Supplementary Material (ESI) for Chemical Communications
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Ratiometric fluorescence chemodosimeters for fluoride anion based on pyrene excimer/monomer transformation

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Electronic Supplementary Information

I. Experimental section

I. Experimental Section

I.1 Materials and instrumentations. All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air and moisture-sensitive reactions were carried out under nitrogen atmosphere in oven-dried glassware. Glassware was dried in an oven at 100 °C and cooled under a stream of inert gas before use. Triethylamine was distilled over calcium hydride. Dry THF was distilled from sodium metal using benzophenone as an indicator under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of the solvent. HRMS were recorded on a Bruker Daltonics microTOF-Q II spectrometer.

1,1,2,2-Tetramethyl-1,2-bis(pyren-1-ylmethoxy)disilane (**1**)

1,2-Dichlorotetramethyldisilane (81μL, 0.43 mmol) was slowly added to a solution of 1-pyrenylmethanol (200 mg, 0.86 mmol) and Et_3N (264 μL, 1.89 mmol) in THF (30 mL). The mixture was stirred over night at room temperature and then filtered. After evaporation of THF, the residue was separated by column chromatography to give a white solid in 77% yield (Hex/EA=9/1; v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15-8.04(m, 10 H), 8.01-7.93(m, 6 H), 7.84(d, J = 9.2 Hz, 2 H), 5.42(s, 4 H), 0.37 (s, 12 H); HR-MS: Calcd. for $C_{38}H_{34}O_2Si_2$ $[M+Na]^+$: 601.1995, found 601.1949.

Dimethylbis(pyren-1-ylmethoxy)silane (**2**)

Compound **2** was obtained as a white solid in 75% yield by following a procedure similar to that of **1**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.06 (m, 4 H), 8.05(s, 2 H), 8.02 (s, 1 H), 7.98(d, J = 8.0 Hz, 2 H), 7.93-7.89(m, 8 H), 7.86 (s, 1 H), 5.35(s, 4 H), 0.32 (s, 6 H); HR-MS: Calcd. for $C_{36}H_{28}O_2Si$ $[M+H]^+$: 520.1859, found 520.1875.

Trimethyl(pyren-1-ylmethoxy)silane (**3**)

Compound **3** was obtained as a solid in 68% yield by following a procedure similar to that of **1**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31(d, J = 9.2 Hz, 1 H), 8.21-8.15 (m, 4

H), 8.13-8.10(m, 1 H), 8.05 (s, 2 H), 8.03-7.99(m, 1 H), 5.45(s, 2 H), 0.23(s, 9 H); HR-MS: Calcd. for $C_{20}H_{20}OSi$ $[M+Na]^+$: 327.1181, found 327.1191

I.2 Procedures of anion sensing

Stock solutions of the anions (1 mM) were prepared with the corresponding salts (tetrabutylammonium fluoride for F^-) in deionized water. A stock solution of **1–3** (1 mM) was prepared in THF. The solution of **1–3** was then diluted to 10 mM with THF/H_2O. In titration experiments, each time a 2 mL solution of **1–3** (10 mM) was filled into a quartz optical cell of 1 cm optical path length, the fluoride anion stock solution was added into the quartz optical cell gradually using a micropipette. In selectivity experiments, the test samples were prepared by placing appropriate amounts of each anion stock solution into a 2 mL solution of **1–3** (10 mM). During fluorescence measurements, the excitation wavelength was 335 nm, and emission spectra were collected between 350–650 nm.

I.3 DFT calculations

The G03W software package[S1] was used to carry out a DFT geometry optimization using the B3LYP functional with 6-31G(d) basis sets.

I.4 Synthesis of PLA nanoparticles

Poly(D,L-lactic acid) (PLA) nanoparticles were prepared by using an oil-in-water (O/W) emulsion and a subsequent solvent evaporation method.[S2] A mixture dispersion of hydrophobic probe **1** and PLA in methylene chloride was poured into an aqueous solution containing F127 ($(EO)_{97}(PO)_{69}(EO)_{97}$) and the solution underwent ultra-sonication using a probe-type sonicator. After the organic solvent was evaporated at room temperature by mechanical stirring and subsequently washed with deionized water several times, PLA nanoparticles incorporating probe **1** were collected. The nanoparticles were centrifuged at 14000 × *g* for 15 min and washed with deionized water. Finally, the resulting nanoparticles solution was filtered with a 220 nm pore size cellulose acetate filter and stored at 4 °C.

I.5 Cell Culture and Confocal Imaging

HeLa cells were maintained following protocols provided by the American type Tissue Culture Collection. Cells were seeded at a density of 1×10^6 cells mL^{-1} for confocal imaging in RPMI 1640 Medium supplemented with 10% fetal bovine serum (FBS), $NaHCO_3$ (2 g/L), and 1% antibiotics (penicillin/streptomycin, 100 U/mL). Cultures were maintained at 37 °C under a humidified atmosphere containing 5% CO_2.

Confocal fluorescence imaging studies were performed on a LSM 710 confocal laser-scanning microscope (Carl Zeiss Co., Ltd.). Prior to imaging, the medium was removed. Cell imaging was carried out after washing cells with PBS for three times. The excitation wavelength was 405 nm, and emission was collected in the ranges of 410–440 nm and 440–600 nm, respectively.

III. References

S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, R. C. Gaussian 03, Gaussian, Inc., Wallingford CT, 2004.

S2 J. Kim, J. E. Lee, S. H. Lee, J. H. Yu, J. H. Lee and T. G. Park, *Adv. Mater.* 2008, **20**, 478;

II Supplementary data

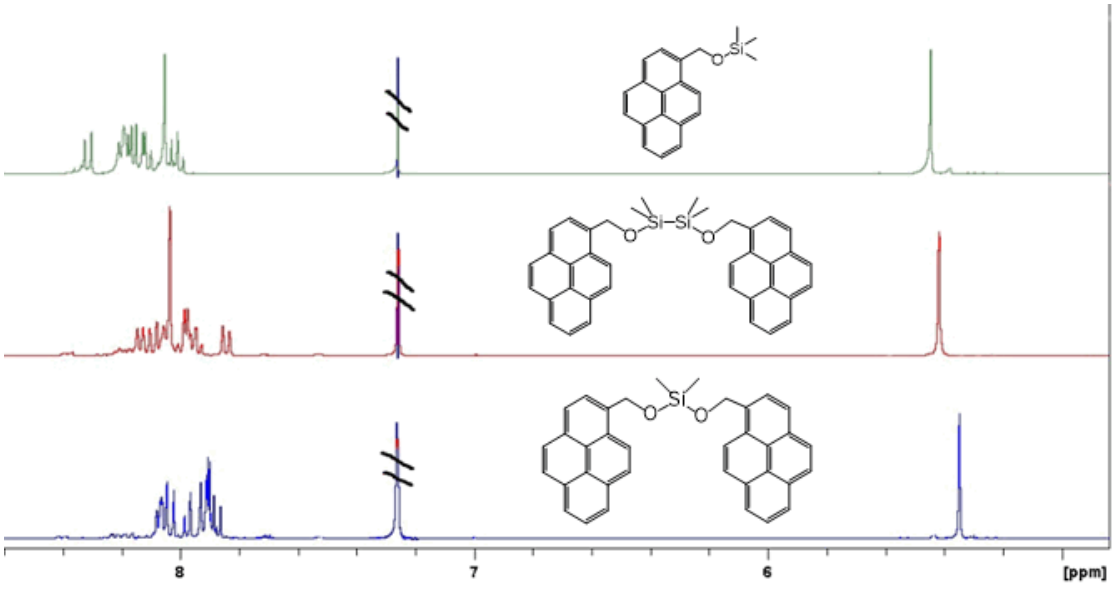

Fig. S1 ^{1}H NMR spectra of **1**–**3**. ($CDCl_3$ solution).

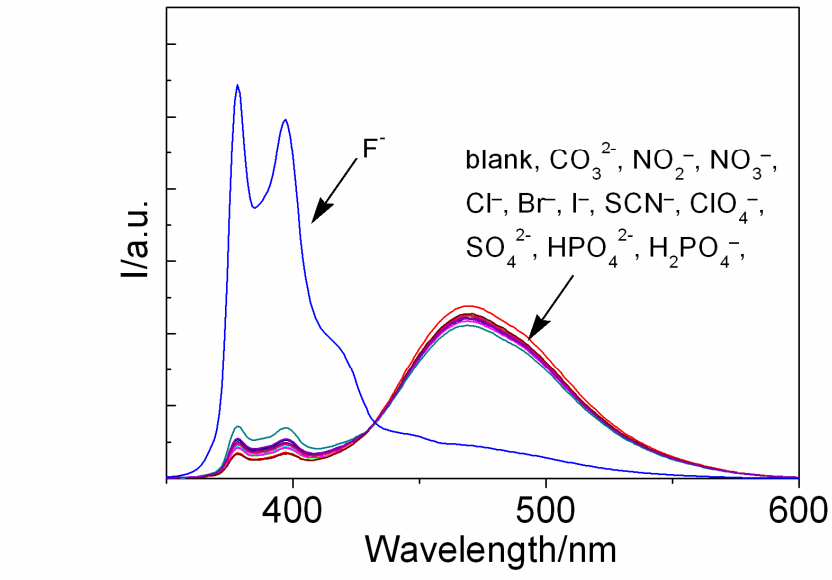

Fig. S2 Fluorescence response spectra of 10 μM **1** in THF/H_2O (v/v, 50/50) after the addition of 10 equiv kind of anion. λex = 335 nm.

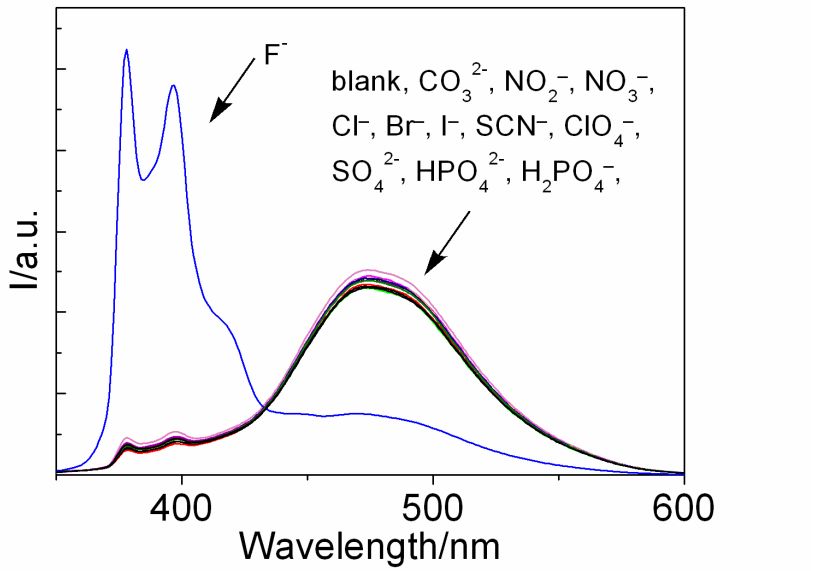

Fig. S3 Fluorescence response spectra of 10 μM **2** in THF/H_2O (v/v, 50/50) after the addition of 10 equiv kind of anion. λex = 335 nm.

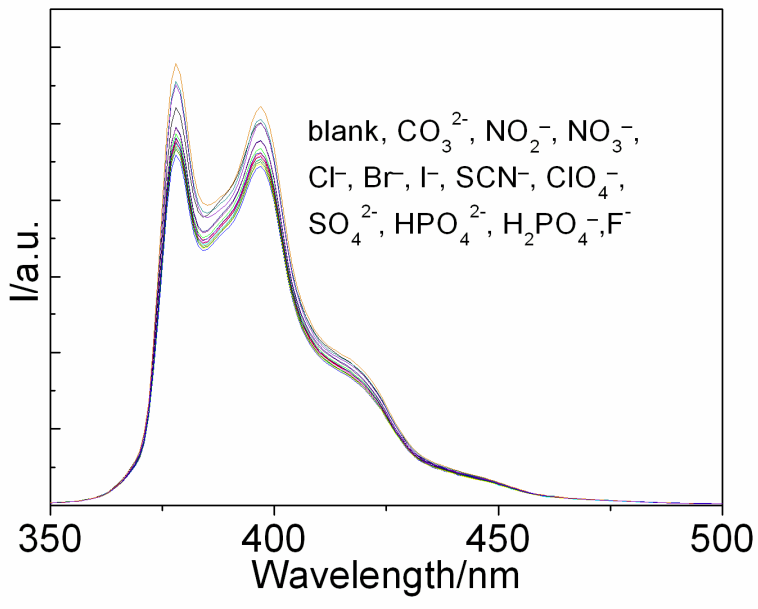

Fig. S4 Fluorescence response spectra of 10 μM **3** in THF/H_2O (v/v, 50/50) after the addition of 10 equiv kind of anion. λex = 335 nm.

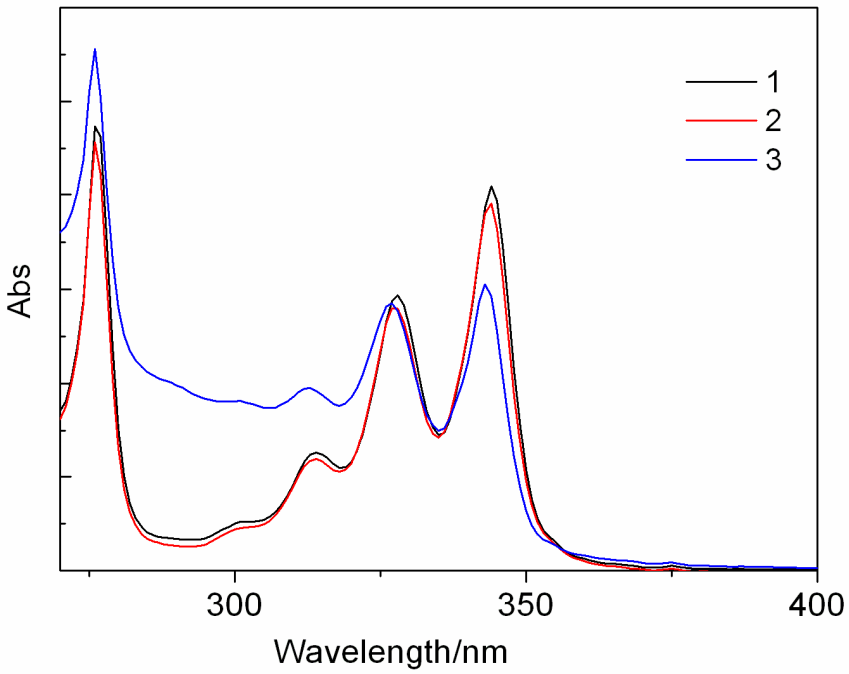

Fig. S5 Absorption spectra of pyrene derivatives **1–3** in THF.

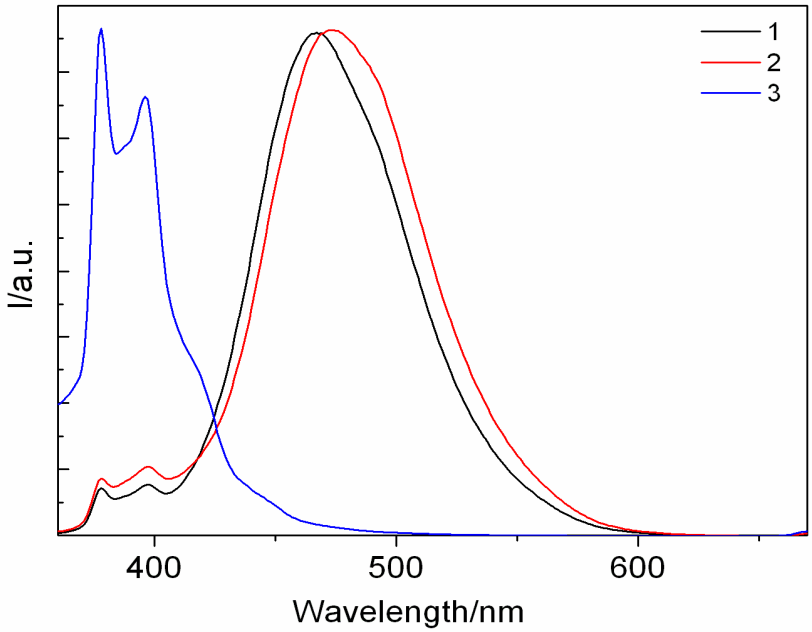

Fig. S6 Fluorescent spectra of pyrene derivatives **1–3** in THF.

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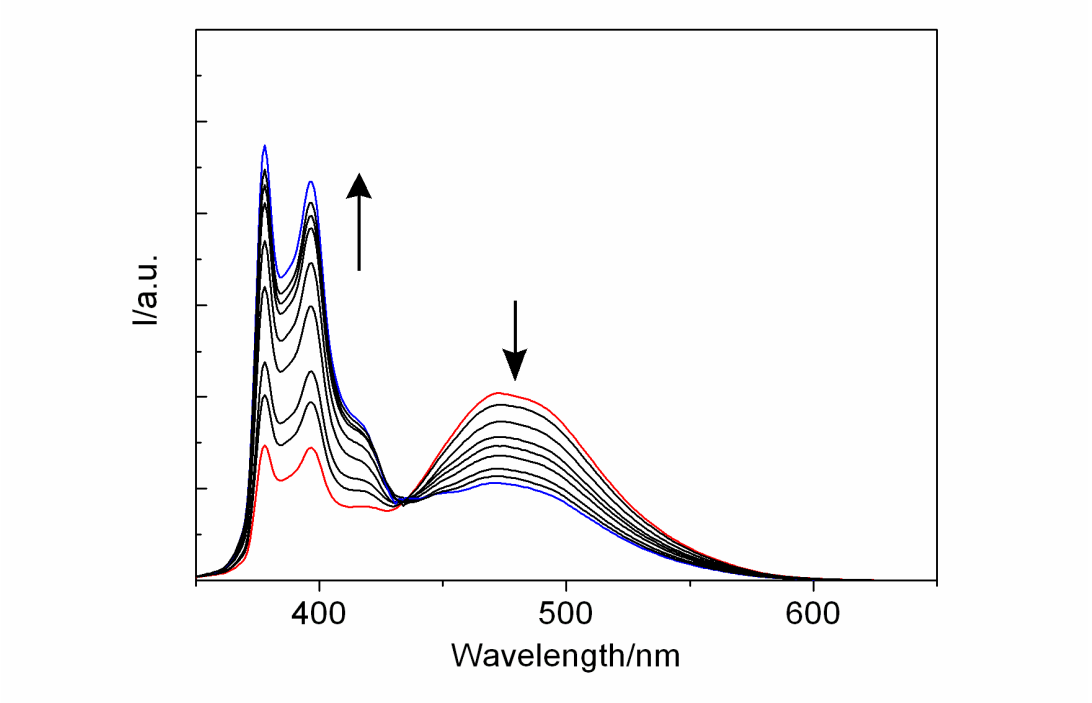

Fig. S7 Fluorescent titration spectra of **2** (10 μM) in THF/H_2O (v/v, 50/50) after the addition increasing of fluoride anion.

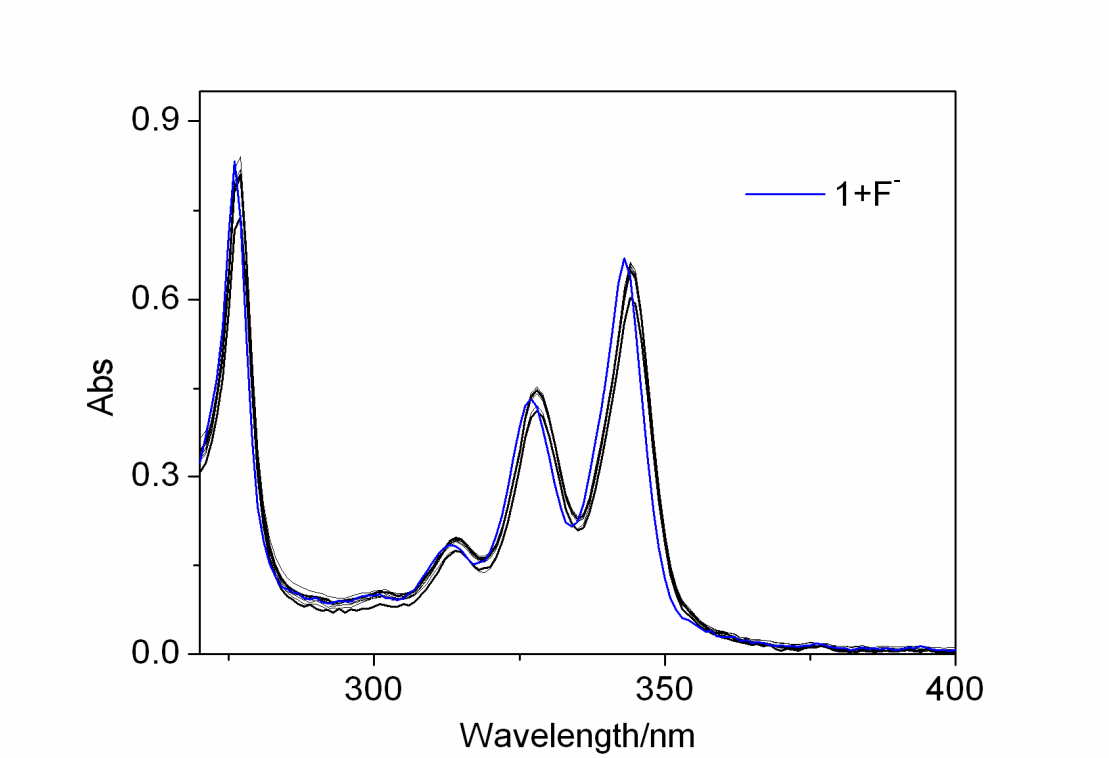

Fig. S8 Absorption spectra of **1** (10 μM) in THF/H_2O (v/v, 50/50) after the addition of 10 equiv kind of anion.

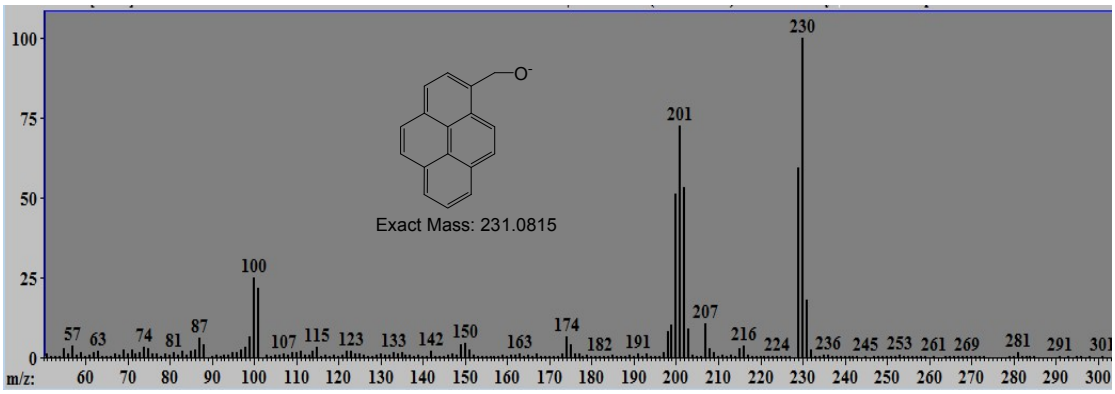

Fig. S9 GC-MS spectrum of **1** with the addition of fluoride anions.

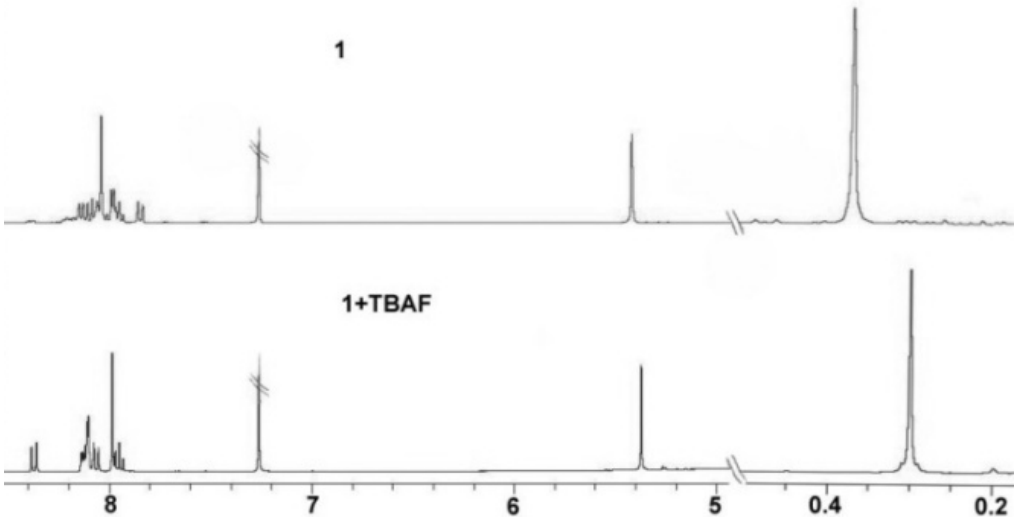

Fig. S10 ^{1}H NMR spectra of **1** and **1** with the addition of fluoride anions ($CDCl_3$ solution).

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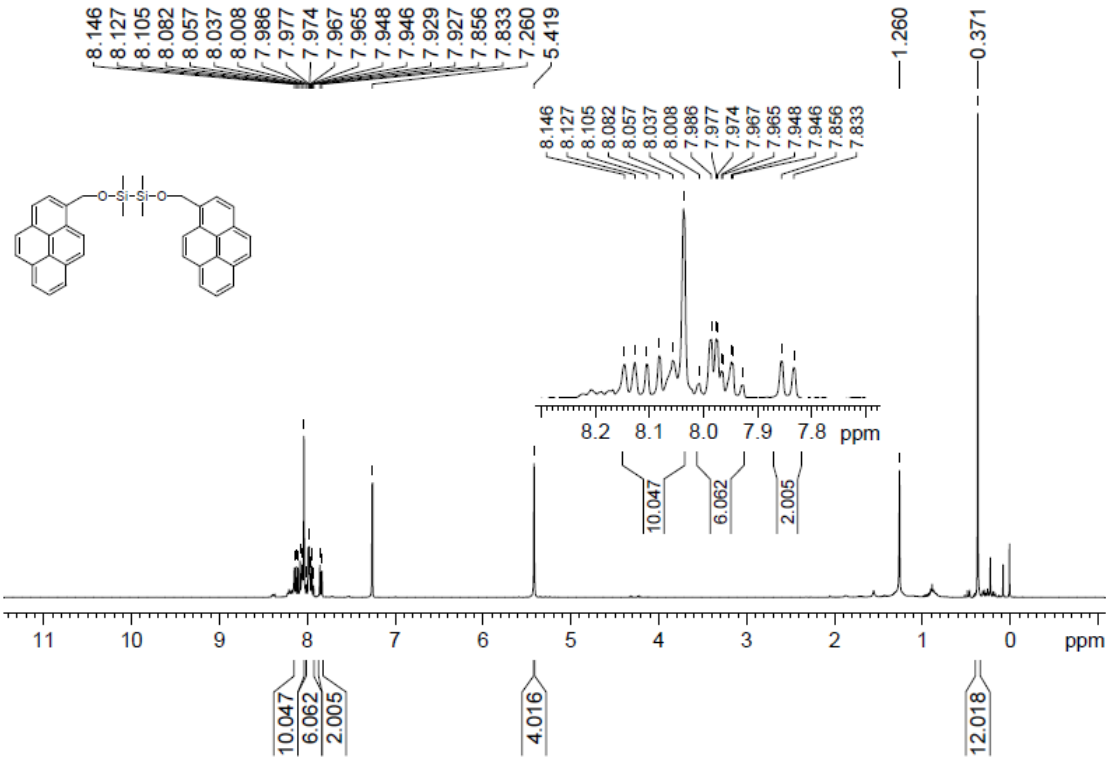

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Comment			

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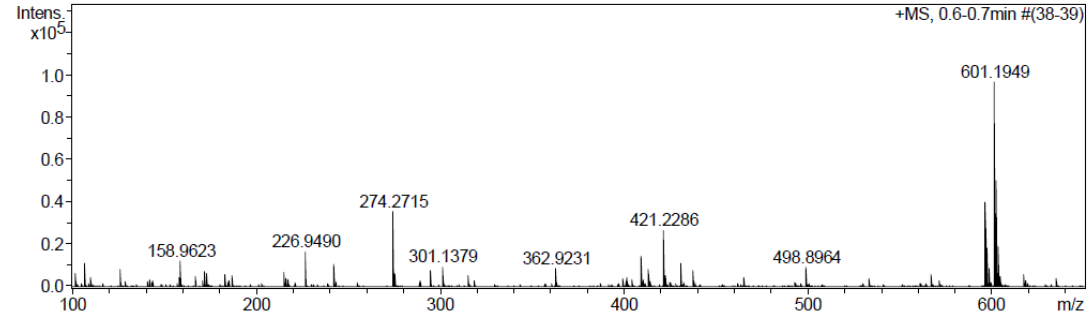

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb e¯ Conf N-Rule

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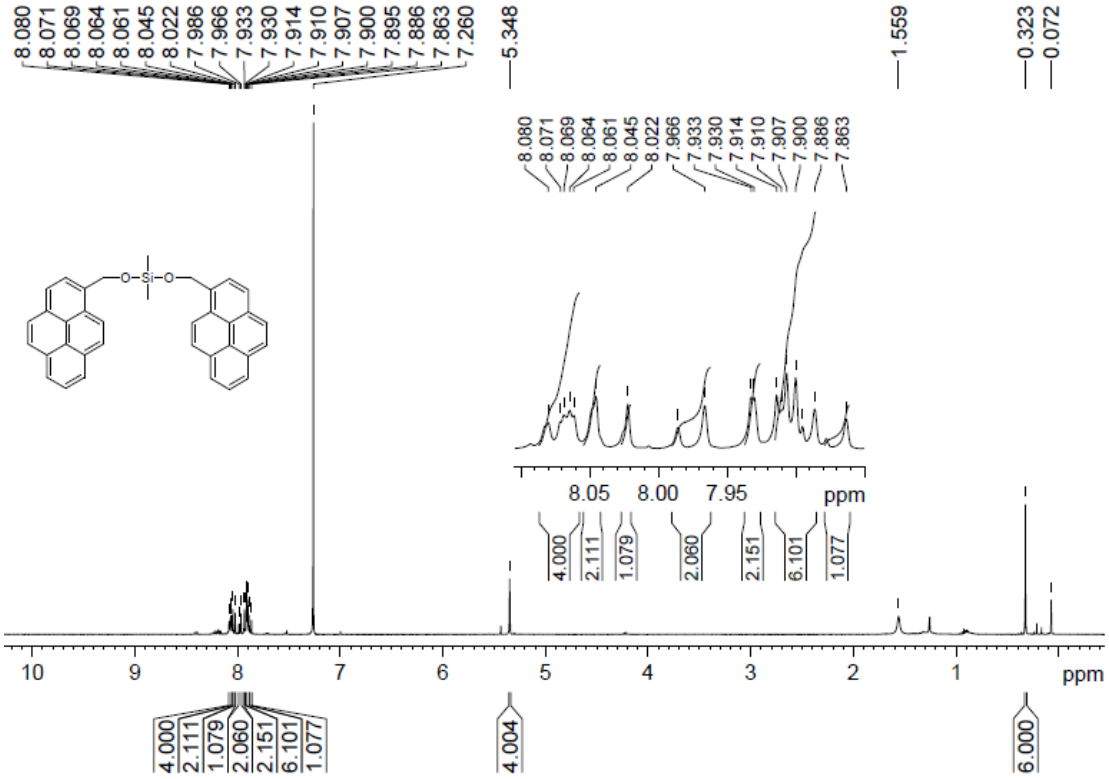

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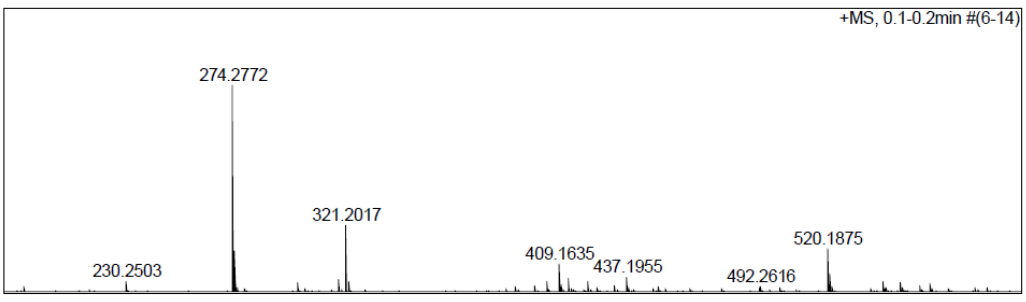

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
520.1875	1	C 32 H 22 N 7 O	100.00	520.1880	0.5	1.0	36.5	25.5	even	ok
	2	C 31 H 26 N 3 O 5	71.99	520.1867	-0.8	-1.5	43.9	20.5	even	ok

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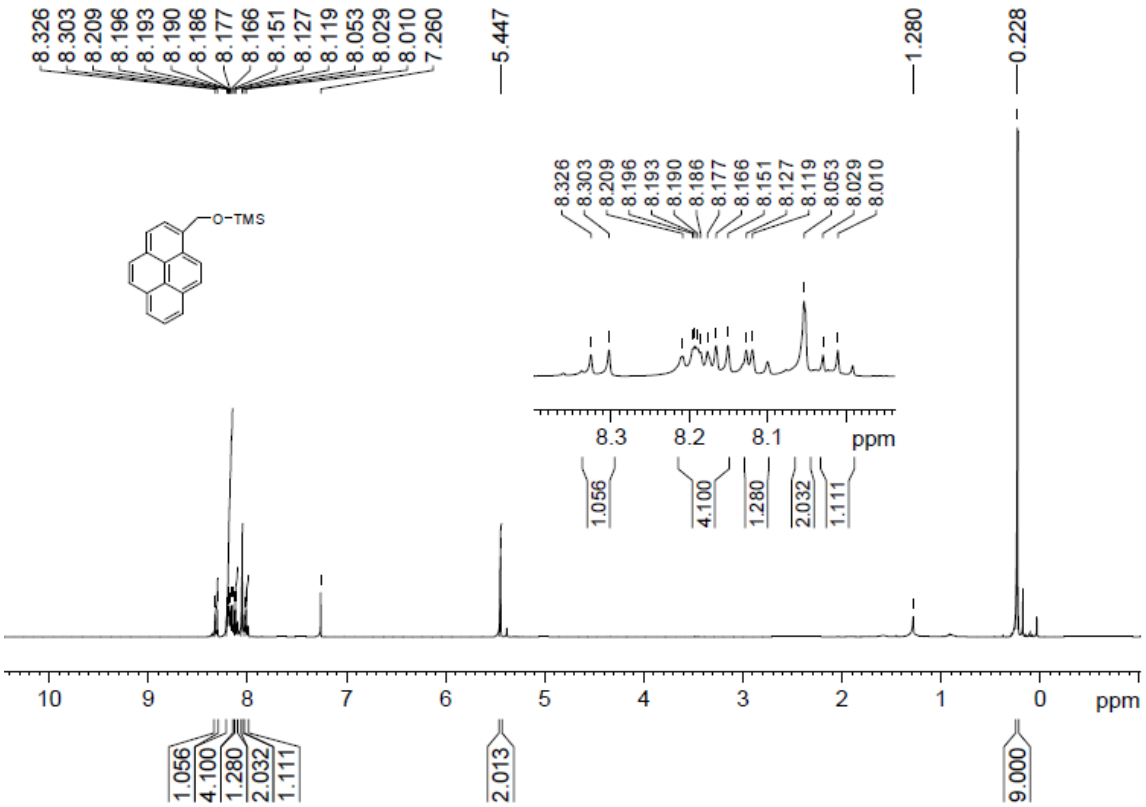

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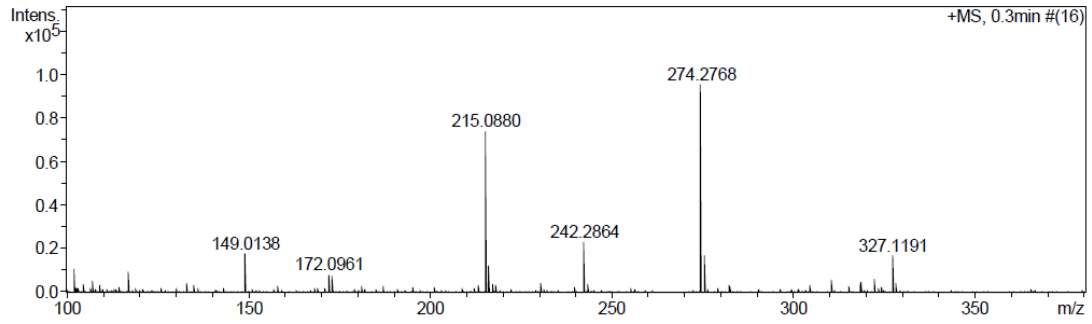

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