Electronic Supplementary Information (ESI)

Silsesquioxane Cage as Fluoride Sensor

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Chemicals and Instruments

1-Bromopyrene, PPh_3, triethylamine and $Pd(OAc)_2$ were purchased from Aldrich, while octavinylsilsesquioxane was prepared according to literature report. The ^{29}Si CP/MAS NMR spectra were acquired at 60 MHz frequency with AVANCE 300 MHz Digital NMR Spectrometer (Bruker Biospin; DPX-300). ^{19}F NMR results were obtained by Bruker-AV 400 of high-resolution magnetic resonance spectrometer. The FT-IR spectra were collected using an attenuated total reflectance (ATR) technique with Bruker model Alpha spectrometer. High-Performance MALDI-TOF analysis was performed on Bruker the new autoflex^{TM} series. UV-Vis spectroscopy was performed on UV-Vis spectrophotometer (Shimadzu UV-2600), while fluorescent spectra was recorded from spectrofluorometer (Horiba FluoroMax4+) and used for quantum yield measurement as well. X-ray Powder Diffraction (XRD) results were obtained by a Bruker D_8 Advance X – Ray diffractometer with a Cu K_α anode (λ = 0.1542 nm). The diffraction patterns were collected at 25 °C, over an angular range of 20 to 80°.

Experimental section

The synthesis of PySQ was simply carried out *via* heck reaction as following methods: 632 mg of OVS (1 mmol), 90 mg of palladium (II) acetate (0.4 mmol) and 210 mg of triphenylphosphine (0.8 mmol) were added into the mixture solvent of THF/Et_3N (45 ml/15 ml) in a 100 ml round bottom flask attached with a condenser. The solution was argon bubbled for 30 min at room temperature, after the mixture was done bubbling 2.474 g of 1-bromopyrene was added, then the mixture was heated to 80 ^oC for 48 h. After cooling at room temperature, the mixture was preliminarily filtrated heterogeneous catalyst out by a Buchner funnel. The mixture was on completion precipitated by adding 5% HCl methanol, the pale-yellow powders were collected. The precipitate product was redissolved in minimal of CH_2Cl_2 and the afterwards purification was performed by column chromatography. The final purification was soxhlet extraction with MeOH and hexane for 1 day each. 0.92 g (41 % yield) of final product was collected as bright yellowish powders.

Quantum yields of PySQ were measured by Horiba, Fluoromax-4 using quantum yield calculation function by the following equation:

$$QY = \frac{Photon\ emiited}{Photon\ absorbed}$$

Firstly, the default function of quantum yield mode was set at slitwidth 3 nm, integration time 1 sec and increment of emission 3 nm/step. After that parabolic spherical barium oxide was used to cover the quartz cell and the Rayleigh scattering of the blank (DMSO and THF) was measured, and the sample was measured emission afterwards. Integration of area as photon emitted/absorbed.

For the kinetic study, at the low concentrations, fluorescent emission intensity(I) was assumed to directly vary to concentration. The rate law could be derived as shown.

$$\ln [I] = kt + ln[I]_0$$

Association constant could be calculated through Benesi–Hildebrand plot. *Ka* was calculated following the equation below (a) fluorescence study and (b) UV-vis study.

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{(I' - I_0)K_a[F^-]} \quad \text{(a)}$$

$$\frac{1}{A - A_0} = \frac{1}{A' - A_0} + \frac{1}{(A' - A_0)K_a[F^-]} \quad \text{(b)}$$

when I and I_0 were the intensity of the solution with and without the presence of fluoride from fluorescence titration method and A_0 is the absorbance of solution in the absence of fluoride, A is the absorbance recorded when added fluoride. The association constant (K) could be calculated from the slope of graph between $1/(A-A_0)$ or $1/(I-I_0)$ against 1/[F-]. When plot according to the equation, K_a which referred to association constant was equal to 3.3×10^4 M^{-1}in fluorescence study and 42.3 M^{-1}in UV-vis study.

The limit of detection and limit of quantitative in emission and absorption spectra was determined from equation below

$$\text{LOD} = 3S_b/S$$

$$\text{LOQ} = 10S_b/S$$

S_b is the standard deviation can be calculated from equation (c) and S is the slope of the calibration curve. Therefore, LOD = 1.61 ppb and LOQ = 5.67 ppb in fluorescence data and equal to 3120 ppm and 10400 ppm in UV-Vis data.

$$s_b = \frac{s_{y/x}}{\sqrt{\sum_i (x_i - \bar{x})^2}}, \quad s_{y/x} = \sqrt{\frac{\sum_i (y_i - \hat{y})^2}{n-2}} \quad \text{(c)}$$

Eyring polanyi equation describe temperature dependence of reaction rate constants

$$\frac{Ink}{T} = \frac{-\Delta H^{\ddagger} 1}{R \quad T} + \frac{Ink_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

Arrhenius equation describe the effect of temperature on the rate constant

$$Ink = InA - \frac{E_a}{RT}$$

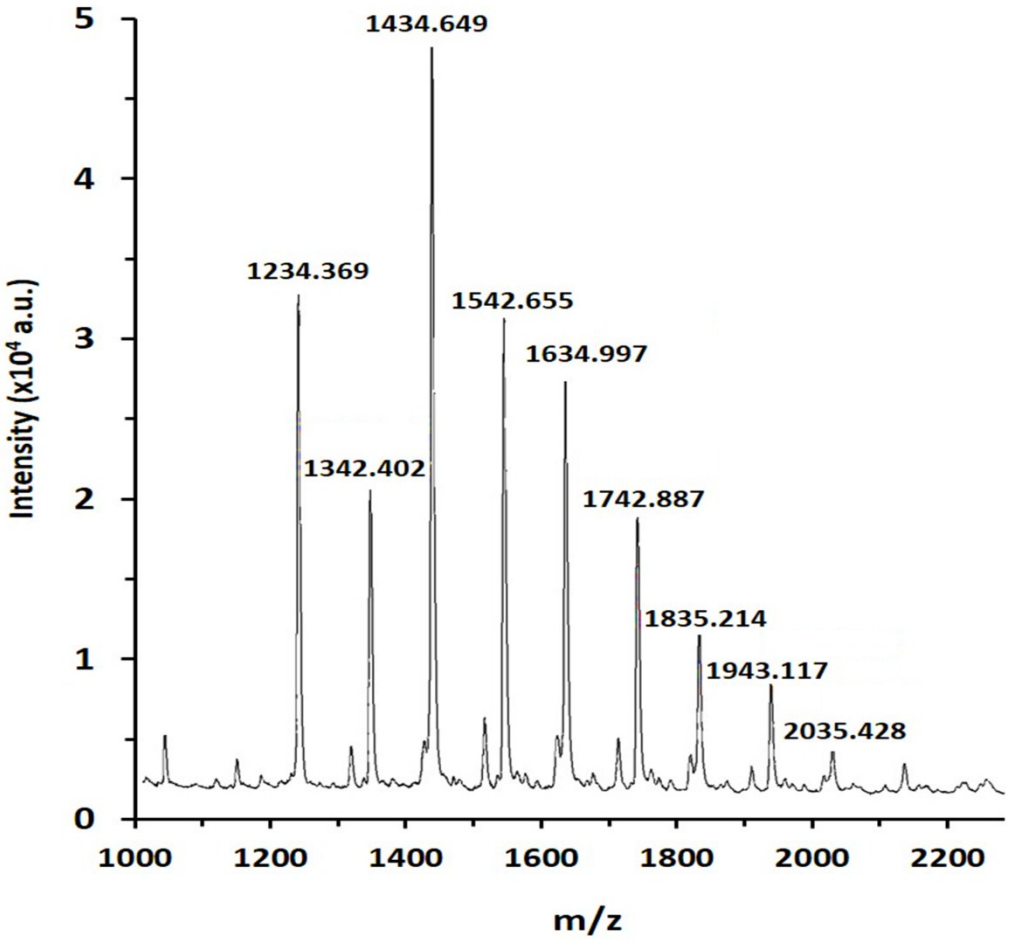

Figure. S1 MALDI-TOF spectrum of PySQ showed the various substitutions.

Table S1 Comparison of a substitution number on T_8 between calculated and experiment values.

Substitution (*n*)	**Formula Structure $[M+H]^+$**	**Calculated Value (m/z)**	**Experimental Value (m/z)**
3	$C_{64}H_{49}O_{12}Si_8^+$	1234.141	1234.369
4	$C_{80}H_{57}O_{12}Si_8^+$	1434.207	1434.649
5	$C_{96}H_{65}O_{12}Si_8^+$	1635.270	1634.997
6	$C_{112}H_{73}O_{12}Si_8^+$	1835.332	1835.241

7	$C_{128}H_{81}O_{12}Si_8^+$	2035.391	2035.428

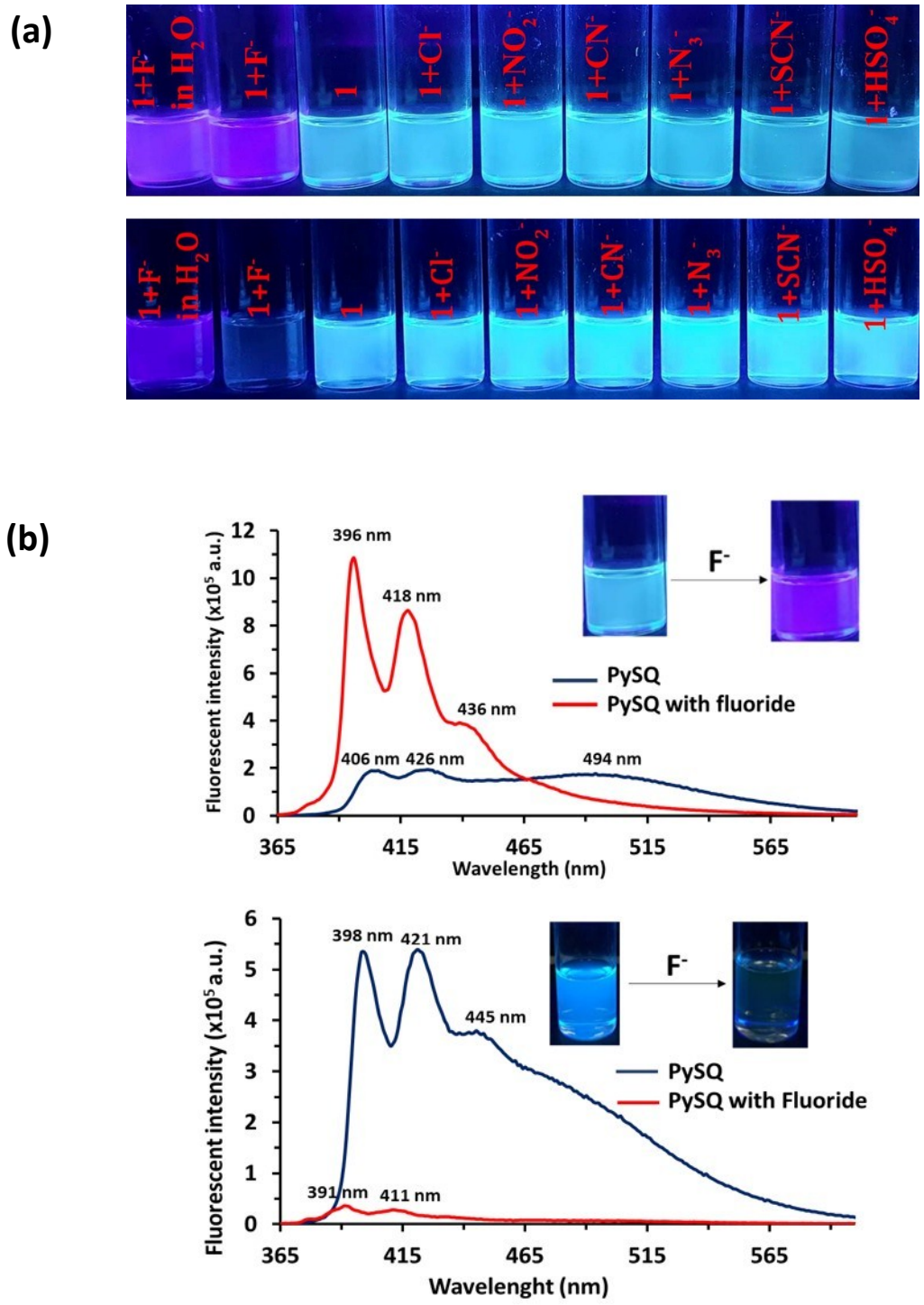

Figure. S2 (a) Selectivity tests of PySQ in DMSO (top) and in THF (bottom) in different ions at the same concentration (150 eq) under UV-lamp(bottom), (b) The Emission

spectrum of PySQ before and after of fluoride addition in DMSO (top) and in THF (bottom) as solvent, all had excitation wavelength at 351 nm.

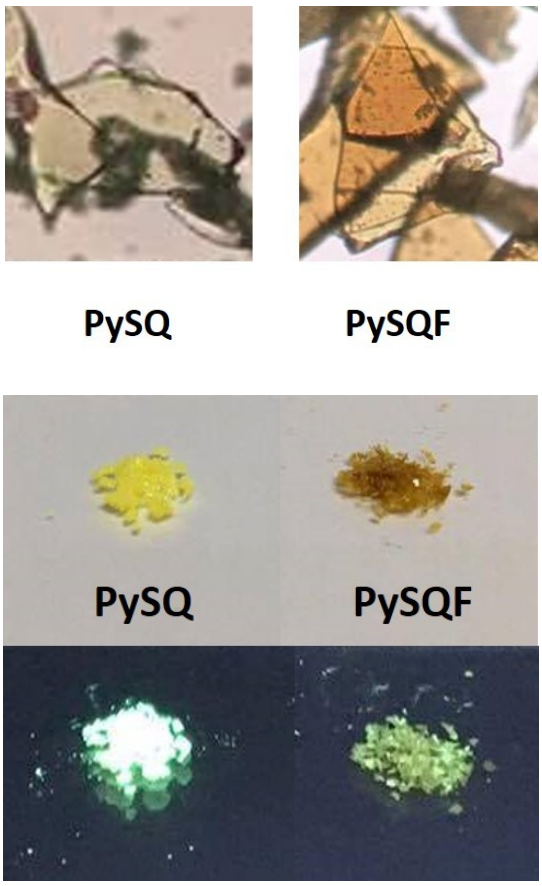

Figure. S3 (top) Crystals of PySQ and PySQ-F^- complexation under microscope,(bottom) Comparison of PySQ and PySQ-F^- in solid state. (top; in room light and bottom; under hand hold UV light).

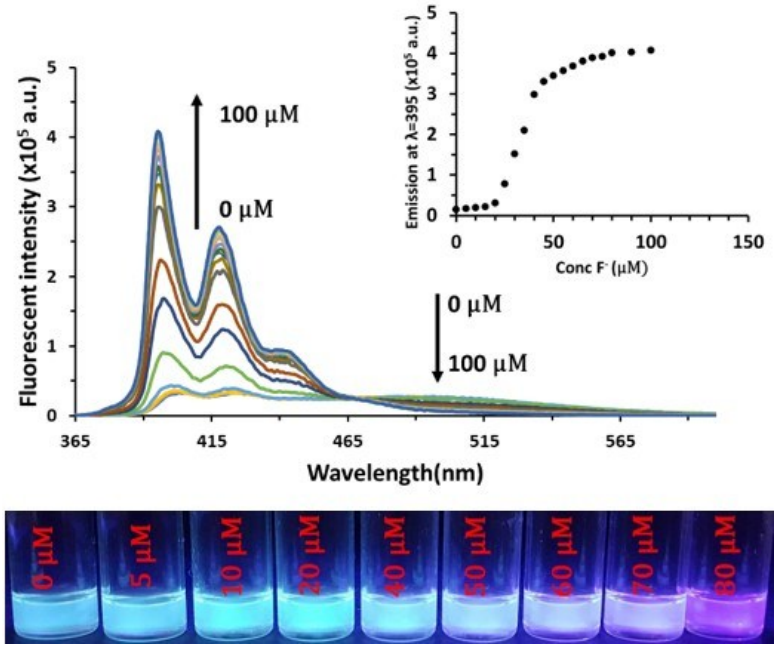

Figure. S4 The emission spectra of PySQ (5.6 µM in DMSO) upon addition of TBAF with excitation wavelength at 351 nm.

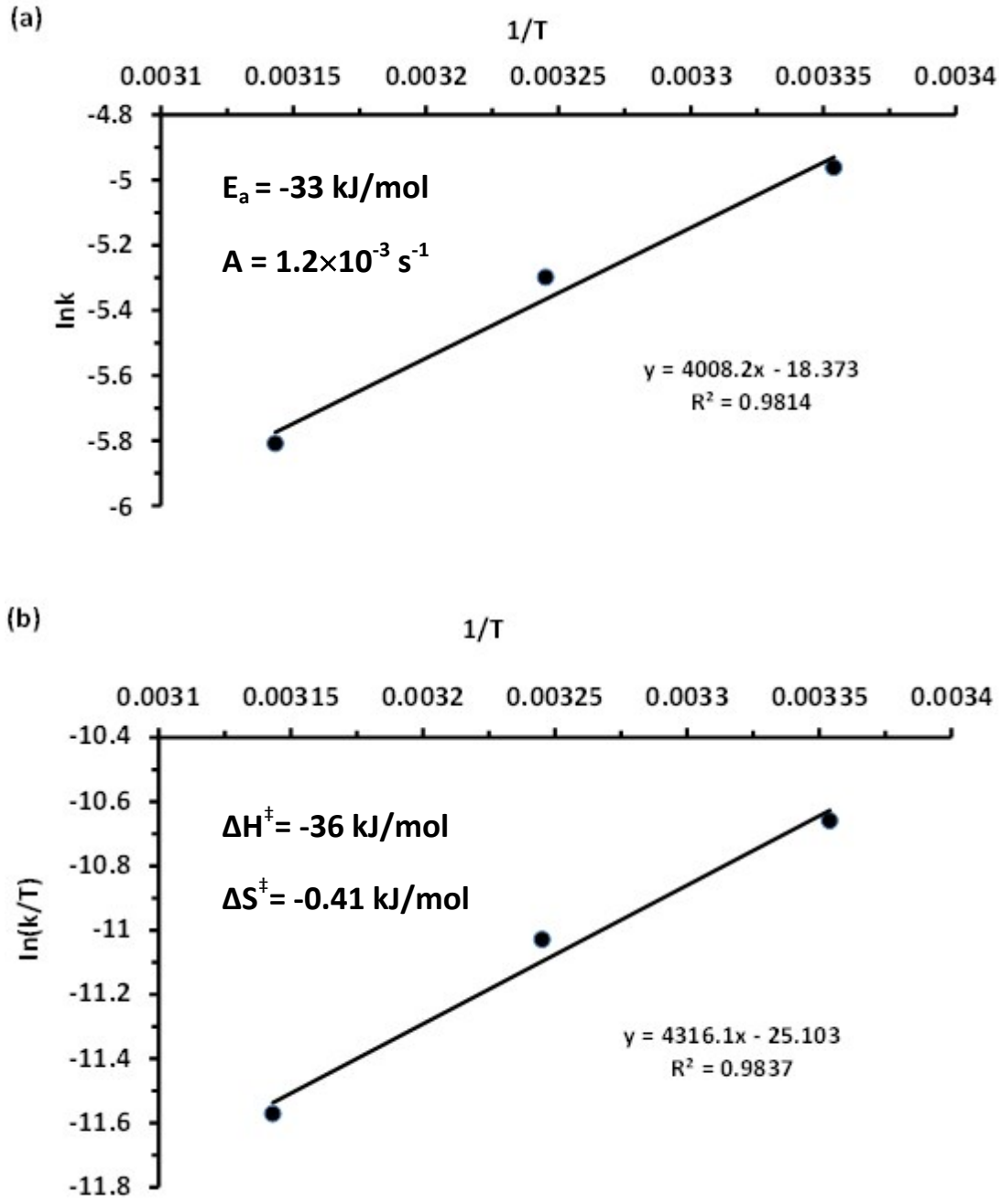

Figure. S5 (top) Arrhenius plot of PySQ between lnk against 1/T(K), (bottom) Eyring–Polanyi plot of PySQ between lnk/T against 1/T(K).

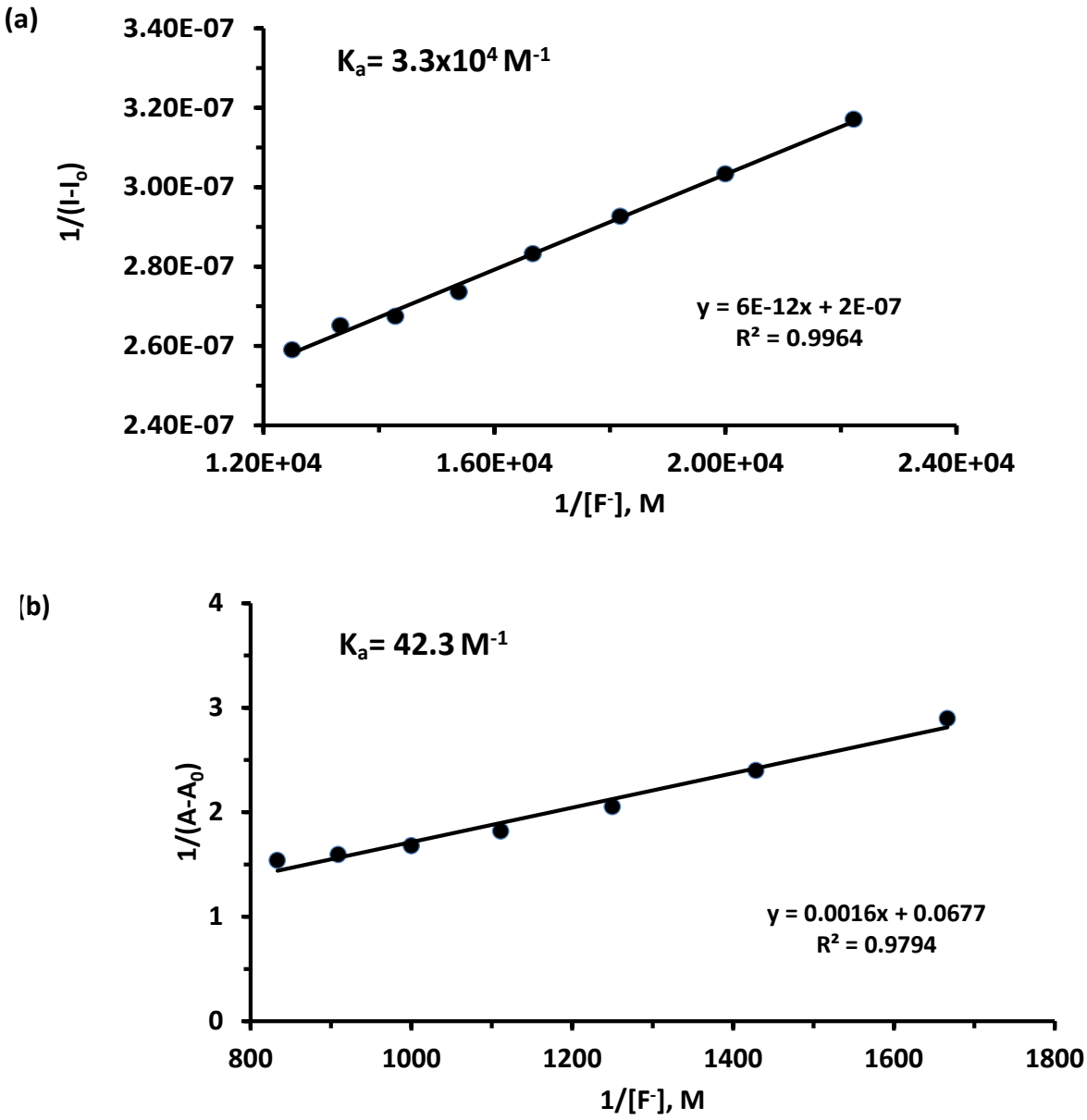

Figure. S6 Benesi–Hildebrand plot from (a) Fluorescence titration data of PySQ at 5.6 μM in DMSO and (b) from Uv-vis titration data of PySQ at 56 μM in THF

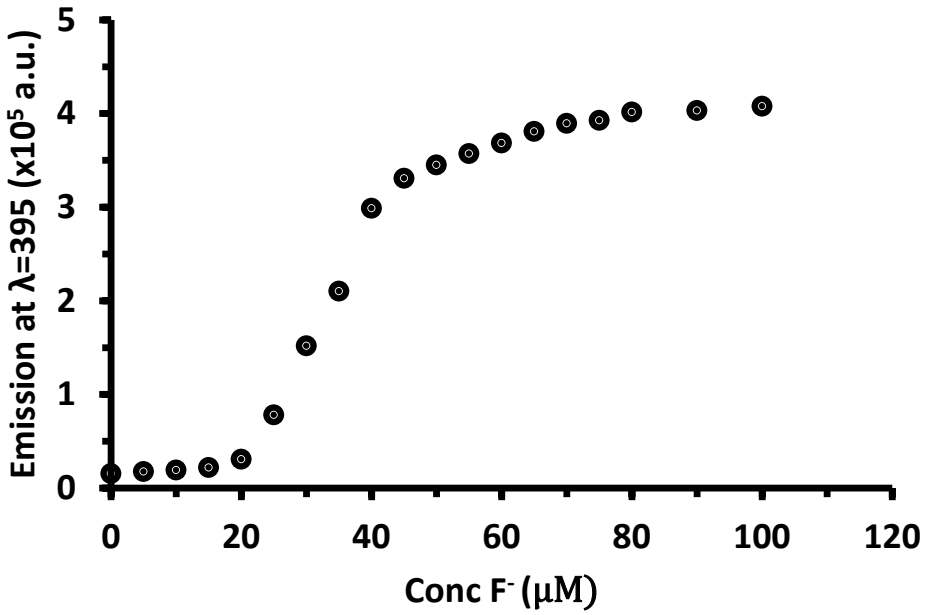

Figure. S7 Titration of 5.6 μM PySQ in DMSO upon addition of TBAF at excitation wavelength 351 nm.

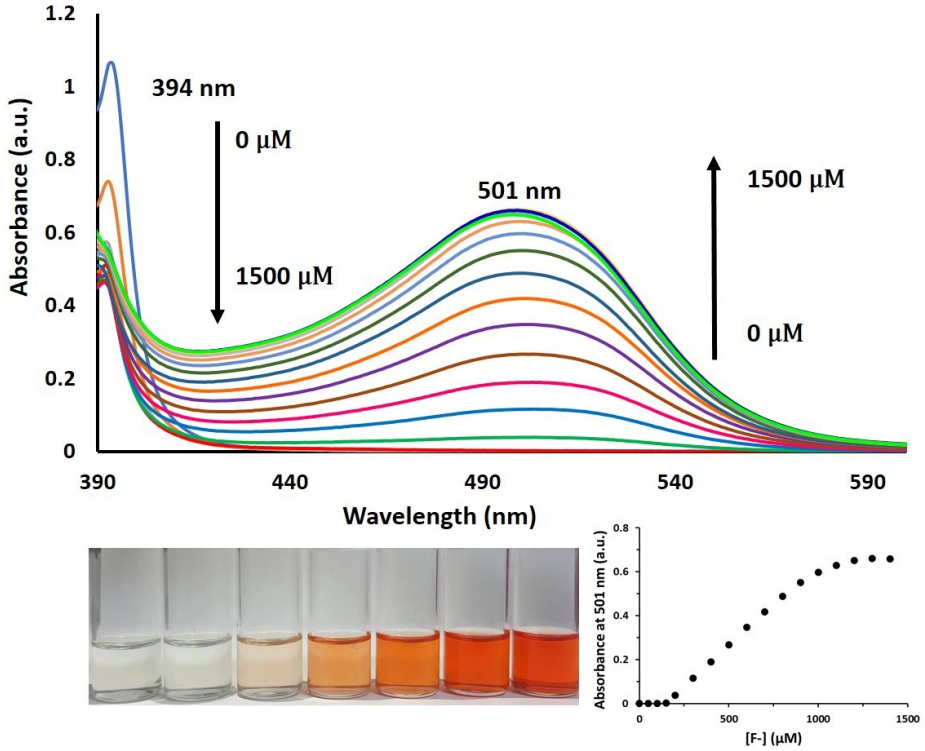

Figure. S8 (top) The UV-Visible absorption spectrum at λ=501 nm of PySQ at 56 μM of PySQ in THF upon addition of 0.01 M TBAF in THF. (bottom left) PySQ 56 μM and various concentration of TBAF. (bottom right) absorbance at λ = 501 of PySQ 56 μM at various concentration of TBAF.

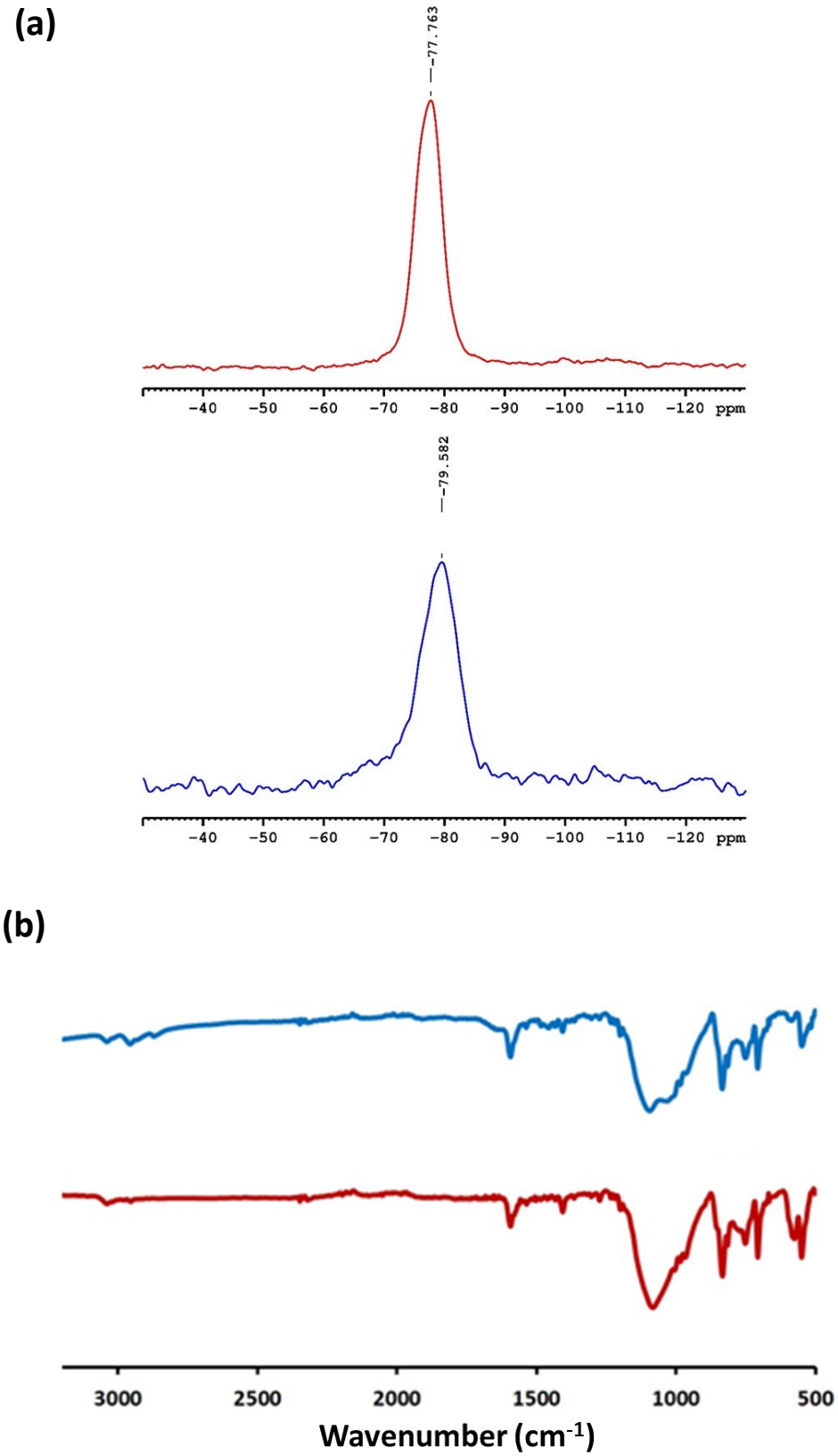

Figure. S9 (a) ^{29}Si CP/MAS NMR spectra of PySQ (top) and PySQ-F^- (bottom), (b) IR spectra of PySQ (bottom) and PySQ-F^- (top).

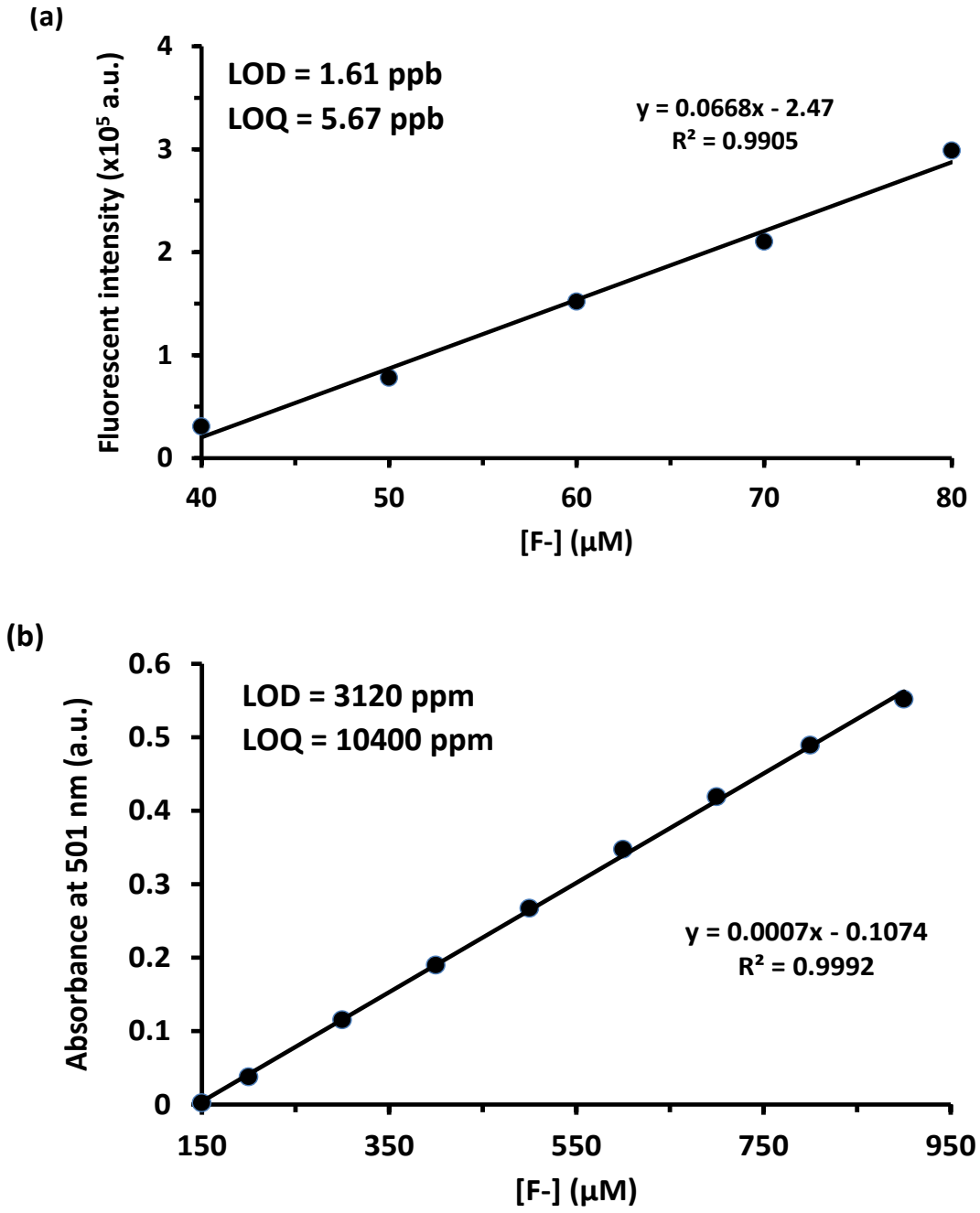

Figure. S10 The calibration curve (a) from fluorescence data of PySQ at 5.6 µM in DMSO at excitation wavelength 351 nm and emission wavelength 395 nm, (b) The calibration curve of PySQ from UV-Vis data of PySQ at 56 µM in THF.

Table S2 Comparison in term of limit of detection (LOD) among reported sensors.

Sensor	LOD (ppb)	References
PySQ	1.61	
2,1,3-benzothiadiazole	16.3	*Dyes and Pigments*, 2016, **124**, 268-276
Resorufin based compound	1.15	*RSC Adv.*, 2014, **4**, 33890-33896
Coumarin based compound	4.1	*Tetrahedron*, 2017, **73**, 1306-1310
Phthalide based compound	19.6	*Chem. Commun.*, 2014, **50**, 5510-5513
Analytical method:		*Anal. Methods*, 2016, **8**, 5338-5352
ICP-MS	0.1	
AAS	160	
Ion-selective electrodes(ISEs)	0.3	

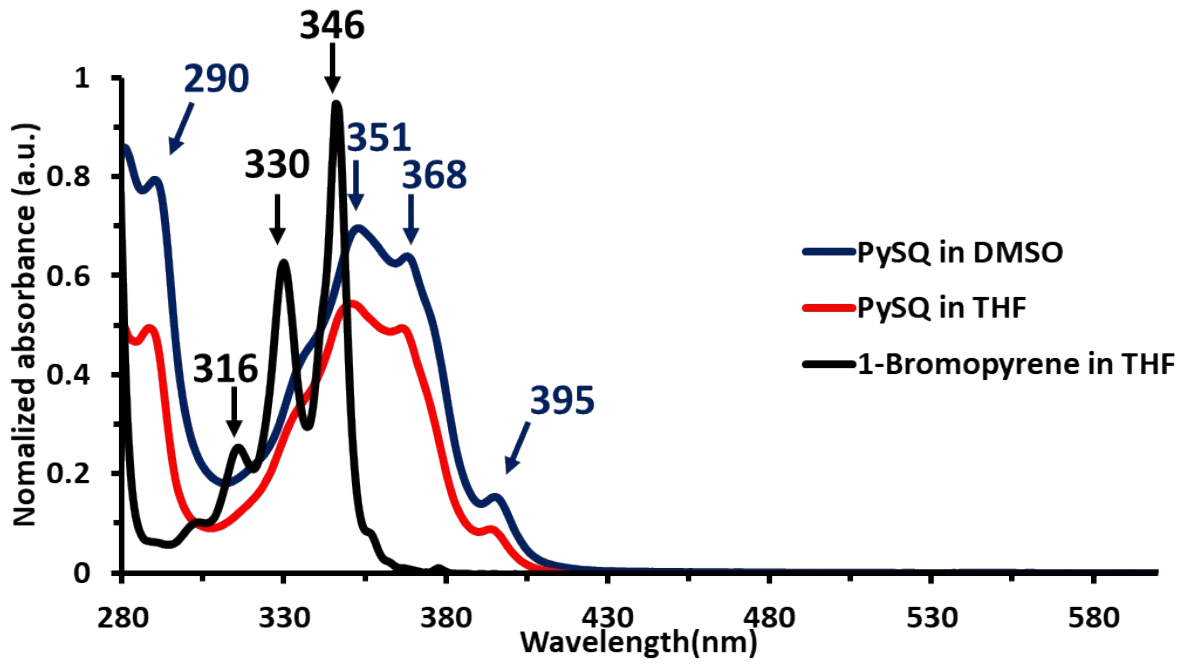

Figure. S11 Absorption spectra of PySQ in DMSO and THF and 1-Bromopyrene, the absorption bands of PySQ in DMSO mostly but intensity

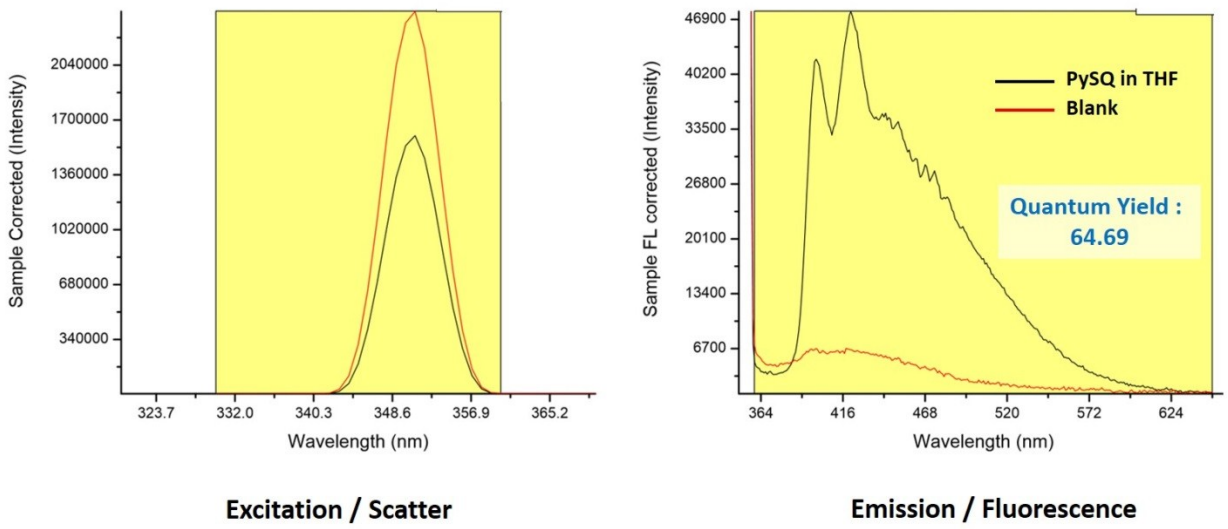

Figure. S12 Quantum yield of PySQ in THF.

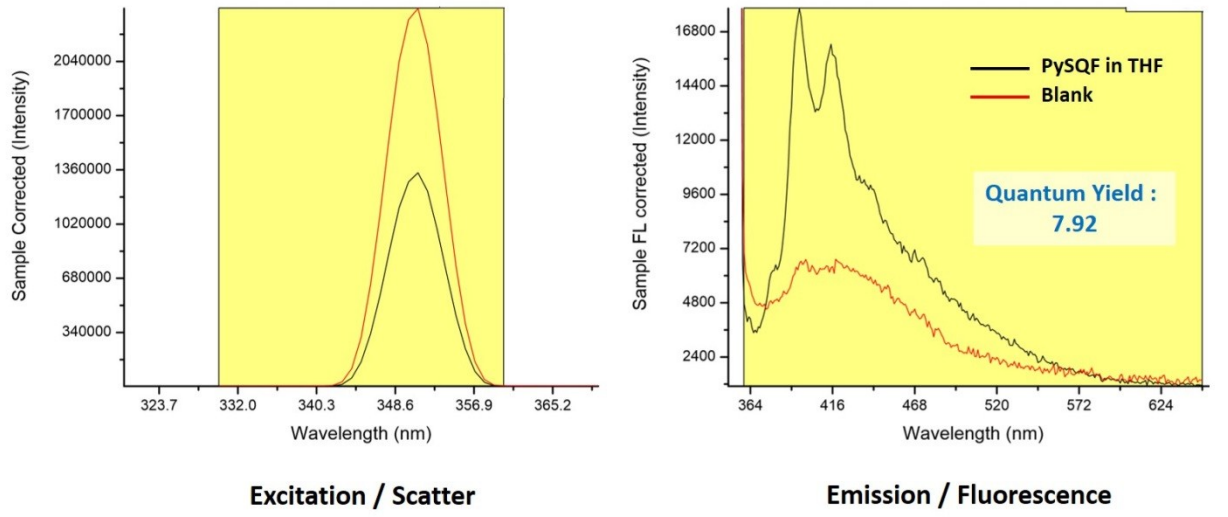

Figure. S13 Quantum yield of PySQ-F^- in THF.

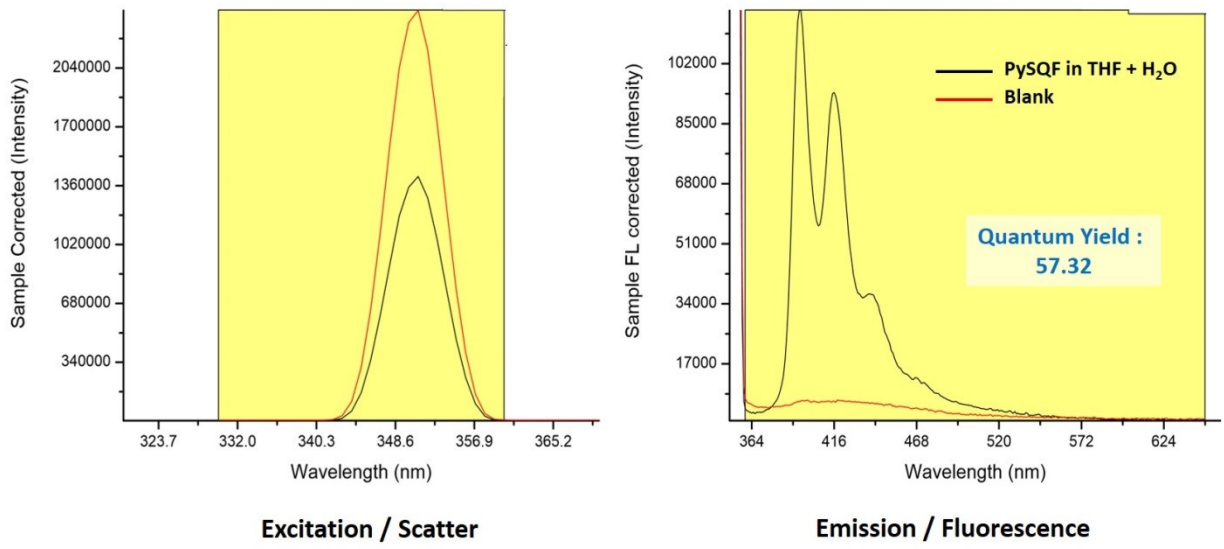

Figure. S14 Quantum yield of PySQ-F^- in THF + H_2O.

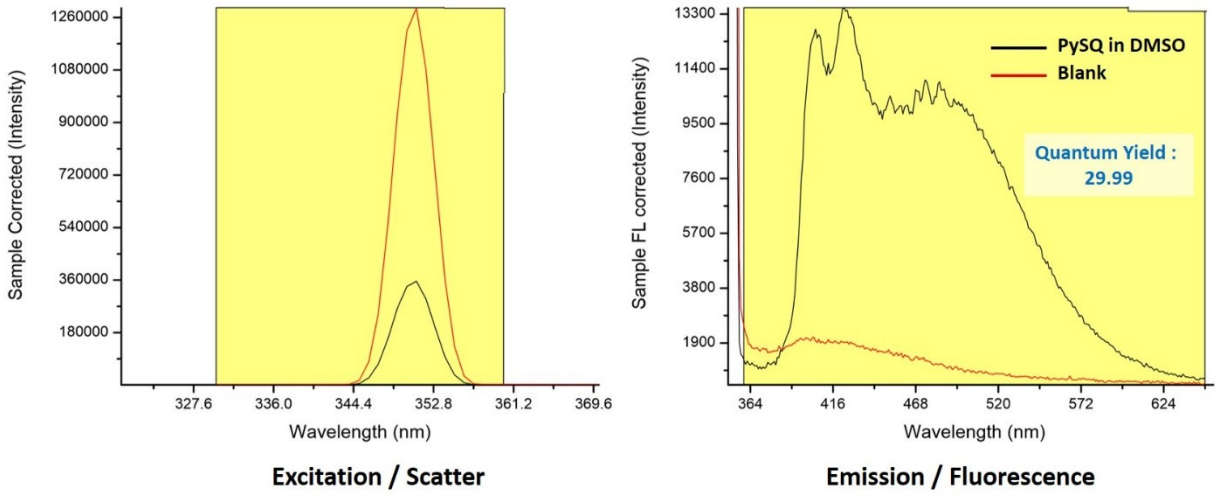

Figure. S15 Quantum yield of PySQ in DMSO.

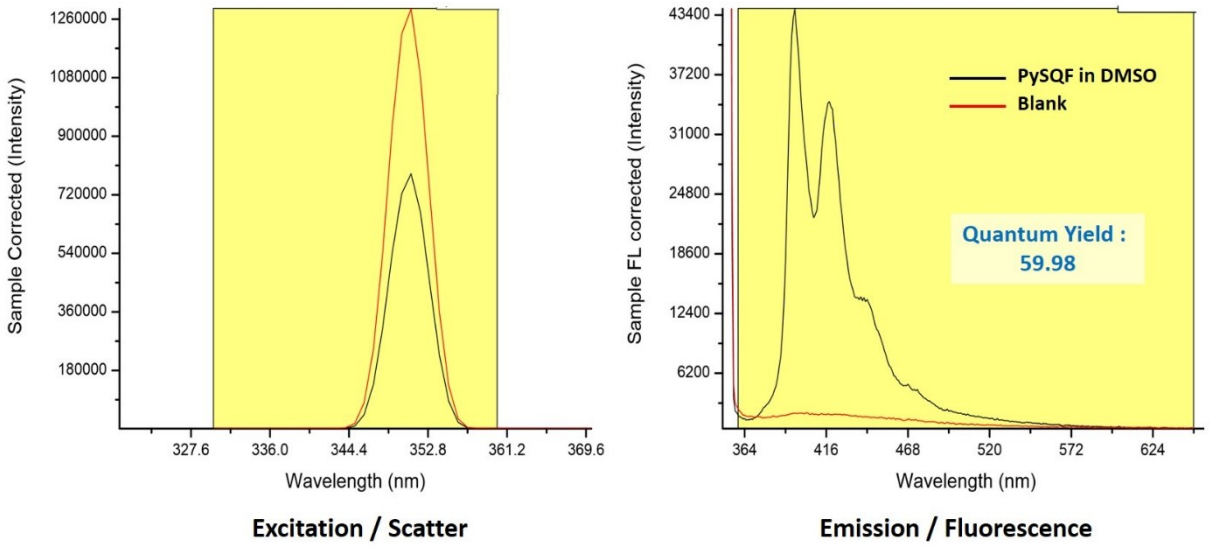

Figure. S16 Quantum yield of PySQ-F^- in DMSO.

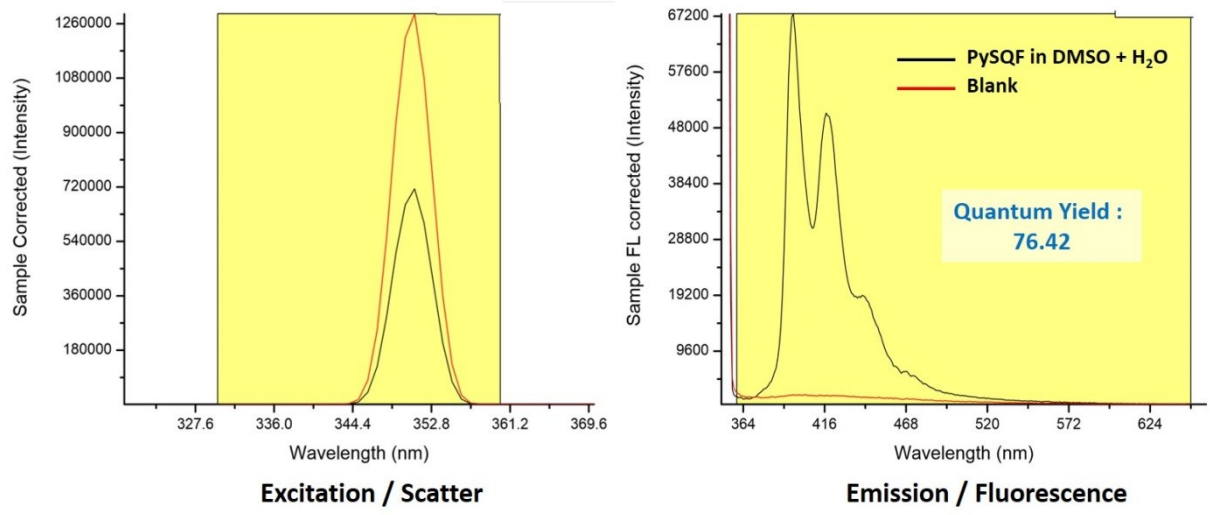

Figure. S17 Quantum yield of PySQ-F^- in DMSO + H_2O.

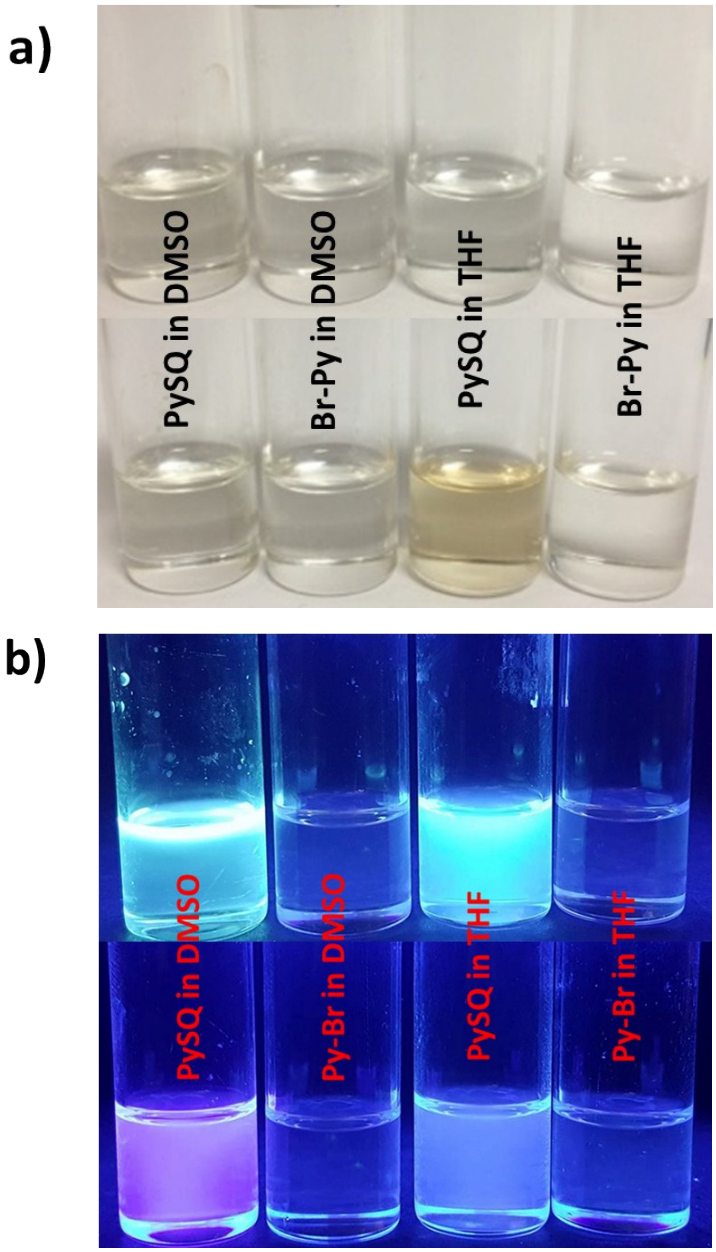

Figure. S18. Comparison of PySQ and 1-bromopyrene solutions at the same concentration (56μM), a) (top) before and (bottom) after addition of TBAF (1 eq) under room light; b) (top) before and (bottom) after addition of TBAF (1 eq) under UV lamp.

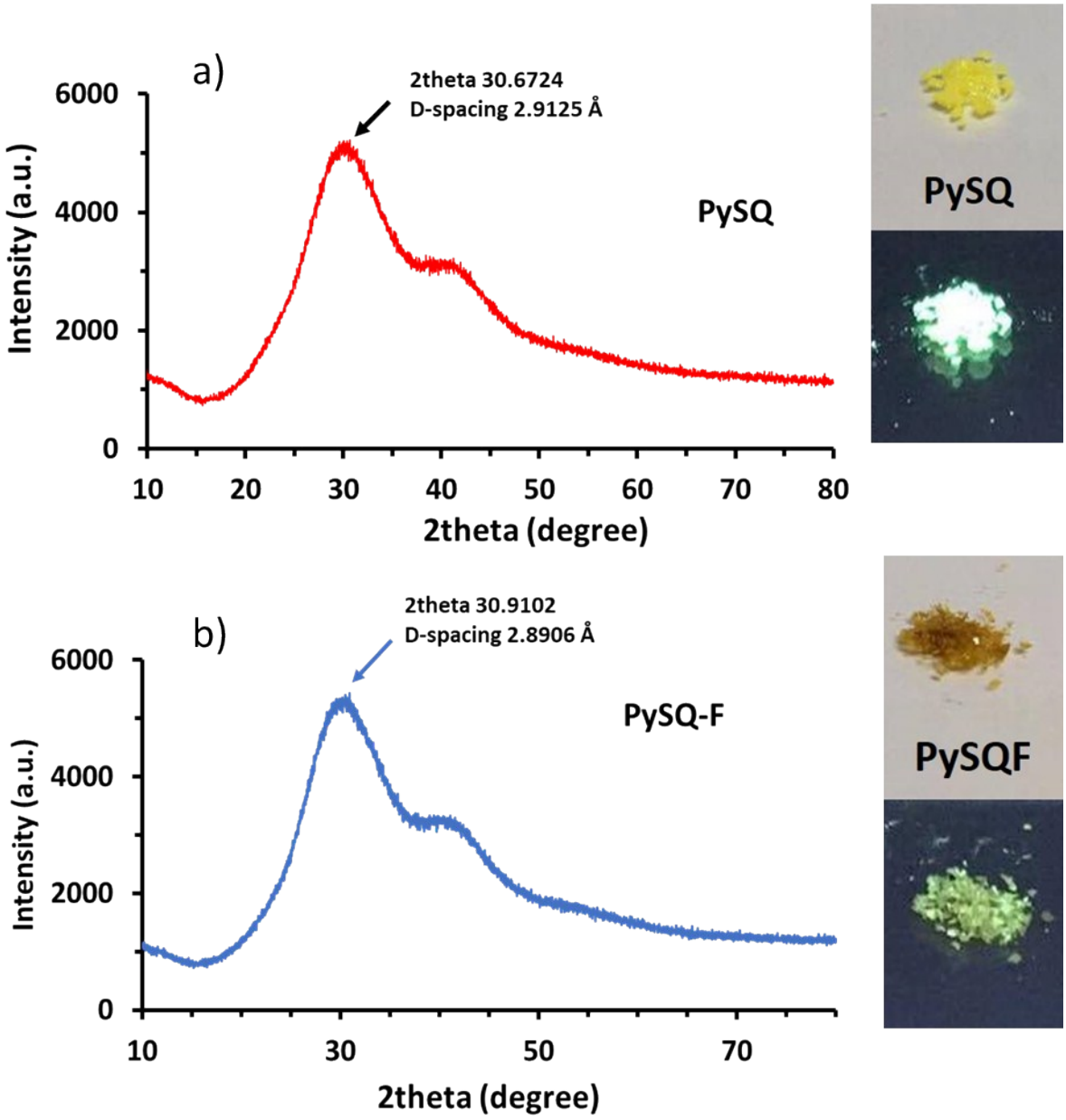

Figure. S19. X-ray Powder Diffraction (XRD) of PySQ and PySQ-F

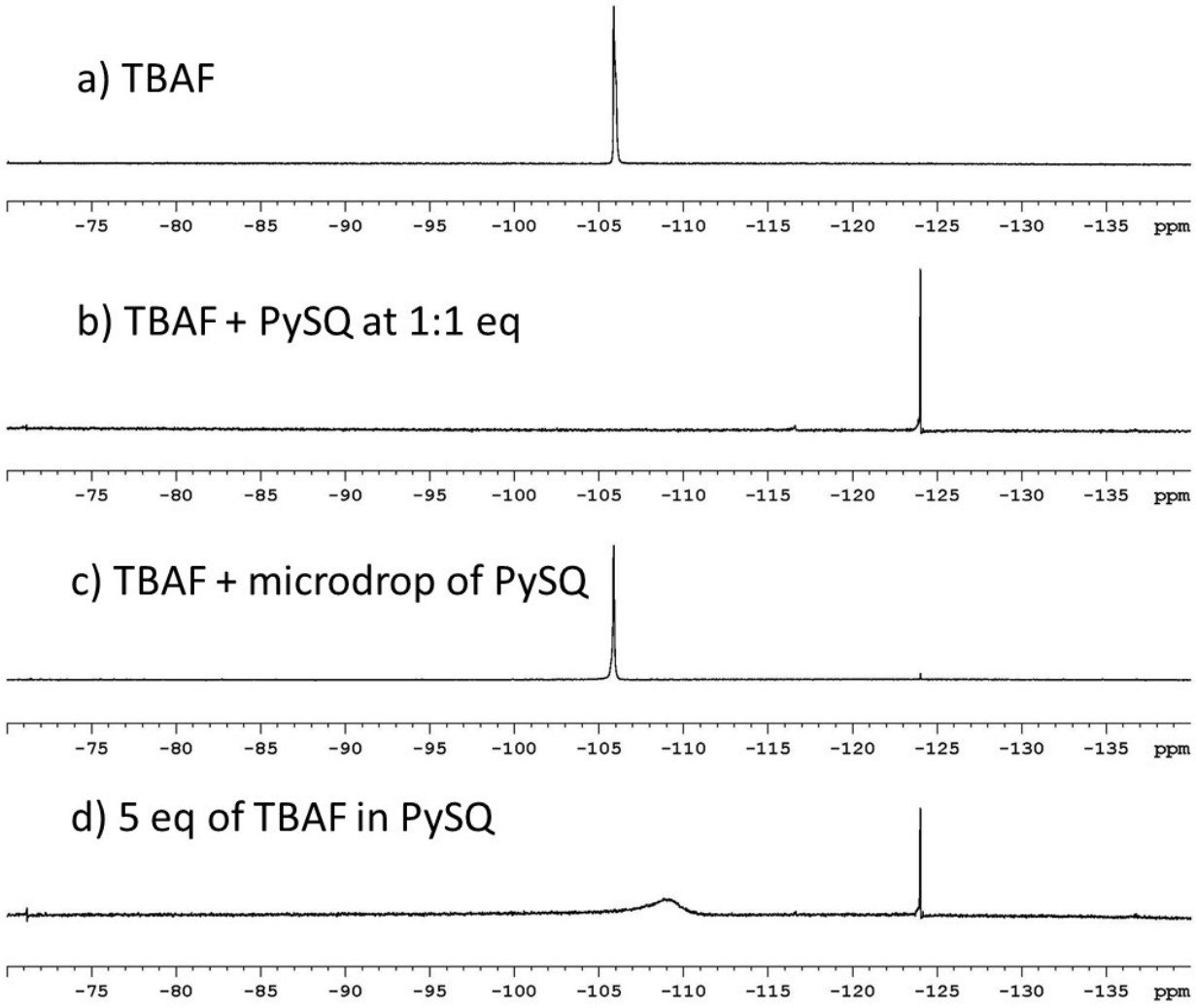

Figure. S20 ^{19}F NMR (376.3 MHz) of TBAF and PySQ in DMSO-d_6 with $CFCl_3$ as calibrator at δ 0 ppm