Electronic Supplementary Information (ESI)

Cyclic Siloxanes conjugated with Fluorescent Aromatic Compounds as Fluoride Sensors

Nicha Prigyai,[a] Supphachok Chanmungkalakul,[a] Sutthiroj Thanyalax,[a] Mongkol Sukwattanasinitt,[b,c] and Vuthichai Ervithayasuporn*[a]

[a] Department of Chemistry, Center of Excellence for Innovation in Chemistry (PERCH-CIC), and Center for Inorganic and Materials Chemistry, Faculty of Science, Mahidol University, Rama VI road, Ratchathewi, Bangkok 10400, Thailand.

[b] Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330 Thailand.

[c] Nanotec-CU Center of Excellence on Food and Agriculture, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330 Thailand.

*Corresponding author: Vuthichai Ervithayasuporn (V.E.)

E-mail address: vuthichai.erv@mahidol.edu

maldiniandg@hotmail.com

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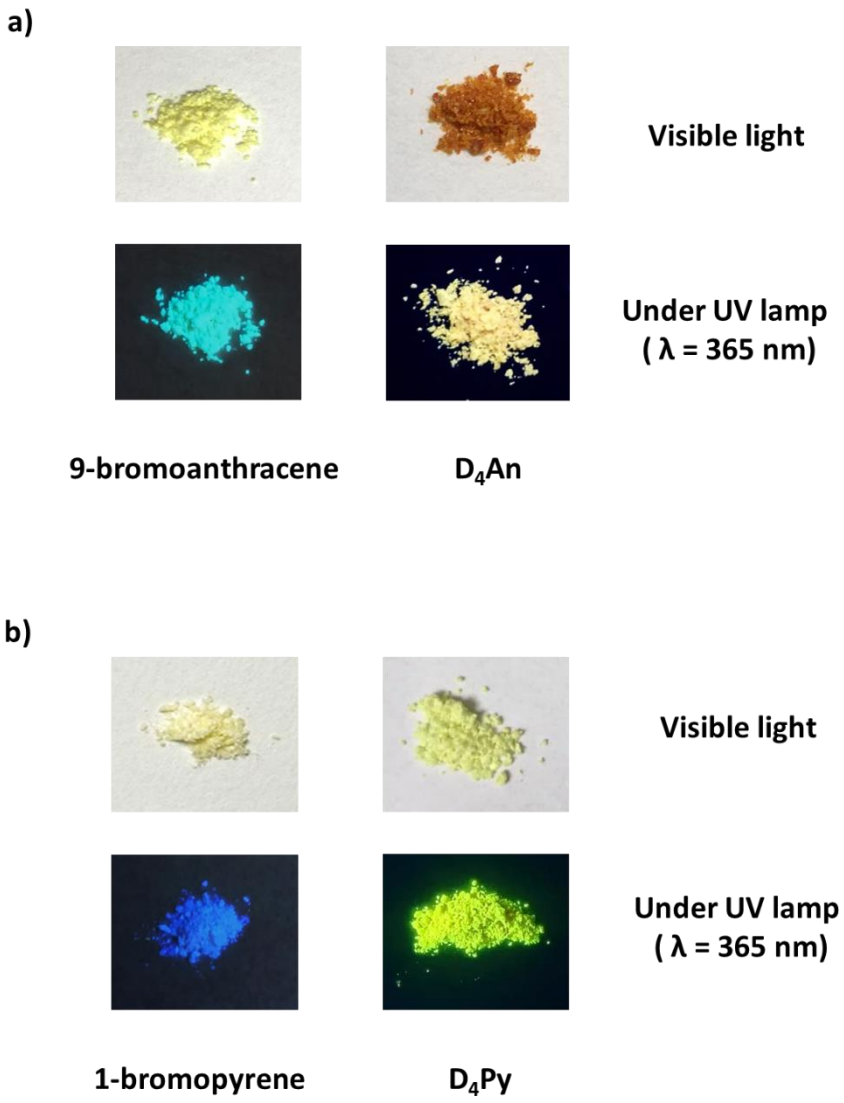

Figure S1. Solid state of 9-bromoanthracene and D_4An (a) and 1-bromopyrene and D_4Py (b) under visible light in top and under UV lamp in bottom.

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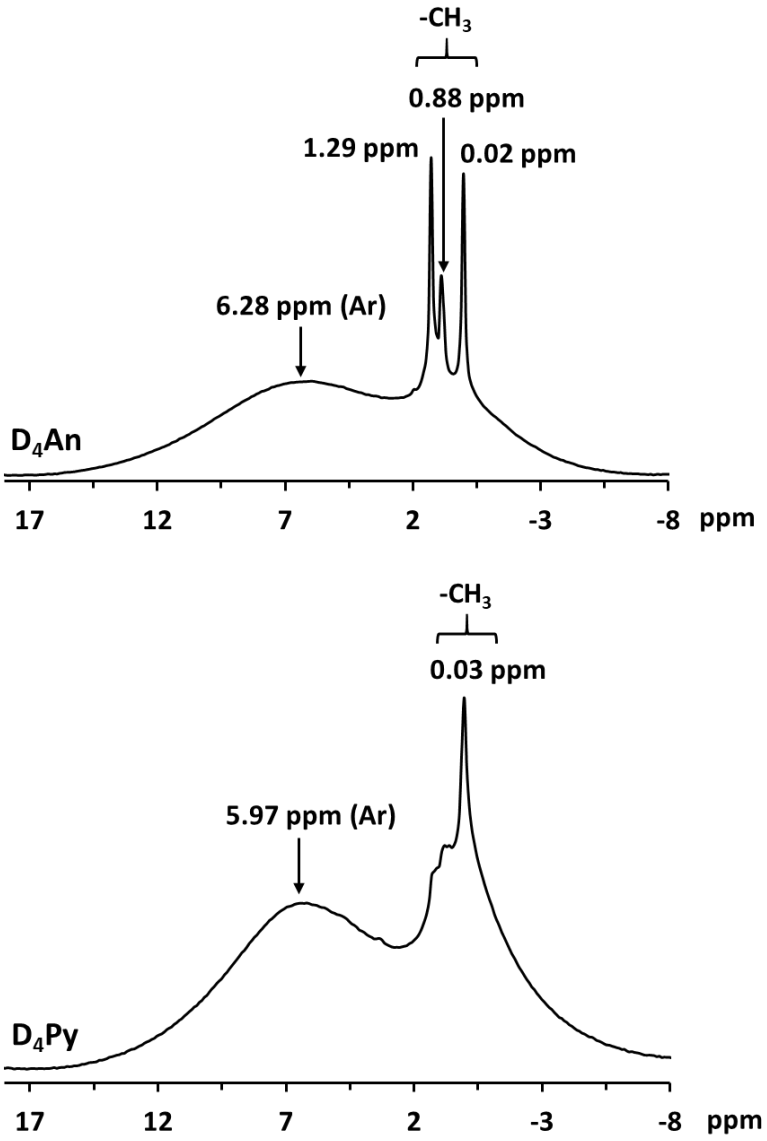

Figure S2. ^{1}H MAS NMR spectra of D_4An and D_4Py.

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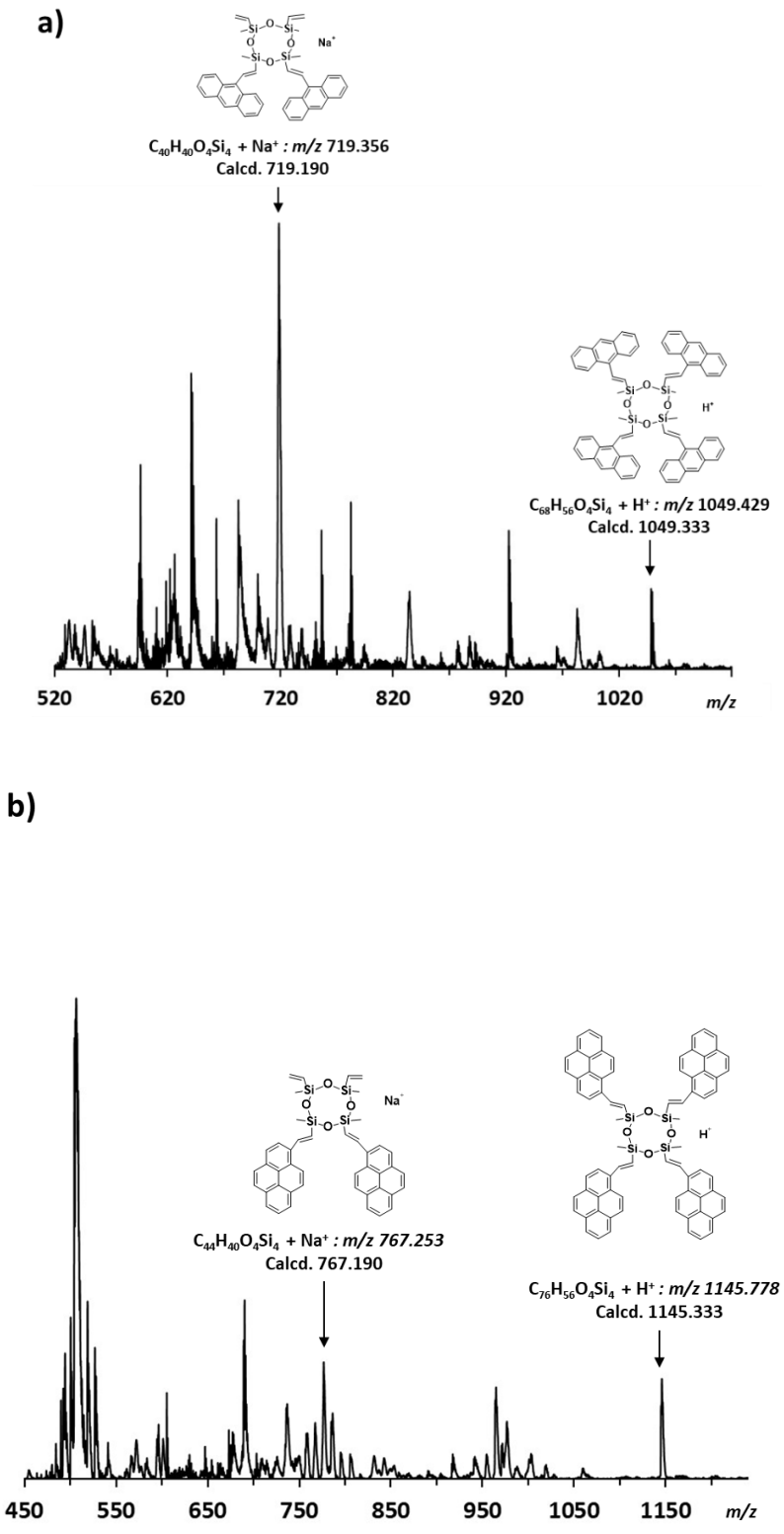

Figure S3. MALDI-TOF spectra of (a) D_4An and (b) D_4Py.

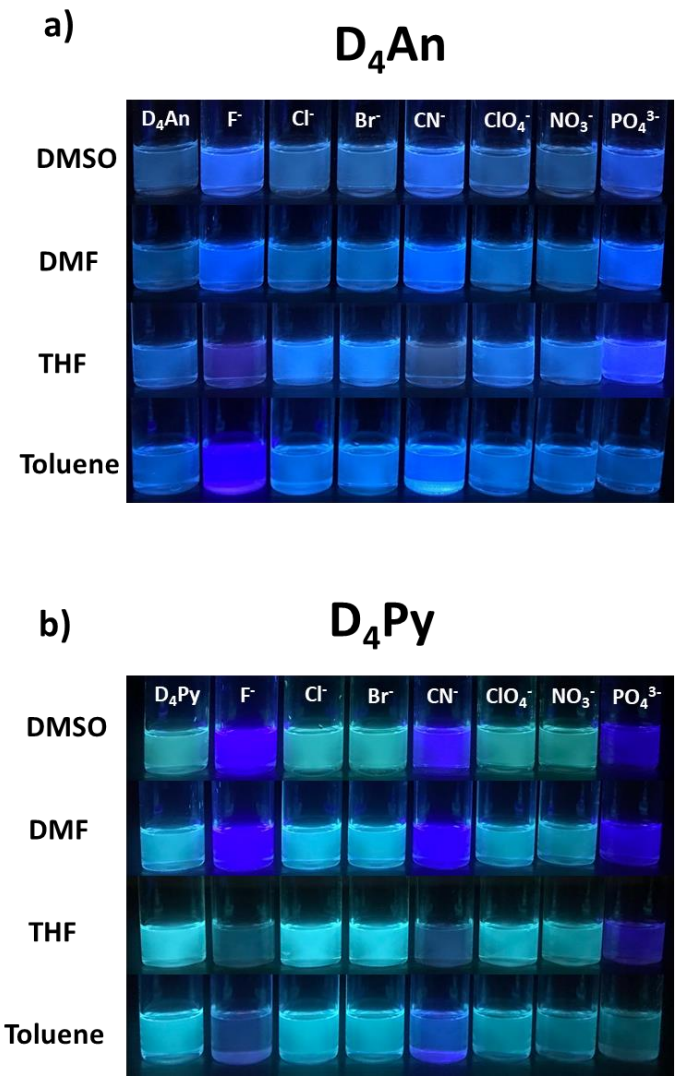

Figure S4. Photograph of a) D_4An (2×10^{-5} M) and b) D_4Py (1×10^{-5}) M after added guest anions (200 equiv.) in various solvents under UV lamp

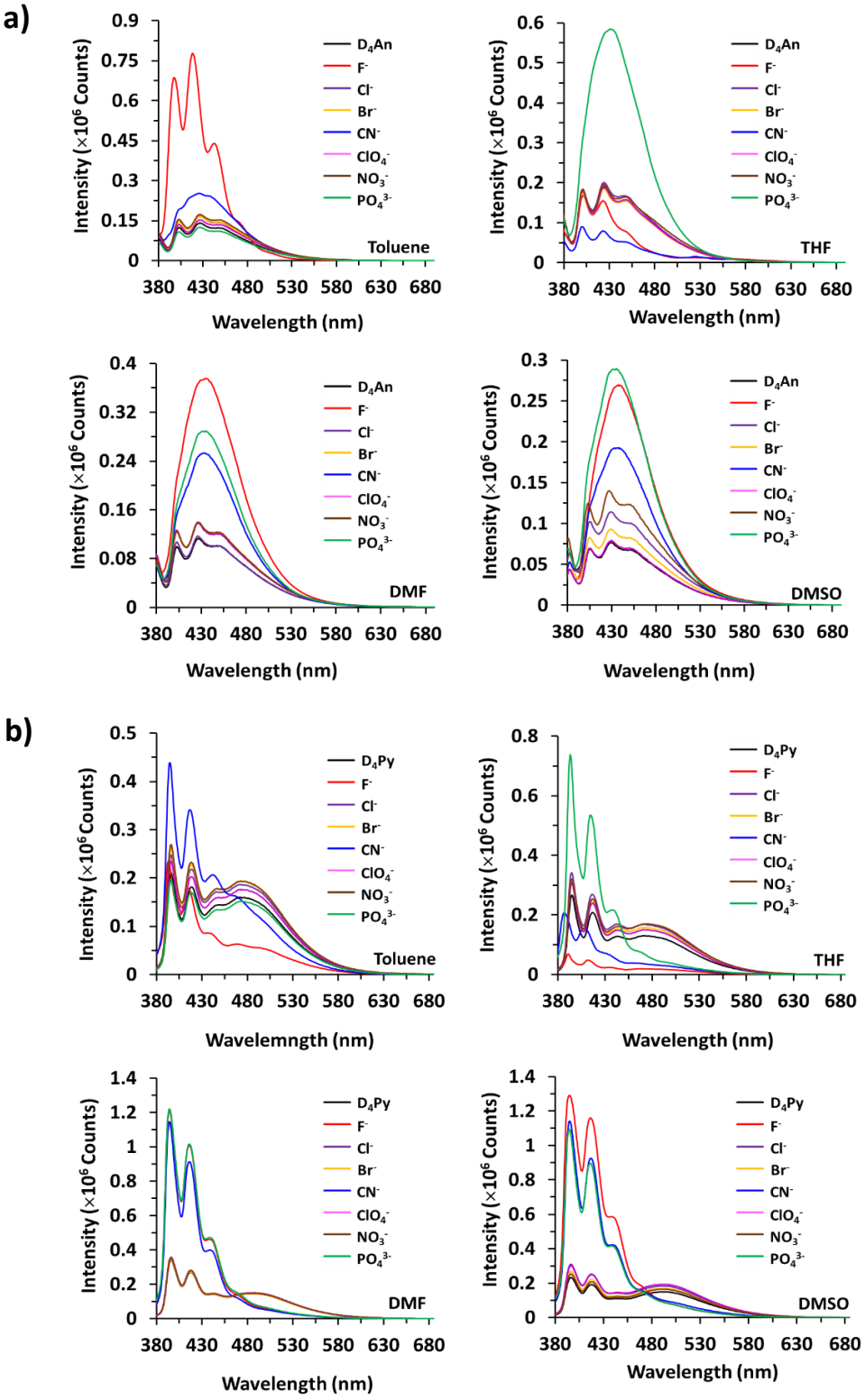

Figure S5. Fluorescence spectra of a) D_4An (2×10^{-5} M) at λ_{ex} = 378 nm and b) D_4Py (1×10^{-5} M) at λ_{ex} = 350 nm in various solvent before and after addition of anions (200 equiv.).

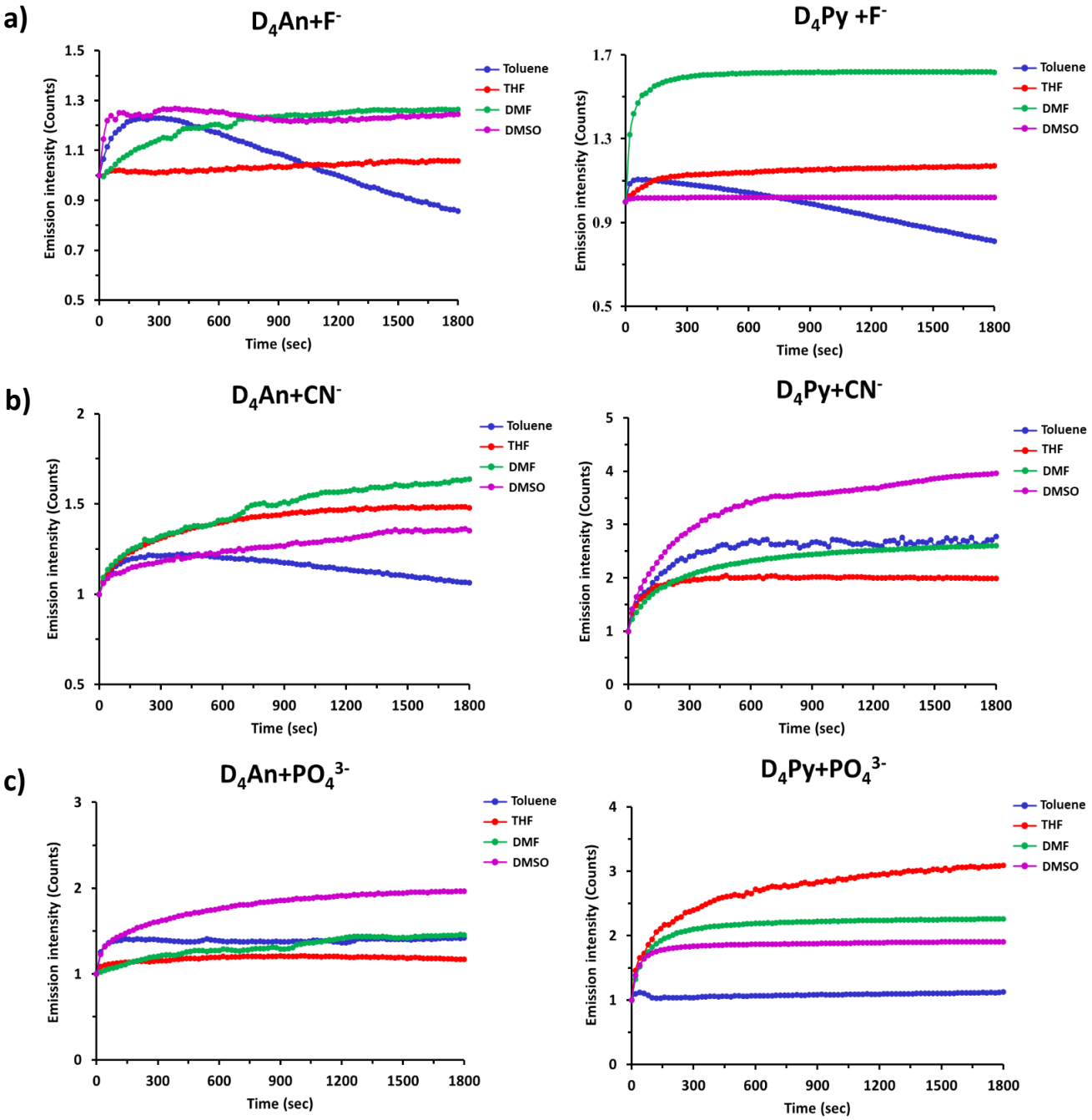

Figure S6. Kinetic studies of D_4An (2×10^{-5} M) (left) and D_4Py (1×10^{-5} M) (right) after addition of excess a) F^-, b) CN^-, and c) PO_4^{3-}.

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Table S1. Kinetic constants (*k*) of fluorescence responses of D_4An and D_4Py with anion guests (200 equiv.)

Kinetic constant (*k*) $\times 10^{-3}$ s^{-1}						
	D4An			D4Py		
Solvent	**F^-**	**CN^-**	**PO_4^{3-}**	**F^-**	**CN^-**	**PO_4^{3-}**
Toluene	3.2	3.1	2.5	0.7	6.3	4.8
THF	0.8	3.4	4.2	1.3	4.9	6.2
DMF	8.4	4.4	1.1	3.6	4.8	6.8
DMSO	6.8	3.0	3.5	0.6	7.5	6.6

Kinetic calculation

At the low concentrations, the kinetic constant was calculated from pseudo-first order equation as following below

$$In\,[I] = kt + In[I]_0$$

When I and I_0 were the fluorescence intensity before and after addition of fluoride, *t* is time (s). The kinetic constant (*k*) could be calculated through the slope of graph between ln [I] against

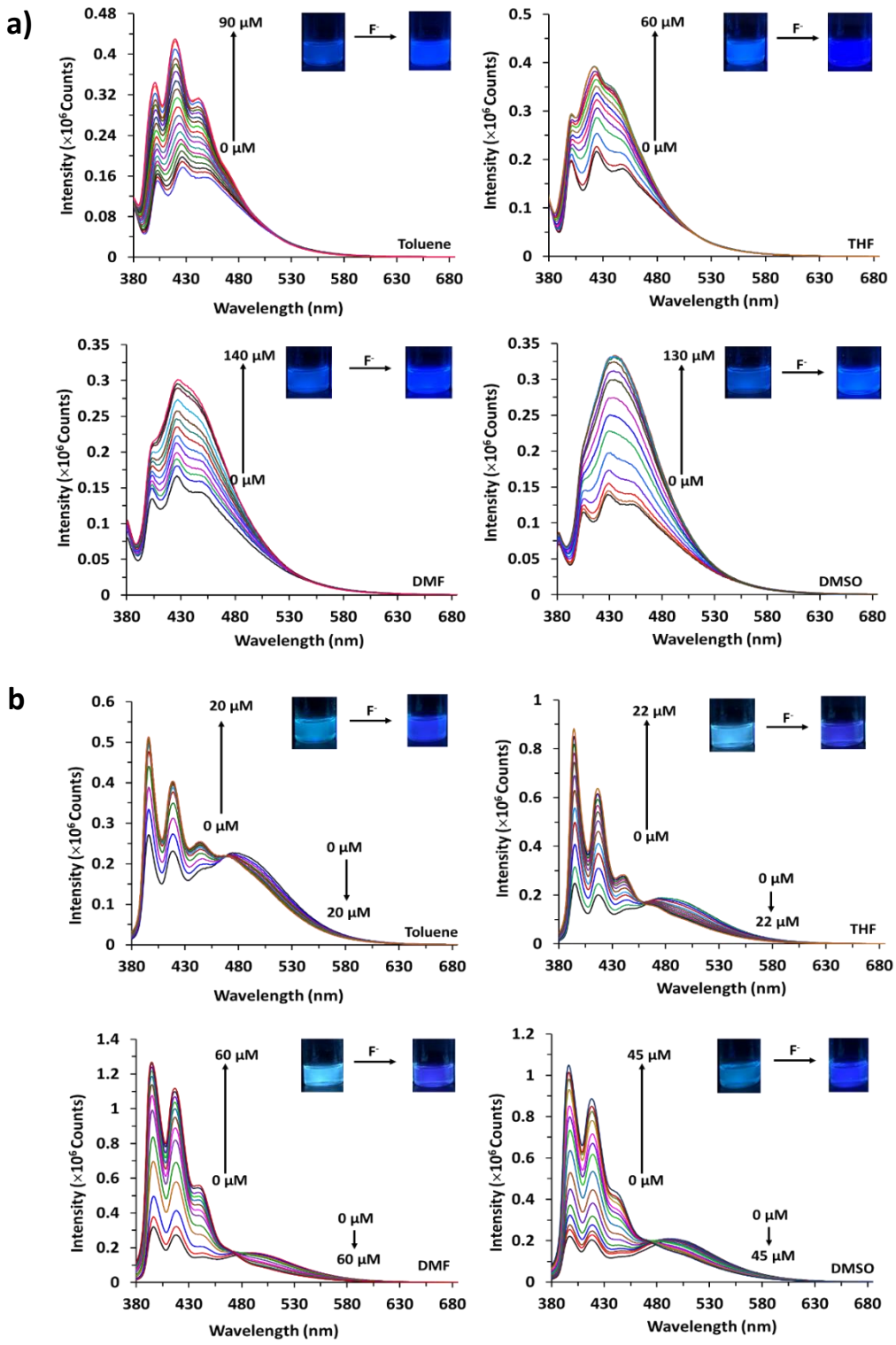


Figure S7. Fluorescence titration spectra of a) D_4An (2×10^{-5} M) at λ_{ex} = 378 nm and b) D_4Py (1×10^{-5} M) at λ_{ex} = 350 nm in various solvents at different concentrations of fluoride

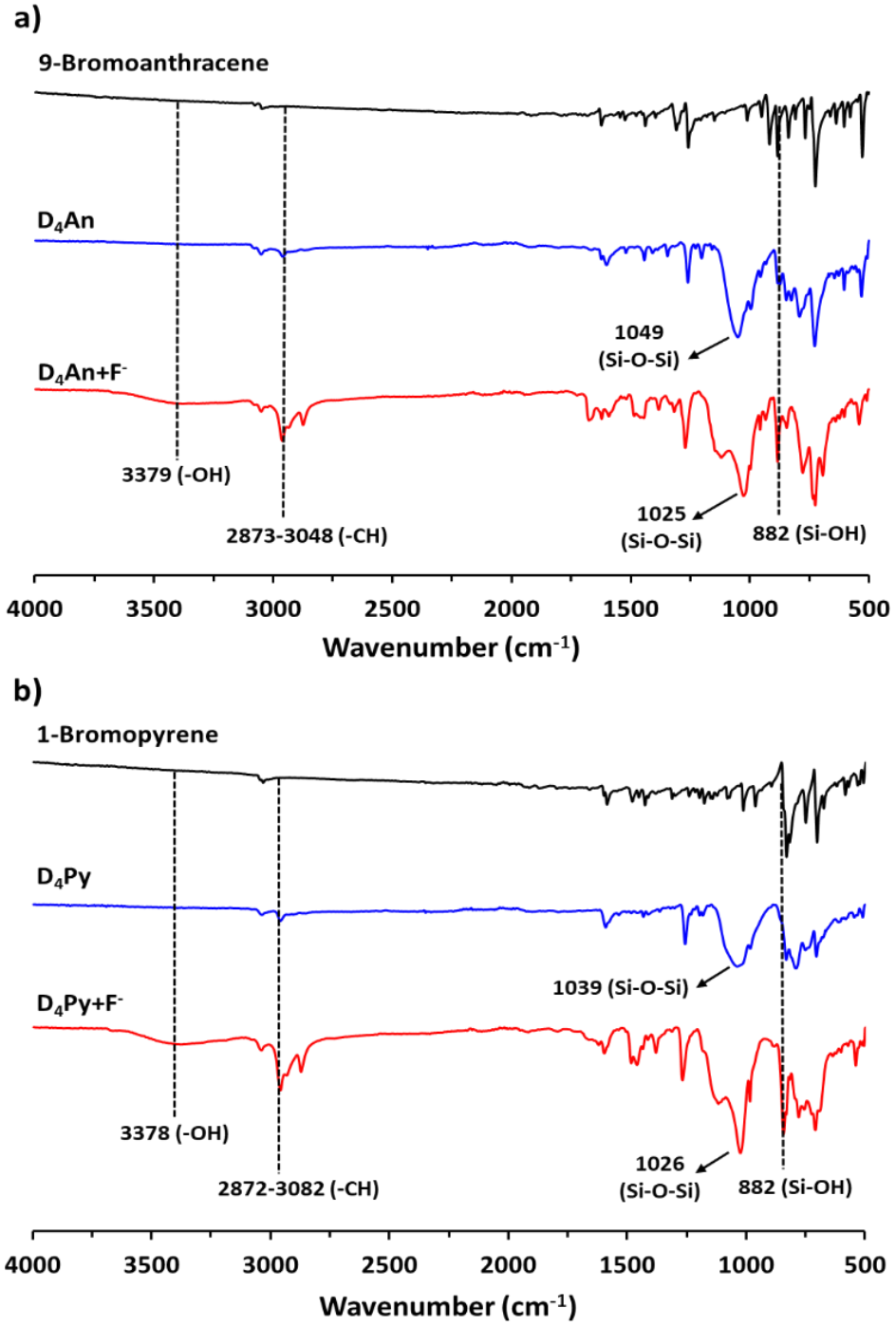


Figure S8. FTIR spectra of a) D_4An and b) D_4Py before and after addition of fluoride (1 equiv).

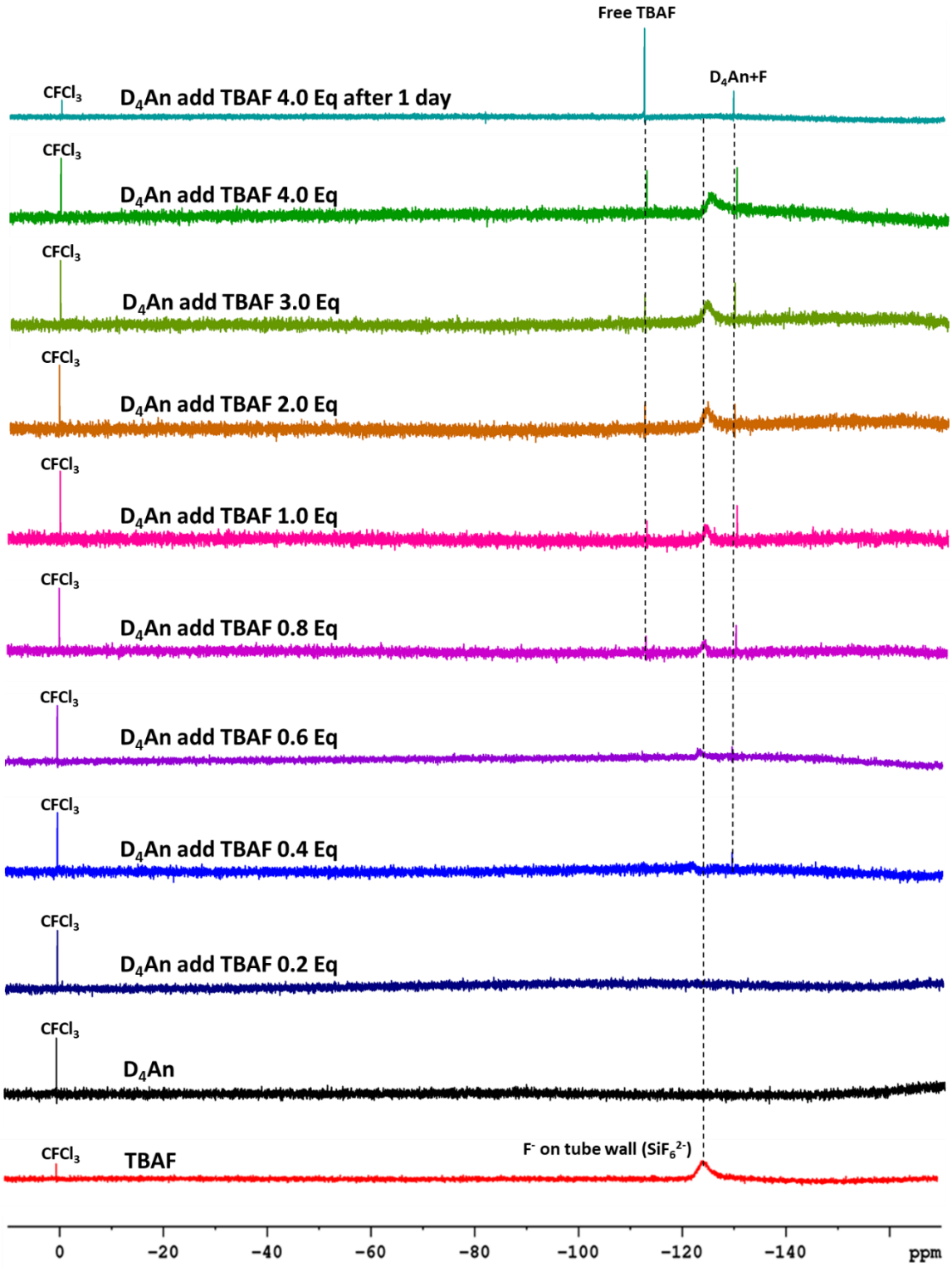


Figure S9. ^{19}F NMR spectra for titration of D_4An in $CDCl_3$ after addition of TBAF

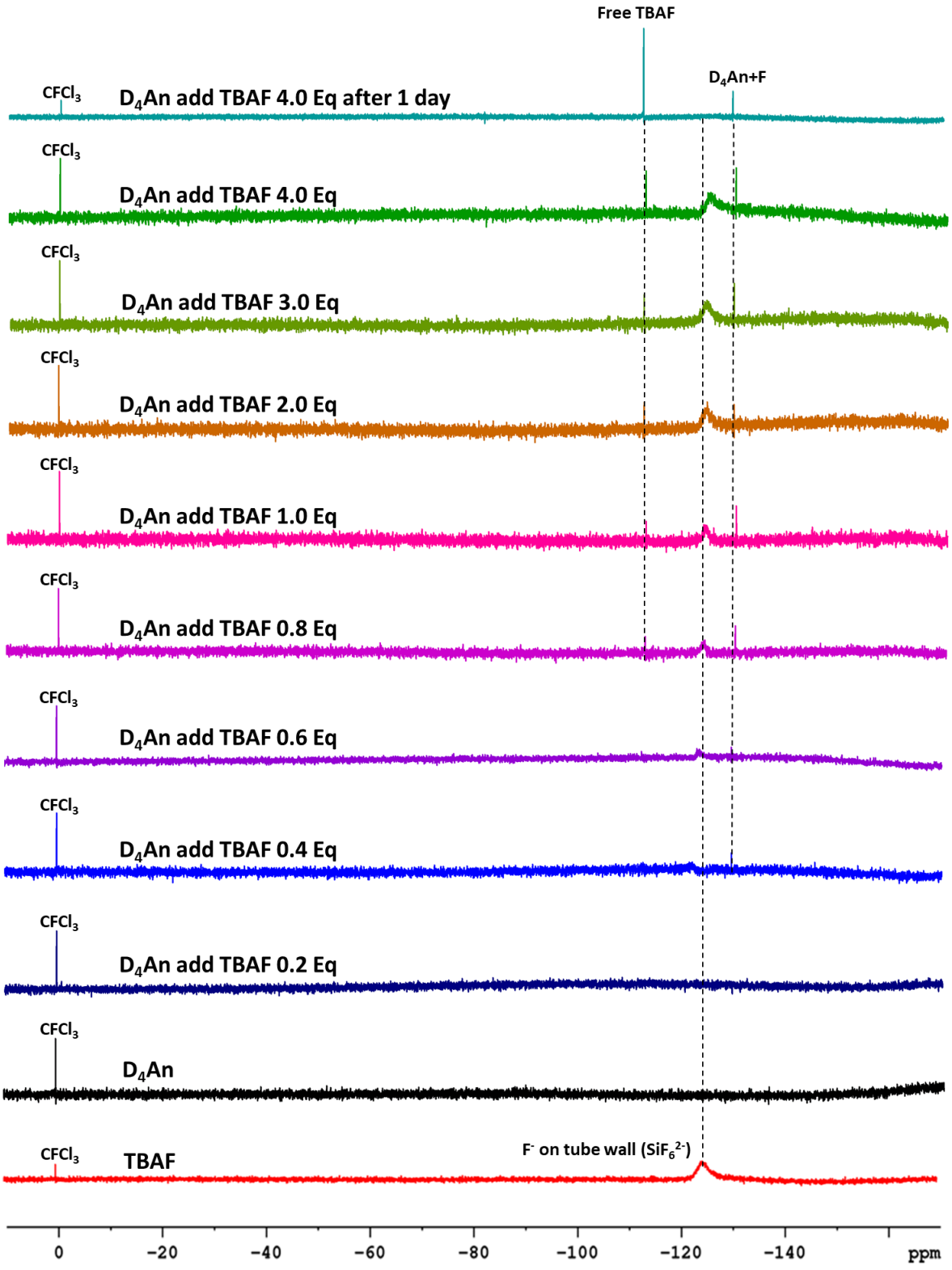
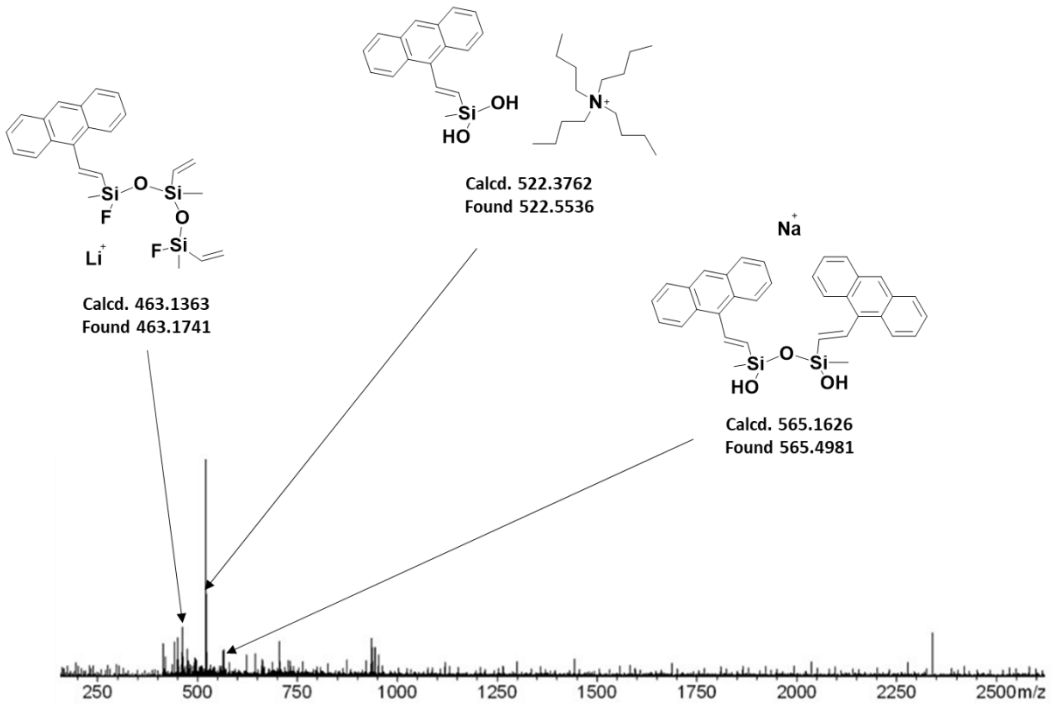
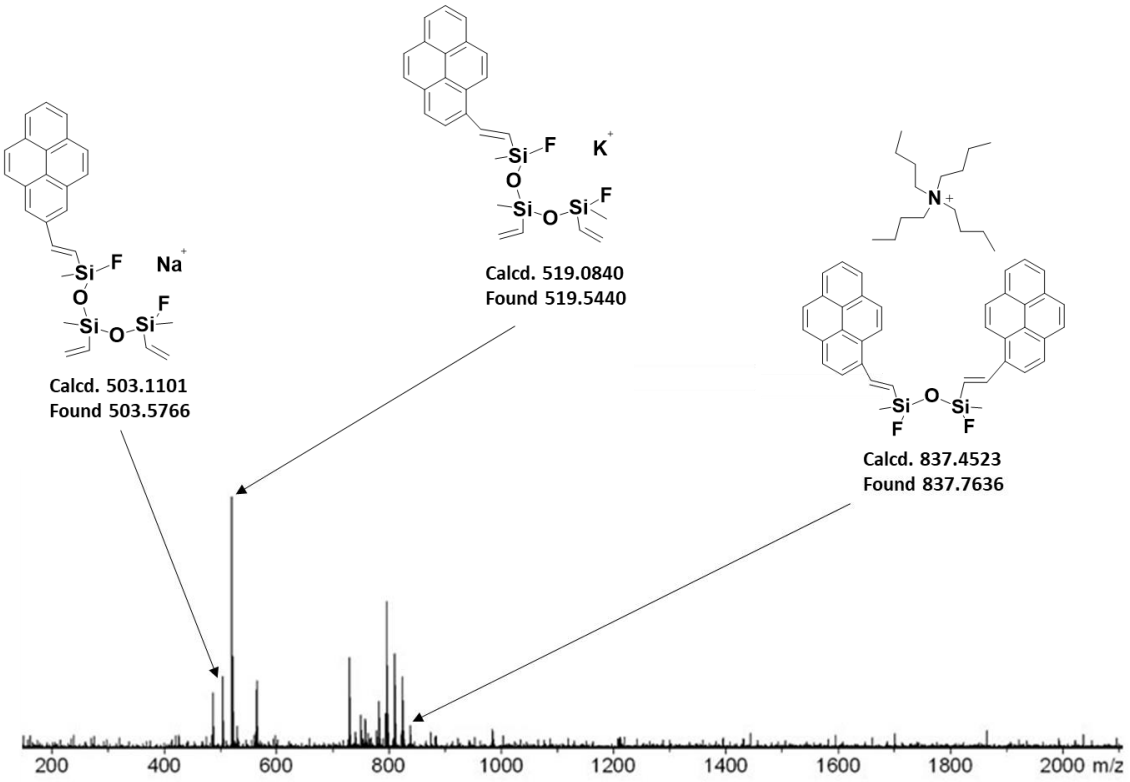


Figure S10. ^{19}F NMR spectra for titration of D_4Py in $CDCl_3$ after addition of TBAF



#	m/z	I	I %	S/N	Res.
1	49.2454	209	10.3	12.6	9815
2	56.3087	206	10.1	12.4	10388
3	101.9802	217	10.7	13.1	14873
4	102.0417	227	11.2	13.8	15009
5	129.9334	285	14.0	17.7	16367
6	413.2745	330	16.3	22.2	5953
7	419.4071	210	10.3	13.4	29287
8	441.3111	347	17.1	22.5	5139
9	450.3533	384	18.9	24.8	5153
10	460.3769	248	12.2	15.2	5343
11	462.3864	479	23.6	30.9	5543
12	463.1741	202	10.0	12.0	4996
13	463.3911	215	10.6	12.9	5454
14	474.2252	283	13.9	17.2	31228
15	493.1570	203	10.0	11.6	5906
16	519.5515	2030	100.0	127.8	6136
17	520.5529	752	37.0	46.1	6094
18	521.5491	779	38.4	47.8	5605
19	522.5536	251	12.4	14.1	5848
20	563.5008	266	13.1	14.8	4646
21	565.4981	278	13.7	15.5	7083
22	622.0506	228	11.2	12.3	6386
23	644.0267	238	11.7	13.0	7052
24	705.6418	351	17.3	20.1	6644
25	935.7199	434	21.4	26.5	6399
26	936.7298	291	14.3	17.1	5456
27	944.0194	296	14.6	17.5	5204
28	952.2041	231	11.4	13.2	48815
29	2339.3246	429	21.1	27.4	75315
30	2339.7690	263	13.0	16.1	74434

Figure S11. ESI-MS spectrum of D_4An after addition of fluoride (1 equiv.)



#	m/z	I	I %	S/N	Res.
1	101.9793	265	12.9	15.3	15334
2	129.9346	248	12.1	14.2	15901
3	486.3824	453	22.1	29.6	5411
4	487.3790	206	10.1	12.4	6597
5	503.5766	601	29.4	39.5	5053
6	504.5860	249	12.2	15.3	5664
7	519.5440	2047	100.0	138.2	5891
8	520.5482	772	37.7	50.9	6220
9	521.5478	768	37.5	50.6	5579
10	522.5444	329	16.1	20.6	7483
11	529.5741	212	10.4	12.5	5036
12	563.4947	503	24.6	32.0	6464
13	565.4938	550	26.9	35.1	5804
14	729.6391	761	37.2	47.4	5445
15	730.6432	439	21.4	26.5	5236
16	749.7246	299	14.6	17.4	5535
17	757.6374	272	13.3	15.7	5452
18	781.7316	411	20.1	24.9	5137
19	782.7364	276	13.5	16.1	5971
20	793.7521	304	14.9	17.9	5454
21	795.7486	1211	59.2	77.2	5728
22	796.7486	699	34.1	43.8	6270
23	797.7475	312	15.2	18.4	8511
24	809.7668	792	38.7	50.0	5014
25	810.7633	539	26.3	33.4	5728
26	811.7680	228	11.1	13.0	5452
27	823.7816	596	29.1	37.2	5177
28	824.7807	413	20.2	25.2	6805
29	837.7636	219	10.7	12.5	7245
30	2339.3389	265	12.9	14.4	74738

Figure S12. ESI-MS spectrum of D_4Py after addition of fluoride (1 equiv.)

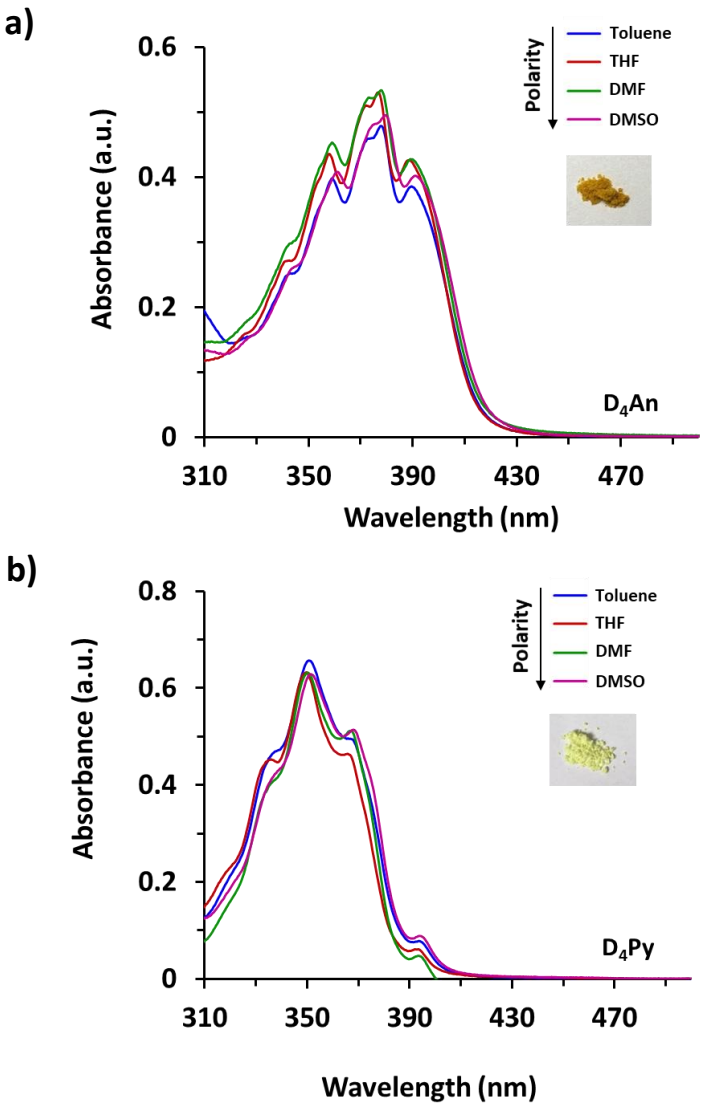


Figure S13. UV-Vis absorption spectra of a) D_4An (4×10^{-5} M) and b) D_4Py (1×10^{-5} M) in various solvents.

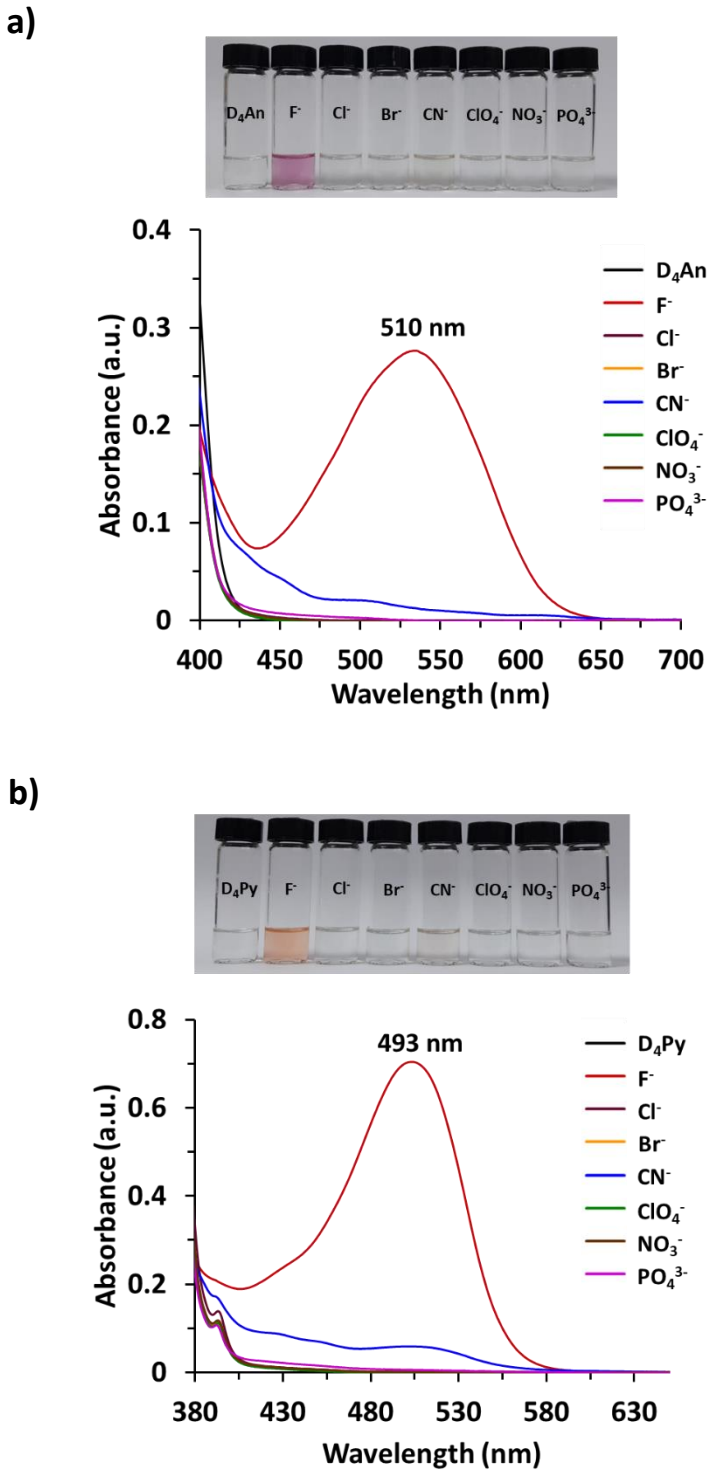


Figure S14. UV-Vis spectra of a) D_4An (4×10^{-5} M) and b) D_4Py (2×10^{-5} M) in THF before and after addition of various anions (200 equiv.)

The association constant (K_a) was calculated according to the Benesi–Hildebrand equation as following below (a) fluorescence experiment and (b) UV-Vis experiment

$$\frac{1}{I - I_0} = \frac{1}{K(I_{max} - I_0)[F^-]} + \frac{1}{(I_{max} - I_0)} \qquad (\boldsymbol{a})$$

$$\frac{1}{A - A_0} = \frac{1}{K(A_{max} - A_0)[F^-]} + \frac{1}{(A_{max} - A_0)} \qquad (\boldsymbol{b})$$

I_o is the fluorescence intensity of solution in the absence of fluoride, I is fluorescence record in the present of fluoride ion and I_{max} is the fluorescence in the addition of $[F^-]_{max}$. While A and A_o are absorbance of solution with and without fluoride, respectively. A_{max} are the absorbance in the presence of $[F^-]_{max}$. The association constant (K_a) could be calculated from the slope of straight line plot between $1/(A - A_o)$ or $1/(I - I_o)$ against 1/[F-].

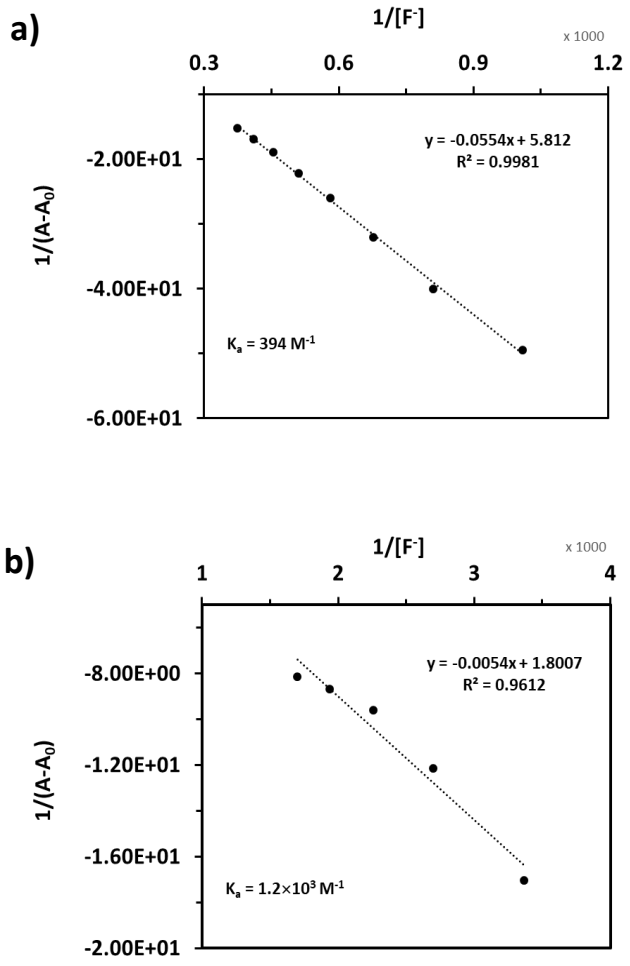


Figure S15. Benesi– Hildebrand plot from UV-Vis titration of a) D_4An (4×10^{-5} M) at 510 nm and b) D_4Py (2×10^{-5} M) at 493 nm in THF with fluoride ion.

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The limit of detection and limit of quantitative for fluoride were calculated from absorption and fluorescence titration which according to the equation

$$LOD = 3\sigma/S$$

$$LOQ = 10\sigma/S$$

Where, σ is the standard deviation of the response and *S* is the slope of calibration curve.

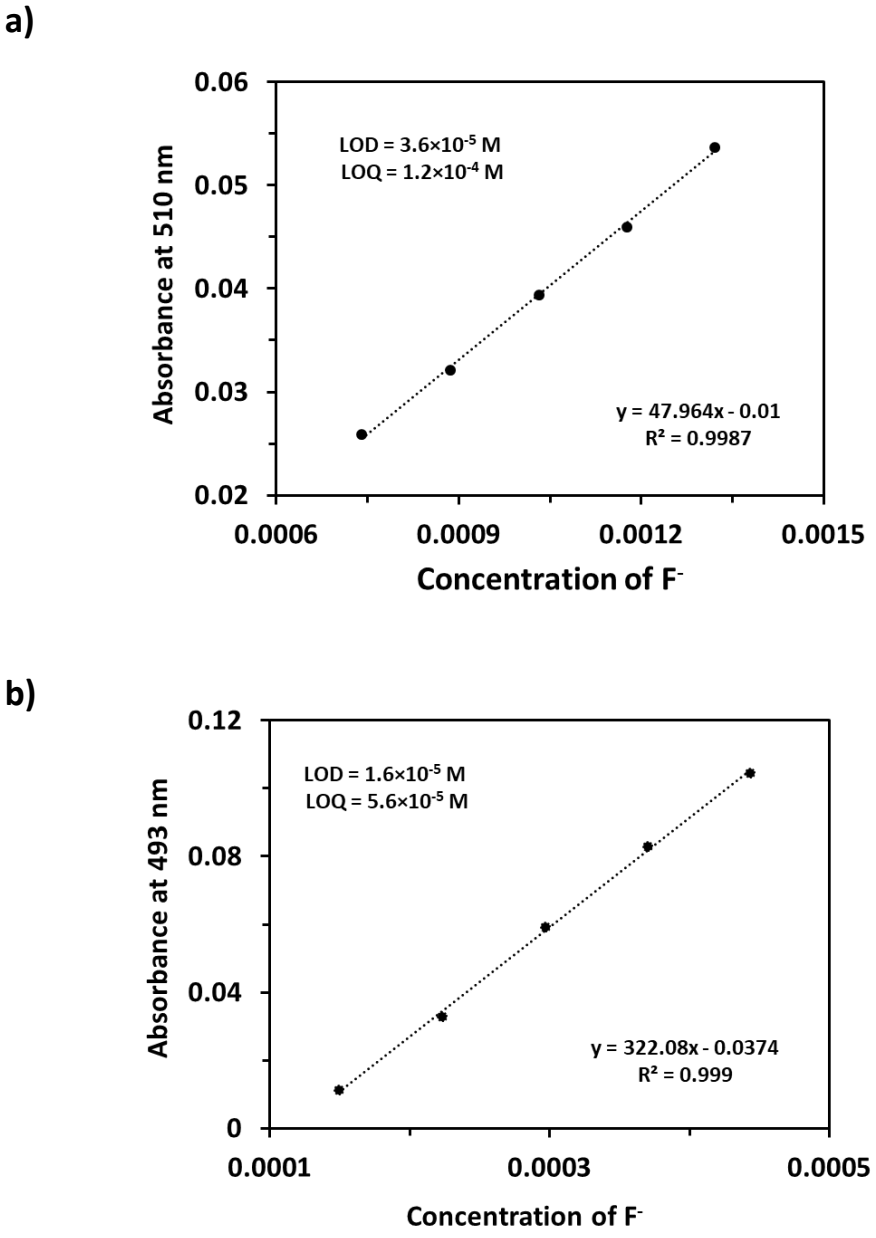

Figure S16. LOD and LOQ plot from UV-Vis titration of a) D_4An (4×10^{-5} M) at 510 nm and b) D_4Py (2×10^{-5} M) at 493 nm in THF with fluoride ion.

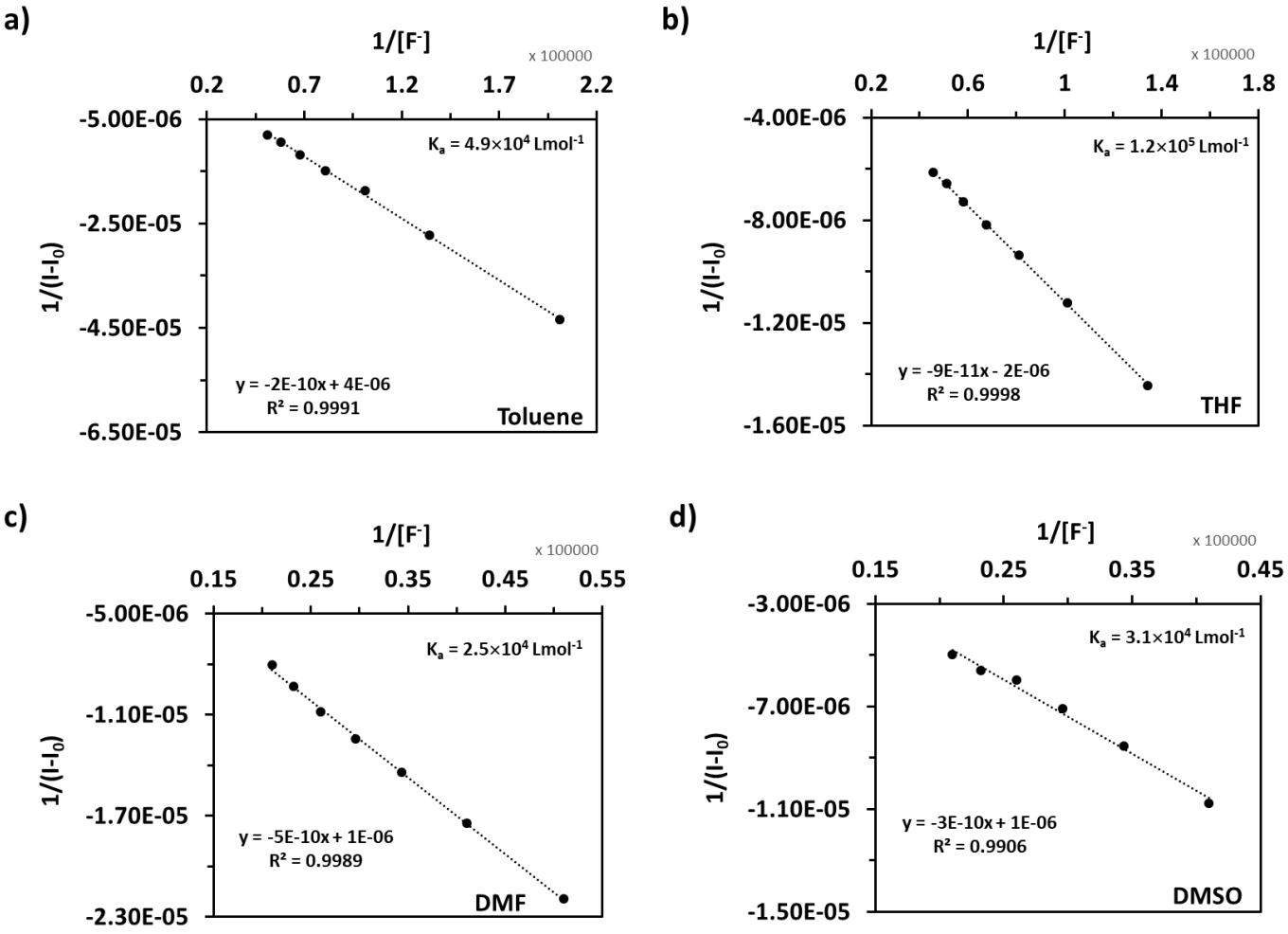

Figure S17. Benesi– Hildebrand plot from fluorescence titration of D_4An (2×10^{-5} M) with fluoride ion in various solvents.

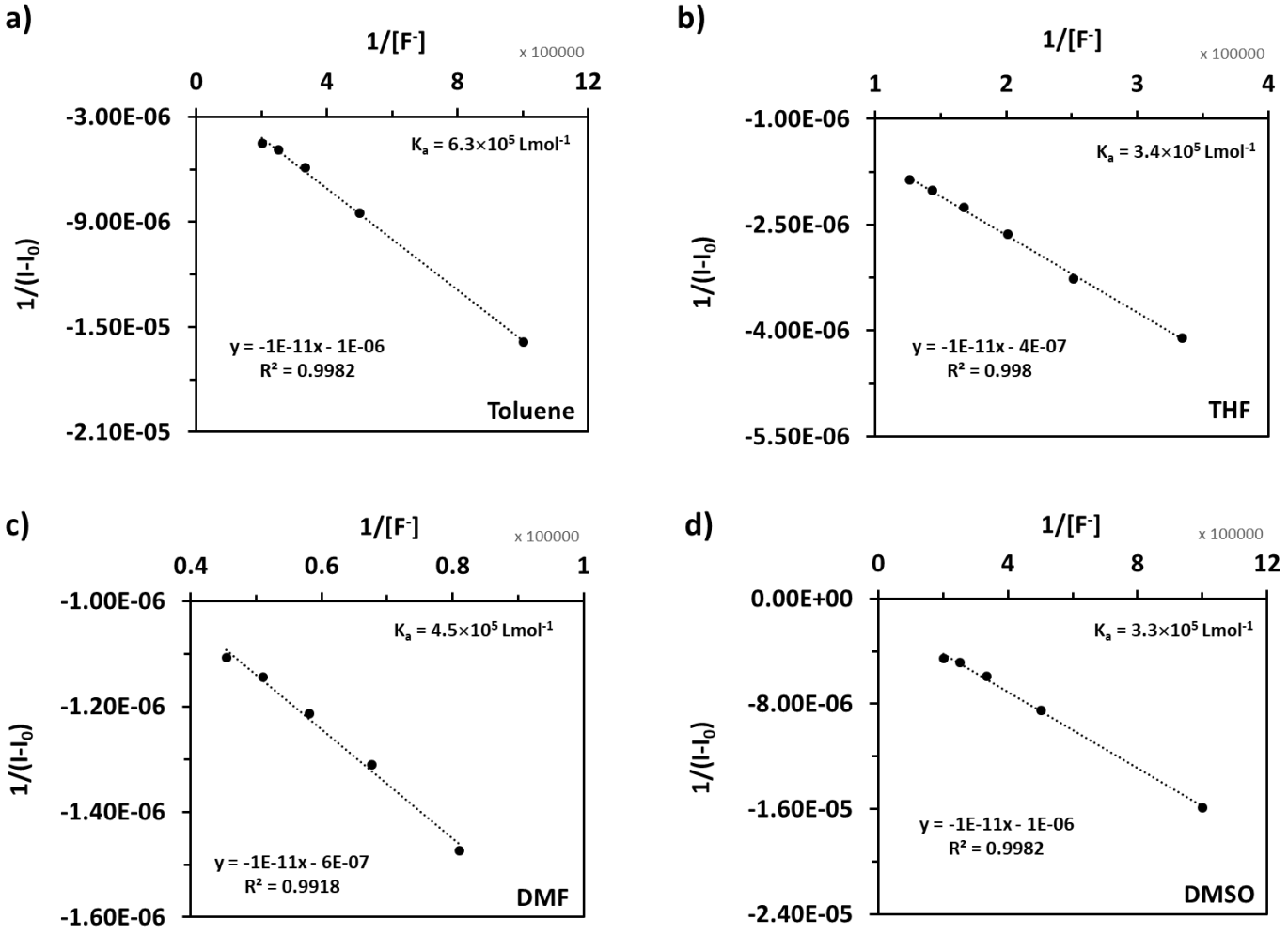

Figure S18. Benesi– Hildebrand plot from fluorescence titration of D_4Py (1 x 10^{-5} M) with fluoride ion in various solvents.

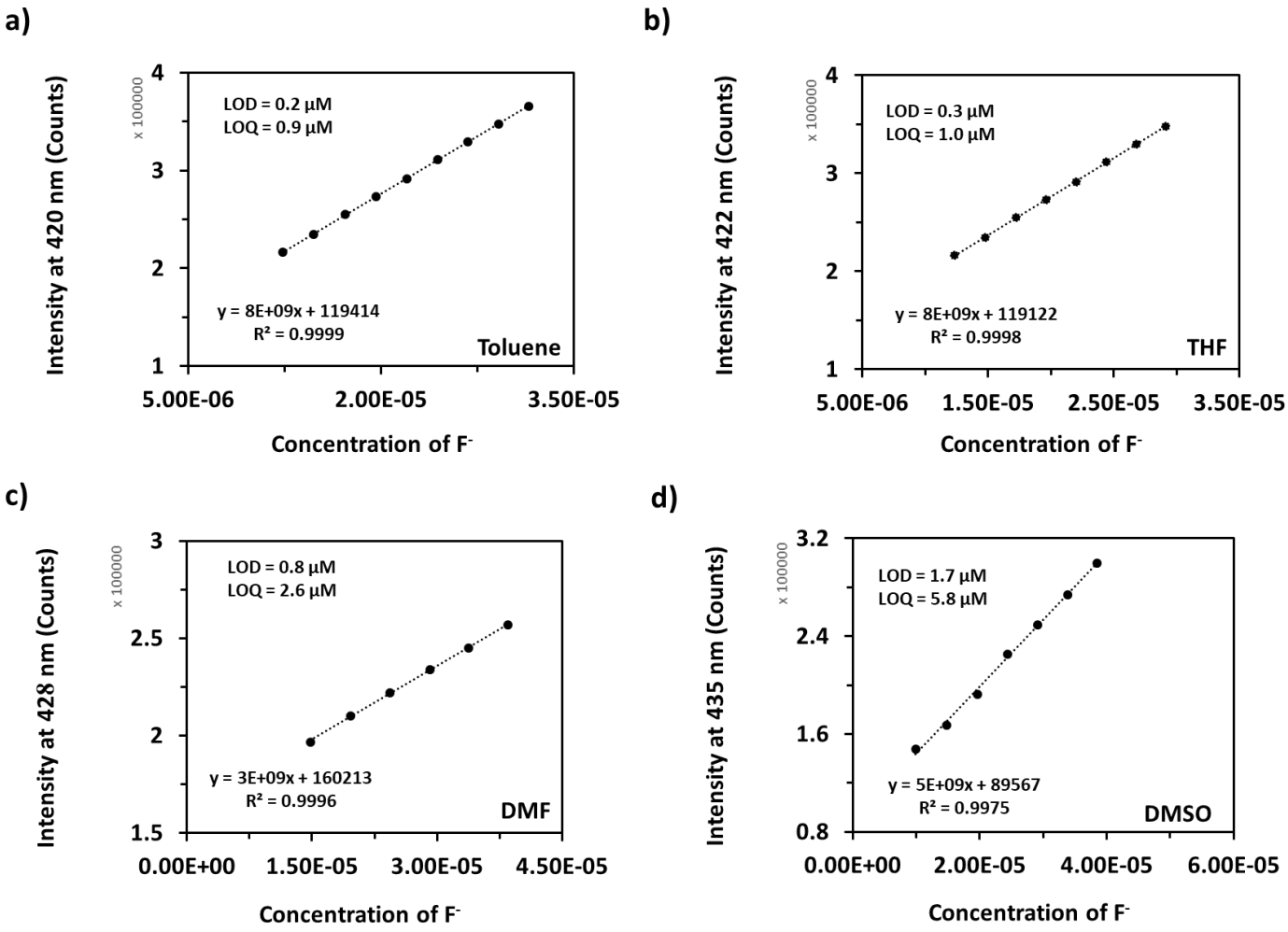

Figure S19. LOD and LOQ plot from fluorescence titration of D_4An (2×10^{-5} M) with fluoride ion in various solvents.

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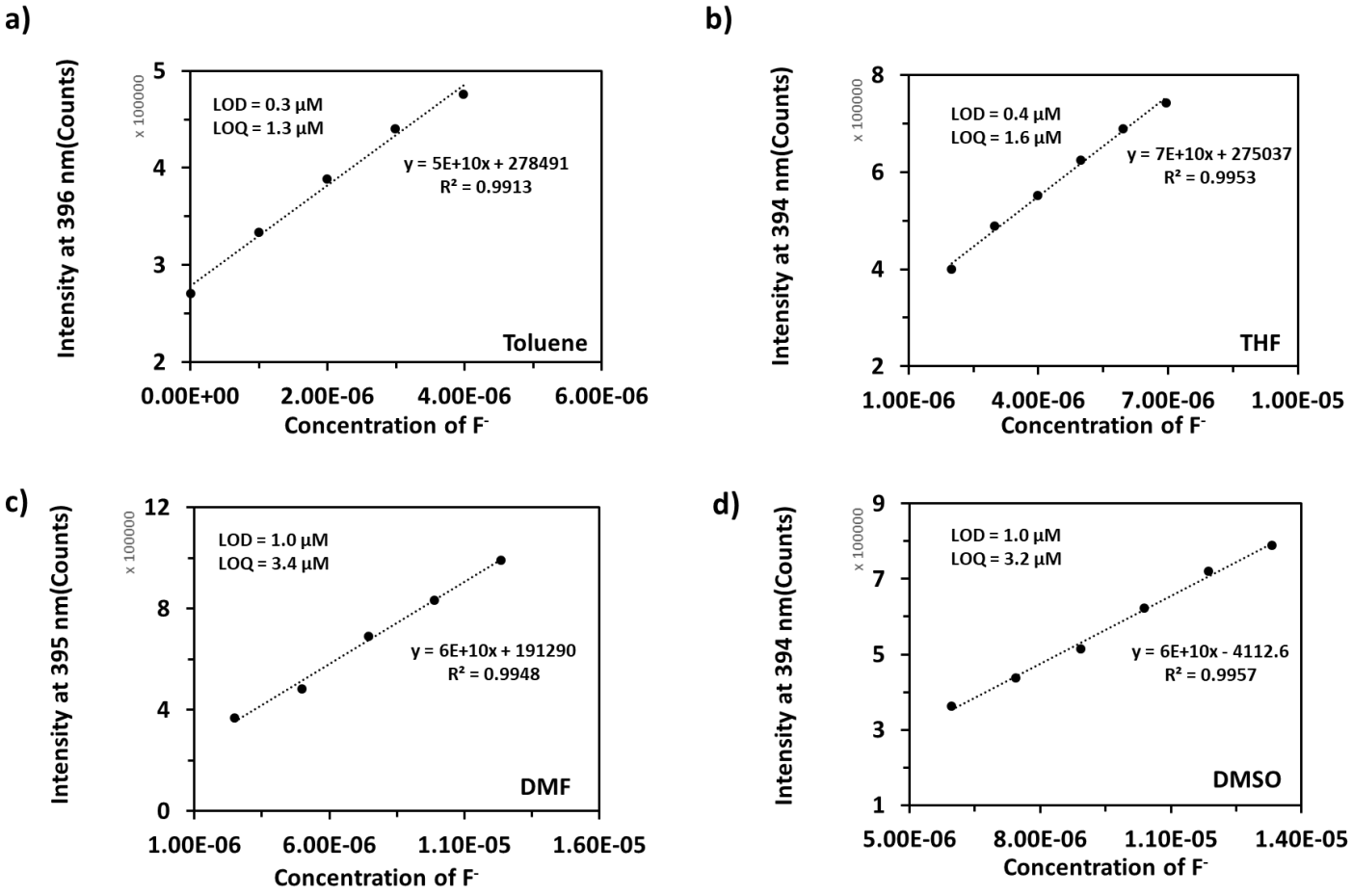
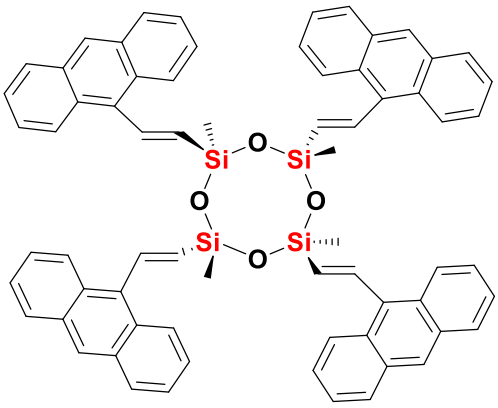


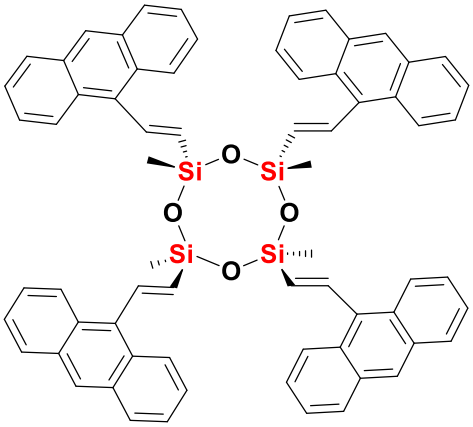
Figure S20. LOD and LOQ plot from fluorescence titration of D_4Py (1 x 10^{-5} M) with fluoride ion in various solvents.

Table S2. Associate constants (K_a), LOD and LOQ of D_4An and D_4Py with fluoride from Uv-Vis absorption and fluorescence emission titration.

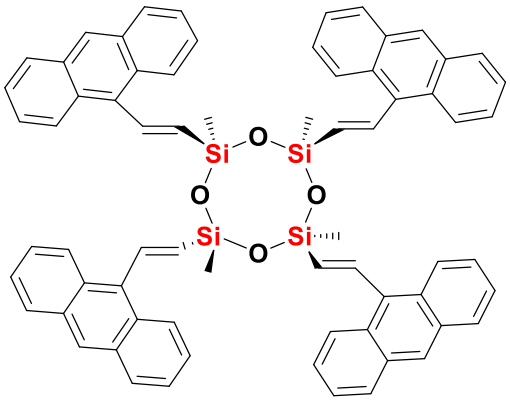
	D_4An						D_4Py					
	Uv-Vis absorption			Fluorescence emission			Uv-Vis absorption			Fluorescence emission		
Solvent	K_a (M^{-1})	LOD (µM)	LOQ (µM)	K_a (M^{-1})	LOD (µM)	LOQ (µM)	K_a (M^{-1})	LOD (µM)	LOQ (µM)	K_a (M^{-1})	LOD (µM)	LOQ (µM)
Toluene	-	-	-	4.9×10^4	0.2	0.9	-	-	-	6.3×10^5	0.3	1.3
THF	394	36	120	11.8×10^4	0.3	1.0	1.2×10^3	16	56	3.4×10^4	0.4	1.6
DMF	-	-	-	2.5×10^4	0.8	2.6	-	-	-	4.5×10^4	1.0	3.4
DMSO	-	-	-	3.1×10^4	1.7	5.8	-	-	-	3.3×10^4	1.0	3.2



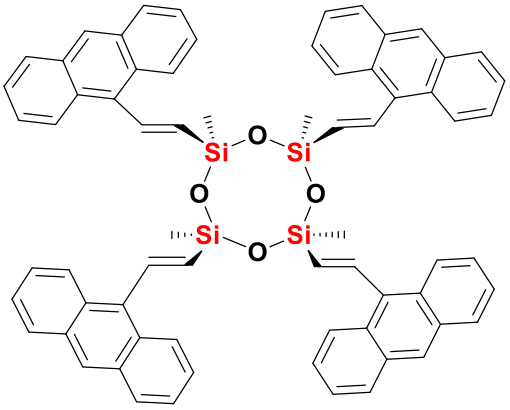
all-*trans*



cis-trans-cis



cis-cis-trans



all-*cis*

Figure S21. Possible D_4 isomers

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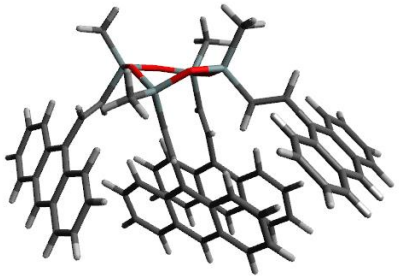
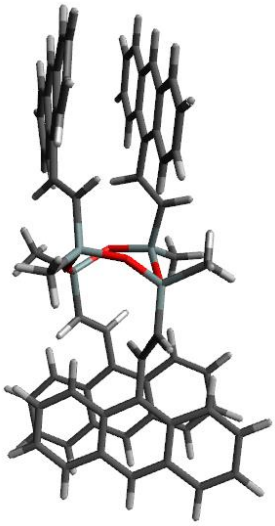
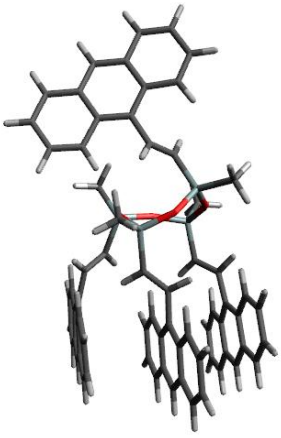
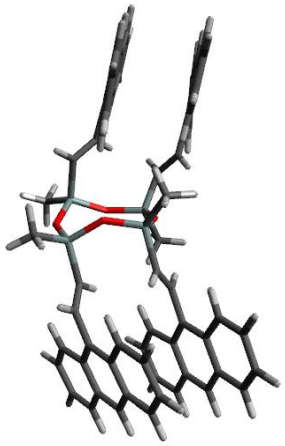
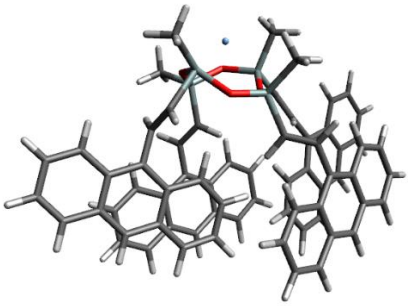
Table S3. Computational optimized of possible D_4 isomers and D_4 after fluoride addition

Isomers	Electronic energy (Hatree)	Geometry
All-*cis*	-4080.587654	
All-*trans*	-4080.596471	
Cis-cis-trans	-4080.585036	

Cis-trans-cis	-4080.586615	
All-*cis* + F^-	-4180.410981	
All-*trans* + F^-	-4180.401083