green solid was obtained (74% yield).

### Synthesis of SB2

Absolute ethanol (30 mL) with aqueous hydrazine (5 mmol, 0.25 g) was dropwise added into 20 mL absolute ethanol of salicylaldehyde (10 mmol, 1.22 g) in a period of 1 h. Then, the mixture was refluxed for 2 h to give crude yellow precipitate. The precipitate was filtered and then recrystallized from ethanol (∼50 mL) in refrigerator to give a yellow solid. After suction filtering, ethanol washing (20 mL), and air drying, 0.92 g pale yellow solid was obtained (77% yield).

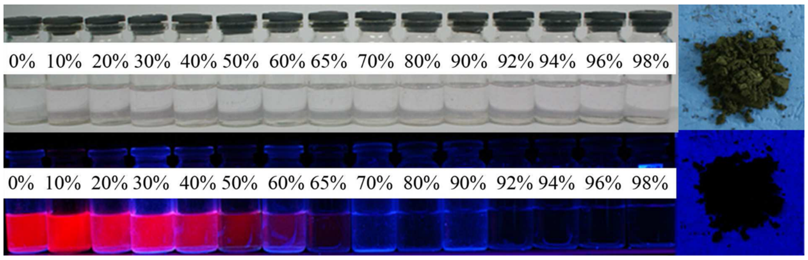

**Figure 4.** Pictures (top, under room light; bottom, under 360 nm UV light) of (left) **SB1** in MeCN/water ($1.0 \times 10^{-6}$ mol/L) with different *f* values and (right) solid **SB1**.

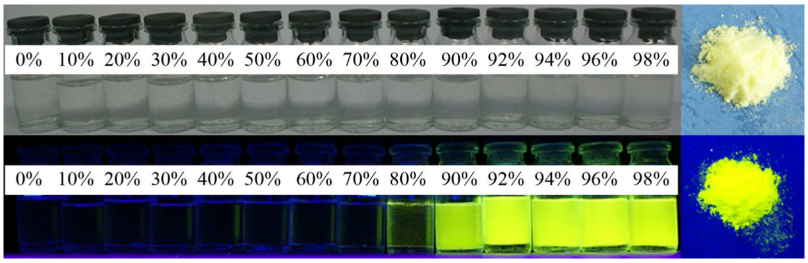

**Figure 5.** Pictures (top, under room light; bottom, under 360 nm UV light) of (left) **SB2** in MeCN/water ($1.0 \times 10^{-5}$ mol/L) with different *f* values and (right) solid **SB2**.

### Fluorescence Analysis

The concentration of **SB1** and **SB2** in MeCN was $1.0 \times 10^{-6}$ and $1.0 \times 10^{-5}$ mol/L, respectively. The aggregated **SB1** and **SB2** in MeCN/water were prepared by adding the high-concentration dye into water (Supporting Information). Fluorescence spectra were obtained using an F-7000 Fluorescence spectrophotometer (Hitachi) at room temperature. Furthermore, a hand-held UV light (360 nm) or LED (385 nm) was used to excite these solution samples for a visual demonstration.

## ■ HAZARDS

For the purpose of safety, students should wear nitrile gloves and goggles at ALL TIMES during the experiment. Chemical reactions should be handled in fume hoods. The dyes might be cancer suspect agents. Caution: Do not directly touch with hand; in case of contact, rinse directly. Because aldehyde and amine are toxic, they touching the skin should be avoided. MeCN and EtOH are flammable. High-energy UV light is harmful to the skin and eyes. Unnecessary exposure of skin and eyes to UV light is not allowed.

## ■ RESULTS AND DISCUSSION

### Synthesis of the ACQ/AIE-Active Dyes

As shown in Figure 3, both **SB1** and **SB2** can be simply and efficiently prepared by a one-pot condensation reaction of 1 equiv of diamine with 2 equiv of salicylaldehyde in ethanol under reflux, according to the previous reports.[19,22] Both **SB1** and **SB2** have good solubility in organic solvents, such as DMSO and MeCN, but they have poor solubility in water or hexane. Both **SB1** and **SB2** are stable in solid and solution for characterization and application.

### Photophysical and ACQ Properties of SB1

The photophysical properties of **SB1** were systematically examined by the previous reports.[19,20,23] The UV/visible absorption and emission spectral data of **SB1** are listed in Table S1 (Supporting Information). As shown in Figure S1, in the dilute solution of MeCN ($1.0 \times 10^{-6}$ mol/L), **SB1** functionalizing a donor−acceptor (DA) systems is liable to produce intramolecular charge transfer from the electron-donating substituent of —$NEt_2$ to the central electron-accepting fragment of —CN, resulting in its low-energy absorption band ($\lambda_{abs}$ = 564 nm) and red emission ($\lambda_{em}$ = 606 nm) with an unexpectedly high $\Phi$ up to 0.80. However, if water is added into the MeCN solution of **SB1**, the fluorescence recedes (Figures 4 and S2), because **SB1** cannot be dissolve in water, which causes **SB1** molecules to precipitate and aggregate. When the volume fraction (*f*) of water is increased to 70%, the fraction of MeCN is too low to dissolve **SB1**, resulting in that most of the **SB1** molecules are in the form of aggregation. Consequently, the aggregation would quenched the fluorescence of **SB1** completely. This ACQ nature of **SB1** in water or solid state even can be visible to a naked eye (Figures 4 and S3).

### Photophysical and AIE Properties of SB2

The photophysical properties of **SB2** were also systematically examined by the previous report.[22] The UV/visible absorption and emission spectral data of **SB2** are listed in Table S1 as well. Contrary to **SB1**, **SB2** in the dilute solution of MeCN ($1.0 \times 10^{-5}$ mol/L) exhibits very weak emission ($\lambda_{em}$ = 509 nm) with an ultralow $\Phi$ of 0.002 (Figure S4). Nonetheless, its fluorescence is strengthened if water is added into MeCN (Figures 5, S5, and S6) due to the formation of aggregation. When *f* of water is increased to 92%, its fluorescence attains the maximum ($\Phi$ = 0.11). The previous work[19] also demonstrated that **SB2** molecules would form nanoparticles (<5 nm) when water was added, which indicates **SB2** molecules are dispersed but not dissolved in water. Unlike **SB1** (Figure 4), **SB2** in solid state emits strong yellow-green emission under 360 nm UV lamp (Figure 5). All of the aforementioned findings confirm that **SB1** and **SB2** own totally opposite ACQ and AIE properties, respectively, in spite of their similar chemical structures.

### Fluorescent pH Sensing Applications of SB1 and SB2

The fluorescent pH sensing applications of **SB1**[20] and **SB2**[22] were reported previously. Because of the time limit of lesson, this part can be demonstrated by teacher. The teacher should emphasize the fact that **SB2** might be better than **SB1** for sensing applications because **SB2** is highly emissive in water due to its nature of AIE, but the ACQ nature of **SB1** would be harmful for the detection in the media of water, and thus, **SB1** must be used in the media of organic solvent. As shown in Figure S7, the emission properties of **SB2** are strongly dependent on pH values. The mixed solvents of MeCN/aqueous Britton−Robinson (B−R) buffer solution (**SB2** $1.0 \times 10^{-5}$ mol/L in MeCN/water, $f$ = 92%) were adopted for fluorescent pH sensing applications. The fluorescence intensity of **SB2** at 536 nm ($I_{536}$) remains unchanged when pH < 8.0, but it weakens when pH values increase from 8.0 to 11.0 and finally remains unchanged again when pH > 11.0, indicating that its p$K_a$ is 9.3. At the same time, $I_{513}$ belonging to the deprotonated **SB2** has a totally adverse pH response (which is zero), increased, and was constant at pHs of <8.0, 8.0−11.0, >11.0, respectively. Moreover, **SB2** provides a perceived color change for rapid visual sensing (Figure 6). It is known that phenol is a weak acid (p$K_a$ = 10).[24] **SB2** (p$K_a$ = 9.3) containing electron-accepting salicylaldimine moiety is more acid than phenol. The electron density of a benzene ring would be decreased by the inductive effect of electron-accepting substituent, which would delocalize the negative charge of phenolic hydroxyl into the benzene ring. And then, the resultant phenolate anion has a better stability to release the proton of phenolic hydroxyl, resulting in the fact that the acidity of **SB2** is bigger than that of phenol.[22]

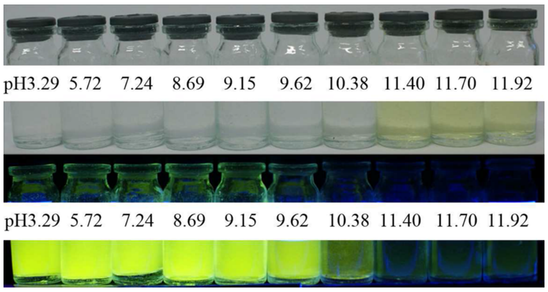

**Figure 6.** Pictures (top, under room light; bottom, under 360 nm UV light) of **SB2** ($1.0 \times 10^{-5}$ mol/L in MeCN/water, $f$ = 92%) in B−R buffer solution at different pH values.

### Molecular Structures/Molecular Arrangements of SB1

Because the molecule structures and arrangements play an important role in ACQ or AIE effect, the X-ray single crystal analysis are carried out by a crystal and molecular structure visualization software, such as Diamond 3.2.[25] The X-ray structures of **SB1**[26] and **SB2**[27] were previously reported and their crystallographic information files (CIF) are available via the Internet. Owing to the time limit of lesson, this part can be demonstrated by teacher as well.

As shown in X-ray single crystal structures of **SB1** (Figure S8), except the carbon and hydrogen atoms in two —$NEt_2$ groups, all other atoms in **SB1** are almost located in one big plane of $\pi$-conjugated system of **SB1**, which provides an efficient way to absorb the excitation energy from UV/visible light. Moreover, the intramolecular hydrogen bonds (1.94 Å) (−OH···N) are observed in **SB1**. These hydrogen bonds would efficiently prevent two phenolic rings from IRs and nonradiative annihilations. Therefore, **SB1** are highly emissive in dilute organic solvent (Figure 7).

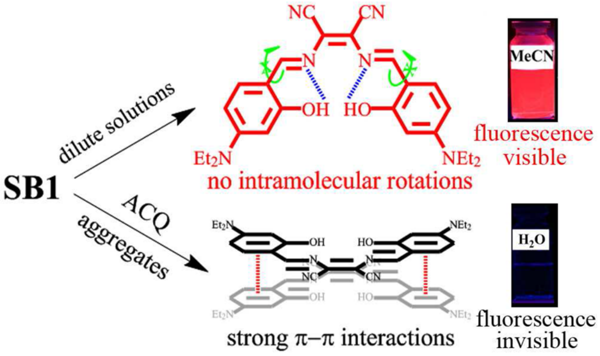

**Figure 7.** Schematic diagram of fluorescence mechanism for **SB1** molecule.

In the aggregates, however, the disc-like **SB1** molecules are face-to-face stacking (Figure S9a) with a very short interplanar distance ($d$) of ~3.05 Å (Figure S9b), resulting in very strong face-to-face $\pi$−$\pi$ interactions between two neighbor **SB1** molecules. These $\pi$−$\pi$ interactions might be expressed directly by the overlaps in two $\pi$-conjugated systems (Figure S9b and S9c) and would facilitate the formation of excimers, which lead to emission quenching and ACQ effect thereby (Figure 7).[18,22] Therefore, if one wants to design luminescent materials for some applications in dilute solution, big $\pi$-conjugated system and less IRs are primary factors to consider.

### Molecular Structures/Molecular Arrangements of SB2

As shown in Figure S10, all atoms in the **SB2** molecule are almost located in one plane of $\pi$-conjugated system of **SB2**. As expected, the similar intramolecular hydrogen bonds (1.90 Å) are also observed in **SB2**, like **SB1**. However, it is obvious that there are still N−N single bond IRs in **SB2** molecules, which would be contributed to the absence of luminescence for **SB2** in the dilute solution of MeCN (Figure 8).

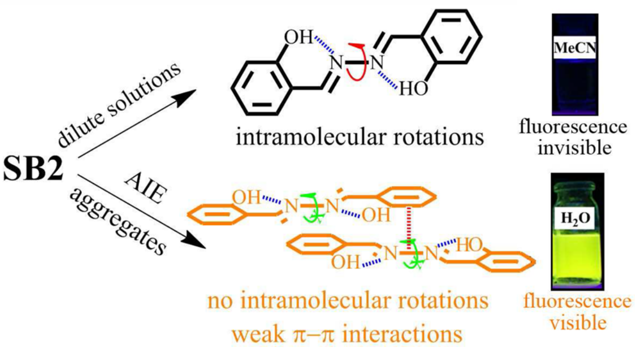

**Figure 8.** Schematic diagram of fluorescence mechanism for **SB2** molecule.

In the aggregates, the cross-stacking (Figure S11a) **SB2** molecules have a short $d$ of ~3.45 Å (Figure S11b). Although this $d$ value is a bit longer than that of **SB1** (~3.05 Å), it is short enough for **SB2** molecules to pack tightly to eliminate N—N single bond IRs and achieve AIE subsequently. Anyway, it is noteworthy that some intermolecular face-to-face $\pi$−$\pi$ interactions between two neighbor **SB2** molecules are still observed (Figure S11b and S11c), but they are much weaker than these of **SB1** molecules (Figure S9b and c). This might be one possible reason for the moderate Φ (0.11) for **SB2**. Therefore, when we design AIE-active materials, we should expect that molecules arrange closely. At the same time, intermolecular face-to-face $\pi-\pi$ interactions should be weak, which means that the overlaps in the $\pi$-conjugated systems of two neighbor molecules had better be small. Close packing and weak $\pi-\pi$ interactions can eliminate IRs and excimer formation, respectively, which are keys for AIE-active materials.[18,22] If one wants to further tune the photophysical properties such as Φ and $\lambda_{em}$, the introduction of different substituents to **SB2** would be a wise choice.[22]

## CONCLUSIONS

Luminescence is one of basic natural phenomena. In general, most organic luminescent materials show luminescence quenching in aggregates due to ACQ, whereas some organic luminescent materials have an exactly opposite effect of AIE. Through this experiment, students would obtain not only training in the preparation, purification, and characterization of samples but also insight into the inherent relationships between molecular structures/molecular arrangements and ACQ/AIE properties. This one-day experiment is suitable for many areas of chemistry, especially for analytical and organic chemistry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00483.

> Absorption and emission spectra, X-ray single crystal structures of **SB1** and **SB2,** materials, experimental procedures, characterization data for the dyes, notes to the instructor, discussion questions, answers to discussion questions, and basic principles of luminescence of organic materials. (PDF)
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>
> **SB1**. (CIF)
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> **SB2**. (CIF)

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### Notes

The authors declare no competing financial interest.

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