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A novel "turn-on" fluorescent chemosensor for the selective detection of Al^{3+} based on aggregation-induced emission[†]

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A water-soluble, 'turn-on' fluorescent chemosensor based on aggregation-induced emission (AIE) has been developed. It exhibits rapid response, excellent selectivity, and sensitivity to Al^{3+} .

Aluminium (Al), as the most abundant metallic element in the earth's crust, was found to be neurotoxic to organisms a long time ago.¹ Al³⁺ has also been linked to Alzheimer's disease.² In 1989, World Health Organization (WHO) listed Al to be one of the food pollution sources and limited Al concentration to 200 μ g L⁻¹ (7.41 μ M) in drinking water. As a result of the close relationship between Al and human health, the investigation of reliable detection methods for Al becomes more and more important. To date, some conventional methods with high sensitivity for Al detection based on atomic absorption or emission spectroscopy have been developed. These methods, however, require expensive instruments and intricate sample preparation processes. It is necessary to find other ways to design new chemosensors for Al³⁺. Recently, considerable attention has been focused on fluorometric and colorimetric online detection methods for Al³⁺, known for their simplicity and selectivity.³

Development of luminogens whose aggregates emit more efficiently than that in solution has aroused much interest in recent years. Tang's group in 2001 first reported that the luminescence of silole molecules is stronger in the aggregate state than that in the solution state. They coined "aggregation-induced emission" (AIE) for this unusual phenomenon.⁴ A variety of luminogens, including distyrylbenzene, fluorene, pentacene, and pyrene derivatives, were successively proved to have the same properties.⁵ Such compounds were regarded as competitive candidates for practical use as highly emissive materials. Moreover, the introduction of functional groups into AIE molecules will favor new development of chemoor biosensors for detecting metal cations, biomolecules, organic vapors, chiral molecules, and explosives.⁶

In our group's previous research, the experimental result indicated that only pentaphenylpyrrole among five aryl-substituted pyrrole derivatives clearly showed an aggregation-induced emission enhancement (AIEE) phenomenon during aggregation in THF–water mixtures. Upon comparing the optical properties and single-crystal structures of these pyrrole derivatives, it is suggested that the more twisted configuration, which prevented parallel orientation of conjugated chromophores, combined with the restricted intramolecular rotation (RIR) effect was the main cause of the AIEE phenomenon.⁷

Herein, we report the synthesis and properties of sodium 4-(2,5-diphenyl-1*H*-pyrrol-1-yl) benzoate (TriPP-COONa), a watersoluble, "turn-on" fluorescein-based sensor that exhibits high selectivity and sensitivity for Al^{3+} . We introduced carboxylic salt into an aryl-substituted pyrrole derivative to enhance its water-solubility. UV spectra of TriPP-COONa show two π - π * transition bands centered at 253 and 298 nm, which can be assigned to benzoate moiety and 2,5-diphenylpyrrole moiety, respectively (Fig. 1).

Since THF is a poor solvent for TriPP-COONa, the molecules of TriPP-COONa must have aggregated in the aqueous/THF mixtures with high THF contents. The experimental result indicates that its fluorescence intensity is toned with THF content in THF–water mixtures (Fig. 2 and Fig. S1 (ESI†)). Upon photo-excitation at 326 nm, the dilute aqueous solution of TriPP-COONa hardly shows any fluorescence (Fig. S1, ESI†). When THF is continually added into the aqueous solution of TriPP-COONa while keeping the luminogen concentration at 10 μ M, the photoluminescence (PL) intensity of TriPP-COONa changed in three stages: almost remain in nullity at "low" THF fraction content (<40%), obviously increased from 40 to 80%, and then sharply enhanced when the THF content is over 80% (Fig. 2). Evidently, the emission of TriPP-COONa is AIE active.

In our previous work,⁷ we found that the highly twisted conformation with large torsion angles between the pyrrole group and the neighbouring phenyl groups, which further fastened by aromatic C–H··· π hydrogen bonds in the aggregation state, is a key factor to the RIR mechanism.⁸ Herein, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of TriPP-COONa were calculated using the B3LYP/6-31 + G** method. The results show that HOMO wave function is located on the pyrrole ring and two neighboring

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Fig. 1 Absorption response of TriPP-COO⁻ (100 μ M) to titration of Al³⁺ in THF–water mixtures (25/75 v/v). The [Al³⁺]_{total} increases from 0 to 23 μ M along the direction of the arrow. Inset: linear relationship between absorbance and Al³⁺ concentration at 298, 253, and 500 nm, respectively.



Fig. 2 Plot of fluorescence intensity of TriPP-COONa (10 μ M) at 406 nm *versus* solvent composition of THF/water mixture.

phenyl rings at 2, 5-positions, while the LUMO is mainly located on the sodium benzoate moiety. Moreover, HOMO and LUMO energy levels of TriPP-COONa proved the existence of two conjugate planes, which provide efficient nonradiative relaxation pathways for the excited states (Fig. S2, ESI†). Unlike most of the other chemosensors, the functional group of TriPP-COONa is binding directly to a fluorophore without any flexible linkages, resulting in a clearer energy level transition and a smaller energy loss that leads to a modification of its AIE property.

As shown in Fig. 3, the fluorescent intensity of 100 μ M TriPP-COO⁻ in 25/75 v/v THF-water mixtures was obviously enhanced with increase of Al³⁺ concentration from 0 to 20 μ M. The increment rate of PL intensity was slowed down when the Al³⁺ concentration was over 20 μ M, and became 0 after 28 μ M. It is indicated that each Al³⁺ cation can couple with almost



Fig. 3 Emission spectra of Tripp-COO⁻ (100 μ M) upon addition of Al³⁺ in THF–water mixtures (25/75 v/v). The Al³⁺ concentrations are 0, 1, 2, 3...28 μ M, from bottom to top. Excitation wavelength: 326 nm. Inset: linear relationship between emission growth ratio and Al³⁺ concentration from 0 to 11 μ M. Curve–fit equation: $(I - I_0)/I_0 = -0.46936 + 0.89971[Al³⁺]$, $R^2 = 0.9925$.

three TriPP-COO⁻ anions. While increasing Al³⁺ concentrations, both the absorption bands of TriPP-COO⁻ at 253 and 298 nm linearly decreased with no blue- or red-shift, demonstrating that there is no chelation or intramolecular charge transfer (ICT) effect in the fluorophore-Al³⁺ system (Fig. 1). Meanwhile, an unsophisticated aggregation has occurred in the emission boosting process, which is evident by the linear increment of light-scattering tails in the long wavelength region of UV-Vis spectra as well as the decrement of transmittance (Fig. 1 and Fig. S4 (ESI[†])). The nano-scaled aggregates formed in the titration process were found to have an average radius of 90 nm and a disorganized morphology, confirmed by dynamic light scattering (DLS) analysis (Fig. S5 (ESI⁺)) and scanning electron microscopy (SEM) measurement (Fig. S6 (ESI⁺)). So we can draw a conclusion that the 'turn on' detection for Al³⁺ is ascribed to the AIE mechanism, in which the non-radiative decay can be suppressed during the aggregation process (Scheme 1).

The fluorescence responds very quickly to the titration of Al^{3+} , owing to the extremely fast aggregation process. Repeated measurements show that the emission intensity immediately enhanced nearly up to maximum after the addition of Al^{3+} (Fig. S7, ESI[†]), providing a potential "zero-wait" detecting method for Al^{3+} . Furthermore, the emission is found to be linearly proportional to the amount of Al^{3+} in the range of 1–10 μ M, which is much lower



Scheme 1 Sensing process based on the AIE mechanism.



Fig. 4 Maximum fluorescent response of TriPP-COO⁻ (100 μ M) upon addition of different metal ions (50 μ M) in THF–water mixtures (25/75 v/v), listed from left to right: (A) blank, (B) Ba²⁺, (C) K⁺, (D) Mg²⁺, (E) Pb²⁺, (F) Cu²⁺, (G) Ce²⁺, (H) Al³⁺, (I) Ca²⁺, (J) Ni²⁺, (K) Cr²⁺, (L) Hg²⁺, (M) Fe³⁺, (N) Ag²⁺, (O) Au³⁺, (P) Zn²⁺, (Q) N(CH₃)₄⁺, (R) Al³⁺ + K⁺, (S) Al³⁺ + Mg²⁺, (T) Al³⁺ + Ca²⁺, (U) Al³⁺ + Ba²⁺, (V) Al³⁺ + K⁺ + Mg²⁺ + Ca²⁺ + Ba²⁺ + Ni²⁺.

than the maximum allowable level ordained by WHO in the quantitative detection scope (Fig. 3).

To explore the selectivity of metal ions, the fluorescence responses of TriPP-COO⁻ to various cations are conducted (Fig. 4). The fluorescence spectra of TriPP-COO⁻ with the existence of other metal ions remain the same as that of free TriPP-COO⁻ except for Pb²⁺, Zn²⁺ and Al³⁺. The PL response of TriPP-COO⁻ to Pb²⁺ and Zn²⁺ is, however, much lower than that of TriPP-COO⁻ to Al³⁺ under the identical conditions. That is, TriPP-COO⁻ shows good selectivity and high sensibility to Al³⁺. To further testify single selectivity of TriPP-COO⁻ for Al^{3+} in practical application, we chose K^+ , Mg^{2+} , Ca^{2+} , Ba²⁺, and Ni²⁺ ions as interfering ions, some of which have a relatively high concentration in biological tissue and drinking water. As shown in Fig. 4, the experimental results indicate that fluorescent intensities of TriPP-COO- at 460 nm enhanced by Al³⁺ are not much affected in the background of the interfering ions, thus providing a potential application for biological detection and the water quality monitoring.

In summary, the single selective and high sensitive watersoluble probe for the rapid "turn-on" detection of Al^{3+} based on the AIE mechanism was successfully prepared. We suppose that the selectivity is probably due to the difference of electrostatic binding ability between metal ions and TriPP-COO⁻ as well as their solubility. Such a detection method based on the AIE mechanism will open up a new way for the designing of chemosensors and biosensors. Further studies on the binding mechanism of TriPP-COO⁻ and Al^{3+} are underway.

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