

Supporting Information

Development of a Fluoride-Ion Sensor based on Aggregation of a Dye-modified Polyhedral Oligomeric Silsesquioxane

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Materials and Methods

Instrumentation

^1H , ^{13}C and ^{29}Si NMR spectra were recorded on JEOL AL400 instruments at 400, 100 and 80 MHz respectively. ^{19}F NMR spectra were recorded on JEOL ECZ400S instruments at 376 MHz. Samples were analyzed in CDCl_3 . The chemical shift values were expressed relative to Me_4Si (^1H , ^{13}C and ^{29}Si) and C_6F_6 (^{19}F , -163 ppm) as internal standards in CDCl_3 . High-resolution mass (HRMS) spectrometry was performed on an EXACTIVE Plus (Thermo Fisher Scientific) at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the high-resolution mass spectra (HRMS) were obtained on a Thermo Fisher EXACTIVE for electrospray ionization (ESI). UV-vis spectra were recorded on a SHIMADZU UV-3600i Plus spectrophotometer, and samples were analyzed at room temperature. Fluorescence emission spectra were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer. Absolute photoluminescence quantum efficiency (Φ_{PL}) was recorded on a Hamamatsu Photonics Quantaaurus-QY Plus C13534-01. Elemental analyses were performed with a MICRO CORDER MT-5 (YANACO CO., Ltd.) at the Microanalytical Center of Kyoto University. Thermogravimetric analysis (TGA) was recorded on a Hitachi High-Tech Science Corporation. TA STA7200RV. Differential scanning calorimetry (DSC) was recorded on a Hitachi High-Tech Science Corporation. TA DSC7020. The sample on the aluminum pan was heated at the rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen flowing (50 mL/min). The dynamic light scattering (DLS) measurements were carried out at 90° scattering angle and 20 ± 0.2 $^\circ\text{C}$ using a FPAR-1000 particle analyzer with a He-Ne laser as a light source. The CONTIN program was used for data analysis to extract information on the average hydrodynamic size. All reactions were performed under nitrogen atmosphere.

Materials.

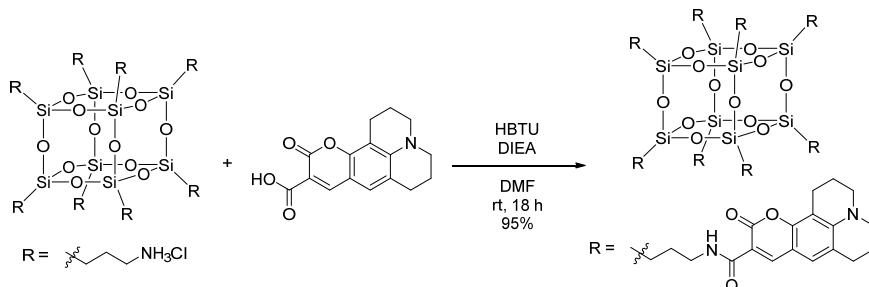
Propylamine, 4-(diethylamino)salicylaldehyde was purchased from Tokyo Chemical Industry Co, Ltd. Tetrabutylammonium fluoride (1 M in THF solution), *N,N*-diisopropylethylamine (DIEA), meldrum's acid, and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) were purchased from FUJIFILM Wako Pure Chemical Corporation. 1-[Bis(dimethylamino)methylene]-1*H*-benzotriazolium 3-oxide hexafluorophosphate (HBTU) was purchased from PEPTIDE INSTITUTE, INC. *N,N*-Dimethylformamide (DMF) (deoxidized grade), and dimethyl sulfoxide (DMSO) (deoxidized grade) were purchased from Wako and used as the reaction solvent. All compounds were used without purification. Octakis(3-aminopropyl) POSS hydrochloride (**Amino-POSS**)¹ and coumarin 343 (C343)² were synthesized according to the literatures.

Sample Preparation for Optical Measurements for Anion Sensing

The stock solution of **C343-POSS** in CHCl₃ (1.6×10^{-3} M per C343 unit) was prepared. This stock solution (30 μ L) was diluted with THF (2970 μ L) and stirred on a Fisher vortex for 30 s with a speed of 8 to obtain **C343-POSS** (1.6×10^{-5} M per C343 unit) in THF/CHCl₃ (99/1 v/v) mixed solution. Diluted TBAF in THF (3 μ L) was added within 30 s and stirred again for 30 s to prepare each concentration. The measurements were initiated 15 min after the end of stirring for Figures 2a and S11, and 1 min after the end of stirring for Figures 2b and 2c to monitor the difference. In the case of anti-interference tests, the anions in THF (3 μ L, 1.0×10^{-5} M) were added within 1 min.

Synthetic Procedures and Characterization

Synthesis of C343-POSS



C343 (55.3 mg, 0.19 mmol) and HBTU (88.3 mg, 0.23 mmol) were placed in a round-bottom flask equipped with a magnetic stirring bar. DMF (10 mL) and DIEA (0.081 mL, 0.47 mmol) were added to the flask. After the mixture was activated at room temperature for 30 min, Amino-POSS (22.8 mg, 0.019 mmol) was added to this solution and stirred for 18 h. The precipitate was collected by filtration, washed with DMF, cyclohexane and dried *in vacuo*. The yellow solid of **C343-POSS** (55.4 mg, 0.0183 mmol, 95%) was then obtained.

^1H NMR (CDCl_3 , 400 MHz) δ 8.81 (t, $J = 5.6$ Hz, 1H), 8.48 (s, 1H), 6.88 (s, 1H), 3.46-3.41 (m, 2H), 3.27-3.22 (m, 4H), 2.77 (t, $J = 6.3$ Hz, 2H), 2.69 (t, $J = 6.2$ Hz, 2H), 1.91 (d, $J = 5.1$ Hz, 4H), 1.77-1.72 (m, 2H), 0.75-0.71 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.3, 162.7, 152.3, 147.7, 147.5, 126.8, 119.2, 109.2, 108.1, 105.4, 50.1, 49.7, 42.1, 27.3, 23.0, 21.1, 20.1, 20.0, 9.4 ppm; ^{29}Si NMR (CDCl_3 , 80 MHz) δ -66.9 (s) ppm. HRMS (ESI) calcd. for $\text{C}_{152}\text{H}_{168}\text{N}_{16}\text{O}_{32}\text{Si}_8$ $[\text{M}+\text{Na}]^+$: 3039.9853, found: 3039.9855.

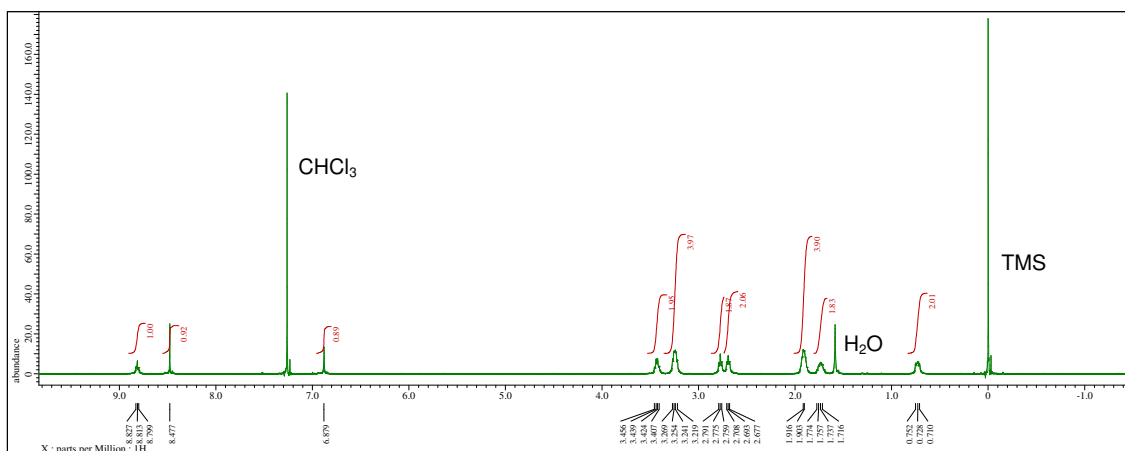


Figure S1. ^1H NMR spectrum of **C343-POSS** in CDCl_3 .

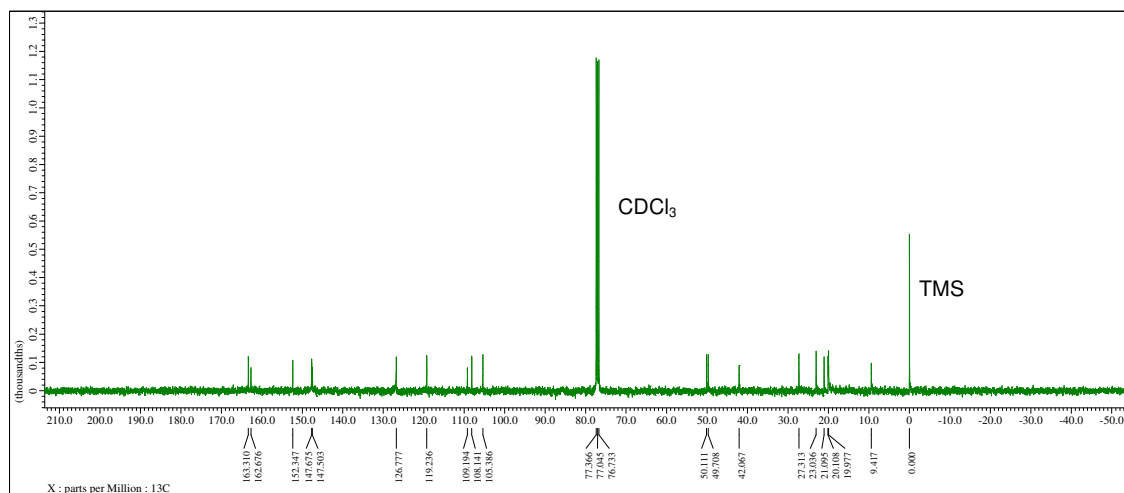


Figure S2. ^{13}C NMR spectrum of C343-POSS in CDCl_3 .

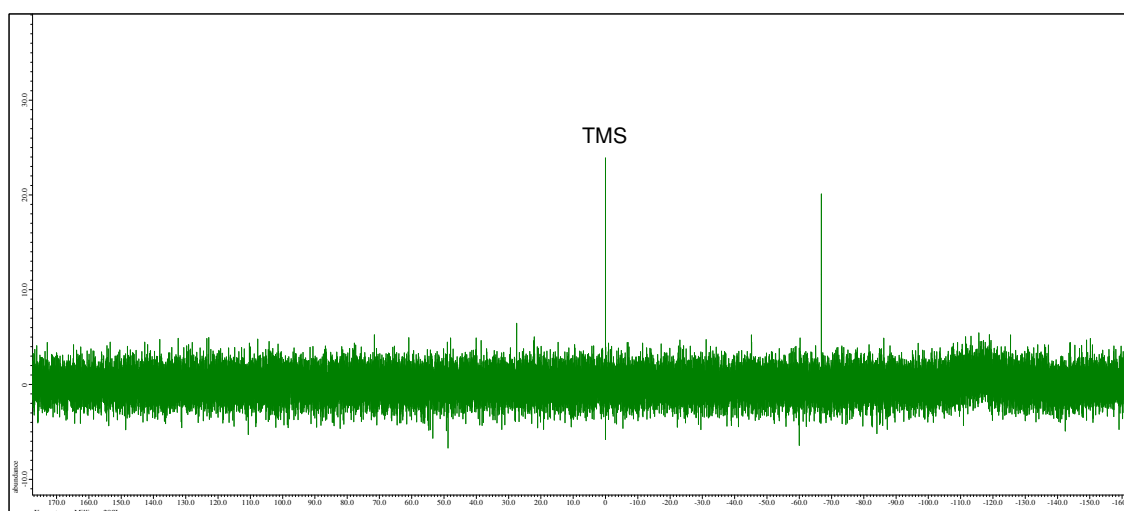
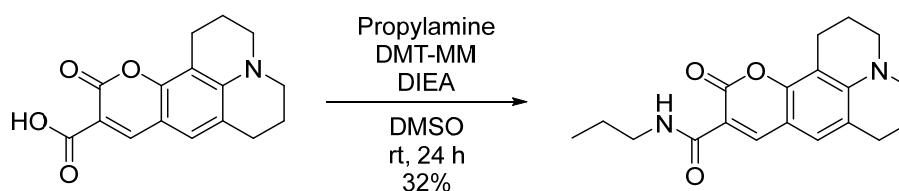


Figure S3. ^{29}Si NMR spectrum of C343-POSS in CDCl_3 .

Synthesis of C343-arm



C-343 (28.5 mg, 0.1 mmol) was dissolved in 5 mL of DMSO in a flask. DMT-MM (55.3 mg, 0.2 mmol) was added to the solution, and the mixture was stirred at room temperature for 30 min, followed by addition of propylamine (5.9 mg, 0.1 mmol) and DIEA (34.8 μL , 0.2 mmol). The mixture was

additionally stirred at room temperature for 24 h and dropped into 250 mL of 0.5 M NaHCO₃ aq. and the products were precipitated. The precipitation was collected by filtration and washed with water and dried *in vacuo*. Recrystallization from hot EtOH/water afforded **C343-arm** as a yellow crystal (10.6 mg, 0.032 mmol, 32%).

¹H NMR (CDCl₃, 400 MHz) δ 8.87 (s, 1H), 8.61 (s, 1H), 7.01 (s, 1H), 3.40 (d, *J* = 5.9 Hz, 2H), 3.33 (s, 4H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 1.98-1.98 (m, 4H), 1.65-1.63 (m, 2H), 0.98 (t, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 163.5, 163.1, 152.6, 148.0, 148.0, 127.0, 119.6, 109.3, 108.3, 105.7, 50.2, 49.8, 41.3, 27.5, 22.9, 21.2, 20.2, 20.1, 11.5 ppm. HRMS (ESI) calcd. for C₁₉H₂₀N₂O₃ [M+Na]⁺: 349.1523, found: 349.1527.

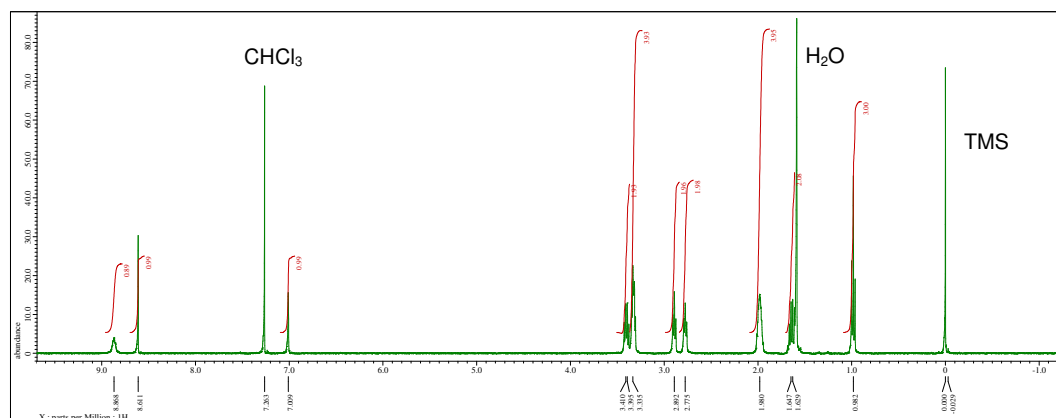


Figure S4. ¹H NMR spectrum of **C343-arm** in CDCl₃.

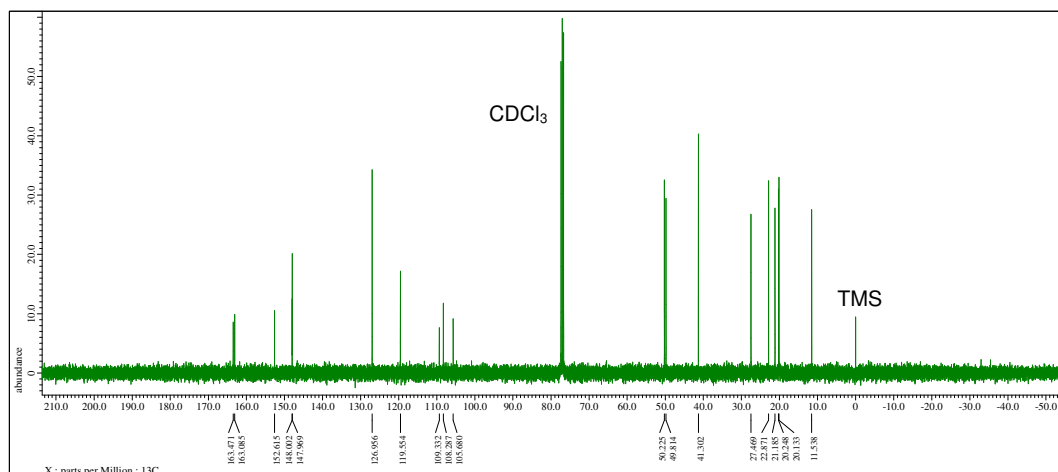


Figure S5. ¹³C NMR spectrum of **C343-arm** in CDCl₃.

IR Spectra

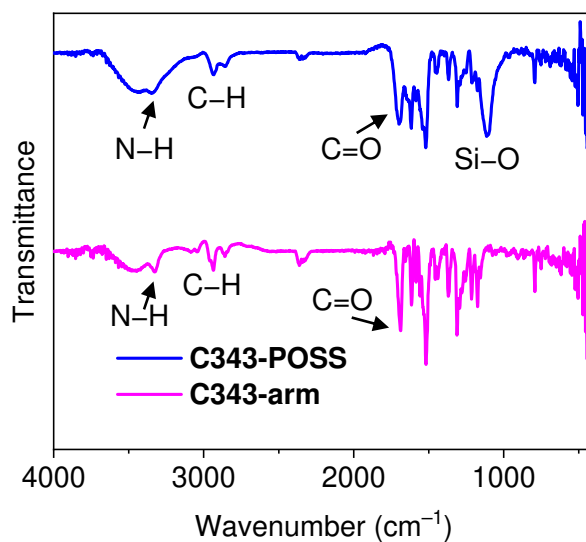


Figure S6. IR spectra of **C343-POSS** and **C343-arm** in KBr pellets.

Optical Properties

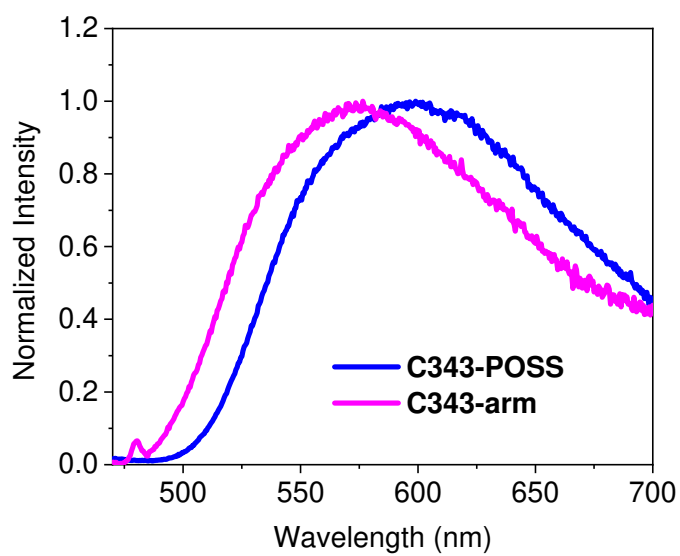


Figure S7. Emission spectra of **C343-POSS** and **C343-arm** in the solid state.

Table S1. Optical data of C343-POSS and C343-arm in solution and solid states

		$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm) ^c	$\epsilon(\text{M}^{-1} \text{cm}^{-1})$ ^d	Φ_{PL} (%)
C343-POSS	CHCl ₃ ^a	429	461	37,300	30
	THF/CHCl ₃ ^b	418	464, 541	20,100	9
	solid	-	596	-	2
C343-arm	CHCl ₃ ^a	432	460	48,000	85
	THF/CHCl ₃ ^b	425	462	43,700	82
	solid	-	574	-	5

^a 1.6×10^{-5} M per C343 unit (absorption), 8.0×10^{-6} M per C343 unit (emission and Φ_{PL}).

^b In THF/CHCl₃ = 99/1 v/v mixed solution, 1.6×10^{-5} M per C343 unit.

^c Excited at the wavelengths of absorption maxima (λ_{abs}).

^d Calculated based on the concentration of C343 unit.

DLS Measurement

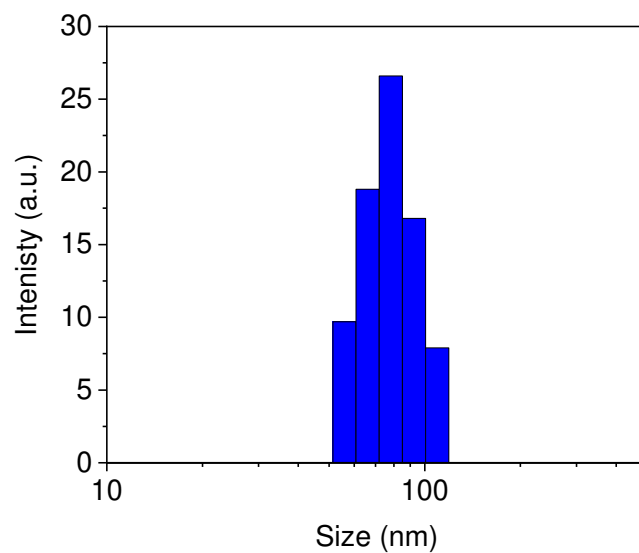


Figure S8. Number-averaged hydrodynamic size distribution of **C343-POSS** (1.6×10^{-5} M per C343 unit) in the THF/ CHCl_3 (99/1 v/v) mixed solution.

Solvent Effect

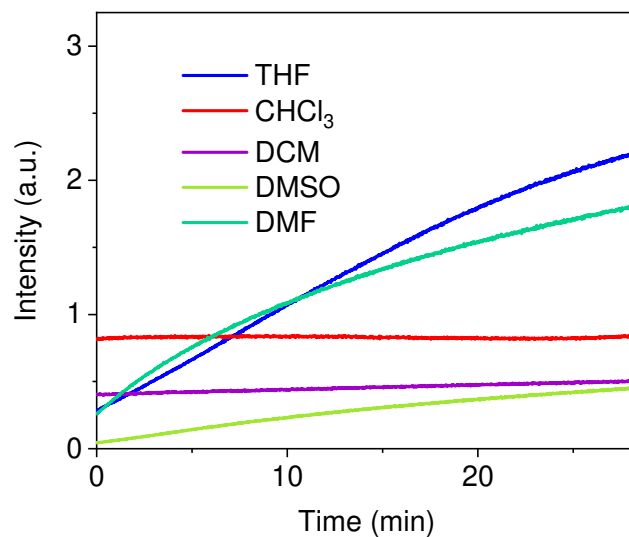


Figure S9. Photoluminescence intensity kinetics of **C343-POSS** (1.6×10^{-5} M per C343 unit) in various solutions (solvent/ CHCl_3 = 99/1 v/v) upon the addition of TBAF (100 equiv.).

Limit of Detection

The calculation of the limit of detection (L_D) was carried out by the data from 0 to 20 μM of TBAF with good correlation between fluoride concentration and fluorescence intensity at low concentration area. This is because at high concentration such as 50 μM (25 equiv. or 3.125 equiv. per C343 unit), fluoride anions should be overconsumed and L_D might be underestimated.

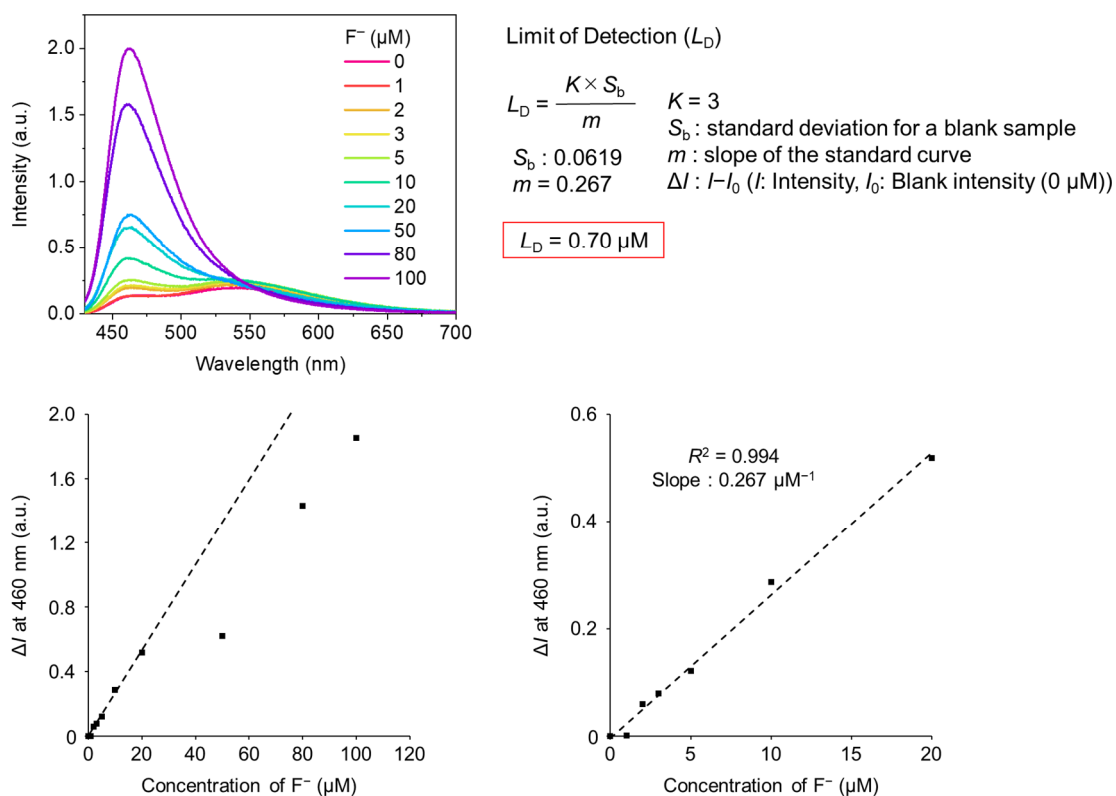
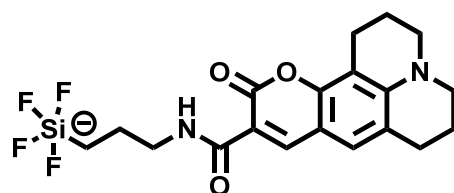


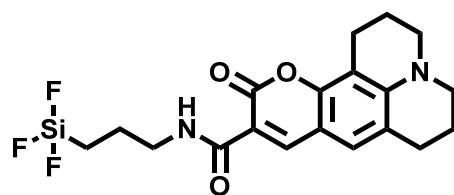
Figure S10. Fluorescence enhancement upon addition of F^- and calculation of limit of detection (L_D). $[\text{C343-POSS}] = 1.6 \times 10^{-5} \text{ M}$ per C343 unit in THF/ CHCl_3 (99/1 v/v) mixed solution. The cation is tetrabutylammonium (TBA).

Mass Spectrometry of Decomposition Compounds



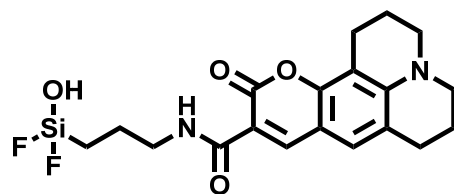
D1

HRMS (ESI) calcd. for $C_{19}H_{21}F_4N_2O_3Si$ $[M-H]^-$: 429.1263 found: 429.1262



D2

HRMS (ESI) calcd. for $C_{19}H_{21}F_3N_2O_3Si$ $[M-H]^-$: 409.1201 found: 409.1200



D3

HRMS (ESI) calcd. for $C_{19}H_{22}F_2N_2O_4Si$ $[M-H]^-$: 407.1244 found: 407.1245

Figure S11. Molecular weights obtained from HRMS spectra of decomposition products.

Mechanism Study

TBAF only

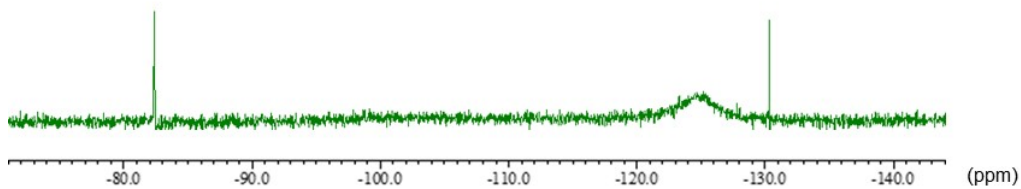
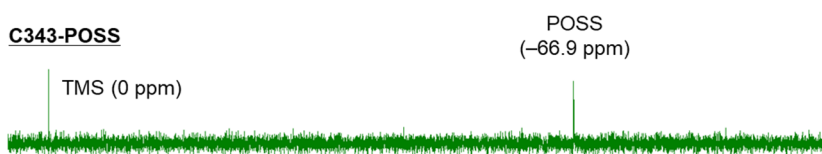


Figure S12. ¹⁹F NMR spectrum of TBAF in CDCl₃ after 12 h of standstill at room temperature.

C343-POSS



C343-POSS + TBAF

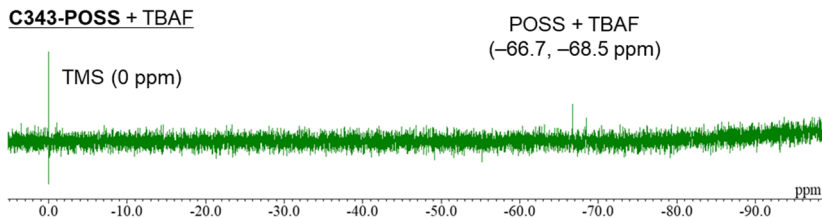
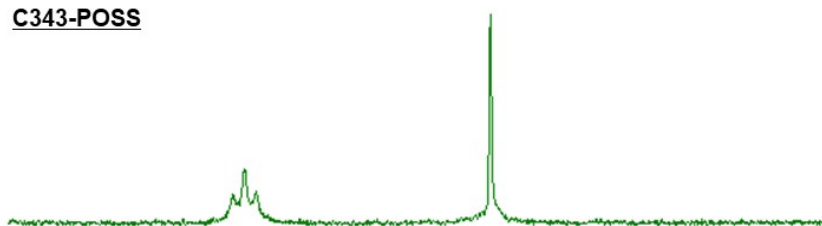


Figure S13. ²⁹Si NMR of C343-POSS before and after the addition of TBAF in CDCl₃.

C343-POSS



C343-POSS + TBAF (4equiv.)

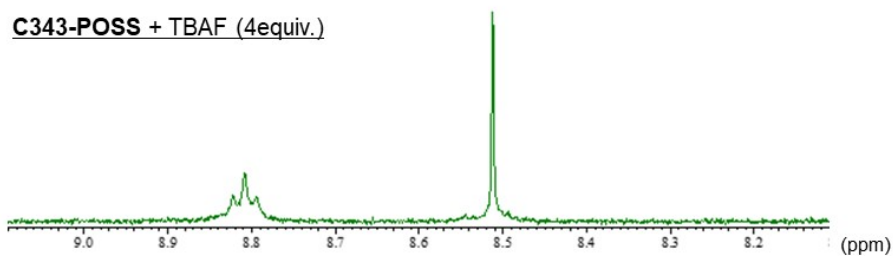
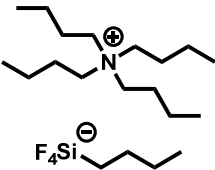
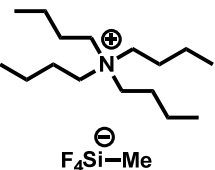
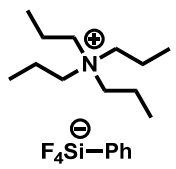
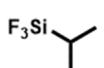



Figure S14. ¹H NMR of C343-POSS before and after the addition of TBAF (4 equiv.) in CDCl₃. The peak of δ 8.81 ppm is attributed to amide proton.

Table S2. ^{19}F NMR data in previous reports

Compound	Solvent	Chemical shift (ppm)	reference
	CD_2Cl_2	-116.6	[3]
	CD_2Cl_2	-110.5	[3]
	CDCl_3	-119.2	[4]
	CDCl_3	-142.2	[4]
	CDCl_3	-137.98	[4]

Thermal analysis

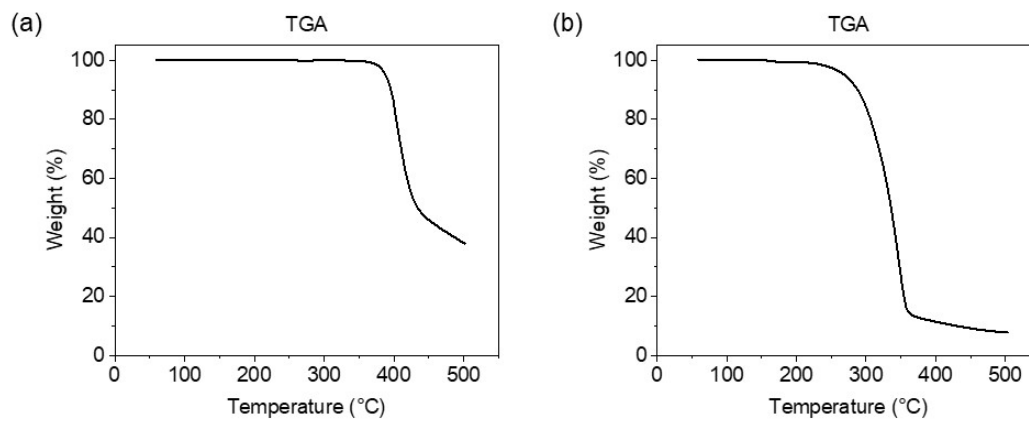


Figure S15. TGA curves of (a) C343-POSS and (b) C343-arm.

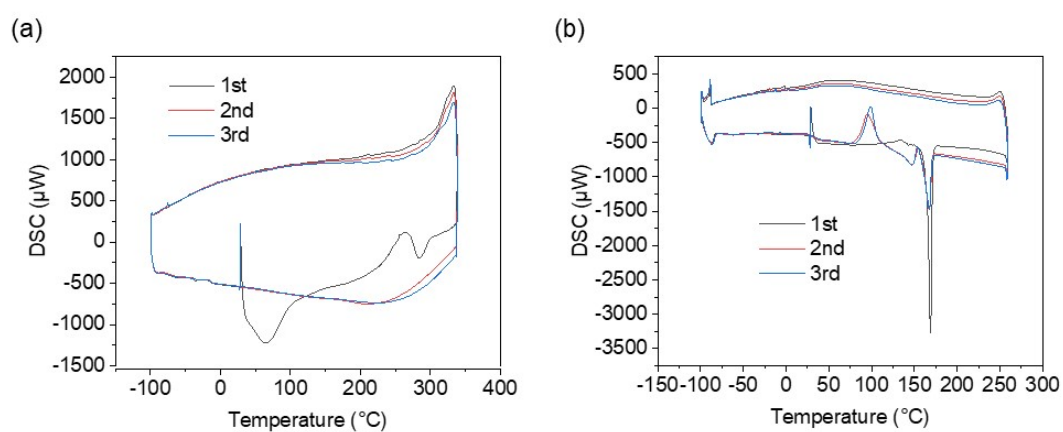


Figure S16. DSC thermograms of (a) C343-POSS and (b) C343-arm.

References

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