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Electronic Supplementary Information

An AIE based tetraphenylethylene derivative for highly selective and light-up sensing of fluoride ion in aqueous solution and in living cells

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Experimental section

All solvents were purified and dried following standard procedures unless special statements. Compound **1** was prepared according to reported procedures.[S1] Compound **3** was synthesized as shown in Scheme 1 according to reported methods.[S2] Other chemical reagent were commercial available and used as received.

^{1}H NMR spectra were obtained on a Brucker DMX-400MHz spectrophotometer. High resolution mass spectra (HRMS) were obtained on Brucker APEX IV (7.0 T) FT_MS. UV-Vis absorption spectra and fluorescence emission spectra were recorded on a Shimadzu UV-1601PC spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Dynamic light scattering (DLS) experiments were carried out with Malvern Instrument (Nano Series). Confocal fluorescence imaging experiments were performed with an Olympus FV-1000 laser scanning microscopy system, based on an IX81 (Olympus, Japan) inverted microscope. The microscope was equipped with 375 nm (CW) laser lines and UPLSAPO 60x/N.A 1.42 objective. Images were collected and processed with Olympus FV10-ASW Ver.2.1b software.

Synthesis of MOPy-TPE (compound 2)

A mixture of compound **1** (220 mg, 0.500 mmol), 4-pyridinylboronic acid (90 mg, 0.730 mmol), Pd(dppf)Cl_2 (80 mg, 0.100 mmol), CH_2Cl_2 (1 mL), Bu_4NI (25 mg, 0.068 mmol) and potassium

carbonate aqueous solution (2 M, 10 mL) in degassed toluene (20 mL) was refluxed under nitrogen atmosphere. After cooling to room temperature, the mixture was washed with brine and extracted with ethyl acetate twice. The organic layer was combined and dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was subjected to column chromatography with ethyl acetate/petroleum ether (1/20~1/2, v/v) as eluent. Compound **2** was obtained as a yellow solid. Yield: 63 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (br, 2H), 7.67 (br, 2H), 7.48 – 7.43 (m, 2H), 7.21 – 7.04 (m, 12H), 6.96 (dd, *J* = 12.2, 8.7 Hz, 2H), 6.69 – 6.94 (m, 2H), 3.76 (s, 3H). HRMS: 440.20082, $[M+H]^+$.

Synthesis of MOTIPS-TPE

To a solution of MOPy-TPE (20 mg, 0.046 mmol) in toluene, compound 6 (31 mg, 0.091 mmol) was added. The mixture was stirred at 110 ℃ overnight at a nitrogen atmosphere. After cooling to room temperature, the mixtures was concentrated and subjected to column chromatography, using dichloromethane/methanol (100/1~10/1) as eluent. MOTIPS-TPE was obtained as an orange yellow solid. Yield: 87 %. ^{1}H NMR (400 MHz, MeOD) δ 8.92 (br, 2H), 8.39 – 8.27 (m, 2H), 7.78 (dd, *J* = 14.9, 8.6 Hz, 2H), 7.43 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.31 – 7.20 (m, 3H), 7.18 – 6.89 (m, 13H), 6.68 (t, *J* = 8.6 Hz, 2H), 5.71 (s, 2H), 3.72 (d, *J* = 4.4 Hz, 3H), 1.26 (m, 3H), 1.12 (d, *J* = 7.3 Hz, 18H). ^{13}C NMR (101 MHz, MeOD) δ 158.85, 158.69, 157.39, 155.87, 148.96, 148.86, 144.01, 143.39, 143.30, 143.15, 142.85, 142.83, 138.74, 138.66, 135.34, 135.28, 132.48, 132.28, 132.19, 131.08, 131.04, 131.02, 130.96, 130.58, 129.58, 128.51, 127.76, 127.65, 127.42, 127.31, 127.22, 126.75, 126.50, 126.46, 125.94, 124.32, 120.51, 113.10, 112.87, 62.95, 54.31, 17.03, 12.48. HRMS: 702.37643, $[M]^+$.

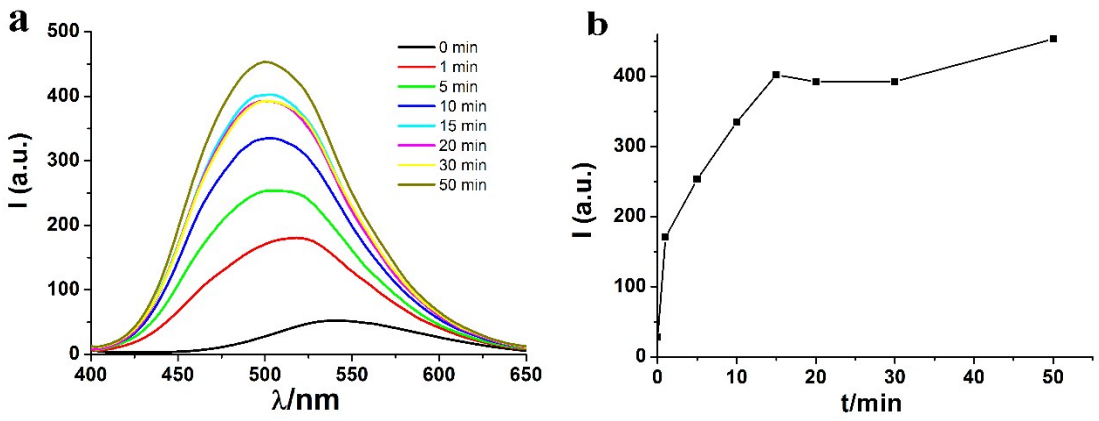

Figure S1. (*a*) Fluorescent responses of MOTIPS-TPE (4 μM) toward F^- (20 μM) at different time points. (*b*) The fluorescence intensity at 504 nm of MOTIPS-TPE (4 μM) incubated with F^- (20 μM) as a function of time. (E_{ex} = 344 nm).

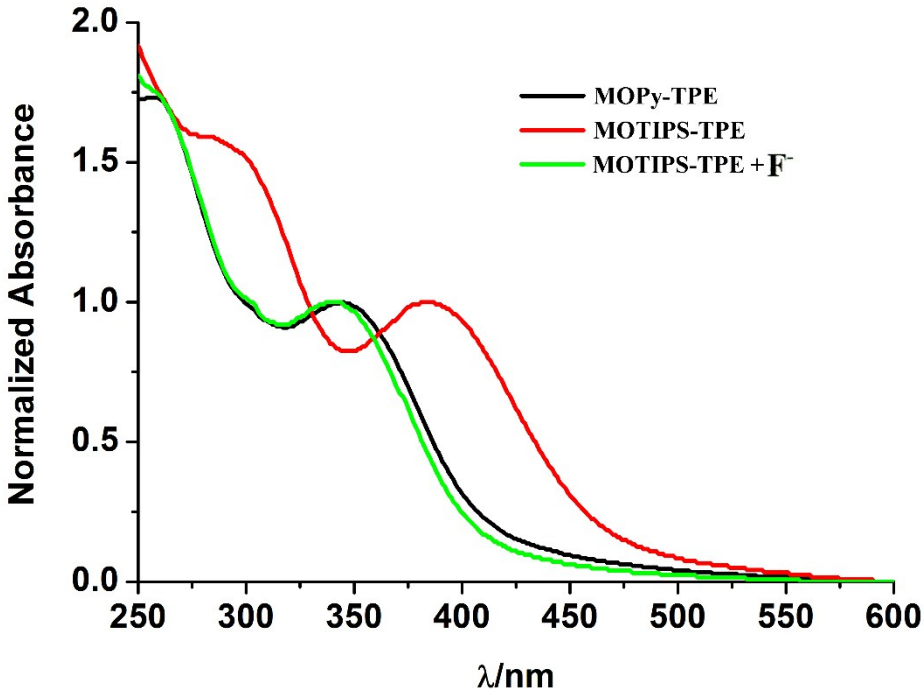

Figure S2. The normalized absorption spectra of MOTIPS-TPE (4.0 μM) in PBS before and after incubation with F^- (20 μM). Normalized absorption spectra of MOPy-TPE were also given for comparation.

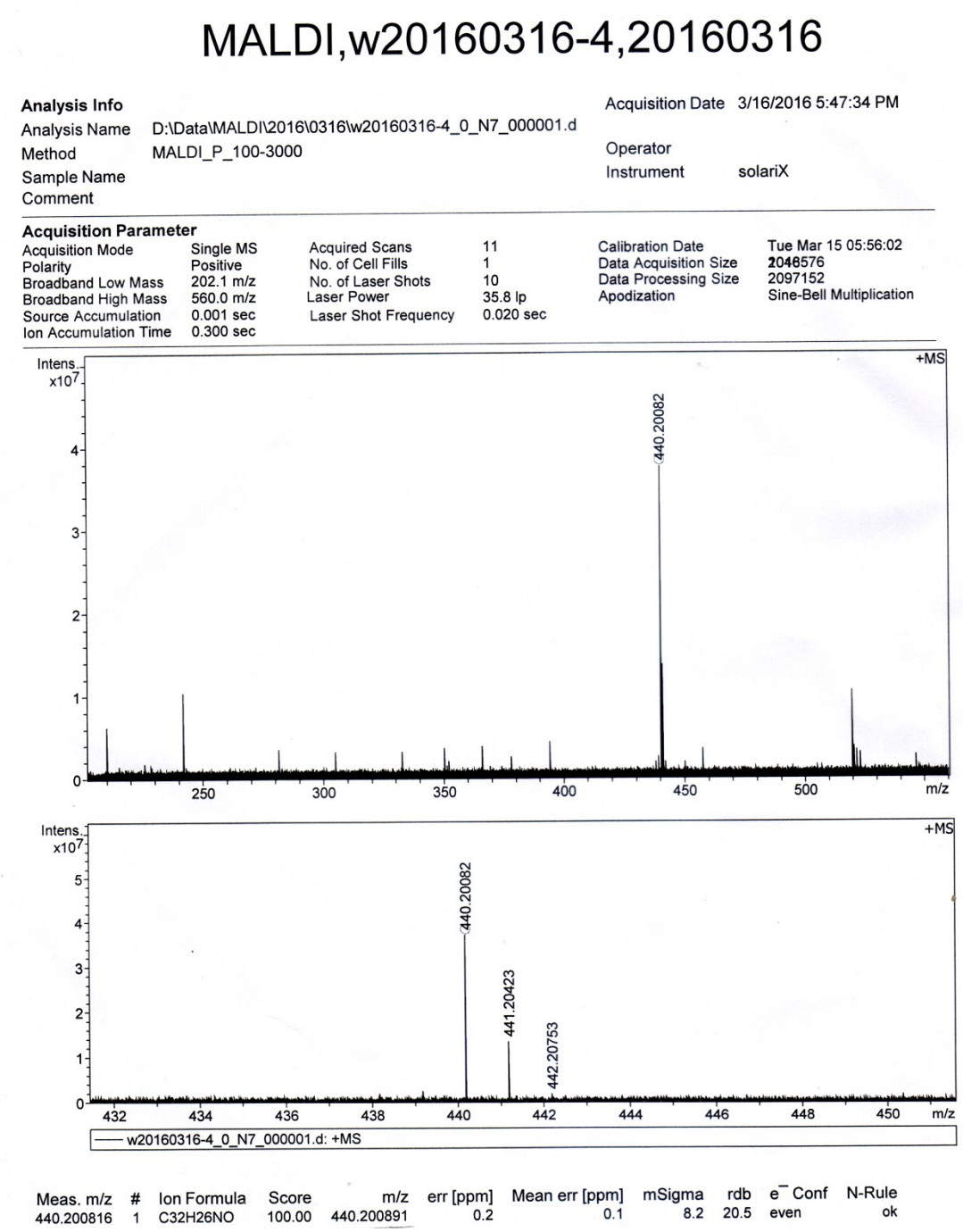

Figure S3. HRMS spectrum of MOTIPS-TPE after 15 min incubation with F^- at 37℃.

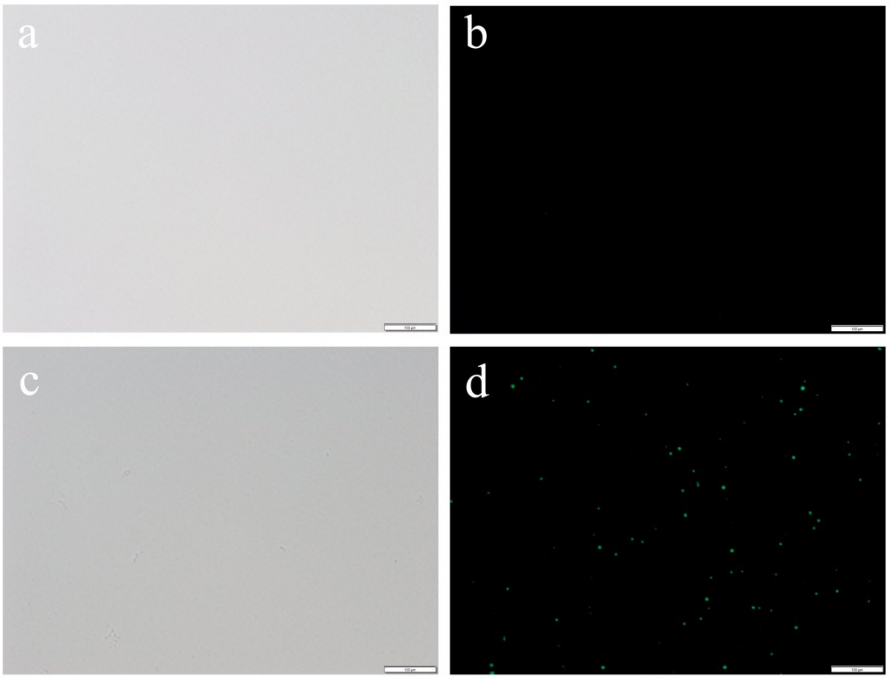

Figure S4. Fluorescence microscope images of MOTIPS-TPE (4.0 μM) in PBS before (a and b) and after (c and d) incubation with F^- (20 μM). Scale bar represents 10 μm.

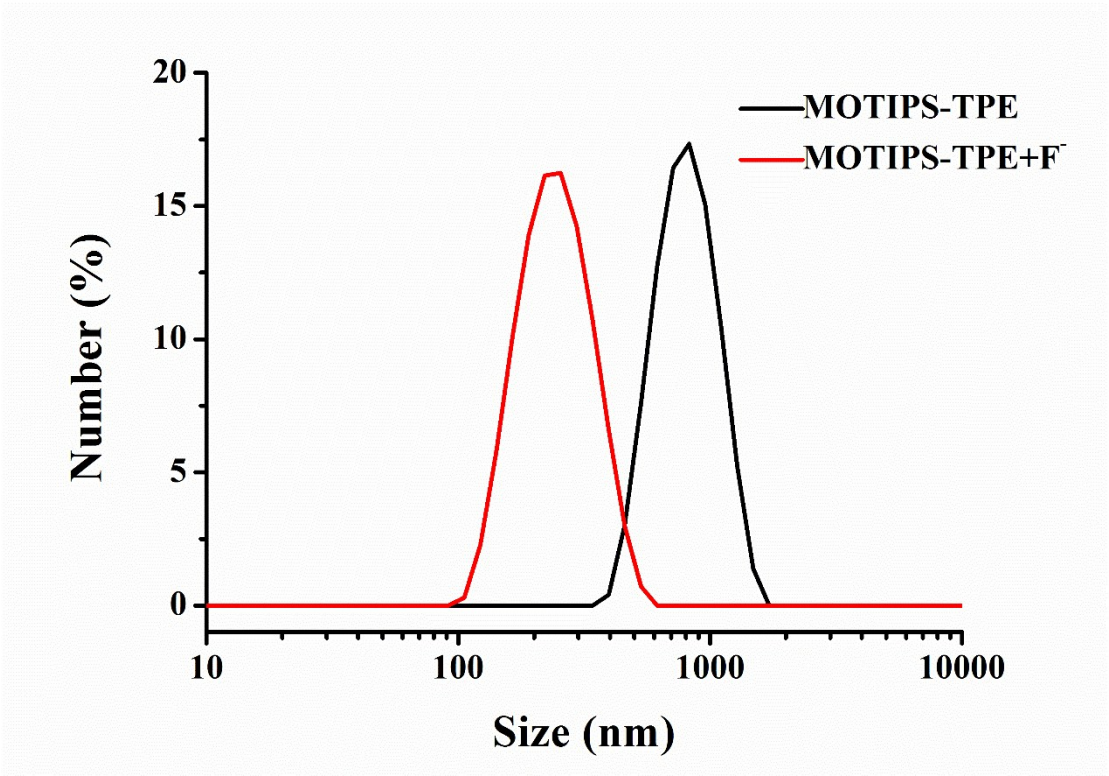

Figure S5. DLS data of MOTIPS-TPE (4 μM) before and after 15 min incubation with 20 μM of fluoride ion in PBS.

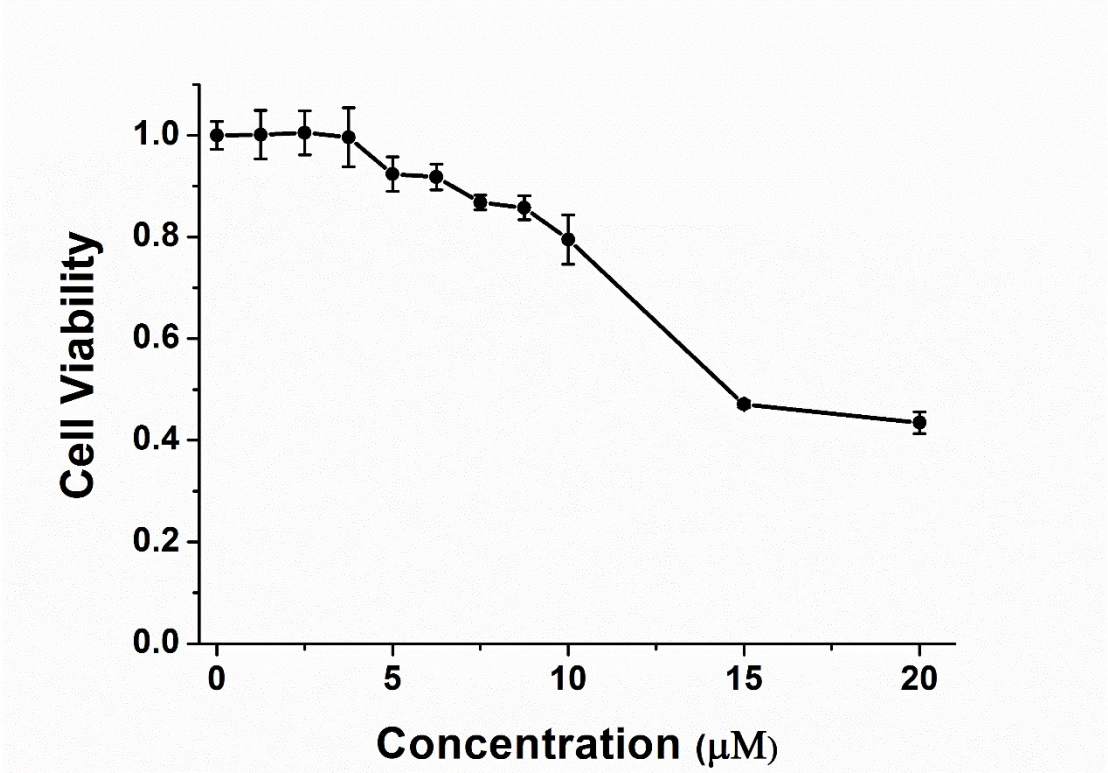

Figure S6. Cell viability of HeLa cells at varied concentrations of MOTIPS-TPE using MTT assay.

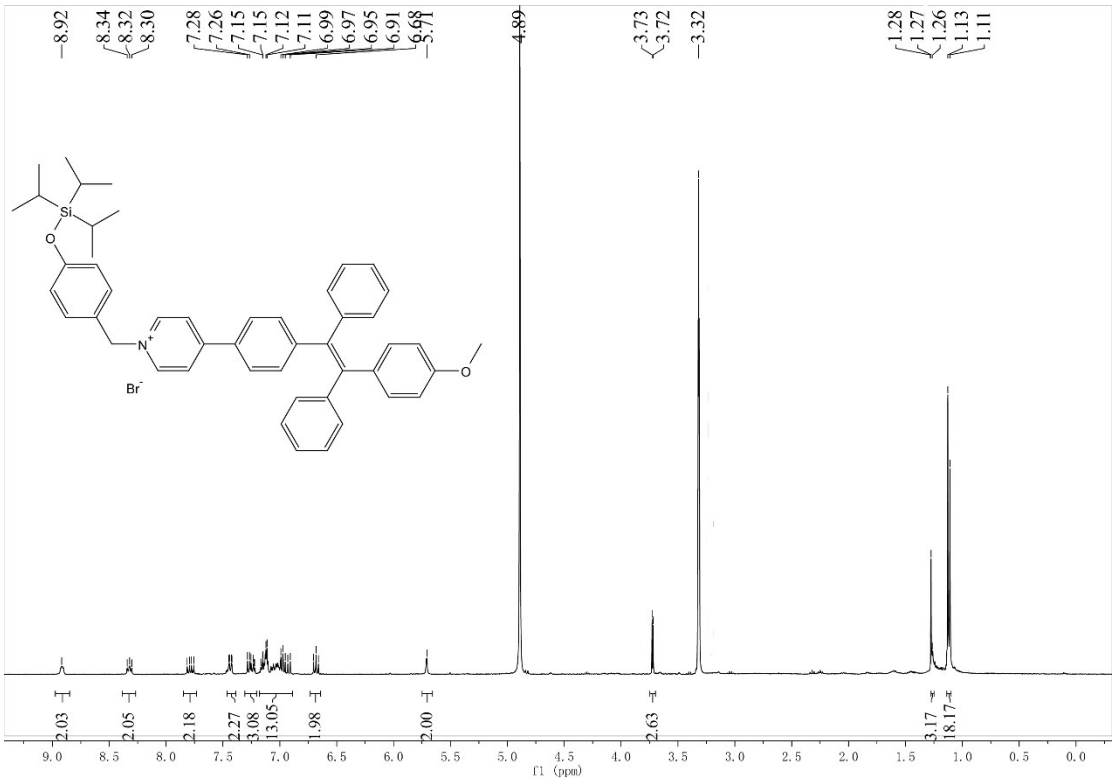

Figure S7. ^{1}H NMR spectrum of MOTIPS-TPE in CD_3OD.

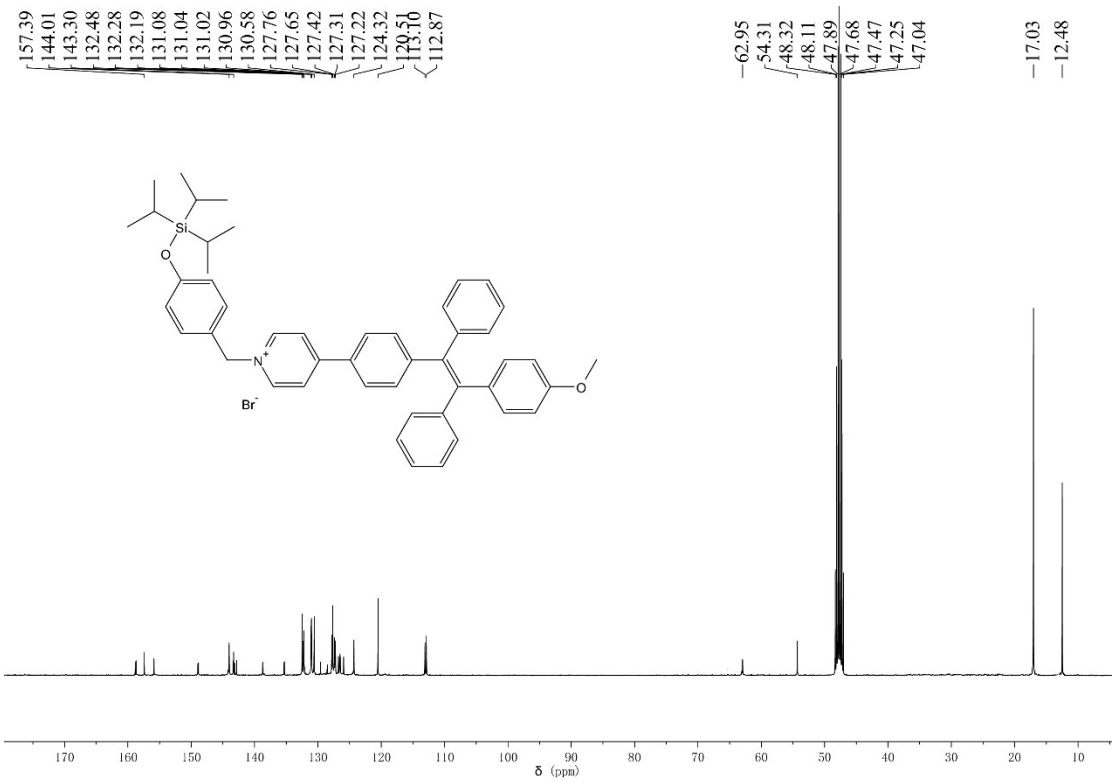

Figure S8. ^{13}C NMR spectrum of MOTIPS-TPE in CD_3OD.

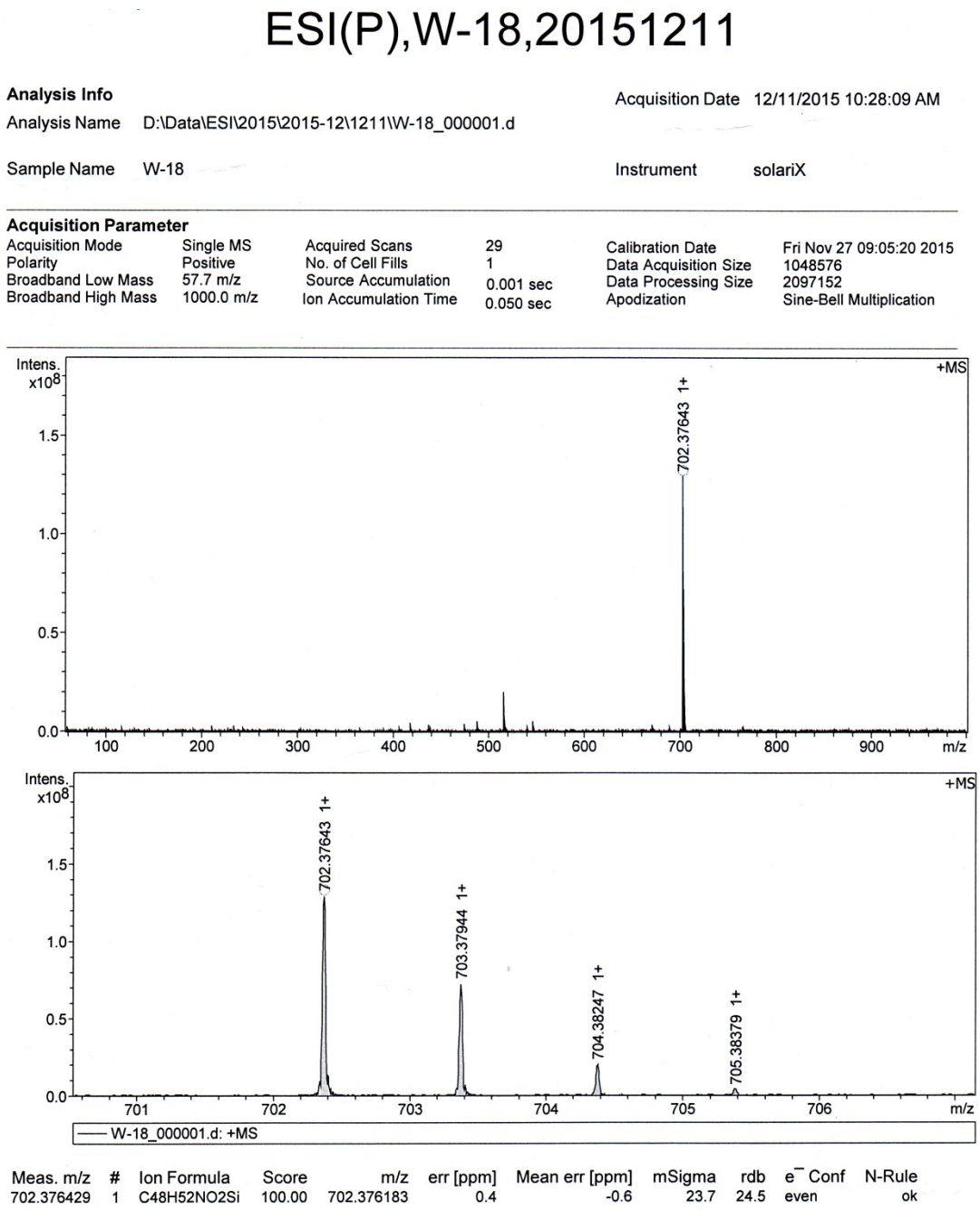

Figure S9. HRMS spectrum of MOTIPS-TPE.

References:

S1. (*a*) X. Gu, J. Yao, G. Zhang, C. Zhang, Y. Yan, Y. Zhao and D. Zhang, *Chem-Asian J.*, 2013, **8**, 2362; (*b*) F. Hu, G. Zhang, C. Zhan, W. Zhang, Y. Yan, Y. Zhao, H. Fu and D. Zhang, *Small*, 2015, **11**, 1335.

S2. J. Xu, S. Sun, Q. Li, Y. Yue, Y. Li and S. Shao, *Anal. Chim. Acta*, 2014, **849**, 36.