Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Endowing Triarylboron Compound of ACQ with AIE Characteristic by Transforming Their emissive TICT State to be Dark

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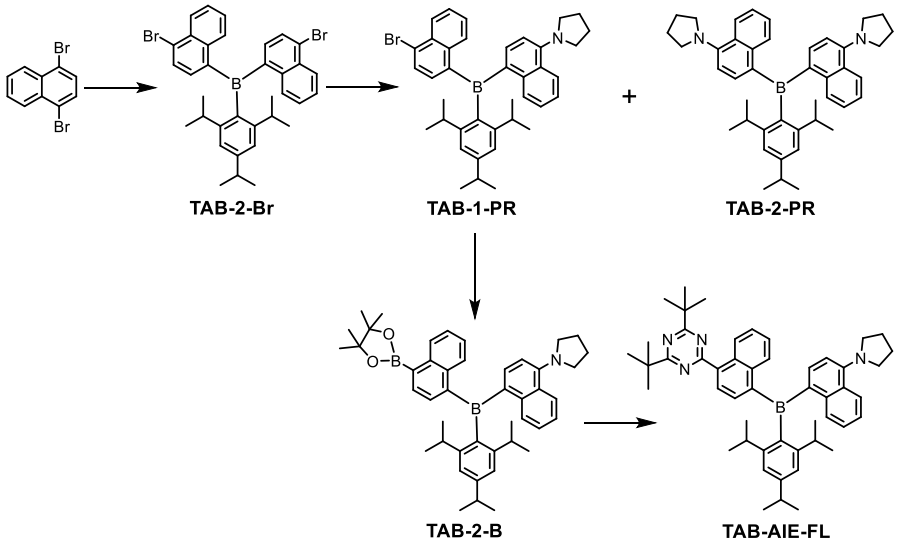
Experimental Details

General Information

All chemical reagents were purchased from J&K (Beijing, China) and used without further purification. Absorption spectra were recorded on Hitachi UV-3010. The fluorescence spectra were obtained on Hitachi F-7000. ^{1}H NMR spectra were obtained on Bruker-Avance III 400 H (400 MHz) spectrometers. Theoretical computation was conducted by density functional theory (DFT) and RB3LYP/6-31G (d) level. NIH/3T3 cells were purchased from Beijing Union Medical College Hospital. Fetal bovine serum (FBS) was purchased from Beijing BioDee Biotechonology Co. Ltd, China.

Synthsis of TAB-2-PR and TAB-AIE-FL.



Scheme S1. The synthetic route to TAB-2-PR and TAB-AIE-FL.

2, 4, 6-triisopropylphenylboronate (TripB(OMe)$_2$) was synthesized according to our previous reports(*Angew. Chem. Int. Ed.* **2011**, 50, 8072-8076).

Synthesis of Compound TAB-2-Br

To a solution of 1,4-dibromonaphthalene (4.72g, 16.5mmol) in anhydrous Et_2O (100mL) at -78 °C under argon, n-BuLi (7.5 mL of 2.22 M solution in n-hexane) was added. The mixture was stirred for 2 h at -78 °C and then warmed room temperature for another 2h. Then TripB(OMe)$_2$ (2.07g, 7.5mmol) was added by injection at -78 °C. The mixture was stirred for 2 h at -78 °C, then recovered to RT and stirred overnight. The reaction solvent was removed by a rotary evaporator, washed with saturated NaCl aqueous solution and extracted with methylene chloride. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by a rotary evaporator, and the crude product was purified by column chromatography (silica gel, hexane as eluent) to afford TAB-2-Br (3.12g, 65%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, 2H), 7.77 (d, 2H), 7.58 (d, 2H), 7.46 (m, 4H), 7.09 (m, 2H), 7.01 (s, 2H), 2.94 (m, 1H), 2.65 (m, 2H), 1.31 (d, 6H), 0.94 (d, 6H), 0.80 (d, 6H); MALDI-TOF (m/z) : $[M-H]^+$ calcd for $[C_{35}H_{35}BBr_2-H]^+$ 625.1, found 625.1.

Synthesis of Compound TAB-1-PR and TAB-2-PR

To a suolution of TAB-2-Br (1.26g, 2mmol), $Pd_2(dba)_3$ (0.20g, 0.2mmol), BINAP (0.26g, 0.40mmol)and sodium t-butoxide (1.20g, 12mmol) were dissolved in anhydrous toluene (20 mL).

Pyrrolidine (0.122g, 2mmol) in 15 mL toluene was added dropwise in the above solution at 80 °C over 2h. Then the mixture was stirred for 12 h at 80 °C. The reaction solvent was removed by a rotary evaporator, washed with saturated NaCl aqueous solution and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by a rotary evaporator, and the crude product was purified by column chromatography (silica gel, eluent: 25% Ethyl acetate in petroleum ether) to afford TAB-1-PR (0.68g, 51.2%) as a yellow powder and TAB-2-PR (0.318g, 26.3%).

TAB-1-PR: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, 1H), 8.17 (m, 1H), 7.75 (d, 2H), 7.65 (d, 1H), 7.57 (d, 1H), 7.42 (m, 2H), 7.24(s,1H), 7.09 (m, 1H), 6.98 (s, 1H), 6.95 (s, 2H), 6.71 (m, 1H), 3.59 (m, 4H), 2.91 (m, 1H), 2.74 (m, 1H), 2.62 (m, 1H), 2.04 (m, 4H), 1.28 (d, 6H), 0.92-0.74 (m, 12H); MALDI-TOF (m/z) : $[M^+]$ calcd for $[C_{39}H_{43}BBrN]^+$ 616.5, found 616.1.

TAB-2-PR: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 2H), 7.74 (d, 2H), 7.49 (d, 2H), 7.15 (d, 2H), 6.91 (d, 4H), 6.72 (d, 2H), 3.44(d,8H), 2.85 (m, 1H), 2.67 (m, 1H), 1.95 (d, 8H), 1.28 (d, 6H), 0.87-0.71 (m, 12H); MALDI-TOF (m/z) : $[M - H]^+$ calcd for $[C_{39}H_{43}BBrN - H]^+$ 606.7, found 605.2.

Synthesis of Compound TAB-2-B

A mixture of 0.66g (1mmol) TAB-1-PR, 0.51g (2mmol) bis(pinacolato)diboron. 0.058(8mol%) Pd(dppf)Cl_2 and 0.588g (60 mol) potassium acetate in DMSO (5mL) was stirred at 80 °C for 24 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, poured into the 50mL ice water, filtrated and then purified by column chromatography on silica gel with dichloreomethane/petroleum ether (1/10) as the eluent to afford TAB-2-B (0.608g, 83.5%) a yellow power. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, 1H), 8.16 (m, 1H), 8.00 (d, 1H), 7.71 (m, 1H), 7.64 (d, 1H), 7.59-7.50 (m, 2H), 7.24(s,1H), 7.35 (m, 1H), 7.02 (m, 1H), 6.97 (s, 1H), 6.94 (s, 2H), 6.71 (s, 1H), 3.58 (m, 4H), 2.90 (m, 1H), 2.75 (m, 1H), 2.65 (m, 1H), 2.05 (m, 4H), 1.42 (s, 9H), 1.29-1.24(m,9H), 0.85(m, 9H); MALDI-TOF (m/z) : $[M-H]^+$ calcd for $[C_{45}H_{55}B_2NO_2]^+$ 662.6, found 662.2.

Synthesis of Compound TAB-AIE-FL

0.332g (0.5mmol) of TAB-1-PR, 0.24g(1.05mmol) of 2-chloro-4, 6-di-t-bytyl-1, 3, 5-triazine, 27mg (0.03mmol) of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), 50mg(0.12mmol) of 2-dicyclohexylphosphino-2', 6'-dimethoxybiphenyl (SPhos), and 2.12g (10.00mmol) of potassium phosphate were mixed, and the mixture was heated to reflux for 2 hours under a nitrogen atmosphere. After the reaction solution was returned to room temperature, ethyl acetate and pure water were added, and the organic layer was extracted. The organic layer was dried with sodium sulfate and subjected to vacuum concentration, and purified by silica gel column chromatography to afford TAB-AIE-FL (277.7mg, 76.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, 1H), 8.37 (d, 1H), 8.10 (d, 1H), 7.77 (dm, 1H), 7.69 (m, 2H), 7.55 (d, 1H), 7.35(m,1H), 7.05 (m, 1H), 6.95-6.89 (m, 3H), 6.65 (s, 1H), 3.53 (m, 4H), 2.86 (m, 2H), 2.62 (m, 1H), 1.97 (m, 4H), 1.41 (s, 18H), 1.35 (m, 12H), 1.23 (m, 6H);MALDI-TOF (m/z) : $[M]^+$ calcd for $[C_{50}H_{61}BN_4]^+$ 728.88, found 728.3. Elemental analysis (%) calcd for $C_{50}H_{61}BN_4$: C 82.39 H 8.44 N 7.69; found: C 82.02 H 8.25 N 7.38.

Preparation of NG-TAB-AIE-FL

TAB-AIE-FL (0.4mg) was dissolved in 20 g of a 500 ppm solution of the polyurethane hydrogel (PU) in an ethanol/water (9:1, v/v) mixture. The resultant ratio of PU/TAB-AIE-FL is 200:4 (w/w). The mixtures were thoroughly stirred for 1 h, then dialyzed against distilled water for 24 h, with

an interval of 2 – 3 h to exchange the water. Finally, the aqueous dispersion of the nanogel was filtered through a 0.2 mm filter to remove large aggregates. The resultant suspension was used in further experiments.

Cell culture and viability assay. Mouse fibroblast cells (NIH/3T3) were cultured in Dulbecco's Modified Eagle Medium (DMEM) with glucose (4.5 g/L), L-glutamine, sodiumpyruvate,and 10% fetal bovine serum (FBS) (Beijing BioDee Biotechonology Co. Ltd, China). The cells were plated on glass bottomed dishes at 37 ℃ under 5% CO_2 atmosphere before imaging. Cell images were obtained using a confocal microscope FV1000-IX81 and were analyzed with FV10-ASW software. NIH/3T3 cells, pre-washed twice, were incubated with 10μM in cultured medium without FBS at 37 ℃ under 5% CO_2 for 30min. Then the cells were washed with PBS to remove unbounded probes for six times before *in situ* imaging by Olympus FV1000-IX81 confocal laser scanning microscopy using oil objective, with excitation by 405nm laser, and4 530-580nm emission light was collected.

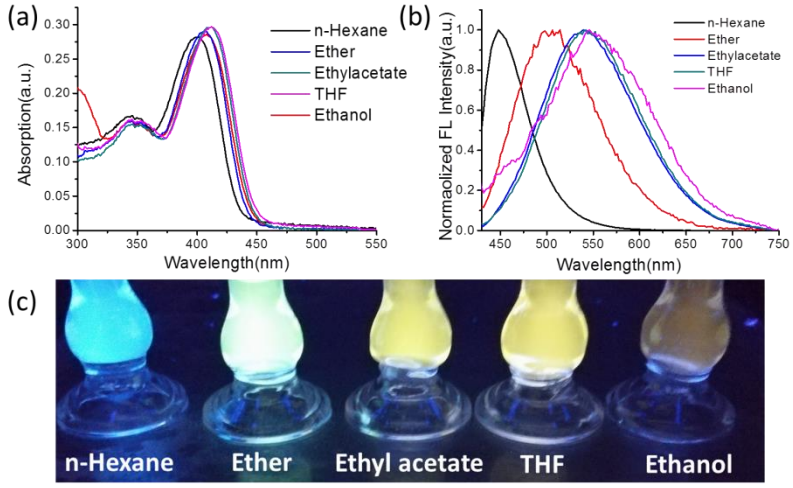


Figure S1. (a) UV absorption spectra and (b) Fluorescence spectra of TAB-2-PR in various solvents; (c) photograph of TAB-2-PR in various solvents under 365nm illumination. (10uM)

Table S1 Quantum yields Φ of TAB-AIE-FL in various solvents

States	solid	In n-Hexane	In THF	In DMSO	In Ethanol
Φ	0.403	0.121	0.010	0.009	0.008

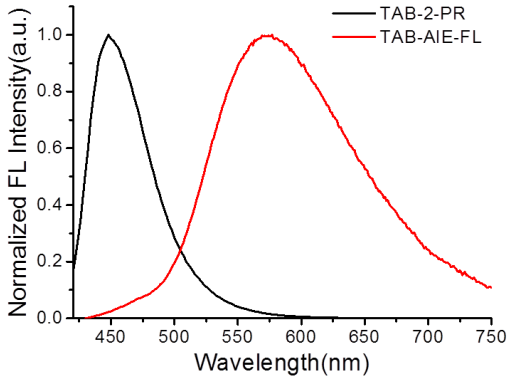


Fig. S2 Fluorescence spectra comparison of TAB-2-PR and TAB-AIE-FL in n-Hexane (10uM).

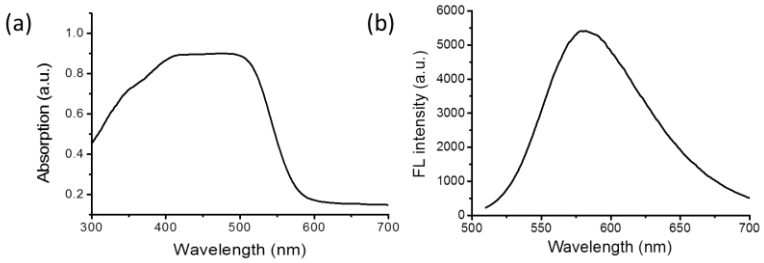


Fig. S3 UV absorption spectra of TAB-AIE-FL (a) and fluorecence spectra of TAB-AIE-FL (b) in solid state.

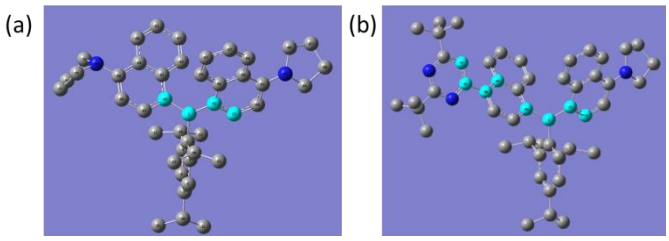


Fig. S4 the dihedral angle used for changing during the computation (atoms labed by cycan).

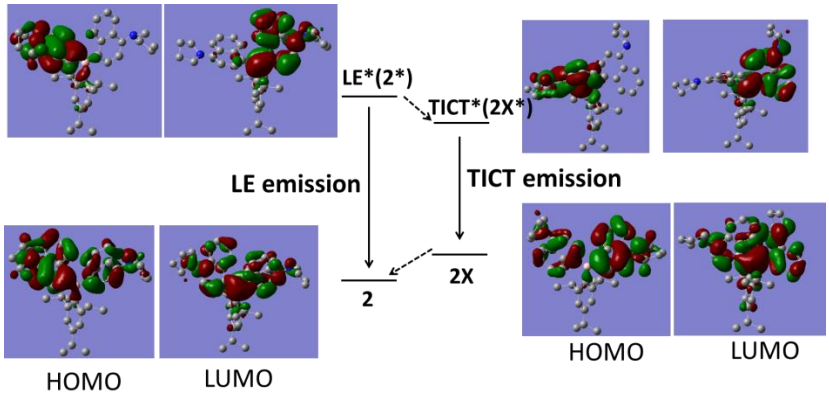


Fig. S5 The front orbital electron cloud distribution of LE state and TICT state of TAB-2-PR.

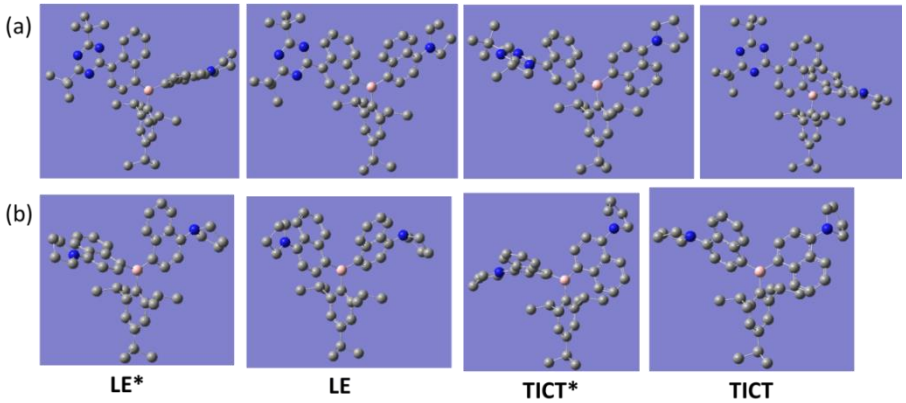


Fig. S6 The optimized ground/excited state geometries for LE (LE*) and TICT (TICT*) of TAB-AIE-FL (a) and TAB-2-PR (b).

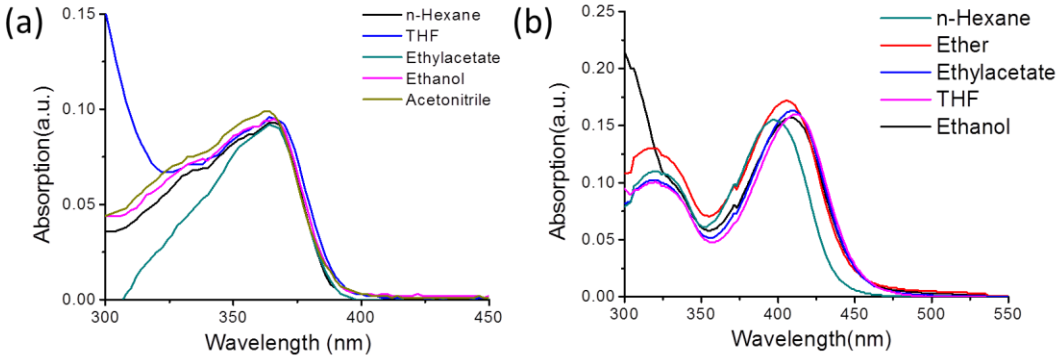


Fig. S7 UV absorption spectra of TAB-2-Br (a) and TAB-1-PR (b) in various solvents (10μM).

By comparing the UV absorption spectra of TAB-2-Br (a) and TAB-1-PR (b) in various solvents, it clearly demonstrated that TAB-1-PR, whose absorption peak appear at around 400nm, bears a larger conjugate plane than TAB-2-Br, whose absorption peak appear at around 360nm.

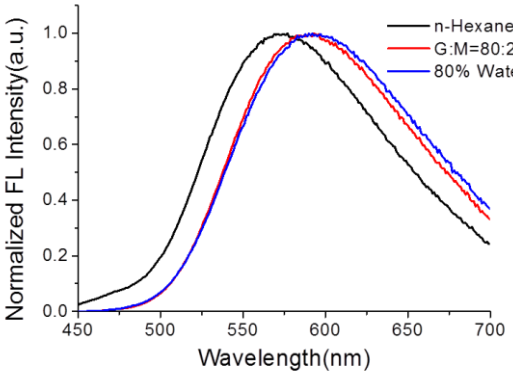


Fig. S8 Fluorescence spectra comparison of TAB-AIE-FL (10μM) in n-Hexane, the mixed solvent of 80% glycerol and 20% methanol, the mixed solvent of 80% water and 20% DMSO; λ_{exc} = 415nm.

By comparing the fluorescence spectra of TAB-AIE-FL in n-Hexane, the mixed solvent of 80% glycerol and 20% methanol, the mixed solvent of 80% water and 20% DMSO, The longer wavelength for the emission of TAB-AIE-FL in the mixed solvent of 80% glycerol and 20% methanol, the mixed solvent of 80% water and 20% DMSO than in n-hexane can attribute the more polarity and $\pi-\pi$ stack in aggregates.

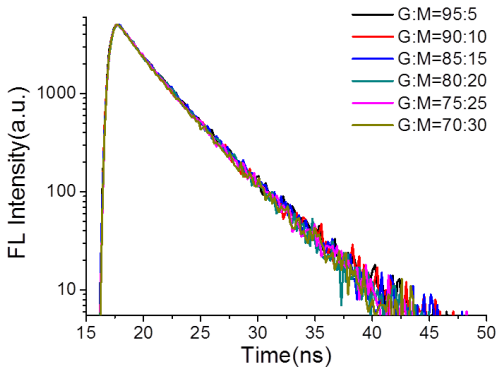


Fig.S9 Changes of fluorescence decay of TAB-AIE-FL (10μM) in the mixed solvents of glycerol and methanol with different ratio; λexc= 405nm.

Figure S9 show the fluorescence lifetime of TAB-AIE-FL is almost unchanged with the increase

of viscosity.

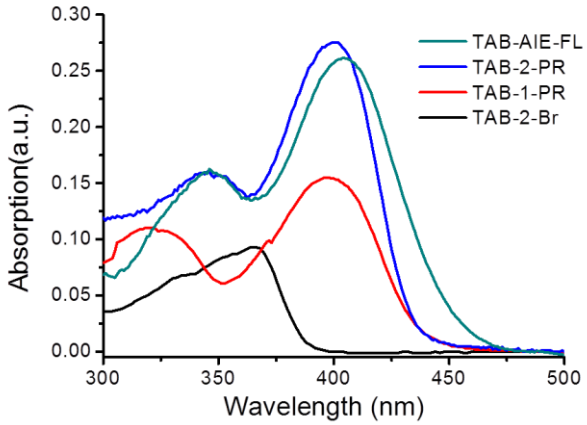


Fig. S10 UV absorption spectra comparison of TAB-2-Br, TAB-1-PR, TAB-2-PR and TAB-AIE-FL in n-Hexane (10μM).

By comparing UV absorption spectra of TAB-2-Br, TAB-1-PR, TAB-2-PR and TAB-AIE-FL in Fig.S10, we can clearly see the TAB-1-PR, TAB-2-PR and TAB-AIE-FL have larger conjugate plane than TAB-2-Br.

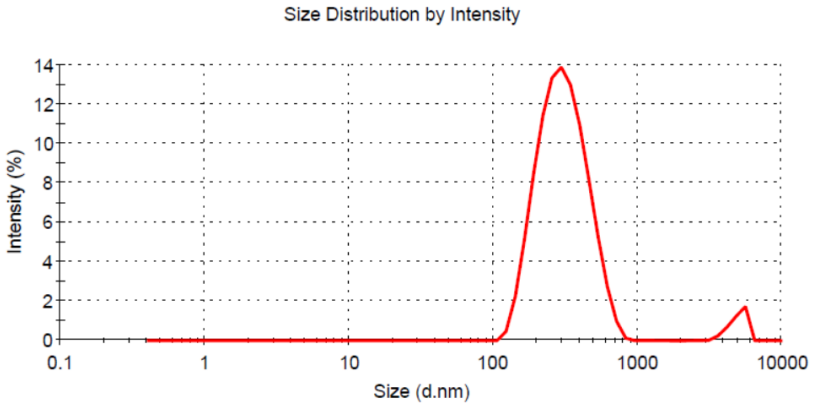


Fig. S11. Size distribution of NG-TAB-AIE-FL measured by DLS.

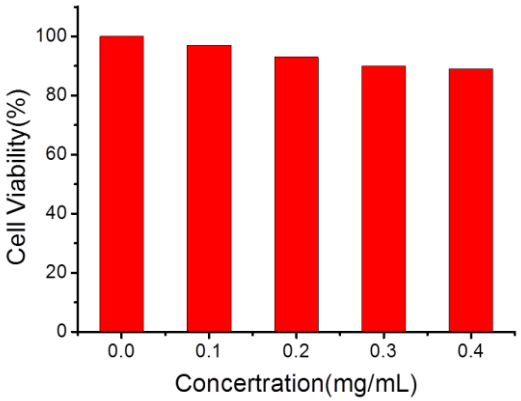


Fig. S12. Cytotoxicity of NG-TAB-AIE-FL on NIH/3T3 cells determined by MTT assay.

Considering biocompatibility is always one of the foremost property for a probe to be practically used in living cells, we further evaluate the cytotoxicity of NG-TAB-AIE-FL on NIH/3T3 cells by a standard 3-(4, 5-dimethyl-2-thiazolyl)-2, 5-diphenyltetrazolium bromide (MTT) assay.(Figure S12) NG-TAB-AIE-FL shows no apparent effects on the cell viability, even at a high concentration of 0.4mg/mL demonstrating a good biocompatibility of NG- NG-TAB-AIE-FL with NIH/3T3 cells.

[1]HNMR and Mass spectra of TAB-AIE-FL