# Supporting Information

# An Aggregation-Induced Emission-Based Fluorescent Chemosensor of Aluminium Ion

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## Experimental

### *Chemicals and Apparatus*

All reagents were of analytical-reagent grade. The reagents of $FeCl_3$, KCl, NaCl, $Mn(CH_3COO)_2$, $CdCl_2$, $Zn(CH_3COO)_2$, $Pb(NO_3)_2$, $CrCl_3$, $CaCl_2$, $CuSO_4$, $CoCl_2$, $MgSO_4$, $Al(NO_3)_3$, $Bi(NO_3)_3$, $NiCl_2$, petroleum ether, dichloromethane ($CH_2Cl_2$), ethanol, acetone, silica gel and tetrahydrofuran (THF) were purchased from Beijing Chemical Co., Ltd. N,N-Dimethylacetamide (DMAC) was bought from Sigma-aldrich. 9,10-Dibromoanthracene, 4-methoxystryrene, $K_3PO_4$, $Pd(OAc)_2$ and 1,3-propanesultone were purchased from Alfa Aesar. Boron tribromide, sodium ethylate (NaOEt) were obtained from Sinopharm Chemical Reagent Co. (China). Water was deionized and further purified using a Milli-Q water purification system (Millipore, Bedford, MA). The pH values were monitoring by a Sartorius PB-10 pH meter (Sartorius, Göttingen, Germany).

The $^1$HNMR and $^{13}$C NMR spectra were measured with a Bruker Avance III 400 MHZ spectrometer (Bruker, Germany). Fluorescence spectra were recorded by a SHIMADZU RF-5301PC spectrophotometer (Shimadzu, Janpan). The photos of fluorescent imaging were obtained by a Vilber Fusion-SL7-3500 imaging system (Vilber Lourmat, French). The elemental analysis was carried out by a vario EL Element Analyzer (Elementar Inc., Germany). Eelectrospray ionization-mass spectrometry (ESI-MS) analysis was carried out by a Thermo LTQ linear ion trap mass spectrometer (Thermo Fisher Scientific, San José, CA). A HITACHI S4800-II FESEM (Blackwood, NJ, USA) was used for recording of scanning electron microscope (SEM) images. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) detection of $Al^{3+}$ concentration in the real sample was carried out by iCAP 6300 (Thermo Fisher Scientific Inc., USA.).

### *Optical Measurements*

The fluorescence spectra were used to study the aggregation behavior of BSPSA. For the measurement of fluorescence responses of BSPSA with the presence of different metal ions, metal ions solutions were added into BSPSA solution dissolved by THF-water (9/1, v/v) in a quartz cuvette. When the solution was mixed thoroughly, the fluorescence spectra were recorded.

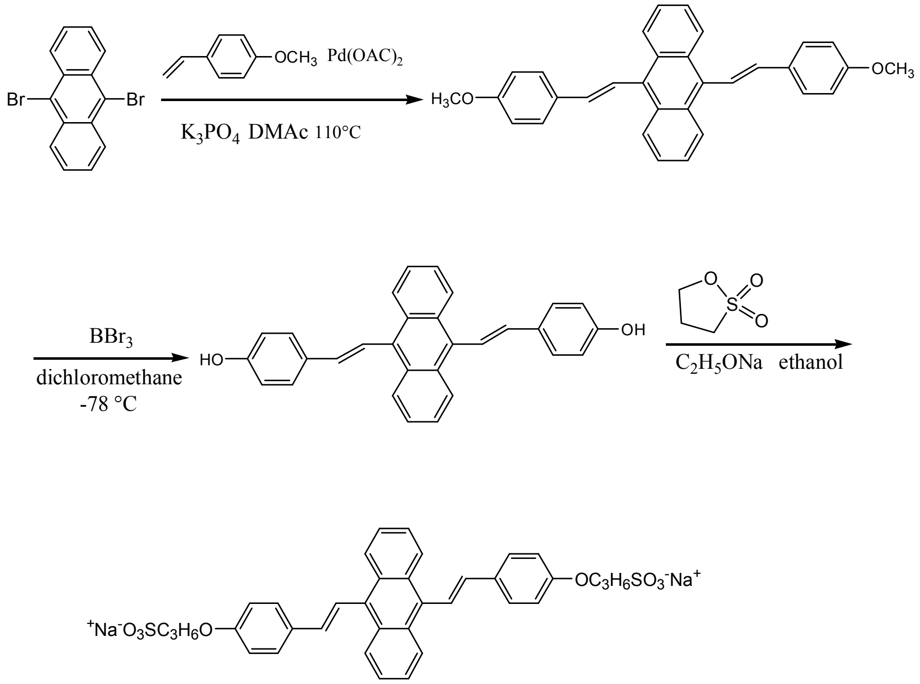
### *Sample Preparation*

The traditional Chinese food of deep-fried dough stick was selected as the sample to test the $Al^{3+}$ concentration. For sample preparation, 8-10 g of sample was heated at 85 °C for 4.5 h, and then crushed and homogenized. 1.20 g of dried sample was added to Teflon vessels containing 9 mL $HNO_3$. The Teflon vessels were closed tightly and put into the microwave oven for digestion. The heating program was 120 °C for 8 min and 180 °C for 8 min. After cooled to ambient temperature, the digests were then quantitatively transferred into Teflon crucibles. With 0.5 mL of $H_2SO_4$ added, the sample was heated to almost dry on the electric hot plate at 160 °C. The residues were diluted with 15 mL water, and at last the solution was transferred to a 50 mL volumetric flask, diluted to the volume.

*Synthesis and Characterizations of BSPSA*

As shown in Scheme 1, the synthesis of BSPSA was according to our previous reports [34]. Briefly, 9,10-Bis(4-methoxystyryl)anthracene was first synthesized by dissolving 1.02 g 9,10-dibromoanthracene, 0.96 g 4-methoxystryrene, 1.92 g $K_3PO_4$ (9 mmol) and 60 mg $Pd(OAc)_2$ in 30 mL DMAC, and then stirred at 110 °C for 24 h. After the extraction, washing, drying, concentrating and chromatographing, 1.26 g (95%) 9,10-Bis(4-methoxystyryl)anthracene was obtained. $^1H$ NMR ($CDCl_3$, 400 MHz): δ8.41 (d, J = 3.3 Hz, 2H), 8.39 (d, J = 3.3 Hz, 2H), 7.79 (d, J = 16.4 Hz, 2H), 7.63 (d, J = 8.6 Hz, 4H), 7.47 (d, J = 3.2 Hz, 2H), 7.45 (d, J = 3.2 Hz, 2H), 7.00 (d, J = 8.6 Hz, 4H), 6.88 (d, J = 16.4 Hz, 2H), 3.89 (s, 6H). Then, 0.67 g 9,10-Bis(4-methoxystyryl)anthracene and 20 mL dry $CH_2Cl_2$ were mixted and cooled to -78 °C, after which boron tribromide/$CH_2Cl_2$ (1.51 g/10 mL) was added. After stirring overnight, 15 mL water was added to obtain 0.52 g (84%) of 9,10-Bis(4-hydroxystyryl)anthracene. $^1H$ NMR (DMSO-$d_6$, 400 MHz): δ9.75 (s, 2H), 8.45 (d, J = 3.3 Hz, 2H), 8.43 (d, J = 3.3 Hz, 2H), 7.95(d, J = 16.4 Hz, 2H), 7.70(d, J = 8.5 Hz, 4H), 7.61(d, J = 3.2 Hz, 2H), 7.59(d, J = 3.2 Hz, 2H), 6.92 (d, J = 8.5 Hz, 4H), 6.86 (d, J = 16.4 Hz, 2H). At last, 0.54 g 9,10-Bis(4-hydroxystyryl)anthracene was added into 20 mL anhydrous under nitrogen, after which NaOEt/anhydrous ethanol (0.20 g/ 20 mL) was slowly added. Then, with the addition of 1,3-propanesultone/ethanol (0.37 g/20 mL), the mixture was vigorously stirred overnight and a yellow product of BSPSA was precipitated. $^1H$ NMR (DMSO-d6, 400 MHz): δ 8.40 (d, J = 3.3 Hz, 2H), 8.38 (d, J = 3.3 Hz, 2H), 7.96 (d, J = 16.5 Hz, 2H), 7.74 (d, J = 8.7 Hz, 4H), 7.55 (d, J = 3.2 Hz, 2H), 7.53 (d, J = 3.2 Hz, 2H), 7.01 (d, J = 8.7 Hz, 4H), 6.86 (d, = 16.5 Hz, 2H), 4.13 (t, J = 6.5 Hz, 4H), 2.58 (t, J = 7.2 Hz, 4H), 2.03 (m, 4H).

Then, the obtained compound was subjected to the further characterizations. By $^{13}$C NMR (100MHz, DMSO-d6), we got the result as follows: δ159.16, 137.20, 132.81, 129.95, 129.46, 128.52, 126.70, 125.87, 122.64, 115.21, 67.27, 48.36, 25.72. By elemental analysis, we obtained the mass fraction of 62.29% (theoretical value: 61. 54%, error: +0.75%) for carbon (C), 5.128% (theoretical value: 4.558%, error: +0.57%) for hydrogen (H) and 8.297% (theoretical value: 9.117%, error: -0.82%) for sulfur (S), respectively. By ESI-MS, we obtained the main ion of m/z 328 in the negative mode. This ion is attribute to $[M-2Na]^{2-}$, which further confirm the successfully synthesis of BSPSA. These data were also in accordance with the previous works. [34, 35]

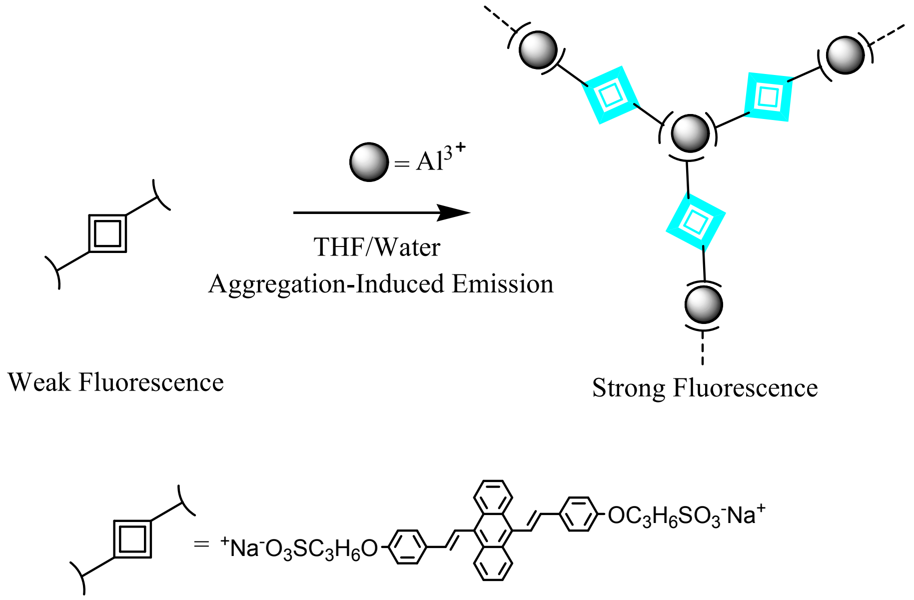


**Scheme S1**. Synthetic route of 9,10-bis[4-(3-sulfonatopropoxyl)-styryl]anthracene sodium salt (BSPSA).

*Optical Properties of BSPSA*

The optical properties of BSPSA were first examined by recording FL signals of BSPSA adding to different THF-water solution. THF was added into different value of water to obtain different THF fractions ($H_2O$ : THF (V/V) = 10:0, 9:1, 8:2, 7:3, 6:4, 2:8, 2:98). As shown in Figure 1A, except for the quite weak emission at 432 nm, no remarkable fluorescence was recorded when BSPSA was dissolved in water (0%). However, when the THF fraction increased to 10%, a quite weak emission at 534 nm appeared. With the further increase of THF fractions (10% - 98% of THF fractions), the intensity of emission at 534 nm increased gradually, which combined with a blue shift. When the THF fraction increased to 80%, the fluorescence intensity was 12.8 times higher than the intensity in water. At 98%, the dramatically increased emission with a 43 times higher intensity than the one in water was resulted. In addition, an obviously red shift was observed (Figure 1A), which might be generated from the different states of aggregation at different fractions of poor solvents.

The fluorescence intensity of BSPSA versus THF fraction is shown in Figure 1B, and the inset is the imaging of BSPSA in different solutions. By naked eyes, we can observe the fluorescence increase with the increase of THF fraction, and find the most dramatically increase from 80% to 98%. In the pure water (THF fraction = 0%), a quite weak blue emission was observed according to the weak emission at 432 nm. The blue-green emission was resulted at the THF fraction of 30%, which was generated from the comparative emissions at both 432 nm and 510 nm. With the further increase of THF, the intensity of emission at 510 nm increased gradually, and showed the green fluorescence at 80% and 98% of THF. Therefore, BSPSA proved to be an AIE luminogen with THF as the poor solvent.



**Scheme S2**. Schematic illustration of the coordination modes between BSPSA and $Al^{3+}$.

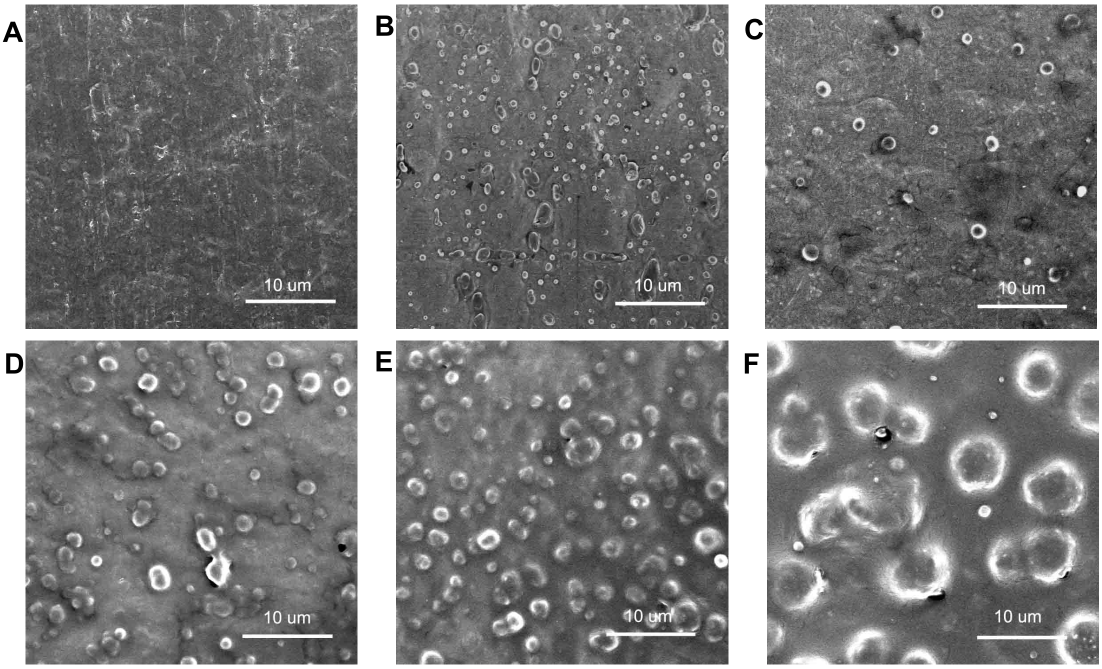


Figure S1. SEM images of $Al^{3+}$ added (50 μM)-BSPSA solution (0.71 μM) with different THF fractions. (A): 10% THF, (B) 20%, (C) 60%, (D) 80%, (E) 95%, (F) 98%.

## Experimental data for Preliminary Study of the Mechanism

To preliminary study the interaction between BSPSA and $Al^{3+}$, the experiments, including the collections of IR spectrum and UV/vis spectrum as well as isothermal titration calorimetry (ITC) data, have been carried out. Comparing with BSPSA (Figure S2-A), the IR band at about 1200 and 1049 $cm^{-1}$ decreased with the addition of $Al^{3+}$ (Figure S2-B), which are attributed to the adsorption of sulfonic group. The decrease of IR adsorption might be the result of the coordination between $Al^{3+}$ and sulfonic group. In addition, the new bands at about 596 and 834 $cm^{-1}$ are observed with the addition of $Al^{3+}$ to BSPSA (Figure S2-B). These bands are the symmeric stretching vibration of Al-O (***ISIT Int.***, 2014, 54, 734-742), which also indicates the coordination.

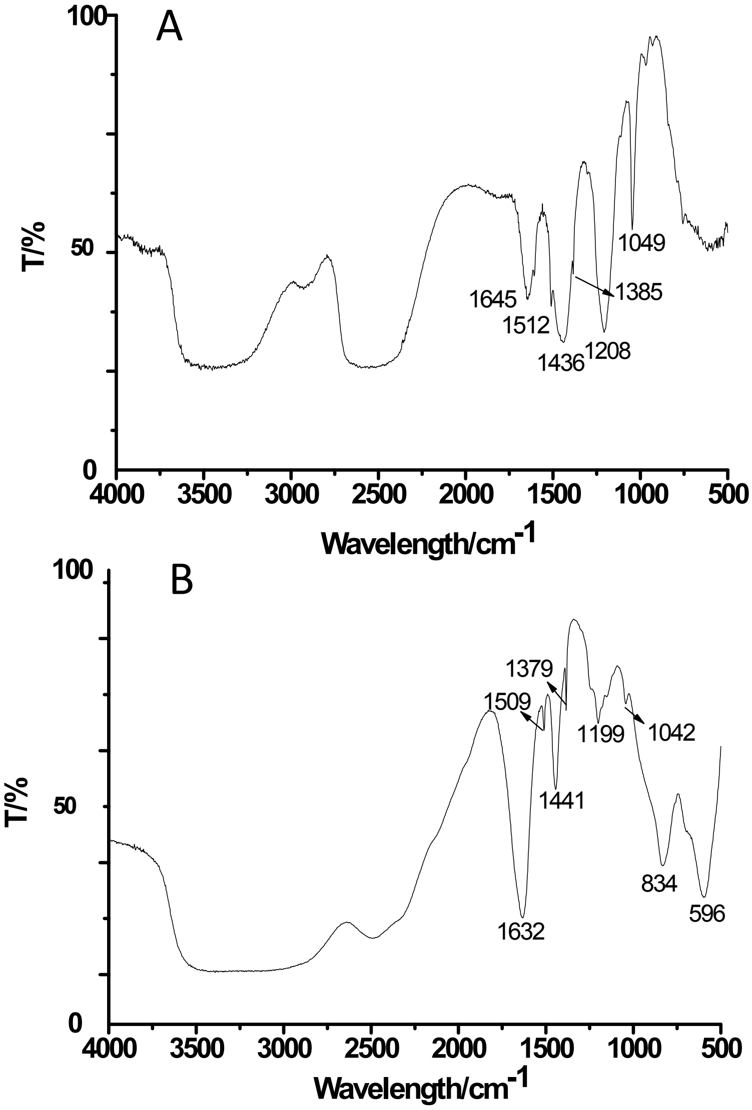


Figure S2. IR spectra of BSPSA (A) and BSPSA with the addition of $Al^{3+}$ (1:2) (B).

Figure S3 shows the variation of the absorption spectrum of BSPSA after the addition of different amount of $Al^{3+}$. The absorption band at around 410 nm decreased gradually and a red-shift was also demonstrated, which could be due to the aggregation by the interaction between BSPSA and $Al^{3+}$ (***Chem. Commun.***, 2001, 1740-1741; ***Chem. Soc. Rev.***, 2011, 40, 5361–5388). In addition, the isothermal titration calorimetry (ITC) experiment of the titration of a BSPSA solution (0.5 mM) into a solution of $Al^{3+}$ (0.025 mM) was also carried out, which resulted the complicated reaction began with an endothermic reaction, and followed by a late exothermic heat reaction, and then an endothermic reaction. This results the multiple sets of independent binding sites with different ΔH, ΔS and K values, which might be associated with a high interaction (***Chem. Eur. J.***, 2013, 19,11261-11269), and not the simple hydrophobic interactions, van der Waals forces, hydrogen bonding or electrostatic interactions. Therefore, based on the data of IR, UV/vis and ITC, the coordination interaction between BSPSA and $Al^{3+}$ could be preliminary concluded.

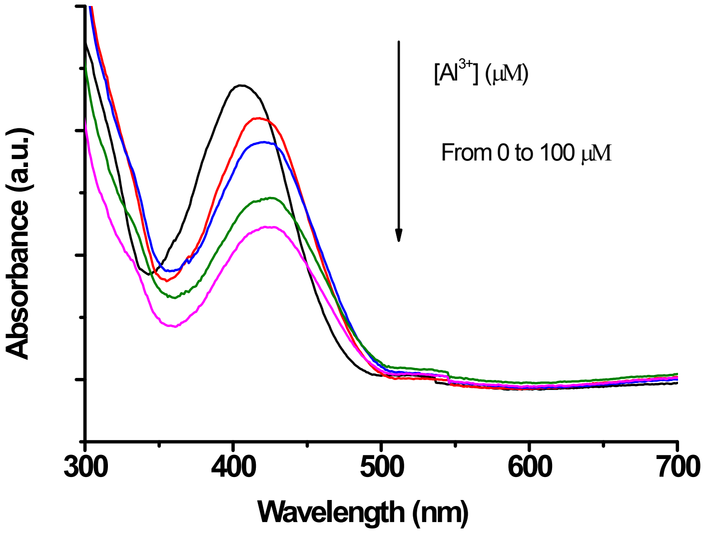


Figure S3. UV/vis spectra of BSPSA with the addition of different amount of $Al^{3+}$. [BSPSA] = 4.75 μM. [$Al^{3+}$] = 0, 25, 50, 75, 100 μM.

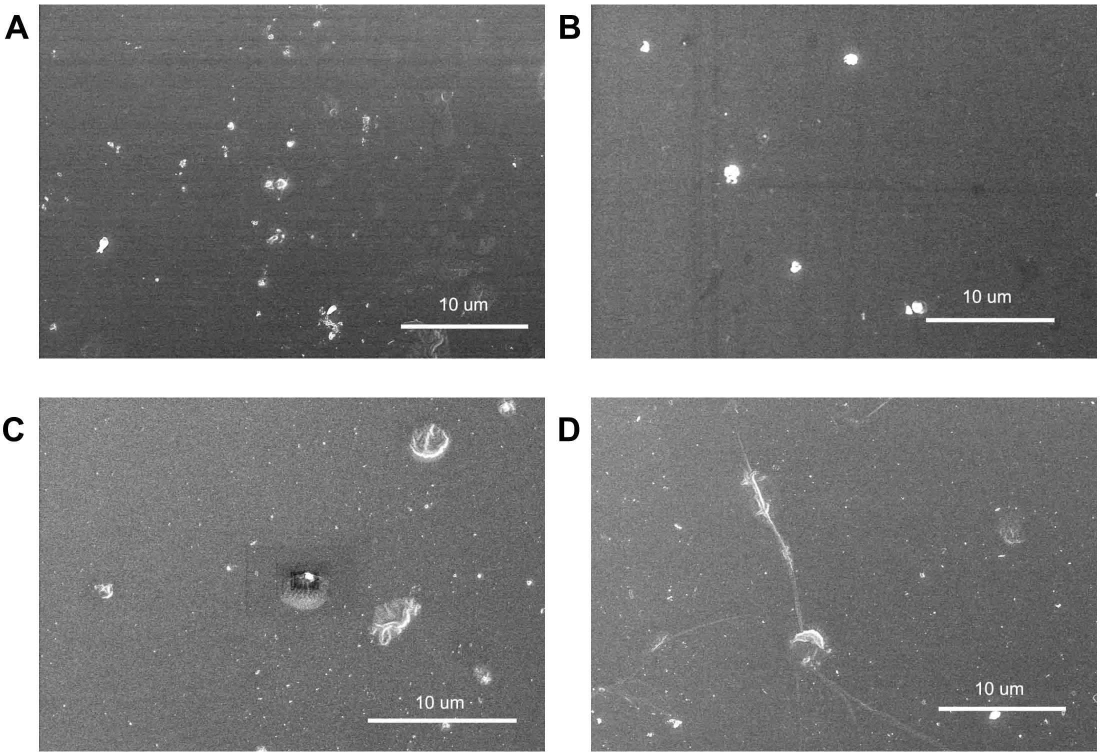


Figure S4. SEM images of BSPSA (0.71 μM) in THF-water (9:1, v/v) with the addition of different metal ions (50 μM). (A): $Cd^{2+}$, (B) $Na^{+}$, (C) $Mn^{2+}$, (D) $Sr^{2+}$.

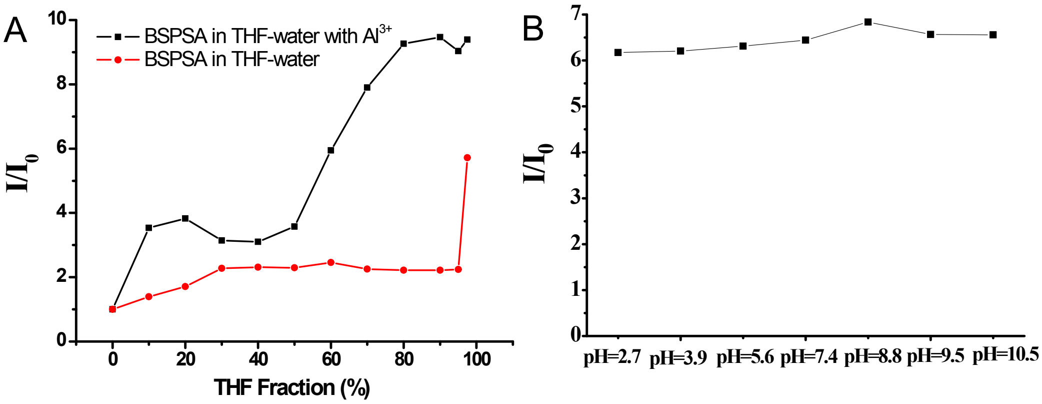


Figure S5. (A) Fluorescent responses of BSP-SA (0.71 μM) as a function of THF fraction with and without $Al^{3+}$ (50 μM). (B) The effect of pH on the FL intensity of $Al^{3+}$/BSPSA solution.

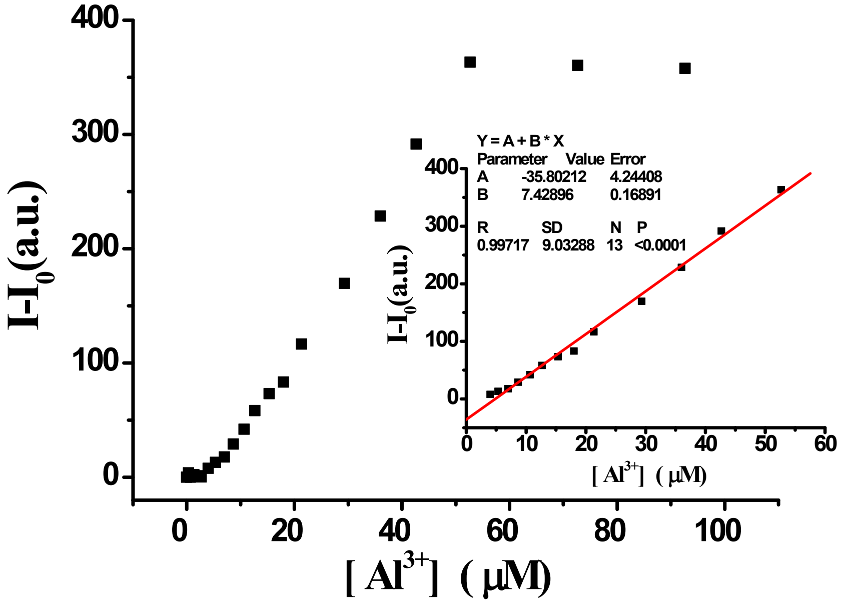


Figure S6. The plot of the fluorescence intensity at 525 nm ($\lambda_{ex}$ = 404 nm) vs [$Al^{3+}$]. The BSPSA was 4.75 μM in THF-water (9/1, v/v).

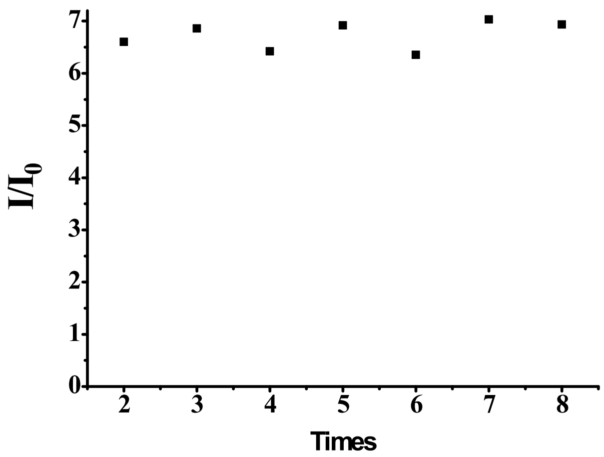


Figure S7. The reproducibility of BSPSA sensing of $Al^{3+}$ for seven times.