Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis and characterization of poly(tetraphenylimidazole)s and their application in the detection of fluoride ions

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Experimental Section

General: Solvents and other general reagents were purified according to standard procedures. Benzil, 4-bromoaniline, 4-vinylphenylboronicacid, di(ethylene glycol) methyl ether methacrylate and ammonium acetate were purchased from Sigma-Aldrich. 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU), tert-butyl(chloro)diphenylsilane and salicylaldehyde were purchased from Alfa-Aesar. Glacial acetic acid and 2,2’-azobis(isobutyronitrile) were obtained from Spectrochem. All 400 MHz ^{1}H, 100 MHz ^{13}C, and 79 MHz ^{29}Si, spectra were recorded on a Bruker ARX 400 spectrometer operating at 400 MHz. All ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. ^{29}Si NMR spectra were referenced externally to TMS in $CDCl_3$ ($\delta = 0$). All NMR spectra were recorded at ambient temperature. Elemental analyses were carried out by using a Thermo quest CE instrument model EA/110 CHNS-O elemental analyzer. ESI mass spectra were recorded on a Bruker, microTOF-QII mass spectrometer. The absorbance spectra were recorded on JASCO V-730 UV-visible spectrometer. The fluorescence spectra were recorded using Edinburgh FS5 spectrofluorometer. The fluorescence spectra were corrected for the instrumental response. Single-crystal X-ray diffraction data was collected on a Rigaku Oxford X-ray diffractometer. The data was collected at 293 K using Cu-Kα radiation (1.54184 Å). Crystallographic data for **3**, details of X-ray diffraction experiments and crystal structure refinements are given in Table S1. The structures were solved and refined with SHELX suite of programs. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. Crystallographic data for the structure **3** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC- 1975843. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk.

Synthesis of 2-(1-(4-bromophenyl)-4,5-diphenyl-1H-imidazol-2-yl)phenol (1):

Benzil (3.00 g, 14.27 mmol) and salicylaldehyde (1.49 mL, 14.27 mmol) were taken in acetic acid, to this mixture 4-Bromo aniline (2.7 g, 15.69 mmol) and ammonium acetate (1.65 g, 21.40 mmol) were added subsequently and refluxed for 24 h. Later the reaction mixture was cooled to room temperature and then water was added, the obtained precipitate was collected by filtration. The white solid was recrystallized from ethyl acetate to get the pure product. Yield: 4.6 g, 69 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.59 (t, J = 8 Hz, 1H), 6.7 (d, J = 8 Hz, 1H), 7.03 – 7.21 (m, 6H), 7.22 – 7.27 (m, 2H), 7.29 – 7.40 (m, 4H), 7.49 (d, J = 8.0 Hz, 2H), 7.56 (d, J =

8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 76.71, 77.02, 77.34, 118.16, 118.45, 123.48, 127.21, 127.67, 128.45, 128.82, 129.03, 129.99, 130.25, 131.27, 132.82, 144.60, 158.00; HR-MS (ESI): calcd. for $C_{27}H_{19}N_2OBr$ ($[M + H]^+$): 467.0754, found: 467.0761.

Table S1: Crystal data and structure refinement parameters for compound **3.**

	3
Empirical formula	$C_{51}H_{44}N_2OSi$
Formula weight	728.97
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.7258(2)
b/Å	17.0253(2)
c/Å	17.5571(3)
α/°	90
β/°	105.6548(18)
γ/°	90
Volume/Å^3	4238.49(13)
Z	4
ρcalcg/cm^3	1.142
μ/mm^{-1}	0.777
F(000)	1544.0
Radiation	CuKα (λ = 1.54184)
2 θ range for data collection/°	6.234 to 148.984
Index ranges	$-18 \leq h \leq 18$, $-21 \leq k \leq 15$, $-19 \leq l \leq 21$
Reflections collected	25771
Independent reflections	8533 [R_{int} = 0.0317, R_{sigma} = 0.0275]
Data/restraints/parameters	8533/0/507
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0535, wR_2 = 0.1564
Final R indexes [all data]	R_1 = 0.0601, wR_2 = 0.1627
Largest diff. peak/hole / e Å^{-3}	0.29 and -0.30

Table S2: Molecular weight and thermal data for polymers

Polymer	M_n,[a] Da	M_w,[a] Da	Z+1	Đ[a]	PDT, °C	T_g, °C
Homo polymer	6665	16750	50787	2.51	320	155
Co polymer	13058	25457	65450	1.95	380	120

[a] GPC-RI in THF *vs* polystyrene standards, Đ – polydispersity index (Đ = M_w/M_n), PDT – polymer decomposition temperature, T_g – glass transition temperature.

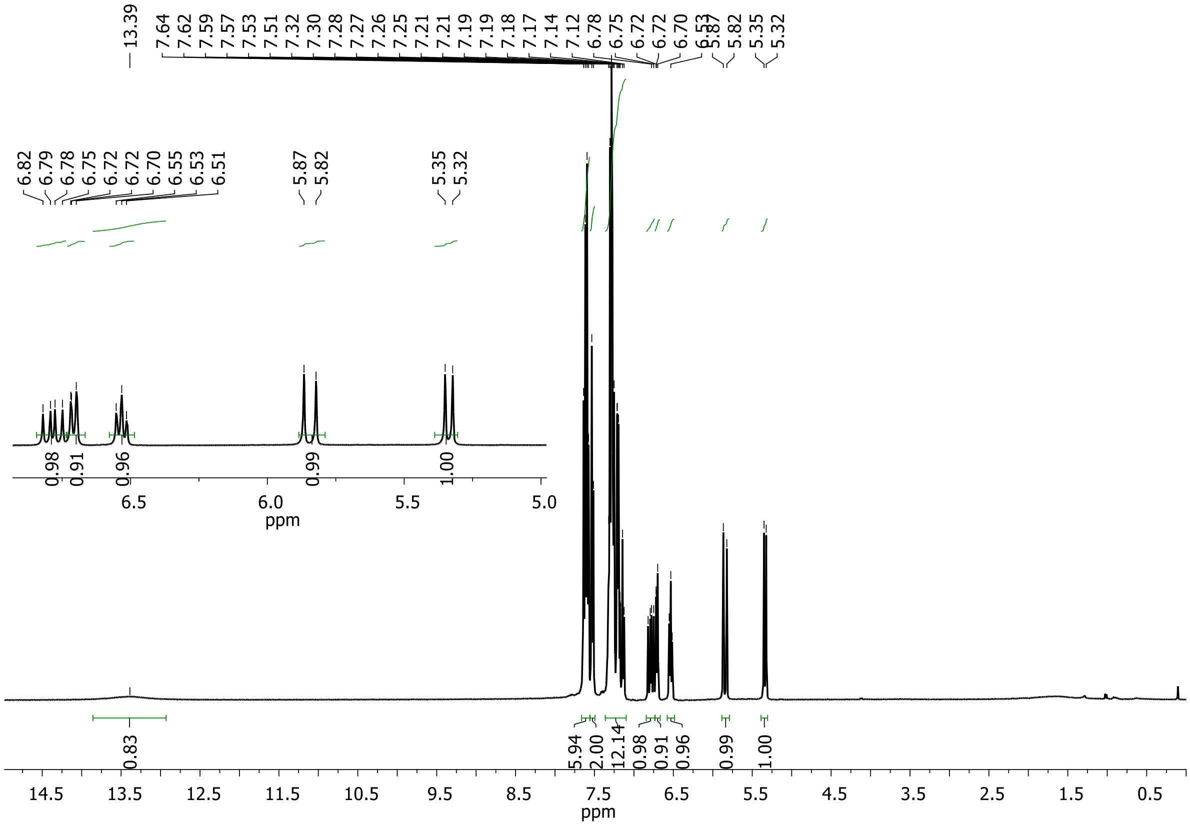


Figure S1: ^{1}H NMR spectrum of the compound **2**

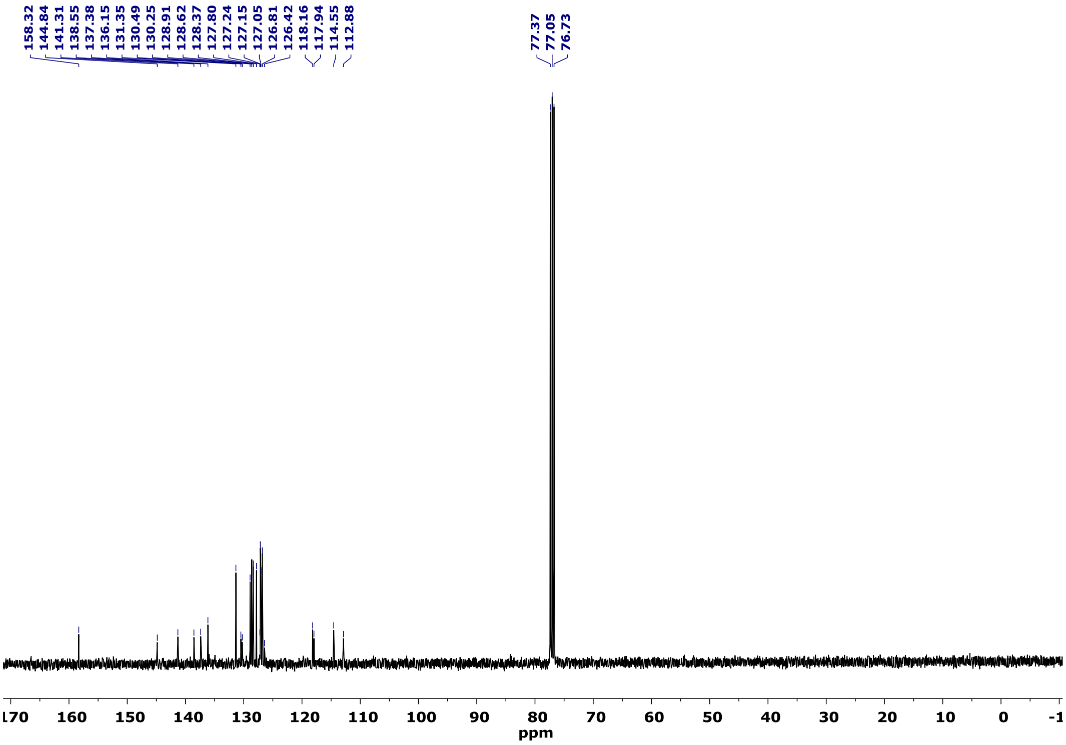


Figure S2: ^{13}C NMR spectrum of the compound **2**

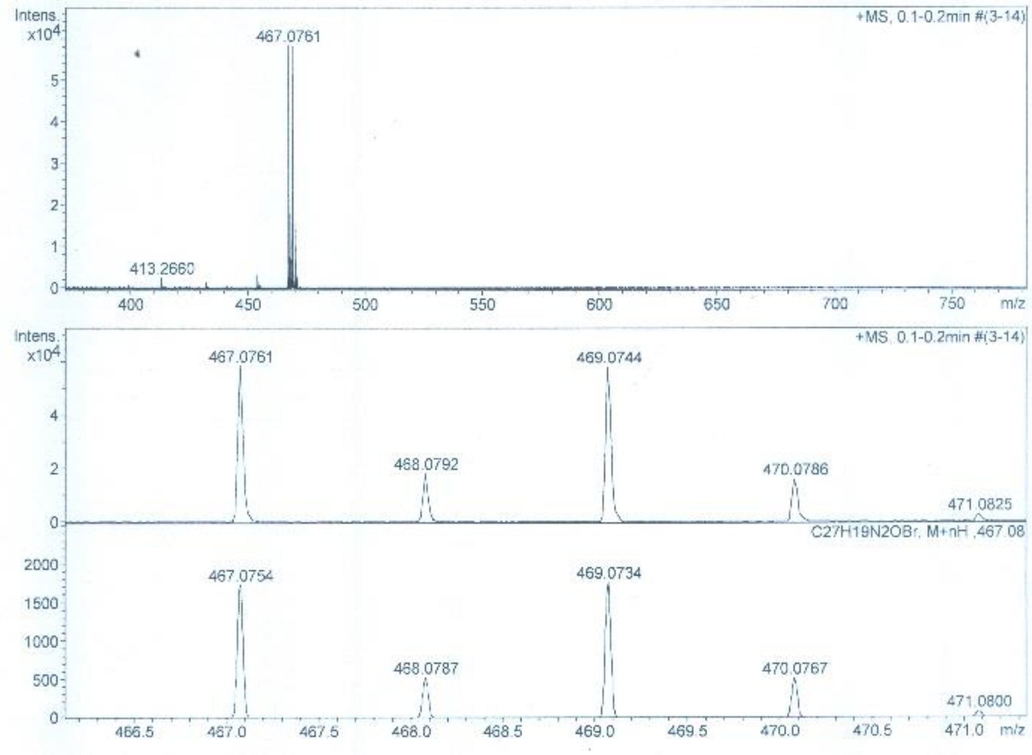


Figure S3: HR-MS data of the compound **2**

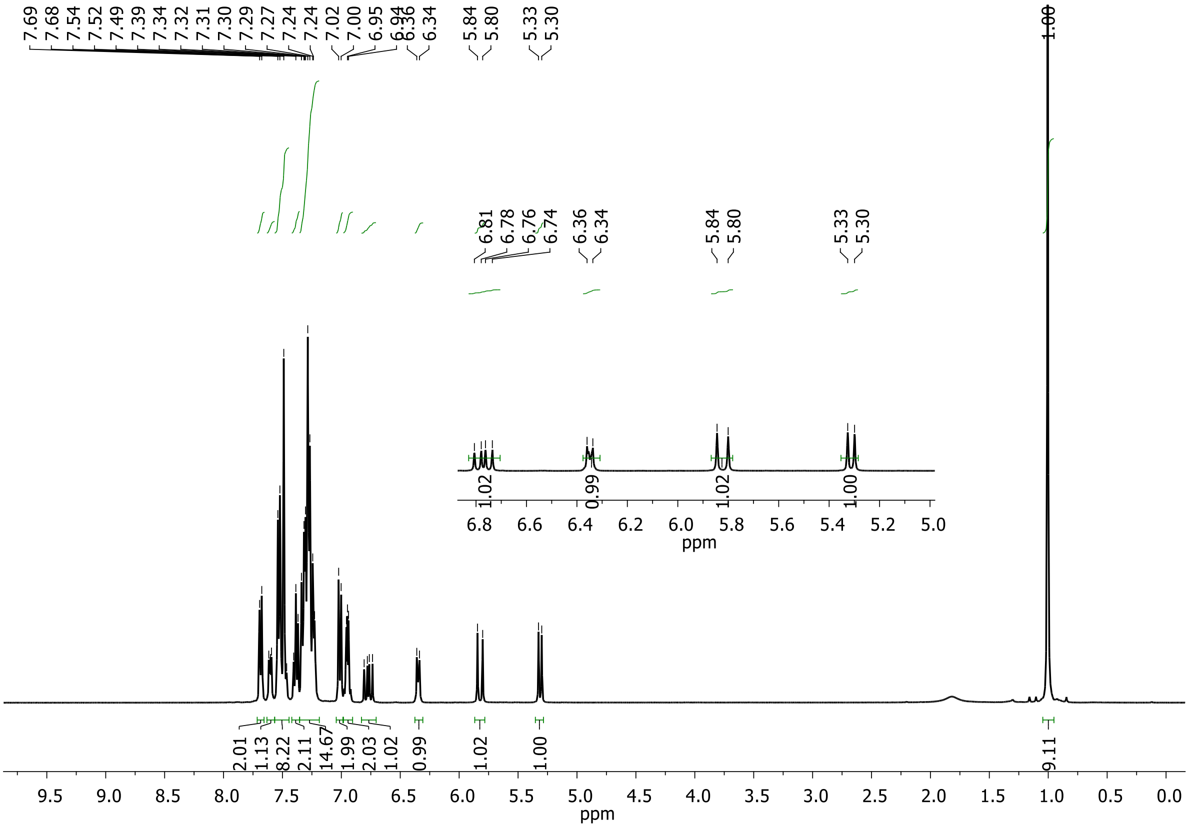


Figure S4: ^{1}H NMR spectrum of the silyl protected monomer (compound **3**)

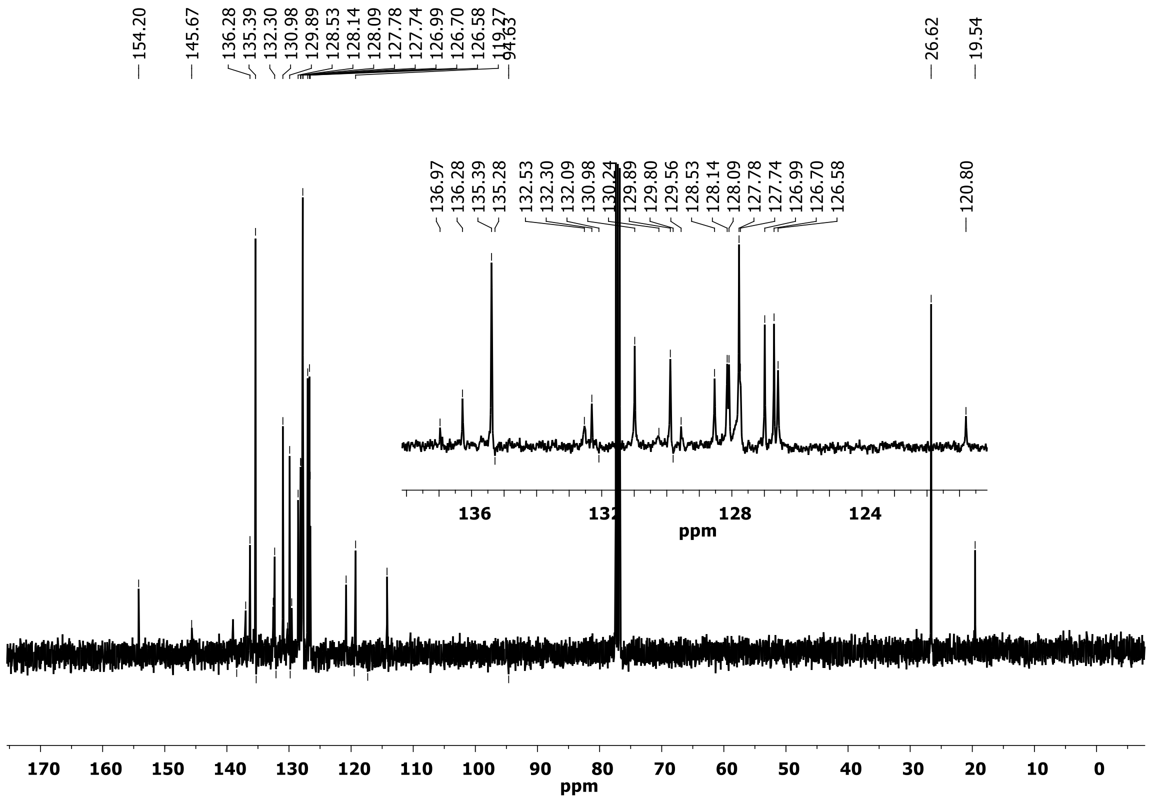


Figure S5: ^{13}C NMR spectrum of the silyl protected monomer (compound **3**)

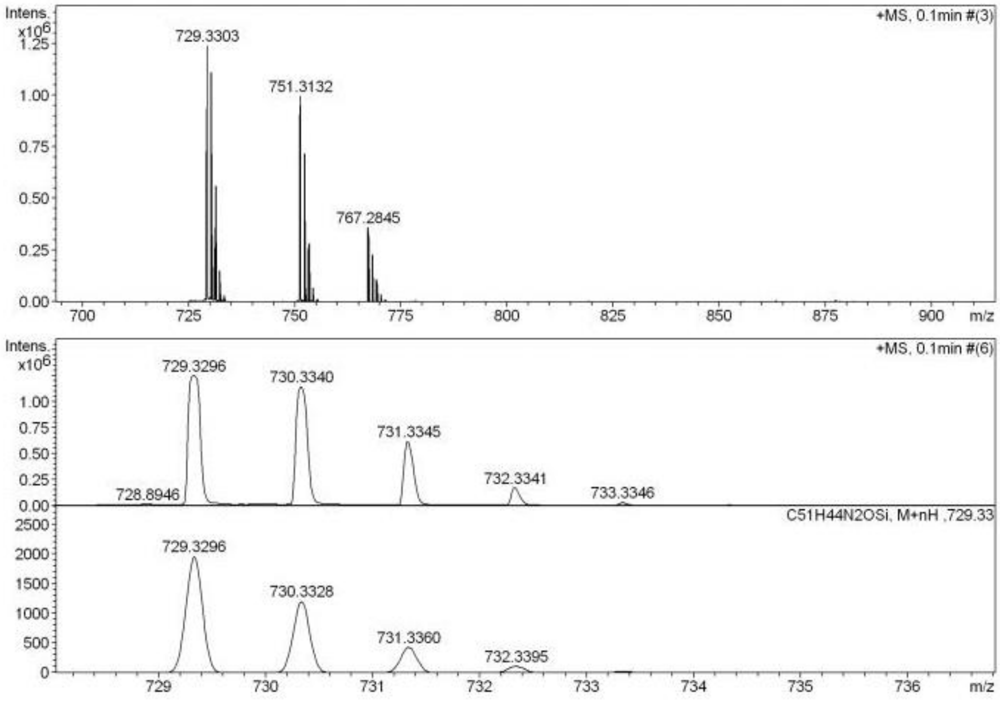


Figure S6: HR-MS data of the compound **3**

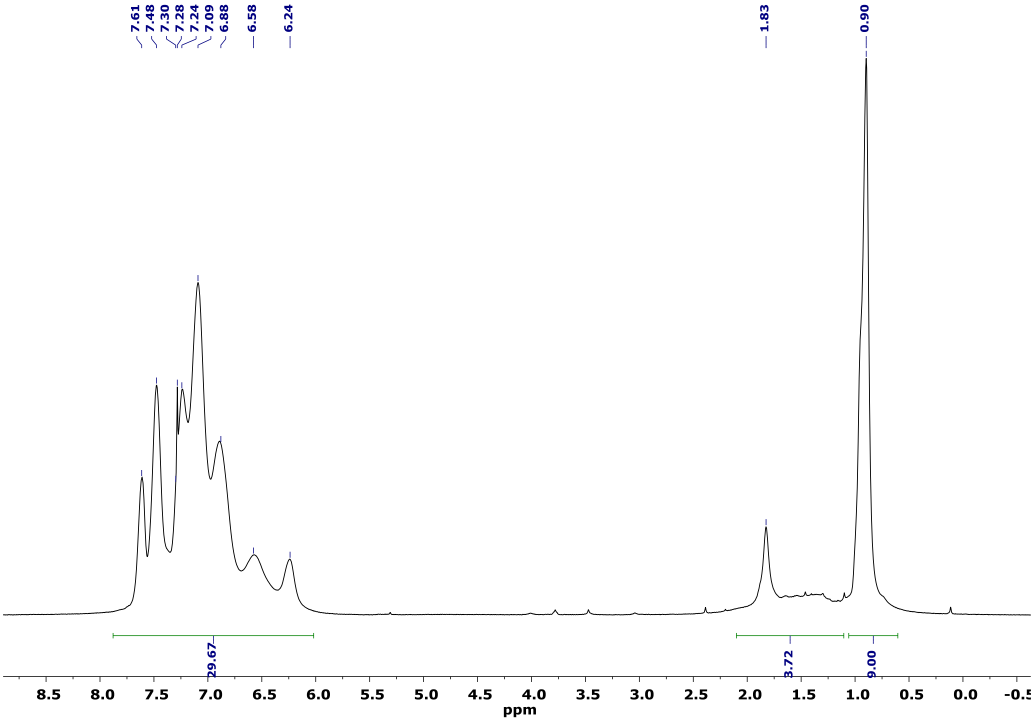


Figure S7: ^{1}H NMR spectrum of the homo-polymer (probe **I**)

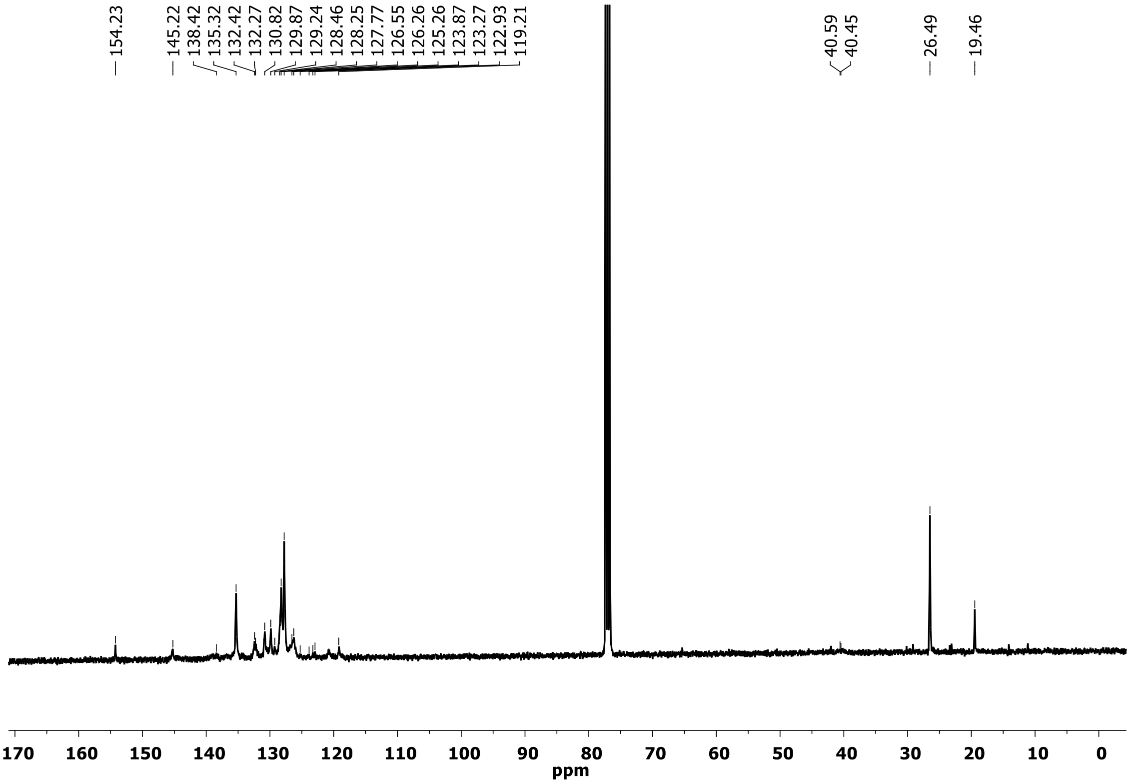


Figure S8: ^{13}C NMR spectrum of the homo-polymer (probe **I**)

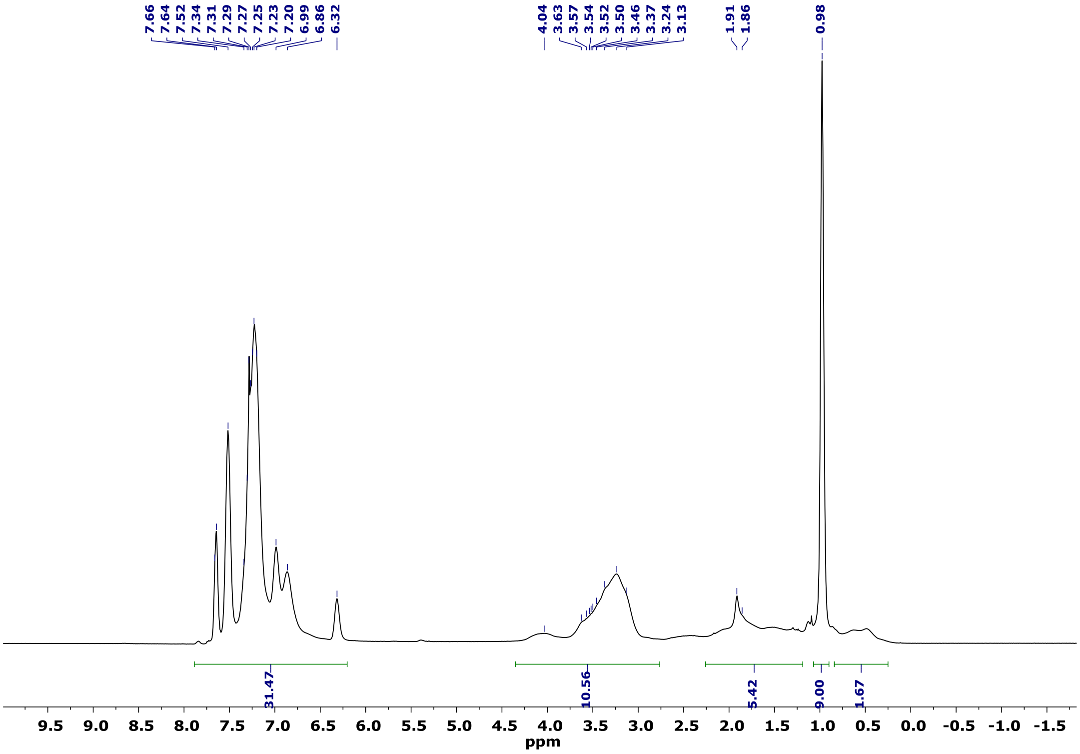


Figure S9: ^{1}H NMR spectrum of the random co-polymer (probe **II**)

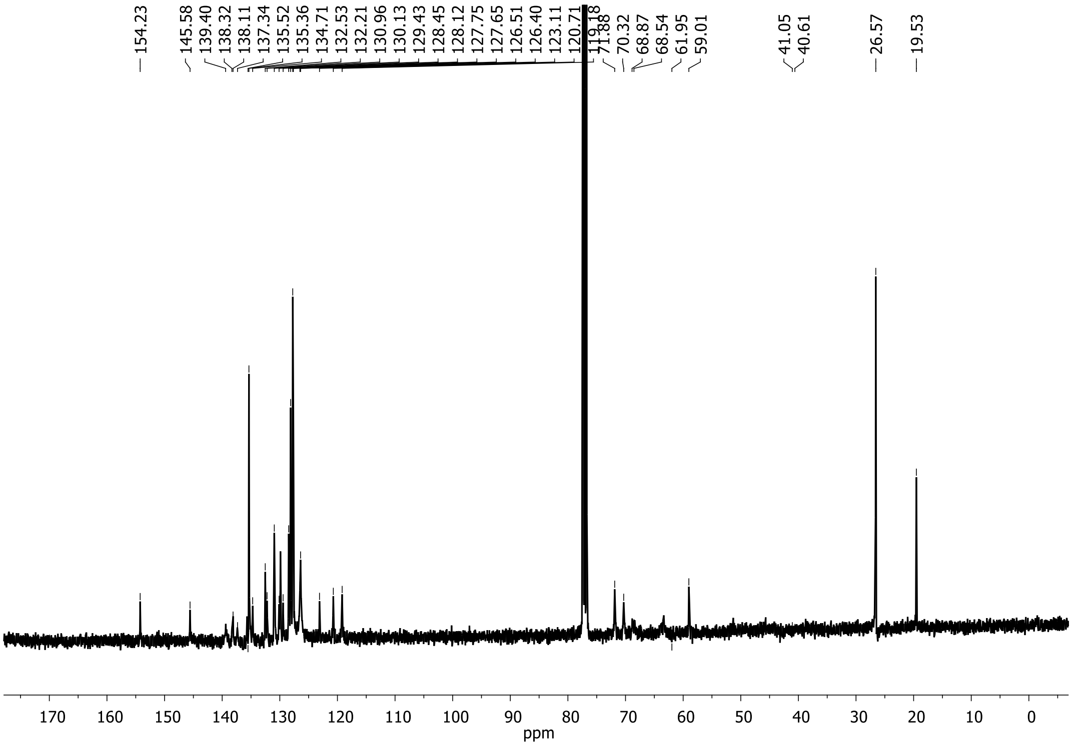
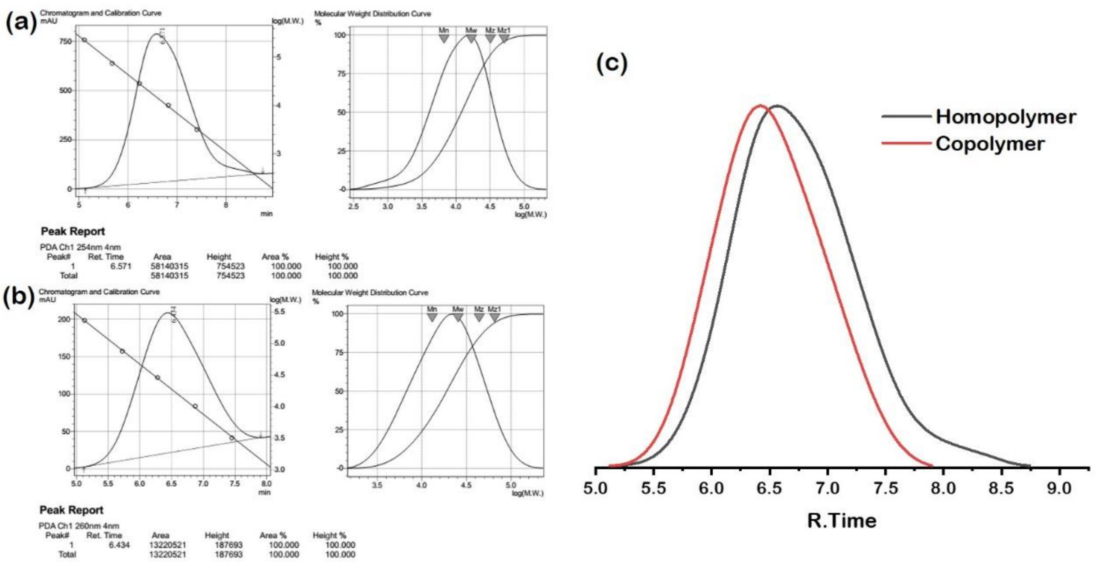


Figure S10: ^{13}C NMR spectrum of the random co-polymer (probe **II**)



Peak Report

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.571	58140315	754523	100.000	100.000
Total		58140315	754523	100.000	100.000

Peak Report

PDA Ch1 260nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.434	13220521	187693	100.000	100.000
Total		13220521	187693	100.000	100.000

Figure S11: GPC traces of the (a) homo-polymer (probe **I**) (b) random co-polymer (probe **II**) and (c) comparison of retention time of both the probes, plot represent normalized RI intensities vs elution time, where THF used as eluent and polystyrene standards were used for calibration.

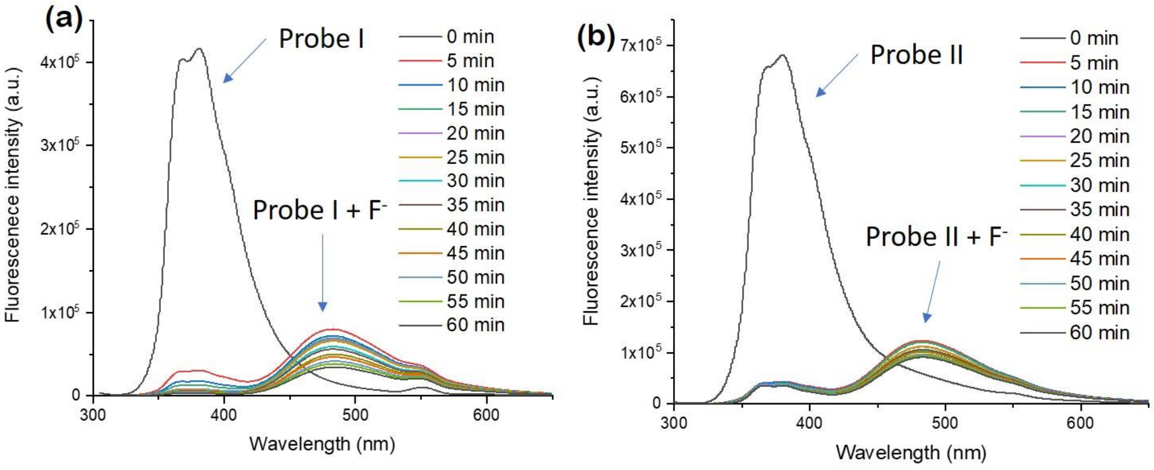


Figure S12: Fluorescence response of both the probes (10 µmol) (a) Probe **I** (homo-polymer) and (b) Probe **II** (random co-polymer) with equi molar fluoride ion (10 µmol) over a period of 60 min.

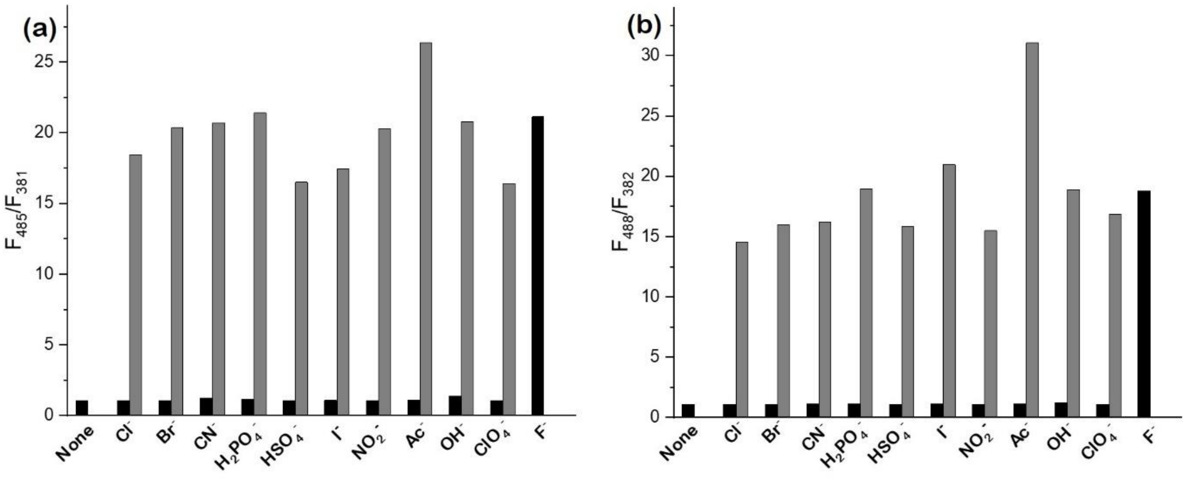


Figure S13: Fluorescence response of both probes (10 µmol) towards various analytes in THF solution. All the data represents the fluorescence intensity ratio (F_{485}/F_{381} for probe **I** (left) and F_{488}/F_{382} for probe **II** (right)). Black bars represent the addition of single analyte including 100 µmol anions (Cl^-, Br^-, CN^-, $H_2PO_4^-$, HSO_4^-, I^-, NO_2^-, Ac^-, OH^- and ClO_4^-). Light gray bars represent the subsequent addition of F^- to the mixture. Each data was obtained after various analytes addition at ambient temperature for 15 min.

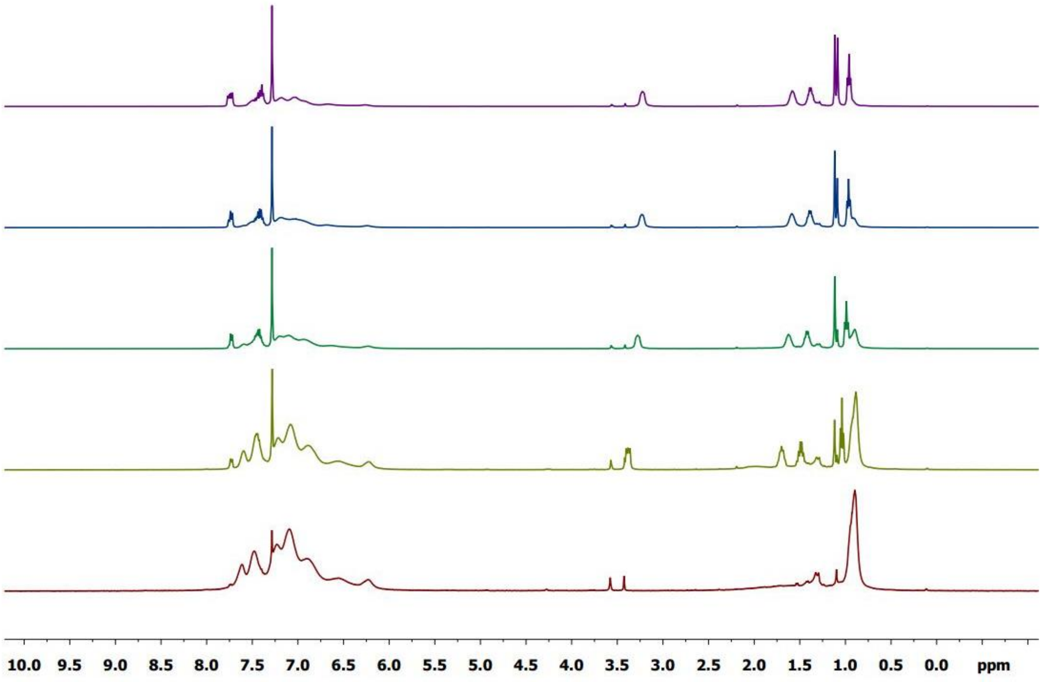


Figure S14: ^{1}H NMR titration spectrum of homo-polymer (probe **I**) 69 mmol with 17, 35, 52 and 69 mmol of fluoride ions in $CDCl_3$ (bottom to top)

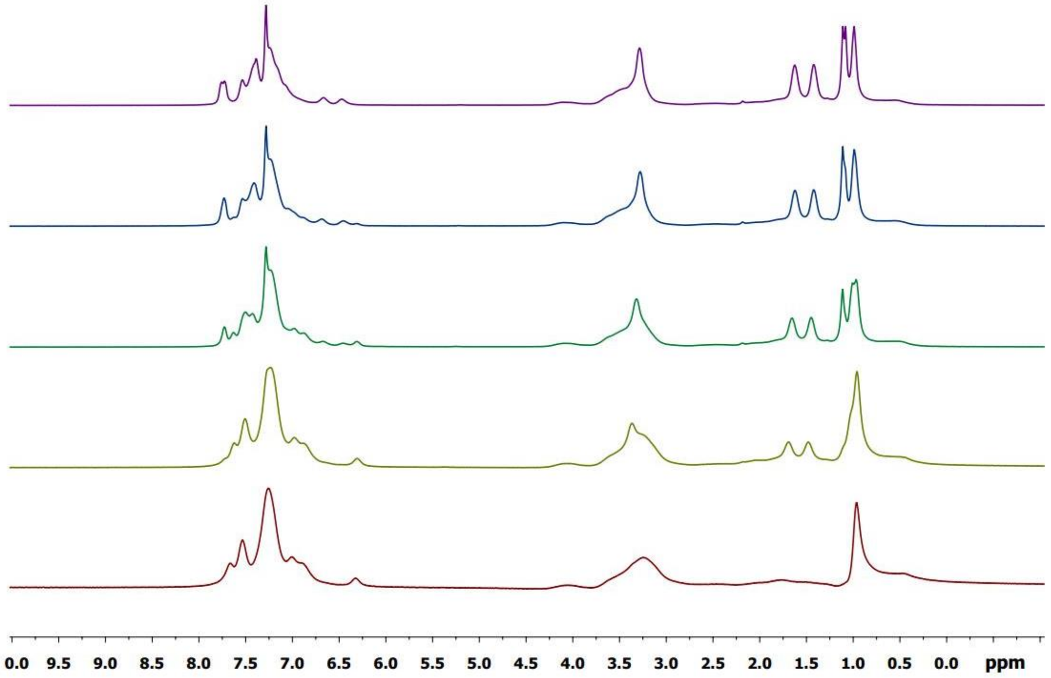


Figure S15: ^{1}H NMR titration spectrum of random co-polymer (probe **II**) 54 mmol with 14, 28, 42 and 56 mmol of fluoride ions in $CDCl_3$ (bottom to top).

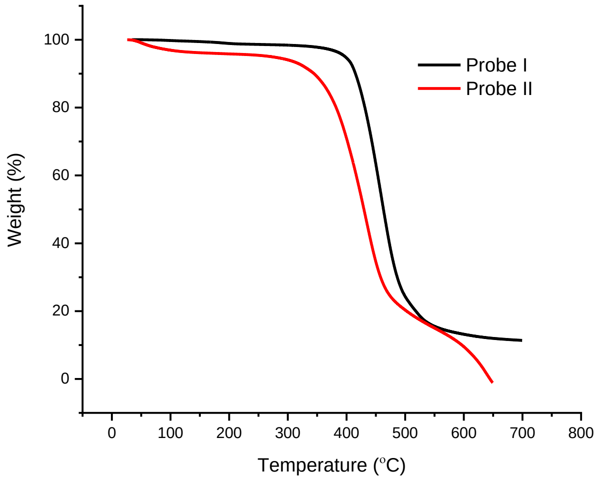


Figure S16: Thermogravimetric analysis traces of probe **I** & **II** recorded under nitrogen at a heating rate of 20 °C/min.

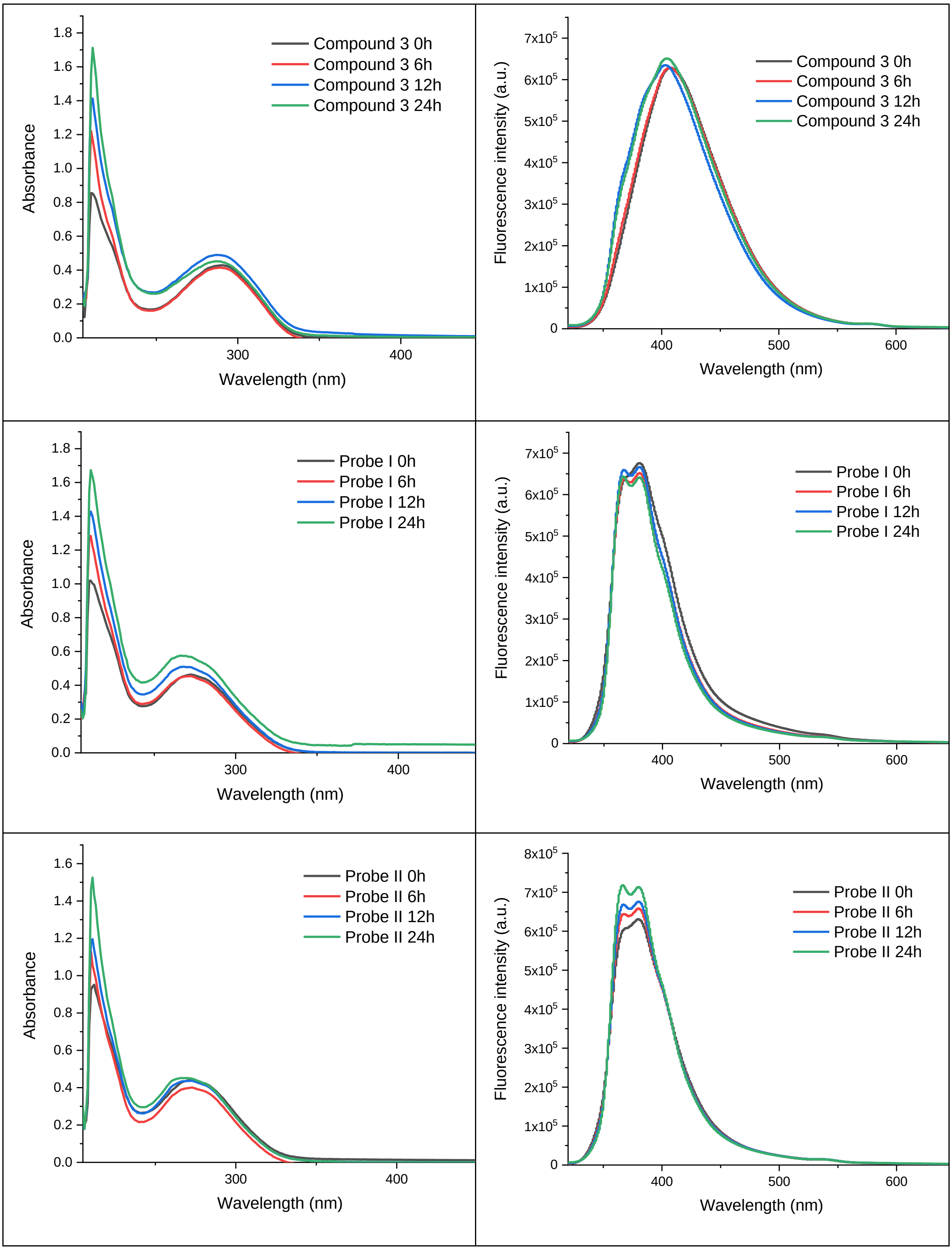


Figure S17: UV-Vis and emission spectra of monomer and the probes **I** & **II** in THF solution at different interval of time.

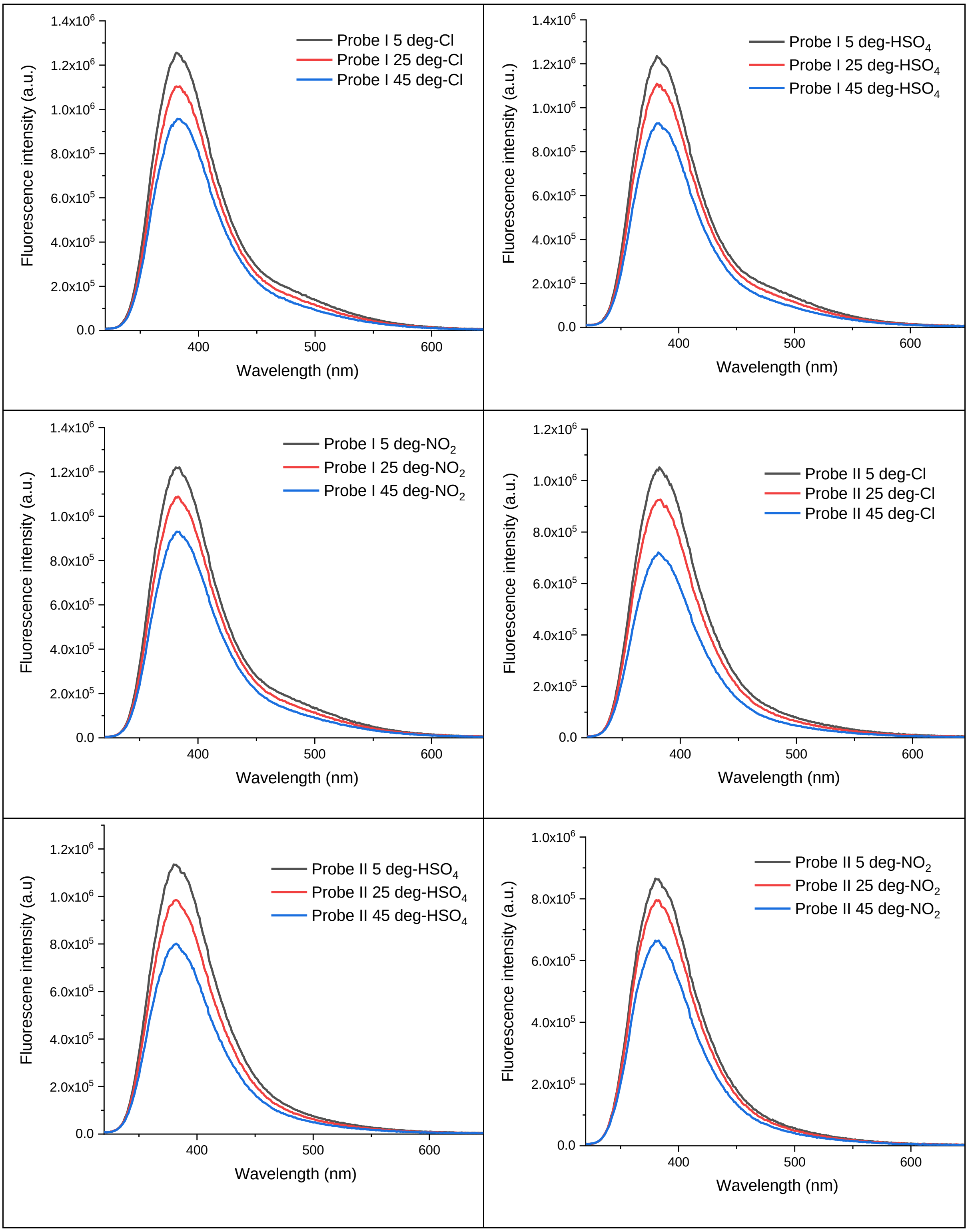


Figure S18: Emission spectra of probes **I** & **II** along with different ions in THF solution at different three different temperatures.

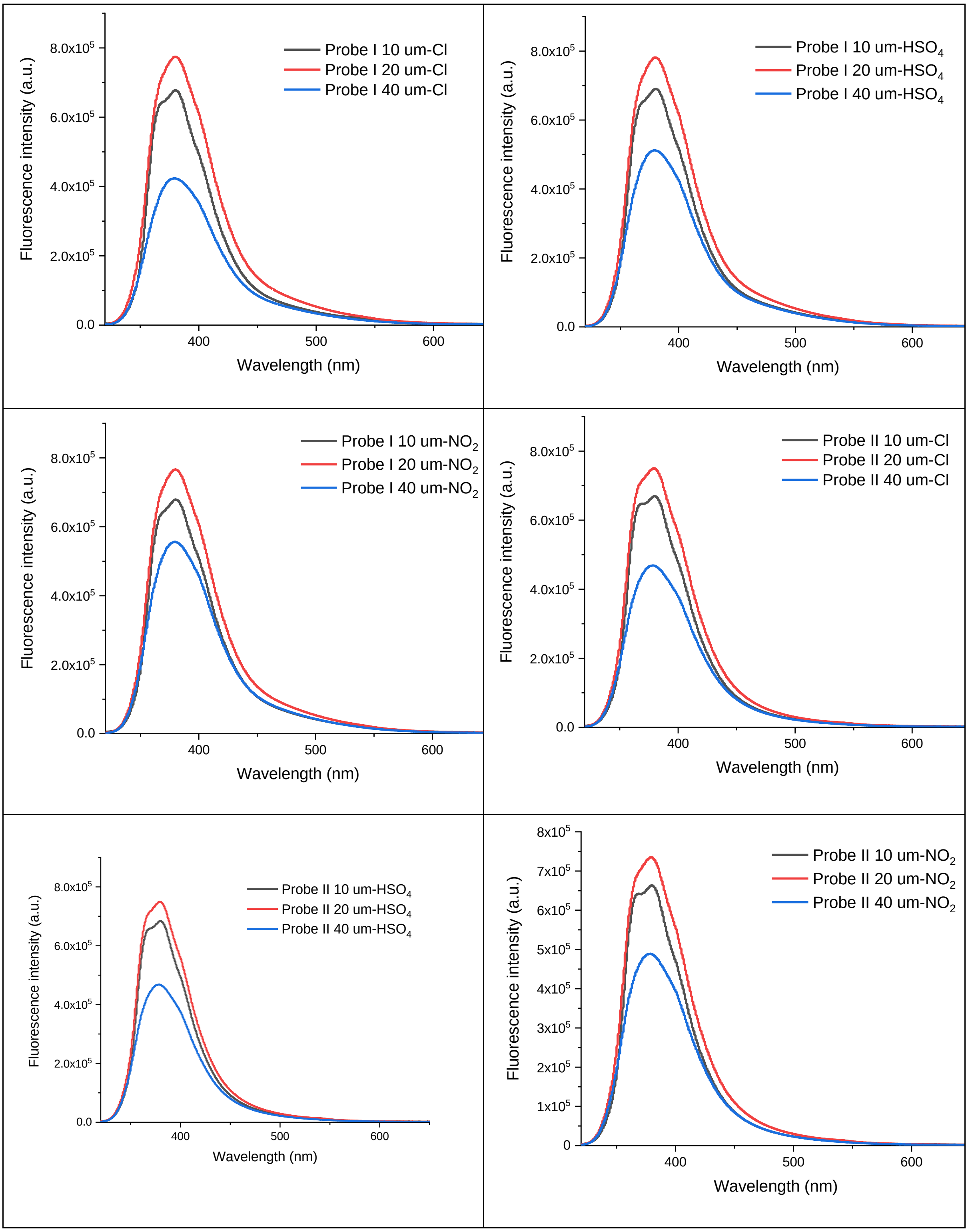
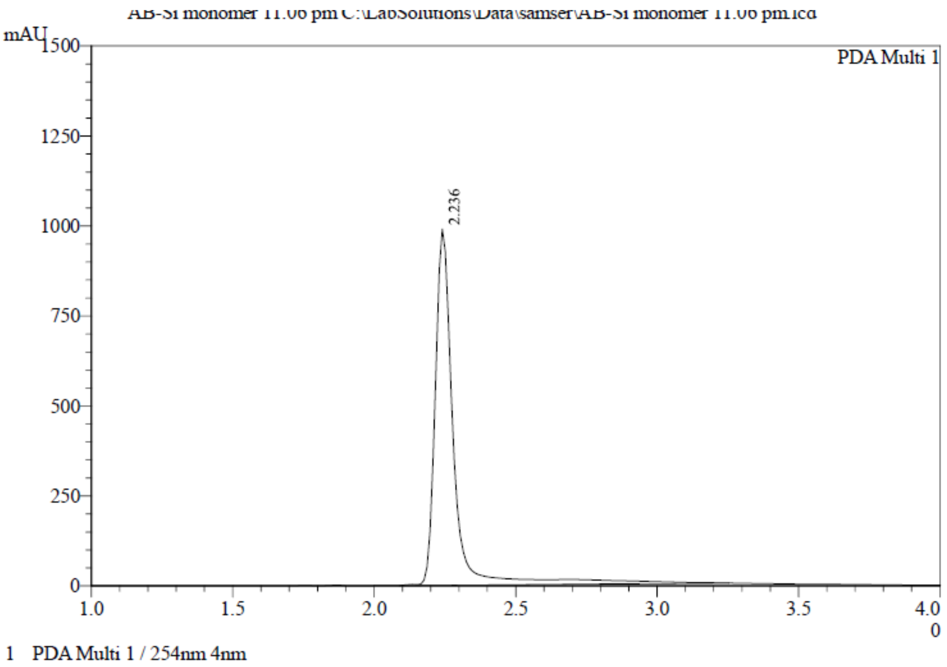


Figure S19: Emission spectra of probes **I** & **II** along with different ions in THF solution at different concentrations.



PeakTable C:\LabSolutions\Data\samser\AB-Si monomer 11.06 pm.lcd

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.236	4519577	989310	100.000	100.000
Total		4519577	989310	100.000	100.000

Figure S20: HPLC trace of compound **3**.