Supporting Information

An ultra-sensitive fluorescence multi-channels and colorimetric probe based on salicylaldehyde hydrazone for Al^{3+} recognition with 3:1 a binding ratio

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Contents

1. Reagents and apparatus

Nicotinic acid hydrazide and 4-(diethylamino)-salicylaldehyde were purchased from J&K Scientific LTD (Beijing). All reagents and solvents (analytical grade) for synthesis and analysis used in the experiments were used without further purification after purchase. Distilled-deionized water was used to prepare all aqueous solutions.

The spectra of the ^{13}C NMR and ^{1}H NMR were recorded on a VARIAN NMR Systems 600 MHz spectrometer and the internal standard was tetramethylsilane (TMS). HRMS spectra were obtained with BRUKER SOLAN X70 FT-MS spectrometer. Fluorescence measurements were carried out on a HITACHI F-4600 fluorescence spectrophotometer, and UV-vis spectra were acquired on a SHIMADZU UV-2700 spectrophotometer.

2. Methods

A stock solution (5.0 mM) of probe SBN was prepared by dissolving in dimethylformamide (DMF). Unless otherwise specified, the test solutions of SBN (20.0 μM) were prepared by diluting the above stock solutions with deionized water. Stock solutions of various metal ions were prepared by dissolving their hydrochloride salts or nitrate salts in distilled water. All tests were performed at room temperature. The excitation wavelengths in the testing of fluorescence emission spectra are 365 and 425 nm, respectively. The emission wavelengths in the testing of fluorescence excitation spectra are 459 and 512 nm, respectively. The limit of detection (LOD) was calculated using the following equation: detection limit = 3S/ρ, where S is the standard deviation of the intensity of the free sensor, and ρ is the slope between fluorescence or UV-vis absorption intensity versus sample concentration.[1, 2] The time interval was 15 min between the various cycles in the reversibility experiments.

3. Fluorescence test paper of SBN

The qualitative filter papers produced by Hangzhou Special Paper Co., Ltd. were cut into 1.5 cm*3.0 cm test paper strips. Then, these test strips were immersed in DMF solution of SBN and dried in air to obtain fluorescence detection test strips.[3, 4]

4. Cell culture

Epinephelus coioides spleen cells were maintained in Leibovitz's Medium (L-15, GIBCO, USA) supplemented with 10 % heat-inactivated fetal bovine serum (FBS, GIBCO, USA) and penicillin (100 IU/ml)/streptomycin (100 mg/ml) at 28 °C for 24 h. Thereafter, the cells were seeded in 24 well-plates with cell climbing slice.[5]

5. Computational details

The ωB97XD density functional[6, 7] including an attractive dispersion term was used to optimize the geometries of SBN-Al^{3+}, and followed by frequency calculations without any symmetry or geometrical constraints to verify the minima nature of optimized structure. In these calculations, the 6-31G (d, p) basis set was used for C, H, O and N atoms and the aluminum atom was treated by SDD[8]. All quantum chemical computations were performed by using the Gaussian09 package of programs [9].

References

1. Z. Ou, M. Wang, Z. Zhang, J. Liang, J. Tang, X. Lei, L. Yang, H. Liu, L. -J. Ma, *Microchem. J.*, 2023, **195,** 109386.
2. X. Lei, Y. Zou, Q. Liang, W. Xu, S. Lao, B. Yang, L. Li, L. Yang, H. Liu, L. -J. Ma, *J. Photochem. Photobiol. A-Chem.*, 2022, **428,** 113854.
3. T. Liu, Z. Huang, R. Feng, Z. Ou, S. Wang, L. Yang, L. -J. Ma, *Dyes Pigm.*, 2020, **174,** 108102.
4. S. Wang, Z. Zhang, Z. Huang, X. Lei, Y. Wang, L. Li, L. Yang, H. Liu, F. Sun, L. -J. Ma, *J. Photoch. Photobio. A-Chem.*, 2021, **418,** 113438.
5. L. -J. Ma, Q. Liang, R. Feng, Z. Lv, F. Cui, L. Li, L. Yang, H. Liu, F. Sun, *J. Photoch. Photobio. A-Chem.*, 2021, **408,** 113086.
6. J. -D. Chai, M. Head-Gordon, *J. Chem. Phys.*, 2008, **128,** 084106.
7. J. -D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections, *Phys. Chem. Chem. Phys.*, 2008, **10,** 6615−6620.
8. D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta*, 1990,

77, 123−141.

9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M.Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford, CT, USA, 2009.

6. ^{1}H NMR and ^{13}C NMR spectra of SBN

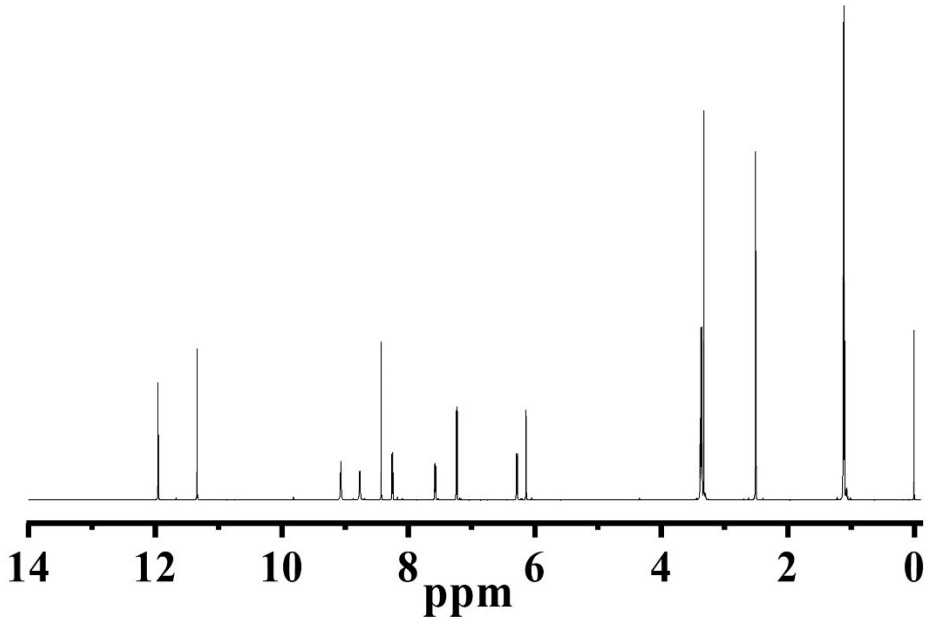

Figure. S1. ^{1}H NMR spectrum of SBN.

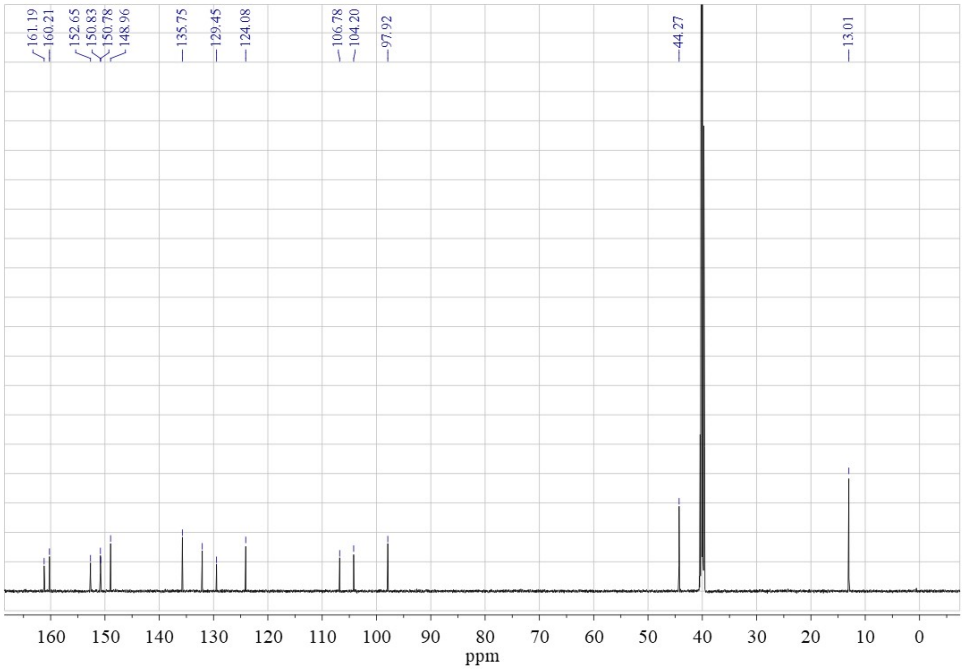

Figure. S2. ^{13}C NMR spectrum of SBN.

7. HR-MS spectrum of SBN

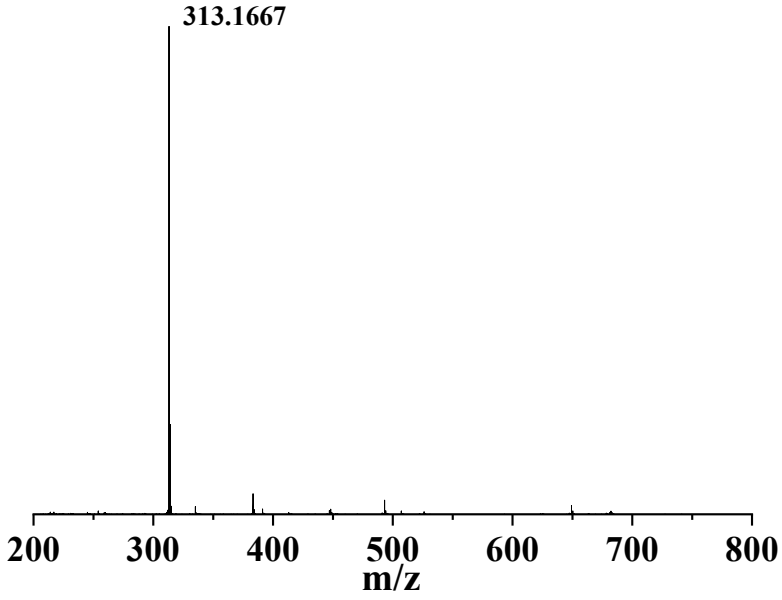

Figure. S3. HR-MS spectrum of SBN.

8. Sensitivity fitting based on UV-vis and fluorescence excitation spectra of SBN

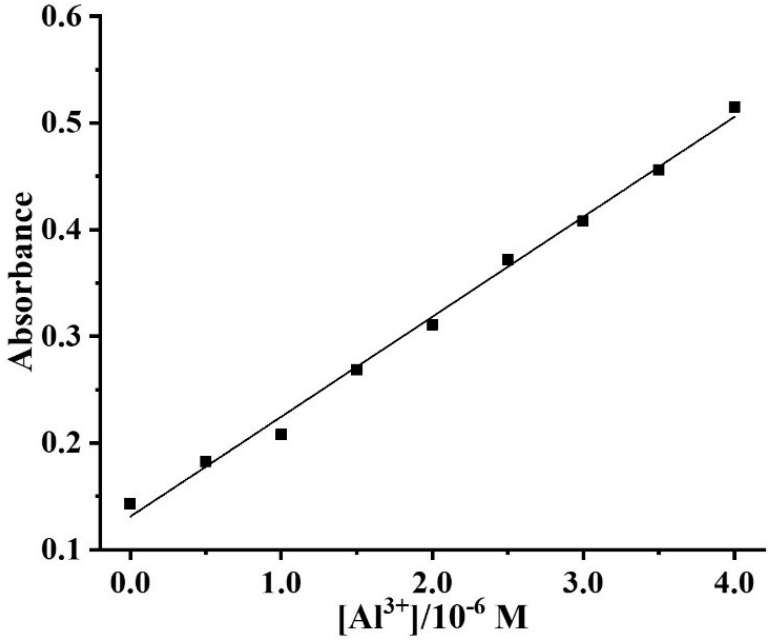

Figure. S4. The linear fitting between the absorption intensity of SBN at 402 nm and Al^{3+} concentration in UV-vis spectra.

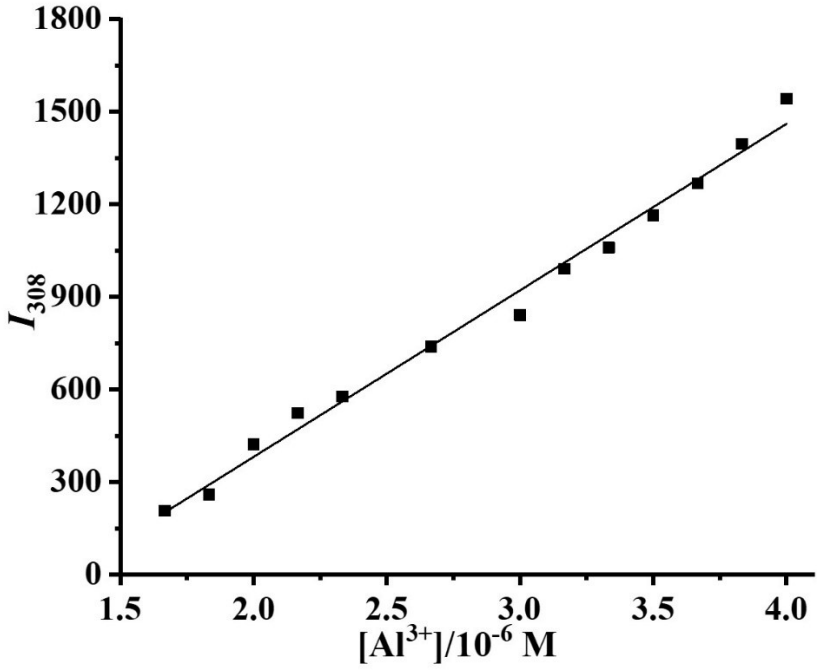

Figure. S5. The linear fitting between the excitation intensity of SBN at 308 nm and Al^{3+} concentration in fluorescence excitation spectra (λ_{em} is 459 nm).

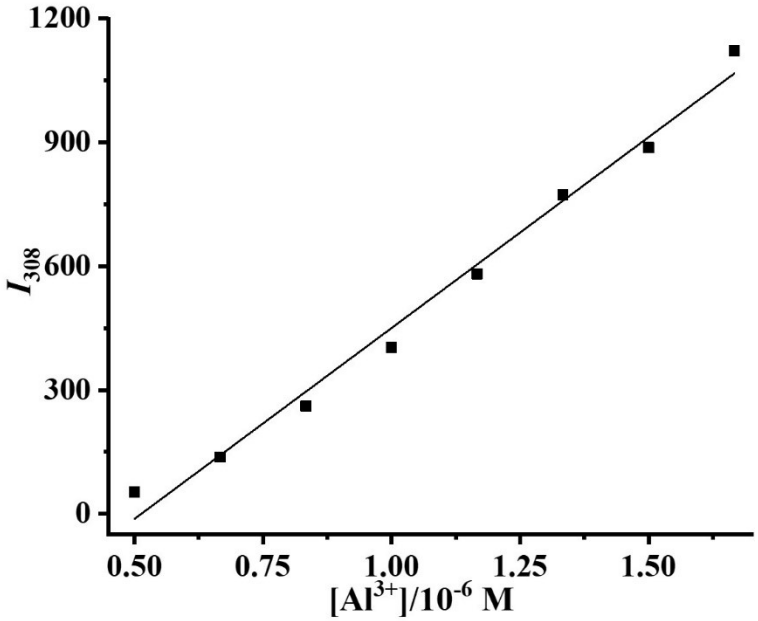

Figure. S6. The linear fitting between the excitation intensity of SBN at 308 nm and Al^{3+} concentration in fluorescence excitation spectra (λ_{em} is 512 nm).