Electronic Supplementary Material (ESI) for Chemical Communications
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## Supporting Information (SI)

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

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## Contents

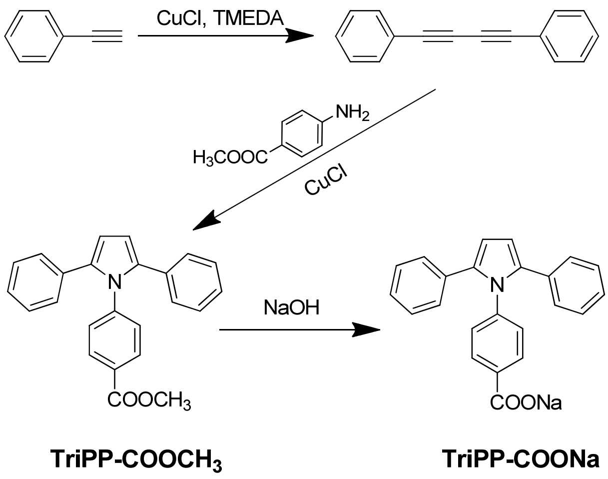
## Section A. Materials and method

All chemicals were purchased from Alfa Aesar and Beijing Chemical Reagent Company without further purification. Solvents were purified according to standard procedures. The structures of the products synthesized in this paper were identified by $^1$H-NMR spectra and elemental analysis through Bruker ARX-400 spectrometer and Elementar Vario EL, respectively. UV-visible absorption spectra were measured by TU-1901 spectrophotometer. The emission spectra were carried out on a Perkin-Elmer VARIAN 55 spectrophotometer. Particle size distribution analysis was determined by an ALV-5000 dynamic laser light scattering (DLS). The morphologies of TriPP-COO$^-$ + Al$^{3+}$ aggregates obtained in THF-water mixtures were observed by Hitachi S4800 scan electron microscopy (SEM). The theoretical ground-state geometry and electronic structure of TriPP-COONa were optimized using the density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31+G(d, p). All the theoretical calculations were performed using Gaussian 03 package[1].

Preparation of TriPP-COONa nanoaggregates in water/THF mixture containing metal ions was described as follows: Solution of TriPP-COONa in water/THF mixtures (25/75 v/v, 100 $\mu$M) was firstly prepared. Aliquots of the solution were transferred to 10 mL volumetric flasks, into which various ions with same concentration and volume were added under vigorous stirring. Five interfering ions of equivalent amounts (K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Ni$^{2+}$) were firstly mixed together, and then added into TriPP-COONa solution, the same condition mentioned above. Emission spectra were immediately performed once the solutions were prepared.

Preparation of DLS and scanning electron microscope (SEM) samples was described as follows: Solution of TriPP-COONa in water/THF mixtures (25/75 v/v, 100 $\mu$M) was firstly prepared. Then 35 $\mu$M of Al$^{3+}$ was added into TriPP-COONa solution, obtaining TriPP-COO$^-$ + Al$^{3+}$ suspension sample for DLS. SEM samples were collected by copper mesh from the above sample.

## Section B. Synthesis of TriPP-COOCH$_3$ and TriPP-COONa



**Scheme S1.** Synthetic route of TriPP-COOCH$_3$ and TriPP-COONa

Compound 1,4-diphenylbuta-1,3-diyne was synthesized according to our previous work[2]. TriPP-$COOCH_3$ was synthesized and purified as follows: A mixture of 1,4-diarylbuta-1,3-diyne (20.0 mmol), copper (I) chloride (2.0 mmol) and methyl 4-aminobenzoate (24.0 mmol) was stirred under argon for 12 h at 110 °C. The crude product was purified by column chromatography (dichloromethane/petroleum ether), then recrystallized from chloroform and *n*-hexane, yield: 42.8%. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.91-7.89 (d, 2H), 7.21-7.17 (m, 6H), 7.07-7.03 (m, 6H), 6.49 (s, 2H), 3.90 (s, 3H). Anal. calcd. for $C_{24}H_{19}NO_2$: C 81.56, H 5.42, N 3.96; found: C 81.36, H 5.42, N 3.97.

TriPP-COONa was obtained as follows: TriPP-$COOCH_3$ (0.8 mmol) and 150 mL of methanol in which dissolved NaOH (5 mmol) was added into a 250 mL round bottom flask, then the mixture was stirred at 65 °C for 8 h and poured into 500 mL dichloromethane, the white precipitate was washed by THF, acetone, and chloroform several times, yield: 85.3%. $^1$H NMR (400 MHz, $D_2O$/$d_8$-tetrahydrofuran), δ (ppm): 8.02-8.00 (d, 2H), 7.29-7.28 (d, 6H), 7.18-7.16 (d, 4H), 7.09-7.07 (d, 2H), 6.52 (s, 2H).

**Section C. Supplementary spectra data (Fig. S1-S7)**

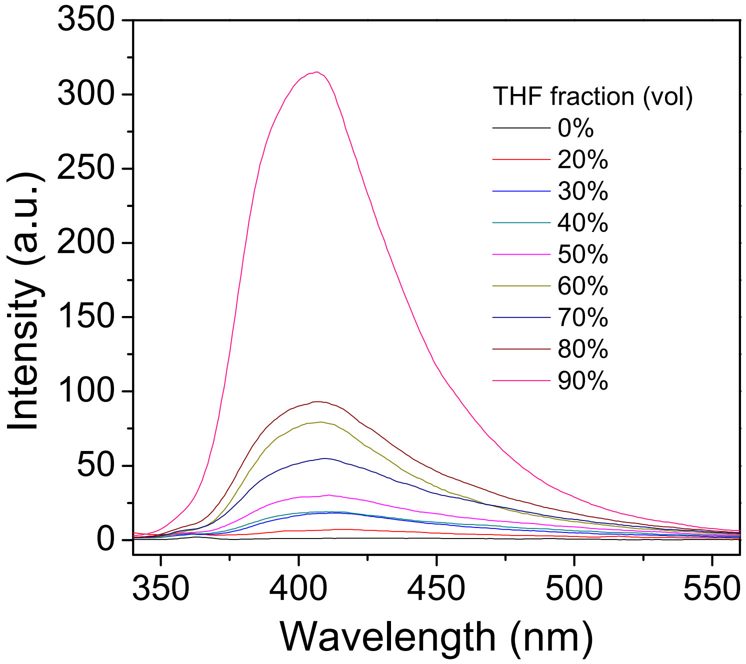


**Fig. S1** Emission spectra of Tripp-COONa (10 $\mu$M) in THF-water mixtures. Excitation wavelength: 326 nm.

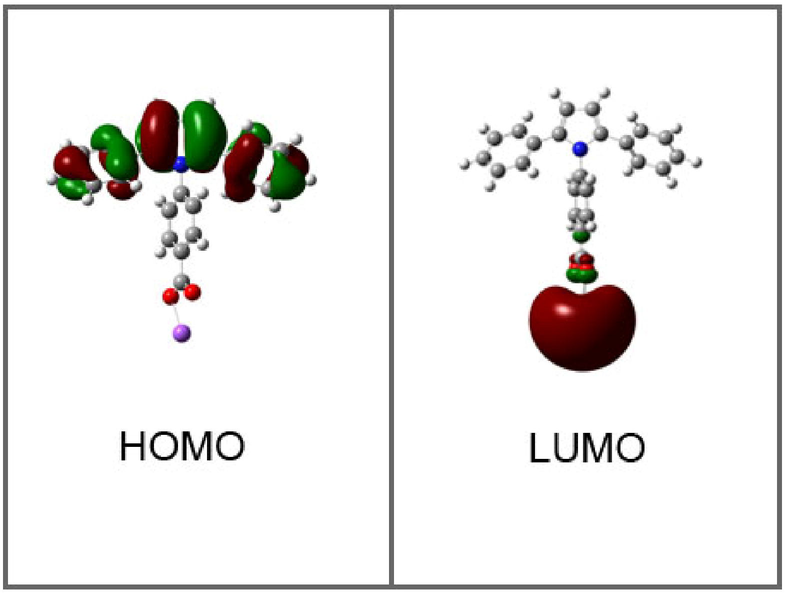


**Fig. S2** Molecular orbital amplitude plots of HOMO and LUMO energy levels of TriPP-COONa calculated with the use of B3LYP/6-31+G** basis set.

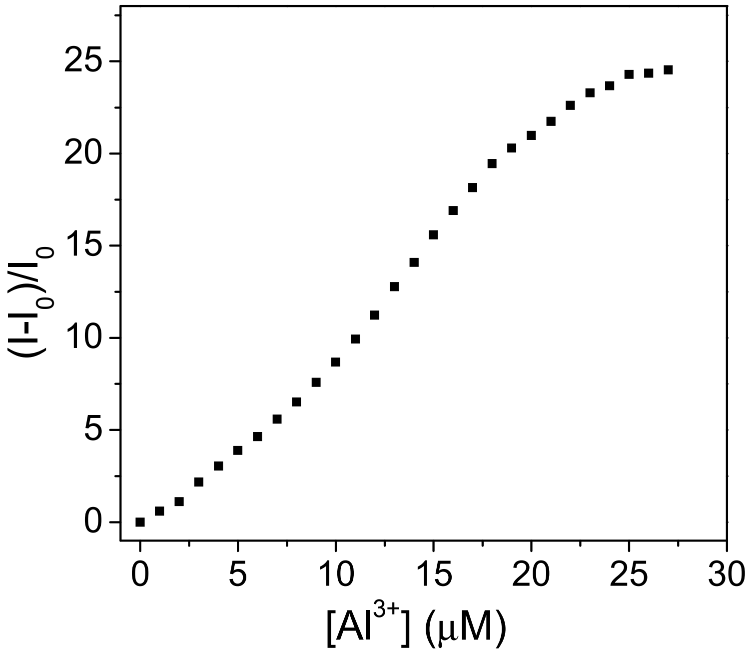


**Fig. S3** Emission intensities of TriPP-COONa (100 μM) in THF-water mixtures (25/75 v/v) as a function of $[Al^{3+}]$ (1 μM-28 μM)

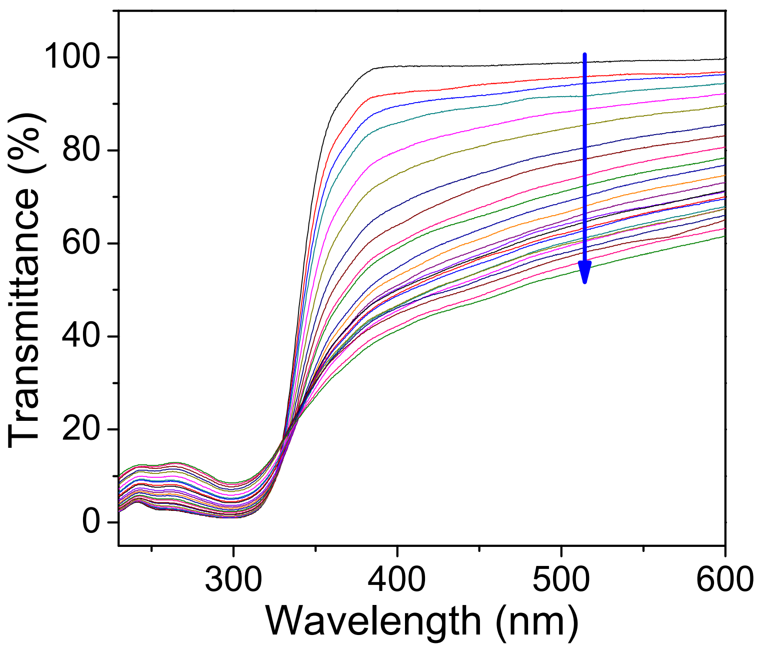


**Fig. S4** Transmittance changes of TriPP-COONa (100 $\mu$M, THF/water: 25/75 v/v) upon titration of $Al^{3+}$. The $[Al^{3+}]_{total}$ increased from 0 $\mu$M to 23 $\mu$M along the direction of the arrow.

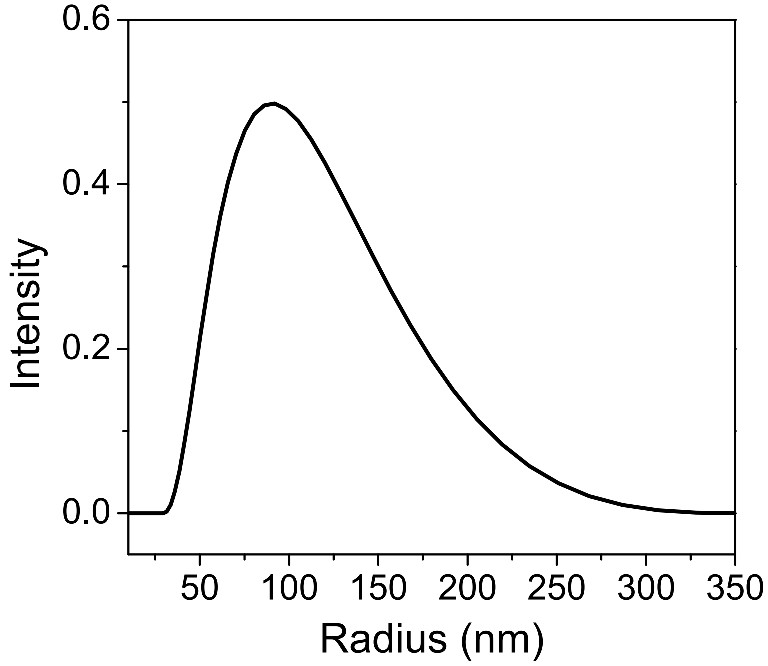


**Fig. S5** Particle size distribution in TriPP-COONa solution (100 $\mu$M, THF/water: 25/75 v/v) determined by DLS upon the addition of $Al^{3+}$ (35 $\mu$M).

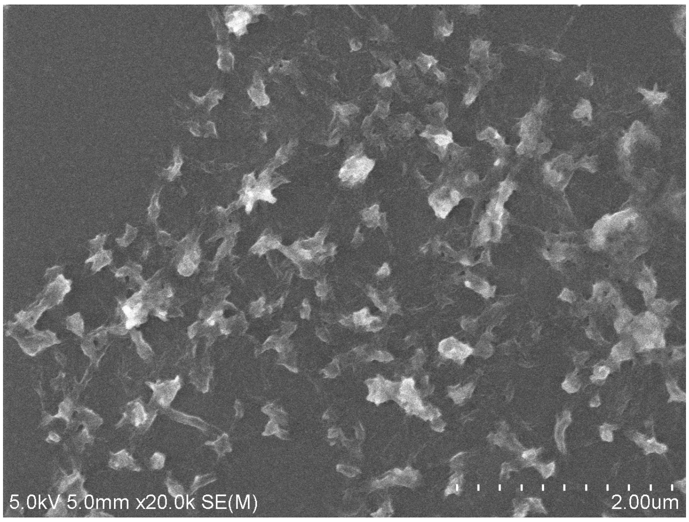


**Fig. S6** SEM of TriPP-COO$^-$ + Al$^{3+}$ aggregates obtained in THF-water mixtures (25/75 v/v, TriPP-COONa: 100 $\mu$M) upon addition of Al$^{3+}$ (35 $\mu$M).

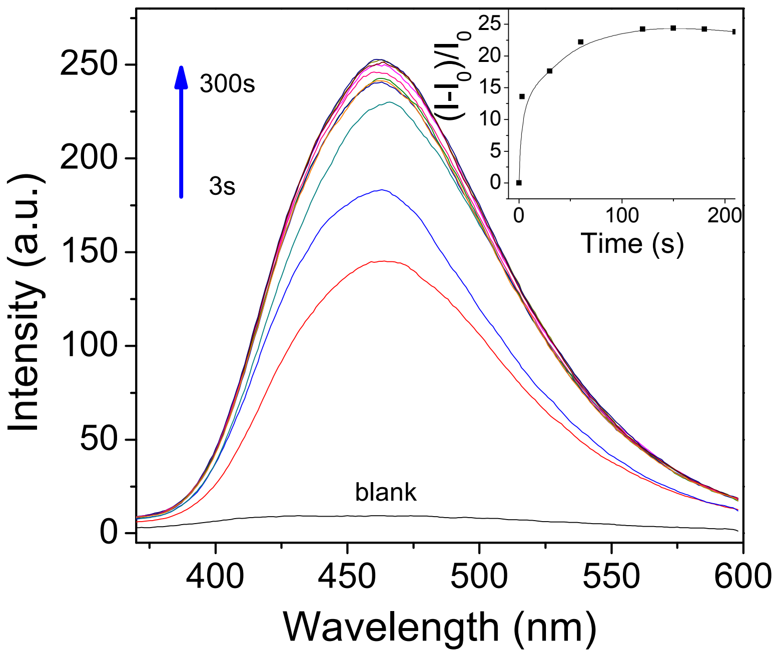


**Fig. S7** Fluorescent spectra of TriPP-COONa (100 $\mu$M) in the presence of 50 $\mu$M Al$^{3+}$ in THF-water mixtures (25/75 v/v) with extended time. Inset: Plot of fluorescent intensity at 460 nm via the leaving time.

## Section D. References

1. Gaussian 03, Revision E.01, M. J. Frisch *et al.*, Gaussian, Inc., Wallingford CT, 2009.

2. X. Feng, B. Tong, J. B. Shen, J. B. Shi, T. Y. Han, L. Chen, J. G. Zhi, P. Lu, Y. G Ma and Y. P. Dong, *J. Phys. Chem. B*, 2010, **114**, 16731.