

Acid Sensors Based on Luminochromism of Solid-State Excimer Emission of Pyrene-Modified Polyhedral Oligomeric Silsesquioxane

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Abstract: To obtain solid-state fluorescence sensors, it is essential to simultaneously obtain solid-state emission and stimuli-responsiveness. In this research, the modified polyhedral oligomeric silsesquioxane (POSS) tethered with pyrenes was synthesized and we confirmed that both demands for developing solid-state fluorescence sensors can be satisfied. The POSS derivative exhibited strong emission even in the solid state. In particular, we found that exposure of the POSS films to trifluoroacetic acid vapor resulted in a significant red-shift of the peak wavelength of the emission band. Excitation spectroscopy and comparison with model compounds suggest that this significant red-shift should be attributable to the formation of static excimer, meaning a preformed dimer in the ground state induced by protonation of the secondary amino groups. These results indicate that POSS is a promising scaffold for a solid-state fluorescence sensor.

Introduction

Solid-state fluorescence sensors have attracted much attention because of their high detection sensitivity, response speed, and ease of measurement.^[1–5] However, common organic chromophores suffer from concentration quenching due to non-specific interactions among luminophores in the solid state.^[6] In addition, to detect molecules, recognition sites for capturing detection targets around luminophores are needed for applications as a fluorescence chemosensor. To satisfy these requirements, Swager *et al.* succeeded in developing a solid-state fluorescent sensor by incorporating a rigid three-dimensional structure into a conjugated polymer to both suppress concentration quenching and provide cavities by isolating luminophores even in the condensed state.^[7]

To meet above demands, such as solid-state luminescence and stimuli-responsiveness, for developing solid-state fluorescence sensors, we have focused on polyhedral oligomeric silsesquioxane (POSS) as a scaffold. POSS is a rigid cubic molecule composed of Si–O bonds possessing organic side-chains on each vertex.^[8–21] Recently, luminophores-integrated POSSs have been applied to organic light-emitting diodes,^[22,23] acceleration of chemiluminescence^[24] and hydrolysis reactions,^[25] and fluorescence sensors^[26–35] because of their high thermal stability and unique three-dimensional structure. Since POSS arranges luminophores in a radial direction, POSS can improve luminescent properties by suppressing their interactions even in the condensed state,^[36–40] and its rigid structure provides sparse space around the core that is

useful for capturing detection targets followed by detecting them.^[41–48] Therefore, POSS is able to be regarded as a versatile platform for constructing solid-state fluorescence sensors based on a preprogrammed design. We also found that the modified POSS derivatives with aromatic rings, such as pyrene, anthracene and naphthalene, through flexible side chains can show excimer emission.^[25,49,50] In particular, their optical properties can be switched by altering tiny environmental factors and adding target molecules. Based on this mechanism, the series of fluorescence sensors were constructed.

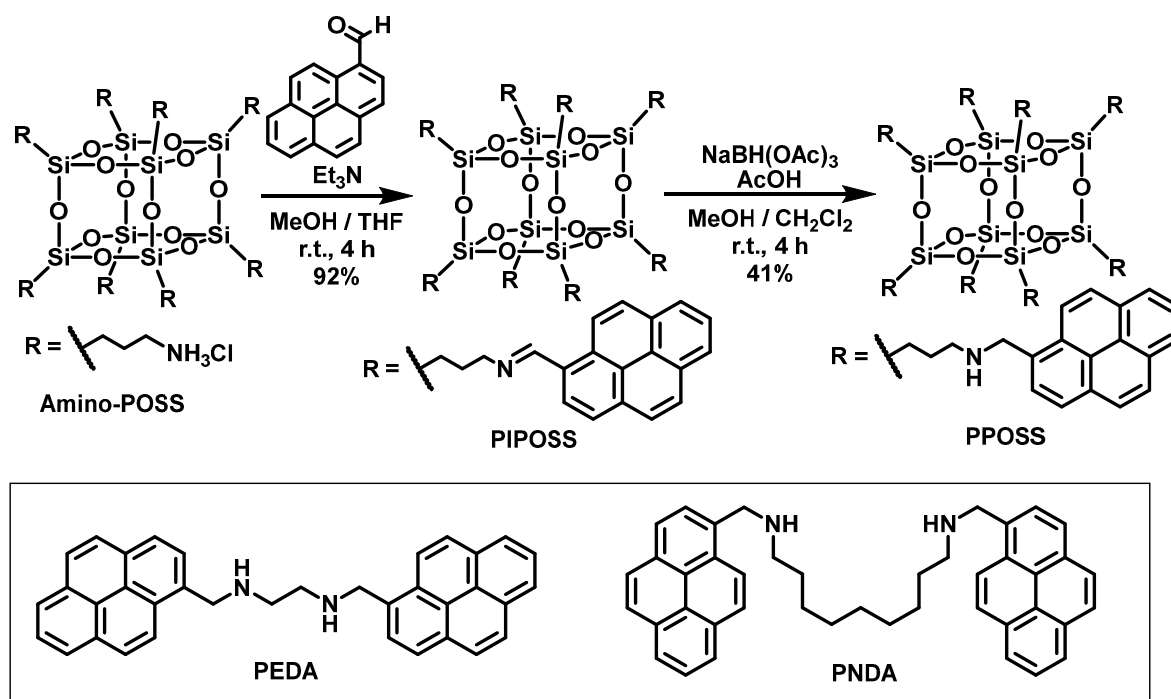
Pyrene is known to exhibit excimer emission even in solution and used in various sensing systems.^[51–59] In addition, there are two types of excimer formation; dynamic excimer and static excimer, where the interaction of luminophores occurs only in the excited state and in both the ground and excited states, respectively.^[53–55] We also presumed to apply excimer emission for sensing because the wavelength of excimer emission can be sensitively altered depending on the overlap of the π -planes and the distance between the luminophores.^[53] Based on this assumption, we synthesized pyrene-integrated POSS having flexible side-chains and introduced amino groups into the side-chains which were electronically independent of the pyrenes and expected to work as acid-responsive units. Considering that almost all acid-responsive systems that induce color changes in the solid state are based on protonation of electronically relevant chromophores,^[60–70] the development of our system is a challenging task. According to the optical measurements, we found that the modified POSS can show solid-state luminescent

properties attributable excimer emission. Interestingly, we discovered that its thin film exhibited significant red-shift over 100 nm by exposure to acid vapor. Protonation of the amine by the acid causes a significant change in the electrostatic interaction and subsequently induces a change in the morphology of the solid state. As a result, strong excimer emission and color changes were observed in the solid state.

Results and Discussion

It was reported that an octasubstituted POSS can be easily obtained by using reductive amination.^[71,72] The octasubstituted POSS with pyrene **PPOSS** was synthesized through two steps of reductive amination from **Amino-POSS** as shown in Scheme 1. In the reduction of the imine, acetic acid was added to allow the reaction to proceed completely. Characterization was performed using NMR spectroscopy and high-resolution mass spectrometric techniques, and it was confirmed that eight pyrenes was able to be introduced. **PEDA** and **PNDA** were also synthesized as model compounds by the similar reaction procedure, in which two pyrene molecules were linked by alkyl chains for comparison (Scheme S1). **PNDA** has the same number of atoms between the two molecules of pyrenes as **PPOSS**.

Scheme 1. Synthesis of **PPOSS** and chemical structures of **PEDA** and **PNDA**



Initially, UV–vis absorption and photoluminescence (PL) spectra were measured in the diluted solutions (Figure 1, Table 1). In the UV–vis absorption spectra, pyrene-derived absorption bands were observed from each compound and there were no significant differences between **PPOSS** and the model compounds. In the PL spectra of **PPOSS**, the band with a vibrational structure derived from monomer emission at around 375 nm and the broad band at around 492 nm were observed. From the fluorescence lifetime measurement, it was shown that this broad emission band had a relatively long fluorescence lifetime of 18.6 ns (Figure S1). This fact is one of the typical characters of excimer emission, indicating that the emission bands in shorter and longer wavelength regions are attributable to locally-excited (LE) emission at pyrene and excimer emission of pyrene, respectively.^[53] Since the measurements were

performed under diluted conditions, the excimer should be obtained through intramolecular interaction between the side-chains of POSS. In the cases of **PEDA** and **PNDA**, the emission bands from excimer were also observed in the longer wavelength regions in addition to the LE emission. The intensity ratio of excimer emission to LE emission (I_e/I_m) of **PPOSS** was 16, whereas that of **PEDA** and **PNDA** were less than 1. These results indicate that the compact POSS structure should be favorable for encouraging intramolecular interactions. The emission band of the excimer emission of **PEDA** was observed in relatively shorter wavelength region than those of **PPOSS** and **PNDA**. It has been reported that emission intensity from the pyrene excimer is maximized when two pyrene units linked by the propylene chain and minimized by the heptylene and octylene chains.^[73] In our case, it is also assumed that the pyrene-to-pyrene overlap might be suppressed due to the restriction of the conformation by the medium length linker.

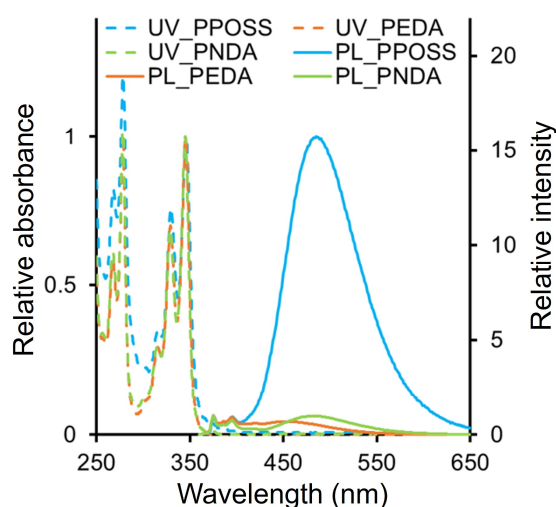


Figure 1. UV–vis absorption and PL spectra normalized at monomer emission of **PPOSS** (1.0×10^{-6} M), **PEDA** (4.0×10^{-6} M), and **PNDA** (4.0×10^{-6} M) in the CHCl_3 solutions excited at 346 nm.

Table 1. Optical properties of pyrene derivatives in diluted solutions ^a

	λ_{abs} (nm)	ε ($\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} (nm)	$I_{\text{e}}/I_{\text{m}}$	Φ_{PL}	τ (ns)	λ_{detect} (nm)	χ^2
PPOSS	346	22.2	375, 485	16	0.29	18.6	485	1.09
PEDA	346	7.5	375, 451	0.70	0.08	15.0	451	1.00
PNDA	345	7.8	375, 481	0.99	0.22	19.0	481	1.06

^a Measure in CHCl_3 (**PPOSS** ($1.0 \times 10^{-6} \text{ M}$), **PEDA** ($4.0 \times 10^{-6} \text{ M}$), and **PNDA** ($4.0 \times 10^{-6} \text{ M}$)) excited at 346 nm.

Optical measurements in the solid state were performed (Figure 2). In the PL spectrum of **PPOSS**, only the broad emission peak derived from excimer was observed at around 490 nm. It is indicated that the pyrene moieties should be close to each other in the condensed state, and the formation of excimer was enhanced. In the case of **PEDA**, the LE emission band was observed at around 405 nm, while both LE and excimer emission bands were observed in **PNDA**. This result suggests that the molecular motion of pyrene units should be restricted in the solid state, and intra/intermolecular interactions of **PEDA** should be strongly suppressed by the medium length linker between pyrene units. The absolute luminescence quantum yield of **PPOSS** was 0.37, which was the highest in the three compounds (Table 2). It is suggested that the high quantum yield in the solid state should originate from the suppression of concentration quenching because of the presence of the steric POSS core. These data indicate that the solid-state luminescent properties were able to be preserved even in the case of POSS.

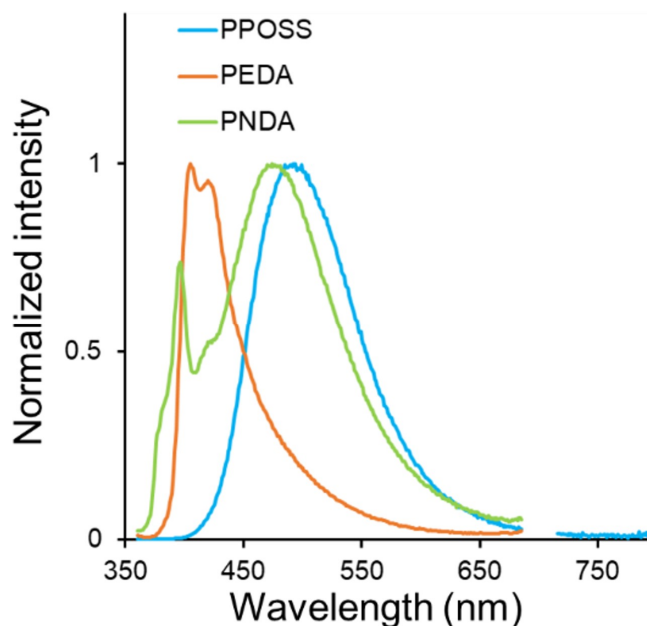


Figure 2. PL spectra of **PPOSS**, **PEDA**, and **PNDA** in the solid states excited at 346 nm. The spectral region derived from the optical overtone of the excitation wavelength was excluded.

Table 2. Emission wavelengths and absolute quantum yields of **PPOSS**, **PEDA**, and **PNDA** in solid

	λ_{em} (nm)	Φ_{PL}
PPOSS	492	0.37
PEDA	405	0.07
PNDA	396, 474	0.12

^a Measured in solid with the excitation light at 346 nm.

To evaluate acid-responsive properties of **PPOSS**, optical measurements were performed in the film states before and after exposure to trifluoroacetic acid (TFA) (Figures 3a and 3b). The thin films were successfully formed by spin-coating methods. From measurements, a significant red-shift of an emission peak over 100 nm was detected. To obtain further information on the mechanism of the red-shift, excitation spectra were measured (Figure 3c). Accordingly, the new absorption band was observed at around 460 nm, which was not observed

before exposure to TFA vapor. This result means that the red-shift could be caused by the change in the interaction between the pyrene units in the ground state. Therefore, it was proposed that this large red-shift should be derived from the formation of static excimer, which means a preformed dimer in the ground state.^[53,74–77] The PL lifetimes of the thin film (7.3 and 25.2 ns) were shortened after exposure to TFA vapor (2.3 and 7.7 ns) (Figure S1), which also supports the formation of the static excimer.^[78] It is likely that intermolecular interactions among pyrene should occur in the condensed state. Although we attempted to neutralize the acidified films with triethylamine (TEA) vapor, the emission wavelength was not completely returned to the same as the pristine film (Figure S2). We assumed that the generation of salts might disturb neutralization in the film. To realize reversible responses, neutralization was performed with TEA in the solution after exposing **PPOSS** powder to TFA vapor. As a result, the spectra of the pristine sample and the neutralized sample were identical (Figure 3d). These results represent that **PPOSS** can be used as a sensor for acidic vapor reversibly.

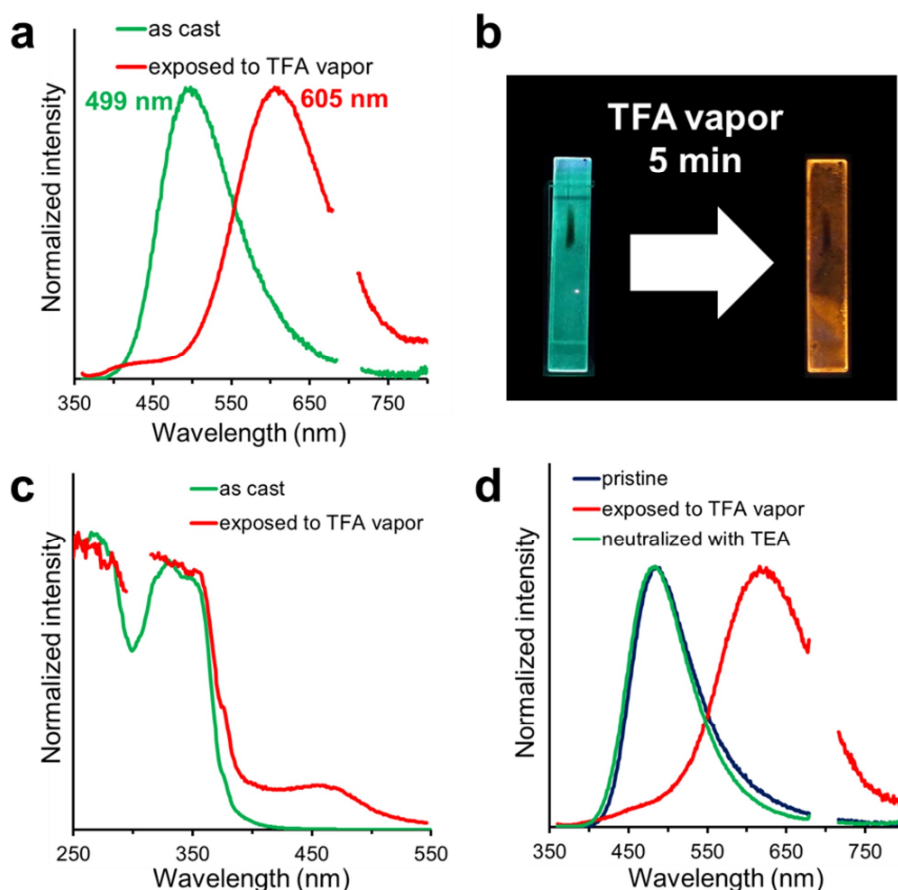


Figure 3. (a) PL spectra excited at 346 nm, (b) photographs excited at 365 nm, and (c) excitation spectra of **PPOSS** in the film state before and after exposure to TFA vapor for 5 min. (d) PL spectra of **PPOSS** in the powder after exposure to TFA vapor and neutralization with TEA excited at 346 nm. The spectral regions derived from the optical overtone of the excitation and monitoring wavelengths were excluded.

To evaluate the effect of protonation on the electronic state, TFA salts of **PPOSS**, **PEDA**, and **PNDA** were synthesized. The optical measurements were performed in both solution and solid states (Figures 4a and 4b). In the solution states, there was no significant difference in the absorption spectra between the neutral **PPOSS** and its TFA salt. In the PL spectra of TFA salts of three compounds, orange emission at around 600 nm did not appear in the solution states. These results showed the red-shifted emission in the solid state was not realized by the change

in the electronic state of pyrene moieties, and the solid state should be essential to induce the orange emission. In the PL spectra in the solid states, **PPOSS** exhibited red-shifted emission at around 600 nm. Considering that the TFA salts of **PEDA** and **PNDA** did not exhibit such red-shifted emission, the POSS framework should play a critical role the orange emission.

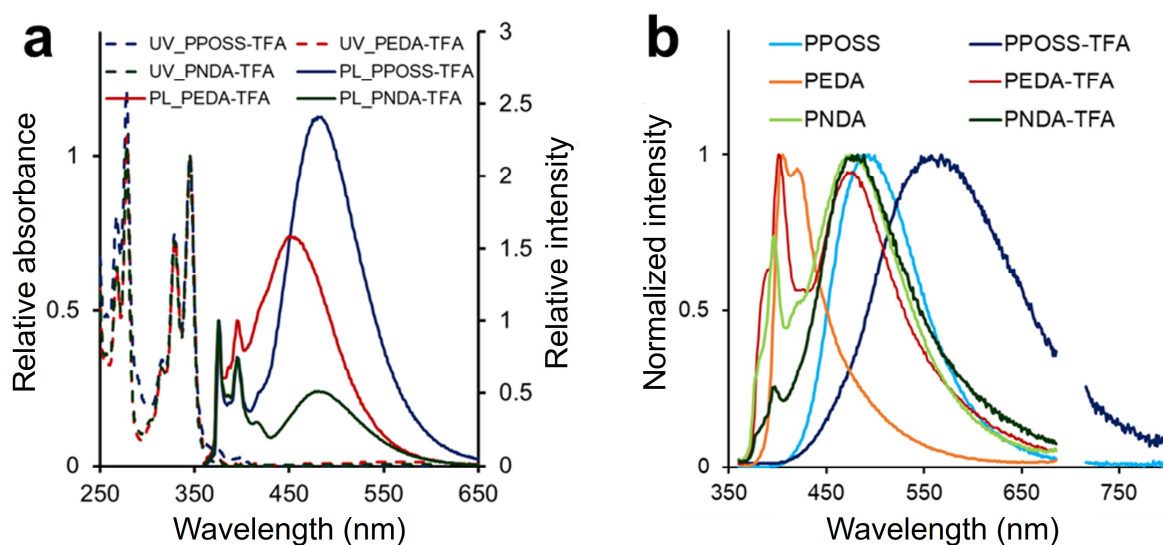


Figure 4. (a) UV–vis absorption and normalized PL spectra at the monomer emission of **PPOSS-TFA** (1.0×10^{-6} M), **PEDA-TFA** (4.0×10^{-6} M), and **PNDA-TFA** (4.0×10^{-6} M) in the CHCl₃ solutions excited at 346 nm. (b) PL spectra of **PPOSS**, **PEDA**, **PNDA**, and their TFA salts in the solid states excited at 346 nm. The spectral regions derived from the optical overtone of the excitation wavelengths were excluded.

We evaluated the effects of counter anions in ammonium salts with various acid salts of **PPOSS**. In the PL spectra, emission peaks were observed in the longer wavelength region in the case of strong acid salts such as TFA, hydrochloric acid, hydrobromic acid, and para-toluene sulfonic acid (Figure 5). On the other hand, in the case of relatively weak acid salts such as acetic acid and formic acid, emission peaks were almost the same as that of neutral **PPOSS**.

These data indicate that ionic interaction strongly affects the red-shifts of emission bands. It is known that the larger difference in pK_a between the acid species and the secondary amines could provide the strong ionicity of the salts.^[79] Therefore, significant changes in PL spectra should be induced in strong acid salts. These results represent that **PPOSS** should be capable of detecting not only acidic vapor but also discriminating the types of acid species by emission wavelength in the solid states.

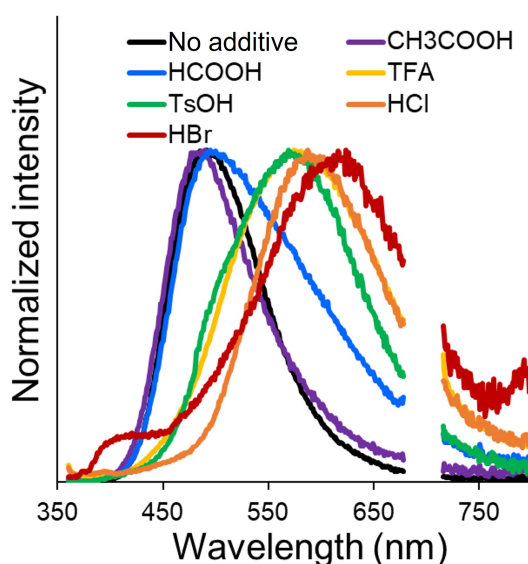


Figure 5. PL spectra of various acid salts of **PPOSS** in the solid states excited at 346 nm. The spectral regions derived from the optical overtone of the excitation wavelengths were excluded.

The plausible mechanism of the acid-responsive properties is discussed (Figure 6). Before the reaction with the acid vapor, the pyrene units interact with each other in the ground state and subsequently form dynamic excimer emission. After the reaction with acid vapor, the assembly state should be drastically changed in the ground state after the generation of ammonium salts. The phase separation-like behavior between the ammonium salt and the

pyrene unit could occur, and the pyrene units strongly interact with each other to form the dimer even in the ground states. As a consequence, the red-shifted emission was able to be induced at around 600 nm. It is because the emission wavelength of the pyrene excimer depends on the stacking situation.^[53] It was reported that similar static excimer emission of pyrenes in the long-wavelength region was observed in the aggregation state of pyrenes-modified dendrimers.^[74] The reason why this phenomenon did not occur in the model compound might be due to the difference in crystallinity. Powder X-ray diffraction (PXRD) measurements exhibited that the **PNDA** powder showed a crystalline peak, whereas **PPOSS** had no diffraction peaks (Figure S3). In other words, the amorphous state of **PPOSS** should contribute to the change in the assembly state of pyrenes. These results propose that the POSS structure is effective for providing solid-state luminescent property and stimuli-responsive properties, which are a useful character for solid-state sensors.

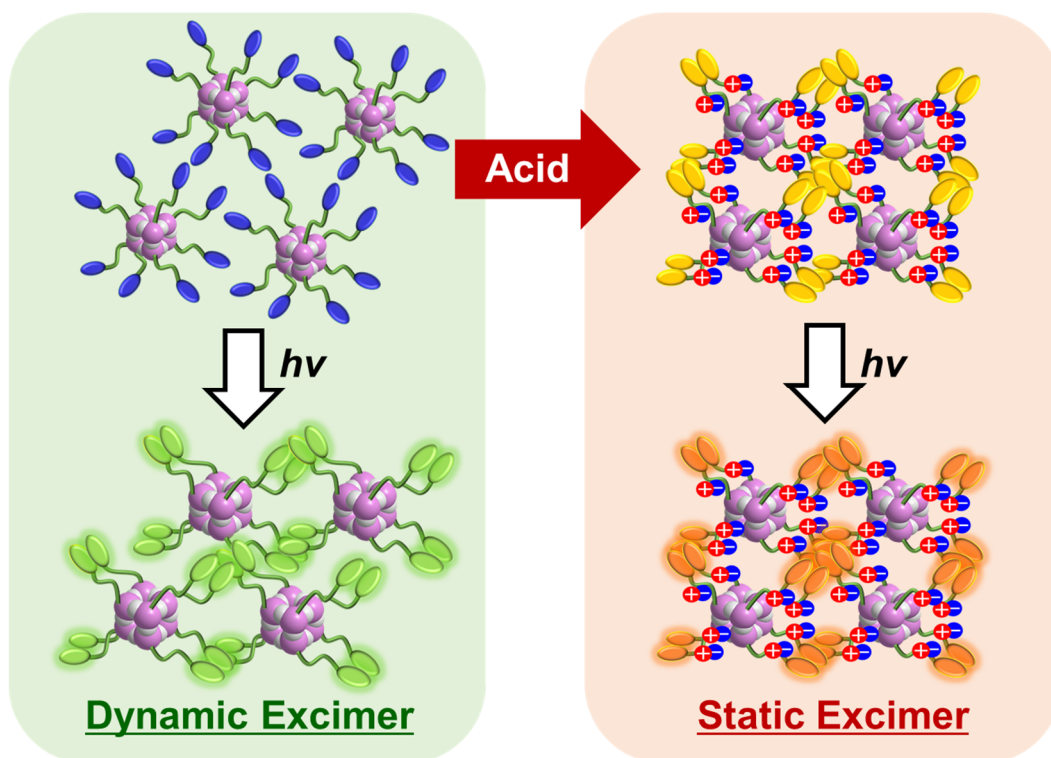


Figure 6. The plausible mechanism of acid-responsive property in **PPOSS**.

Conclusion

We successfully synthesized the modified POSS consisting of eight pyrenes linked by flexible side chains using reductive amination. Highly efficient excimer emission was observed under dilute solution conditions, indicating that intramolecular interactions between the side chains can easily occur. **PPOSS** showed excimer emission with high quantum yield even in the solid state. By exposing the thin film of **PPOSS** to TFA vapor, a significant red-shift of the emission peak was observed. This was attributed to the formation of static excimer. The absence of such stimuli-responsive properties in the model compound powders suggests that the unique three-dimensional structure of POSS should contribute to the acid-responsive property. By introducing the luminophores into the rigid POSS core, both solid-state luminescence and

stimuli-responsive properties were obtained. In this study, we also achieved creating a solid-state acid sensor based on luminochromism with the luminophores that are electronically independent of the protonation sites. Based on our results, it might be possible to develop acid-responsive systems exhibiting dramatic color changes by using alterations both in the electronic state of the π -conjugated system and in the mechanism of the excimer formation, such as **PIPOSS**. Our findings represent that POSS is a promising scaffold for constructing solid-state fluorescence sensors although POSS itself does not have significant optical properties.

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Supporting Information

Acid Sensors Based on Luminochromism of Solid-State Excimer Emission of Pyrene-Modified Polyhedral Oligomeric Silsesquioxane

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General

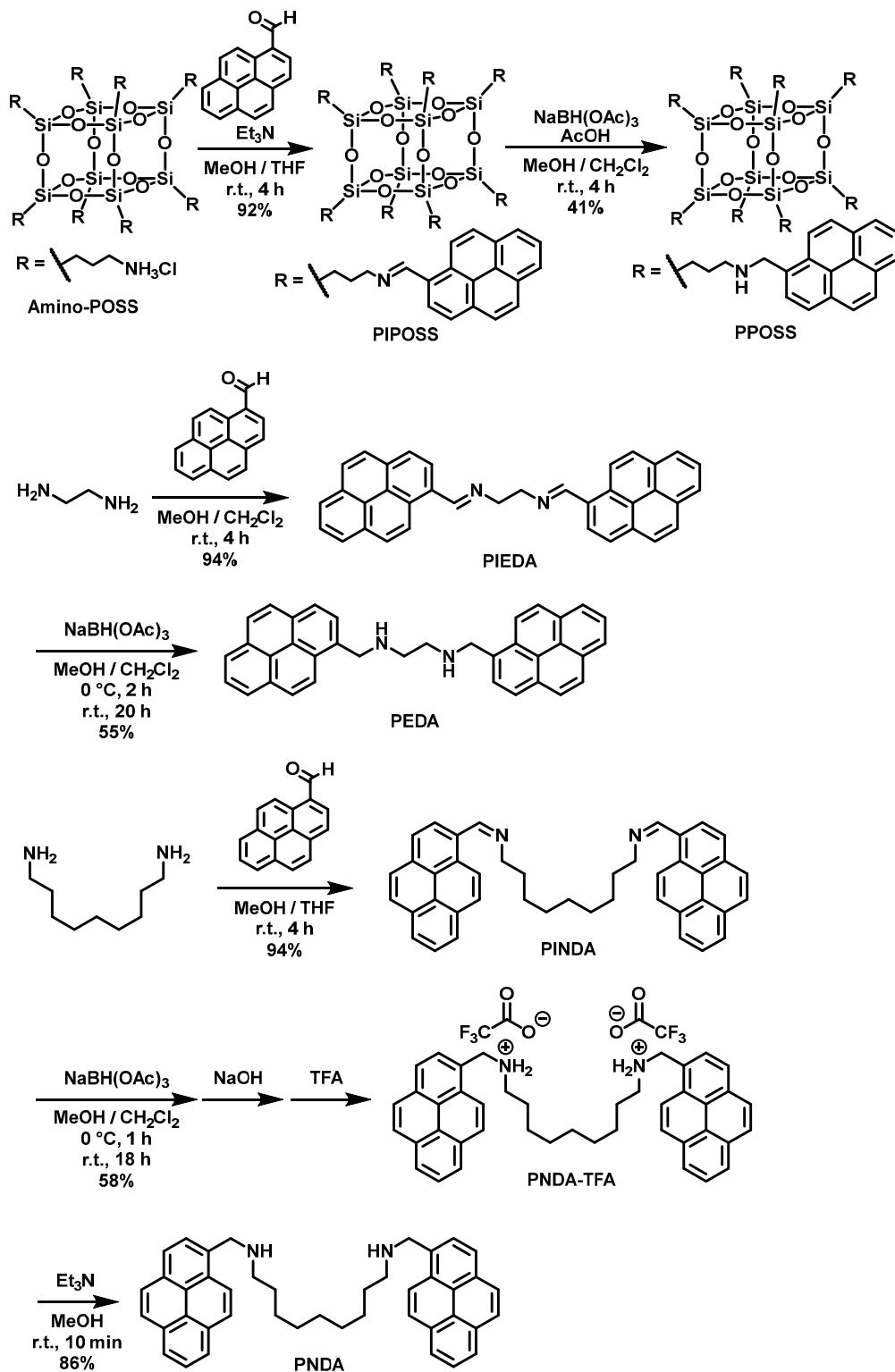
^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{29}Si NMR spectra were recorded on JEOL EX400 and AL400 instruments at 400, 100 and 80 MHz, respectively. Samples were analyzed in CDCl_3 , and the chemical shift values were expressed relative to Me_4Si as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-MS700 spectrometer for electron ionization (EI), a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI) and Thermo Fisher Scientific OrbitrapXL spectrometers for matrix assisted laser desorption/ionization (MALDI) using 1,8-dihydroxy-9,10-dihydroanthracen-9-one (DIT) as a matrix. UV-vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed at room temperature. PL spectra were measured with HORIBA JOBIN YVON FluoroMax-4P at 25 °C using a 1 cm path length quartz cell. Absolute photoluminescence quantum efficiency (Φ_{PL}) was recorded on a Hamamatsu Photonics Quantaaurus-QY Plus C13534-01. The PL lifetime measurement was recorded on a Horiba FluoroCube spectrofluorometer system and on a Horiba DeltaFlex spectrofluorometer system; excitation was carried out by using UV diode lasers (NanoLED 375 nm and DeltaDiode 375 nm), respectively. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Powder X-ray diffraction (PXRD) patterns were taken by using $\text{CuK}\alpha$ radiation with a Rigaku Miniflex.

Materials

Amino-POSS^[1] was synthesized according to the literature. 1-pyrenecarbox aldehyde (PyrCHO), ethylenediamine, $\text{NaBH}(\text{OAc})_3$, 3-aminopropyltriethoxysilane, were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. *N,N*-diisopropylethylamine (DIEA), NaBH_4 , 1,9-diaminononane, TFA, hydrochloric acid, formic acid, acetic acid, hydrobromic acid, *p*-trifluoromethanesulfonic acid, Na_2SO_4 , 1.0 N NaOH aq., MeCN (dehydrated grade), DMSO (dehydrated grade), MeOH, CHCl_3 , CH_2Cl_2 , THF, acetone were purchased from FUJIFILM Wako Pure Chemical Corporation. and used without further purification. Et_3N (Kanto Chemical Co., Inc.), Et_2O (dehydrated grade, FUJIFILM Wako Pure Chemical Corporation) and THF (dehydrated grade, FUJIFILM Wako Pure Chemical Corporation) were purified by passage through solvent purification columns under N_2 pressure. CDCl_3 and $\text{DMSO}-d_6$ was purchased from Nacalai Tesque. Deionized water was purified using an Autopure WEX3 system from Yamato Scientific Co., Ltd. Thin films were prepared using a spin-coating method

(1000 rpm, 30 s) from chloroform solution (100 μ L, 5 mM) on a quartz substrate (0.9 cm $\times$ 5 cm).

Scheme S1. Overview of syntheses of **PPOSS**, **PEDA**, and **PNDA**.



Synthesis of PIPOSS

Amino-POSS (4.7 g, 4.0 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling Ar three times, MeOH (400 mL) and Et₃N (11.8 mL, 8.10 g, 16.0 mmol) were added to the flask, and the reaction mixture was stirred at room temperature for 10 min. To the reaction mixture was added a solution of PyrCHO (9.22 g, 40.0 mmol) in THF (100 mL) and the reaction was carried out at room temperature for 4 h under an argon atmosphere. The solvent was removed by decantation and the residue was washed with MeOH and acetone. The residue was purified by recrystallization with CH₂Cl₂/acetone. The crystal was collected with filtration and dried *in vacuo* to afford **PIPOSS** (9.55 g, 92%) as a pale yellow crystal. ¹H NMR (CDCl₃, 400 MHz) δ 9.03 (s, 8H), 8.57 (d, *J* = 9.2 Hz, 8H), 8.23 (d, *J* = 8.2 Hz, 8H), 7.96 (d, *J* = 7.0 Hz, 8H), 7.87–7.69 (m, 40H), 7.64 (d, *J* = 8.9 Hz, 8H), 3.81 (t, *J* = 6.7 Hz, 16H), 2.11 (m, 16H), 1.00 (t, *J* = 8.1 Hz, 16H) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 159.6, 132.3, 130.9, 130.3, 129.4, 128.5, 128.1, 128.0, 127.1, 125.9, 125.7, 125.4, 125.2, 124.6, 124.4, 124.3, 122.2, 64.9, 24.8, 10.0 ppm; ²⁹Si NMR (CDCl₃, 80 MHz) δ –66.3 ppm. HRMS (APCI) calcd. for C₁₆₀H₁₂₉N₈O₁₂Si₈ [M+H]⁺: 2577.7879, found: 2577.7951.

Synthesis of PPOSS

PIPOSS (2.0 g, 0.776 mmol), NaBH(OAc)₃ (4.6 g, 21.8 mmol), CH₂Cl₂ (80 mL), MeOH (4 mL), and acetic acid (1.24 mL, 21.8 mmol) were placed in a round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 4 h. To the reaction mixture was added Et₃N (12 mL, 86.9 mmol) and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was poured into 240 mL of MeOH and the solvent was removed by decantation, and the residue was washed with MeOH. The residue was dissolved in CHCl₃ and precipitated in MeOH. The residue was washed with MeOH by decantation and dried *in vacuo* to afford **PPOSS** (0.828 g, 41%) as a pale yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ 8.11 (d, *J* = 9.0 Hz, 8H), 8.02 (d, *J* = 7.6 Hz, 8H), 7.96 (d, *J* = 7.6 Hz, 8H), 7.88–7.75 (m, 48H), 4.24 (s, 16H), 2.69 (t, *J* = 7.3 Hz, 16H), 1.68 (m, 16H), 0.68 (t, *J* = 8.1 Hz, 16H) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 133.8, 131.2, 130.7, 130.4, 128.7, 127.3, 127.3, 126.8, 126.5, 125.6, 124.9, 124.8, 124.8, 124.7, 124.5, 122.9, 52.4, 51.5, 23.4, 9.6 ppm; ²⁹Si NMR (CDCl₃, 80 MHz) δ –66.5 ppm. HRMS (APCI) calcd. for C₁₆₀H₁₄₅N₈O₁₂Si₈ [M+H]⁺: 2593.9131, found: 2593.9146.

Synthesis of PPOSS-TFA

PPOSS (40 mg, 0.154 mmol), CHCl_3 (10 mL), and TFA (23.6 μL , 35.1 mg, 0.308 mmol) were placed in a round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 30 min and poured into 30 mL of Et_2O . The precipitate was collected with filtration and washed with Et_2O , and dried *in vacuo* to afford **PPOSS-TFA** (33.6 mg, 62%) as an orange solid. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 9.33 (br, 32H), 8.34 (d, $J = 9.3$ Hz, 8H), 8.29 (m, 8H), 8.20 (d, $J = 7.8$ Hz, 8H), 8.15–7.97 (m, 48H), 4.85 (br, 16H), 3.10 (br, 16H), 1.80 (br, 16H), 0.70 (br, 16H) ppm. The ^1H NMR signals from CH_2Cl_2 and MeOH were detected because CH_2Cl_2 and MeOH were used as the solvent to synthesize **PPOSS**.

Synthesis of PIEDA

Ethylenediamine (334 μL , 301 mg, 5.00 mmol) and MeOH (100 mL) were placed in a round-bottom flask equipped with a magnetic stirring bar after degassing and filling Ar three times. To the reaction mixture was added a solution of PyrCHO (2.30 g, 10.0 mmol) in CH_2Cl_2 (20 mL) and the reaction was carried out at room temperature for 4 h. The precipitate was collected with filtration and washed with MeOH/ CH_2Cl_2 (4:1, v/v) and dried *in vacuo* to afford **PIEDA** (2.27 g, 94%) as a pale yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 9.32 (s, 2H), 8.68 (d, $J = 9.2$ Hz, 2H), 8.52 (d, $J = 8.1$ Hz, 2H), 8.15 (d, $J = 8.2$ Hz, 4H), 8.09–7.99 (m, 6H), 7.93 (t, $J = 7.6$ Hz, 2H), 7.79 (d, $J = 9.3$ Hz, 2H), 4.35 (s, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 162.2, 132.8, 131.1, 130.5, 129.8, 128.8, 128.5, 128.3, 127.4, 126.2, 126.0, 125.7, 125.5, 124.9, 124.8, 124.5, 122.5, 62.5 ppm. HRMS (ESI) calcd. for $\text{C}_{36}\text{H}_{25}\text{N}_2$ $[\text{M}+\text{H}]^+$: 485.2012, found: 485.2014.

Synthesis of PEDA

PIEDA (969 mg, 2.00 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling Ar three times, CH_2Cl_2 (50 mL) and MeOH (10 mL) was added to the flask. NaBH_4 (1.84 g, 8.00 mmol) was slowly added to the reaction mixture at 0 $^\circ\text{C}$ and the reaction was carried out at 0 $^\circ\text{C}$ for 2 h and then stirred at room temperature for 20 h. To the reaction mixture was added 100 mL of 1.0 M NaOH aq. and 50 mL of CH_2Cl_2 . The organic layer was extracted and washed with 1.0 M NaOH aq. The solution was cooled to -20 $^\circ\text{C}$ to precipitate the product. The precipitate was collected with

filtration and purified by recrystallization in toluene. The crystal was collected with filtration and dried *in vacuo* to afford **PEDA** (305 mg, 55%) as a pale yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 8.29 (d, J = 9.3 Hz, 2H), 8.14 (d, J = 7.5 Hz, 2H), 8.09–7.90 (m, 14H), 4.43 (s, 4H), 2.98 (s, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 134.0, 131.3, 130.8, 130.6, 129.0, 127.5, 127.4, 127.0, 126.9, 125.8, 125.0, 125.0, 124.9, 124.9, 124.6, 123.2, 51.8, 49.3 ppm. HRMS (ESI) calcd. for $\text{C}_{36}\text{H}_{29}\text{N}_2$ $[\text{M}+\text{H}]^+$: 489.2325, found: 489.2329.

Synthesis of PEDA-TFA

PEDA (98 mg, 0.20 mmol), toluene (30 mL), and TFA (153 μL , 228 mg, 2.00 mmol) were placed in a round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 10 min. The precipitate was collected with filtration and washed with toluene, and dried *in vacuo* to afford **PNDA-TFA** (171 mg, quant.) as a pale yellow solid. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 9.22 (br, 4H), 8.53 (d, J = 9.2 Hz, 2H), 8.39–8.35 (m, 8H), 8.28–8.20 (m, 6H), 8.14 (t, J = 7.7 Hz, 2H), 5.04 (s, 4H), 3.50 (br, 4H) ppm.

Synthesis of PINDA

1,9-Diaminononane (317 mg, 2.00 mmol) and MeOH (20 mL) were placed in a round-bottom flask equipped with a magnetic stirring bar. To the reaction mixture was added a solution of PyrCHO (967 mg, 4.20 mmol) in THF (5 mL) and the reaction was carried out at room temperature for 4 h. The precipitate was collected with filtration and washed with MeOH/THF (5/1, v/v). The precipitate was dried *in vacuo* to afford **PINDA** (1.11 g, 94%) as a pale yellow solid. ^1H NMR (CDCl_3 , 400 MHz) δ 9.27 (s, 2H), 8.88 (d, J = 9.3 Hz, 2H), 8.51 (d, J = 8.0 Hz, 2H), 8.20–7.98 (m, 14H), 3.83 (t, J = 6.6 Hz, 4H), 1.85 (m, 4H), 1.53–1.43 (m, 10H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 159.4, 132.6, 131.2, 130.6, 129.7, 128.9, 128.5, 128.3, 127.4, 126.2, 126.0, 125.7, 125.5, 124.9, 124.8, 124.7, 122.6, 62.8, 31.2, 29.6, 29.4, 27.5 ppm. HRMS (ESI) calcd. for $\text{C}_{43}\text{H}_{39}\text{N}_2$ $[\text{M}+\text{H}]^+$: 583.3108, found 583.3114.

Synthesis of PNDA-TFA

PINDA (291 mg, 0.50 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing and filling Ar three times, CH_2Cl_2 (20 mL) and MeOH (5 mL) was added to the flask.

NaBH₄ (461 mg, 2.00 mmol) was slowly added to the reaction mixture at 0 °C and the reaction was carried out at 0 °C for 1 h and then stirred at room temperature for 18 h. To the reaction mixture was added 30 mL of 1.0 M NaOH aq. The organic layer was extracted and washed with 1.0 M NaOH aq. The solution was dried over Na₂SO₄ and the solvent was removed with a rotary evaporator. The residue was dissolved in toluene (20 mL) and TFA (153 μ L, 228 mg, 2.00 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 10 min. The precipitate was collected with filtration and washed with toluene, and dried *in vacuo* to afford **PNDA-TFA** (236 mg, 58%) as a white solid. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.95 (br, 4H), 8.53 (d, *J* = 8.9 Hz, 2H), 8.40–8.34 (m, 8H), 8.28–8.21 (m, 6H), 8.14 (t, *J* = 7.4 Hz, 2H), 4.93 (s, 4H), 3.11 (t, *J* = 8.0 Hz, 4H), 1.67 (m, 4H), 1.32–1.26 (m, 10H) ppm.

Synthesis of PNDA

PNDA-TFA (163 mg, 0.20 mmol), MeOH (50 mL), and Et₃N (557 μ L, 405 mg, 4.00 mmol) were placed in a round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 10 min. The precipitate was collected with filtration and washed with MeOH, and dried *in vacuo* to afford **PNDA** (101 mg, 86%) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ 8.36 (d, *J* = 9.2 Hz, 2H), 8.18–8.12 (m, 8H), 8.03 (s, 4H), 8.02–7.97 (m, 4H), 4.49 (s, 4H), 2.78 (t, *J* = 7.1 Hz, 4H), 1.53 (br, 4H), 1.35–1.26 (br, 10H) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 134.3, 131.4, 130.9, 130.6, 129.1, 127.6, 127.5, 127.0, 127.0, 125.9, 125.1, 125.0, 125.0, 125.0, 124.7, 123.2, 52.0, 50.1, 30.2, 29.6, 29.5, 27.4 ppm. HRMS (ESI) calcd. for C₄₃H₄₃N₂ [M+H]⁺: 587.3421, found: 587.3427.

Preparation of Various Acid Salts of PPOSS

PPOSS (52 mg, 0.02 mmol, 1 eq.), CHCl₃ (5 mL), and acid (1.0 mmol, 50 eq.) were placed in a round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 10 min. The precipitate was collected with filtration and washed with CHCl₃, and dried *in vacuo* to afford various acid salts of **PPOSS**.

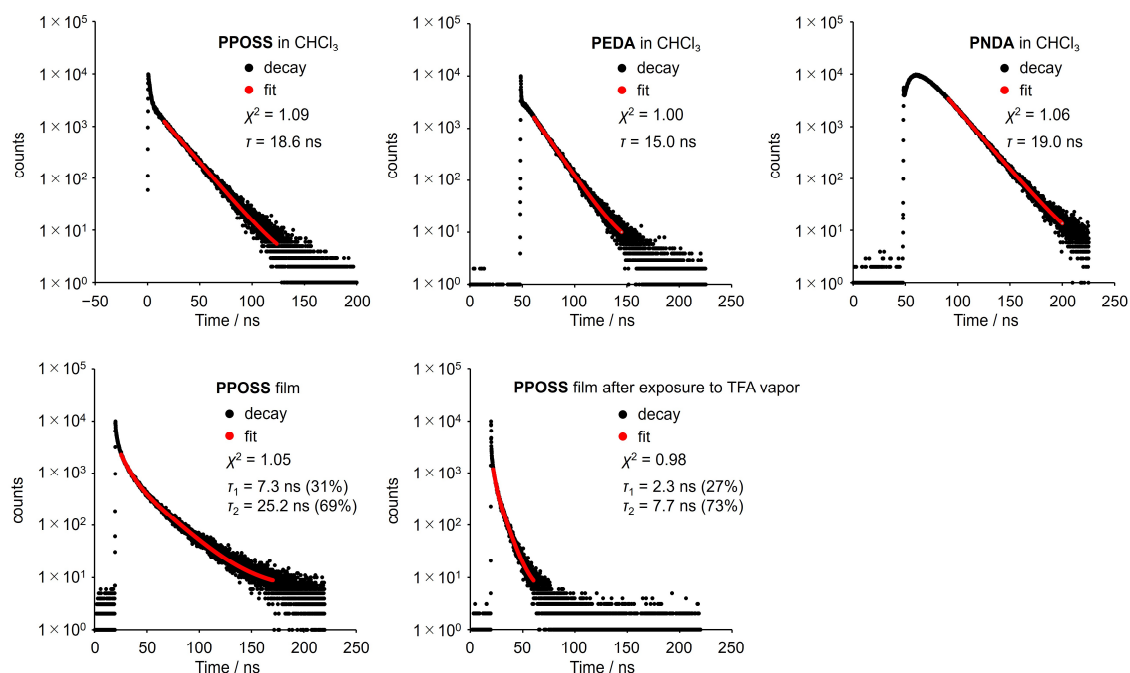


Figure S1. PL decay curves of **PPOSS** (1.0×10^{-6} M), **PEDA** (4.0×10^{-6} M), and **PNDA** (4.0×10^{-6} M) in the CHCl_3 solutions with a Horiba FluoroCube spectrofluorometer, and **PPOSS** in the film state before and after exposure to TFA vapor for 5 min with a Horiba DeltaFlex spectrofluorometer, excited at 375 nm. Their maximum PL wavelengths of excimer emission were monitored. The PL lifetime of excimer emission was evaluated by a tail fit of the decay curve.

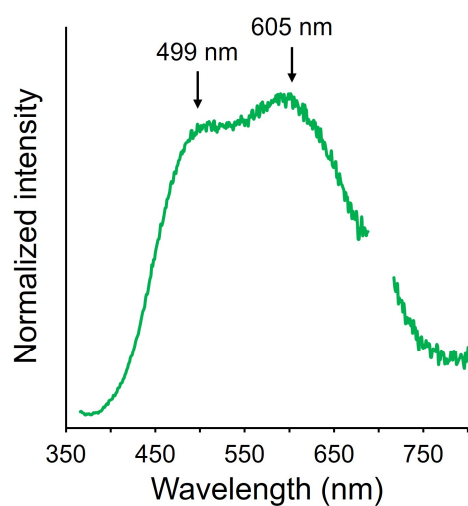


Figure S2. PL spectrum of **PPOSS** in the film after exposure to TFA vapor and neutralization with TEA vapor excited at 346 nm. The spectral region derived from the optical overtone of the excitation wavelength was excluded.

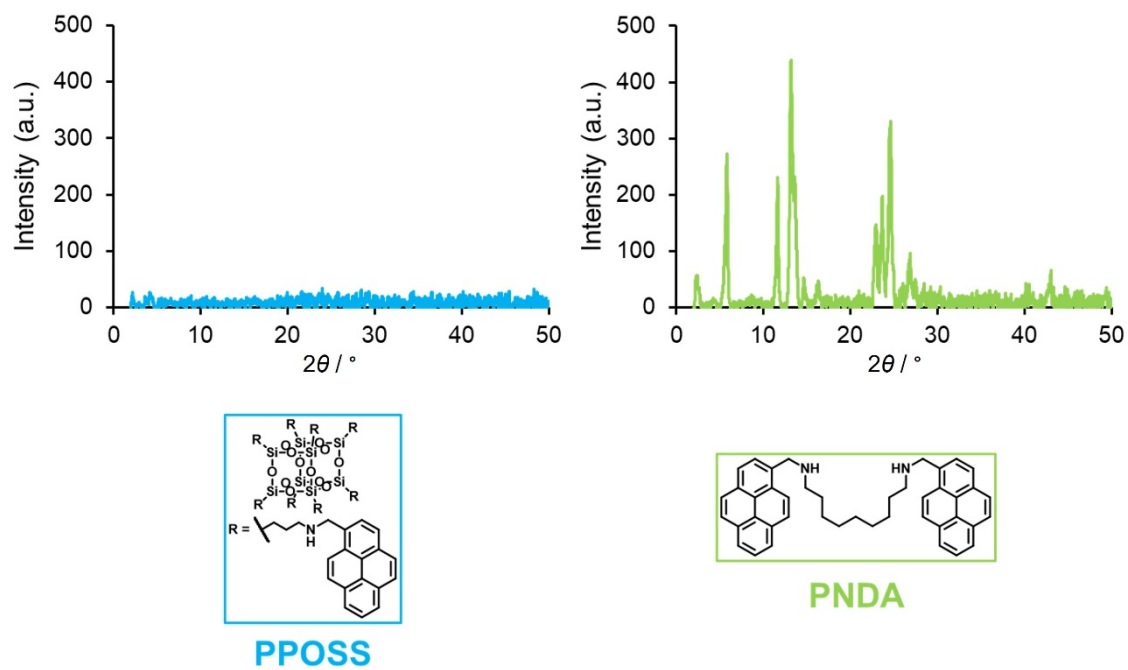


Figure S3. Powder X-ray diffraction patterns of **PPOSS** and **PNDA**.

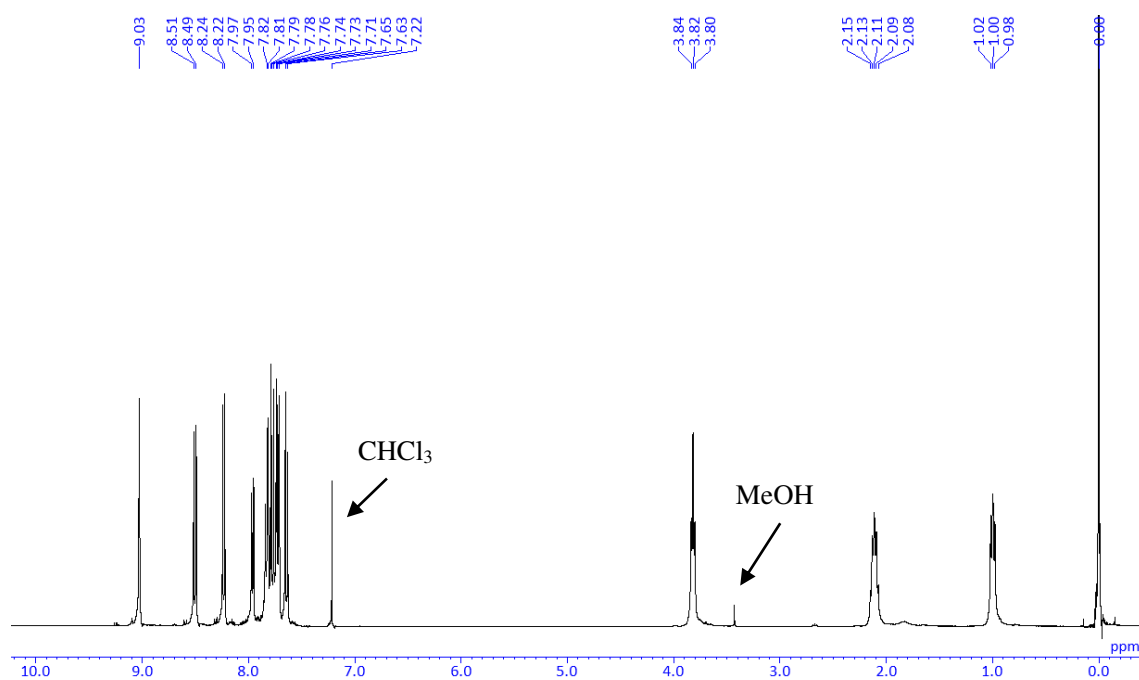


Chart S1. ¹H NMR spectrum of PIPOSS in CDCl₃.

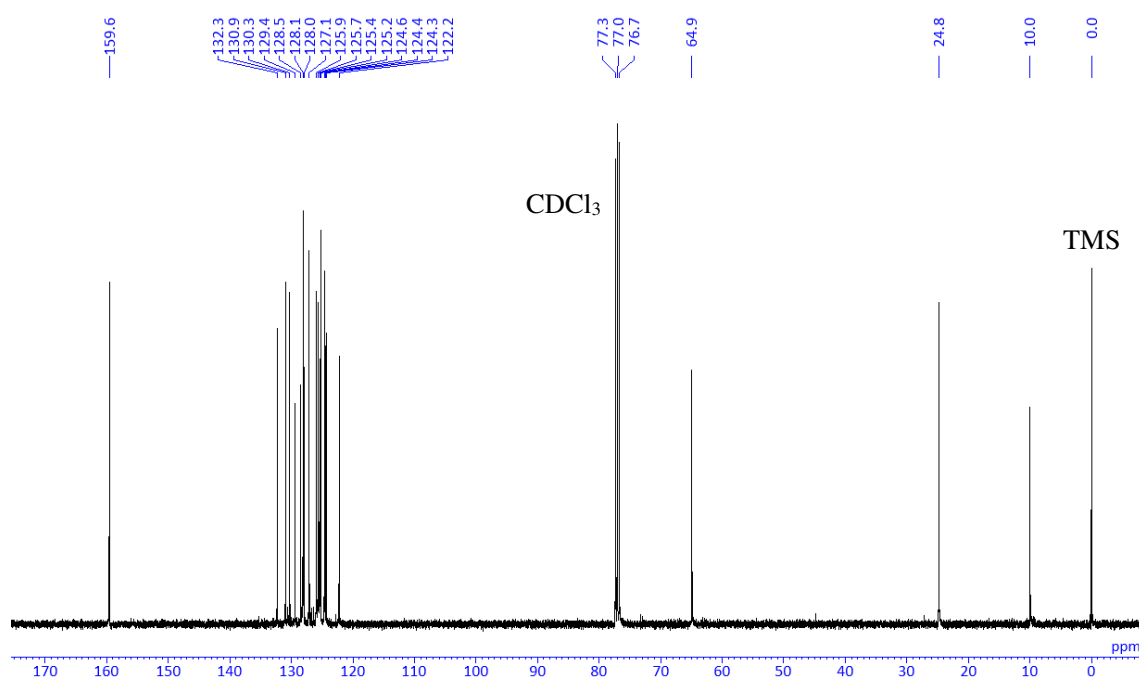


Chart S2. ¹³C{¹H} NMR spectrum of PIPOSS in CDCl₃.

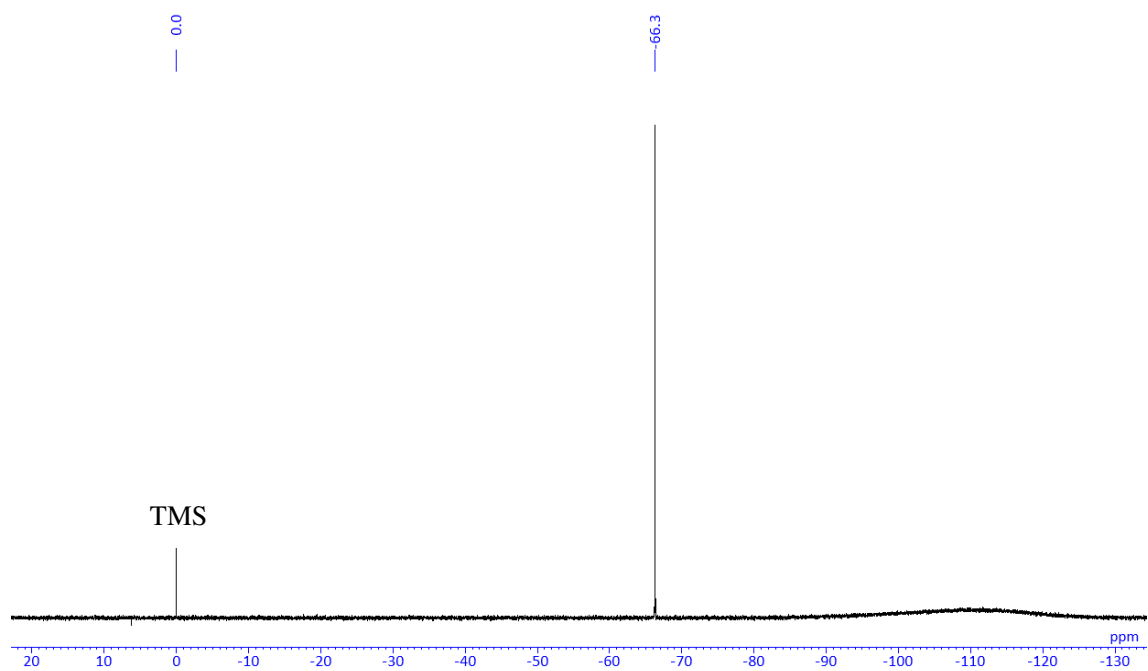


Chart S3. ^{29}Si NMR spectrum of **PIPOSS** in CDCl_3 .

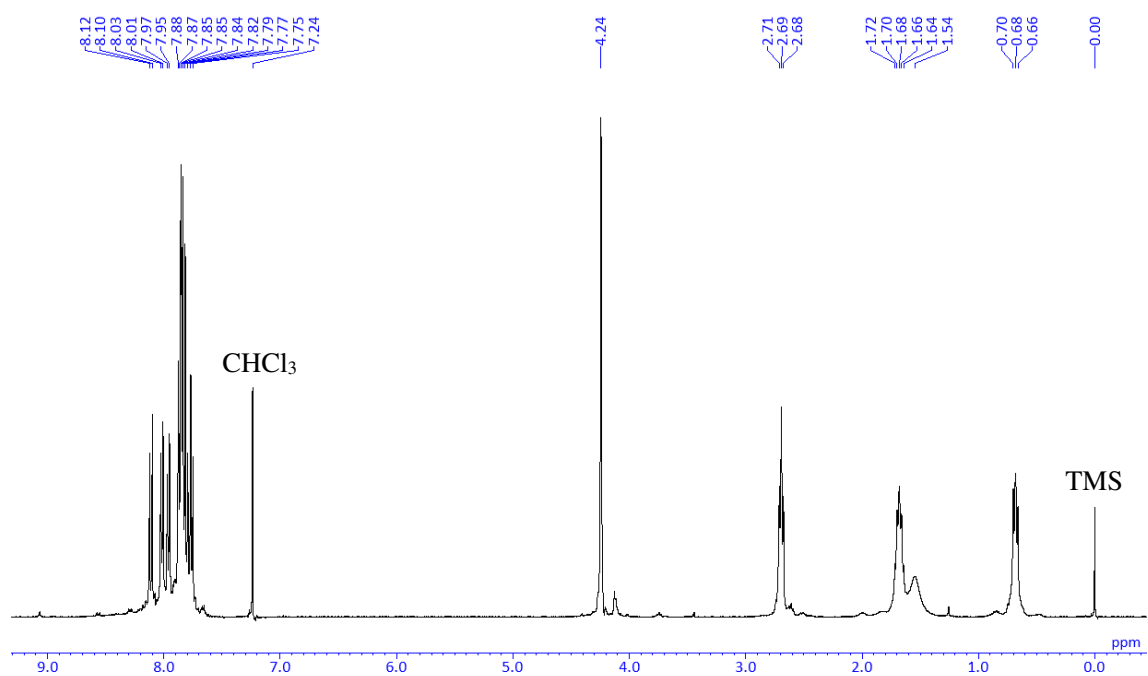


Chart S4. ^1H NMR spectrum of **PPOSS** in CDCl_3 .

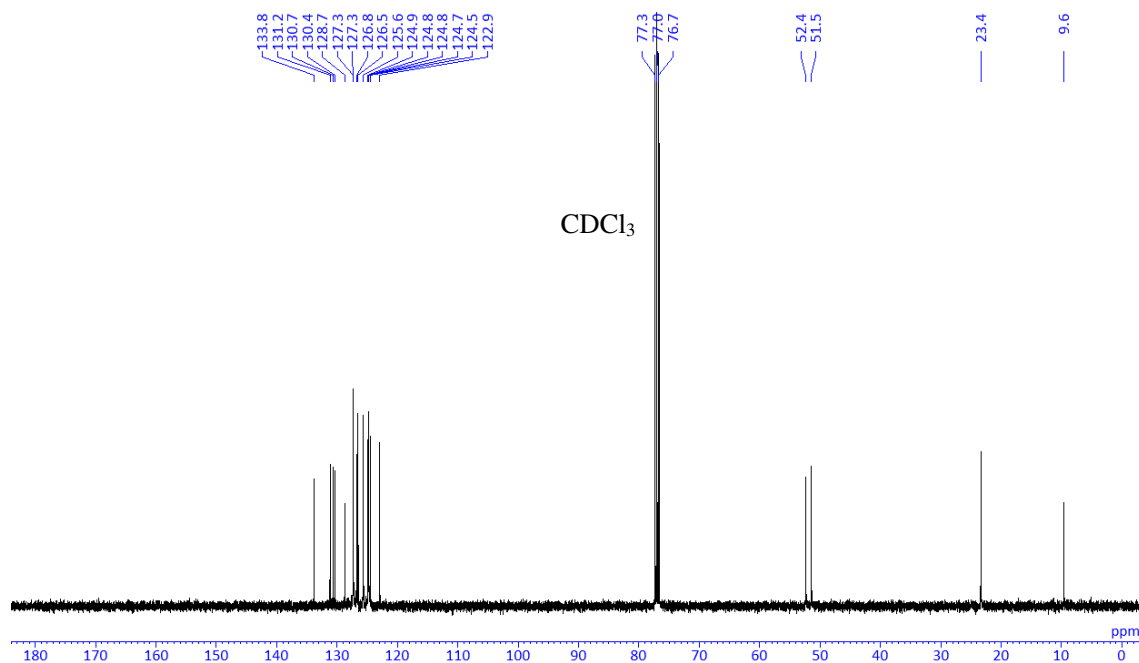


Chart S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of PPOSS in CDCl_3 .

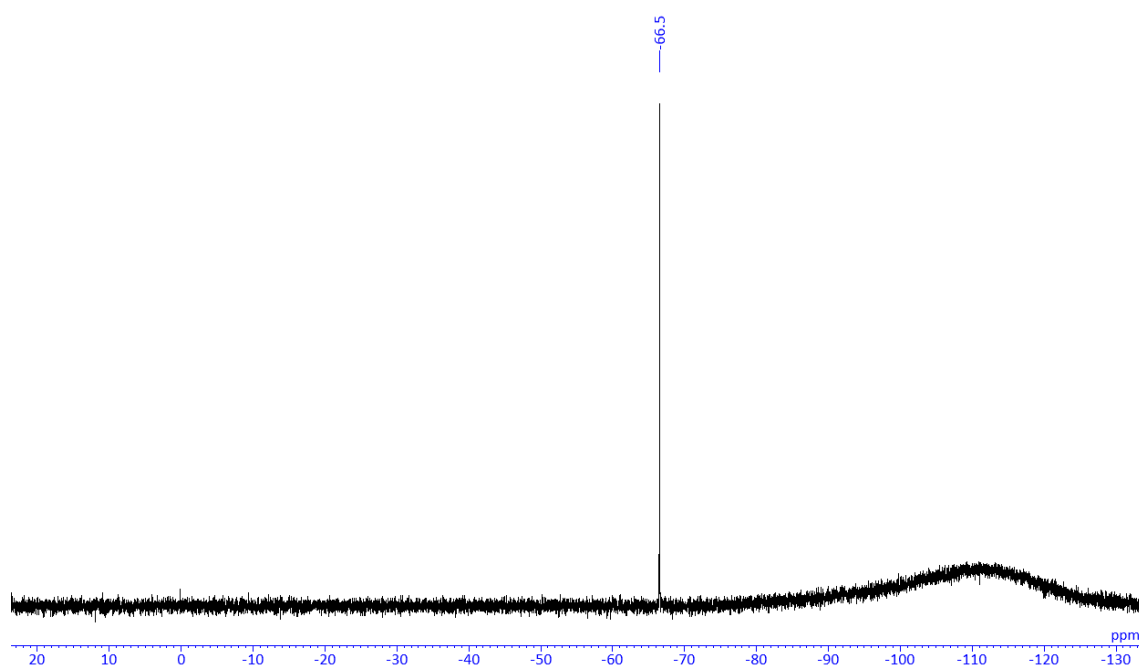


Chart S6. ^{29}Si NMR spectrum of PPOSS in CDCl_3 .

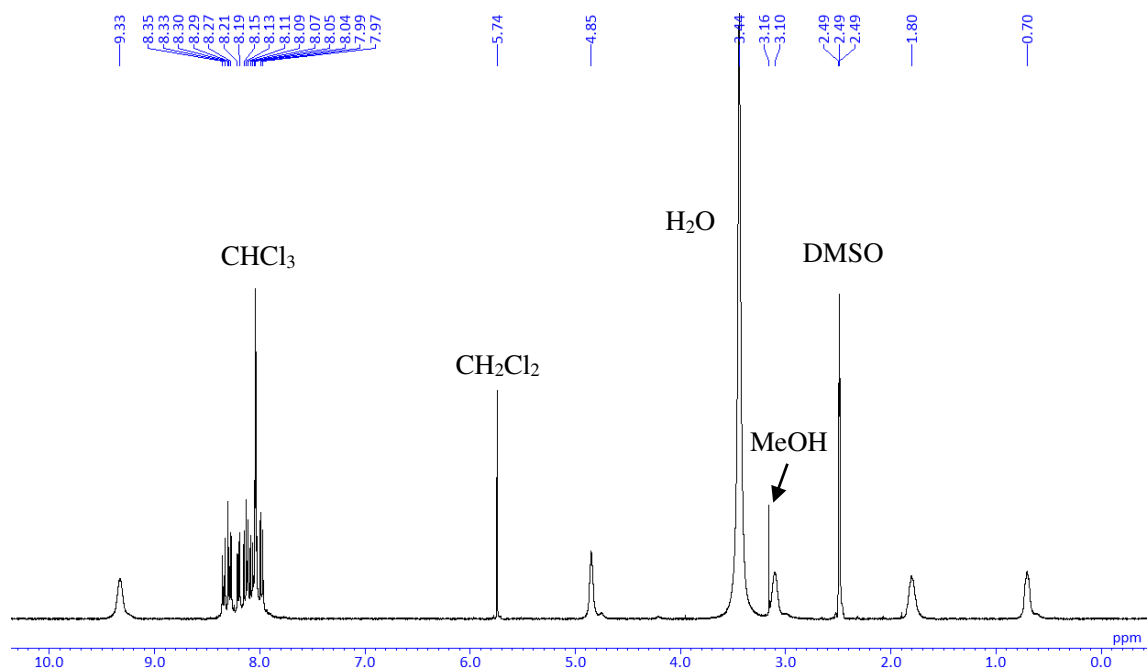


Chart S7. ¹H NMR spectrum of **POSS-TFA** in $\text{DMSO-}d_6$.

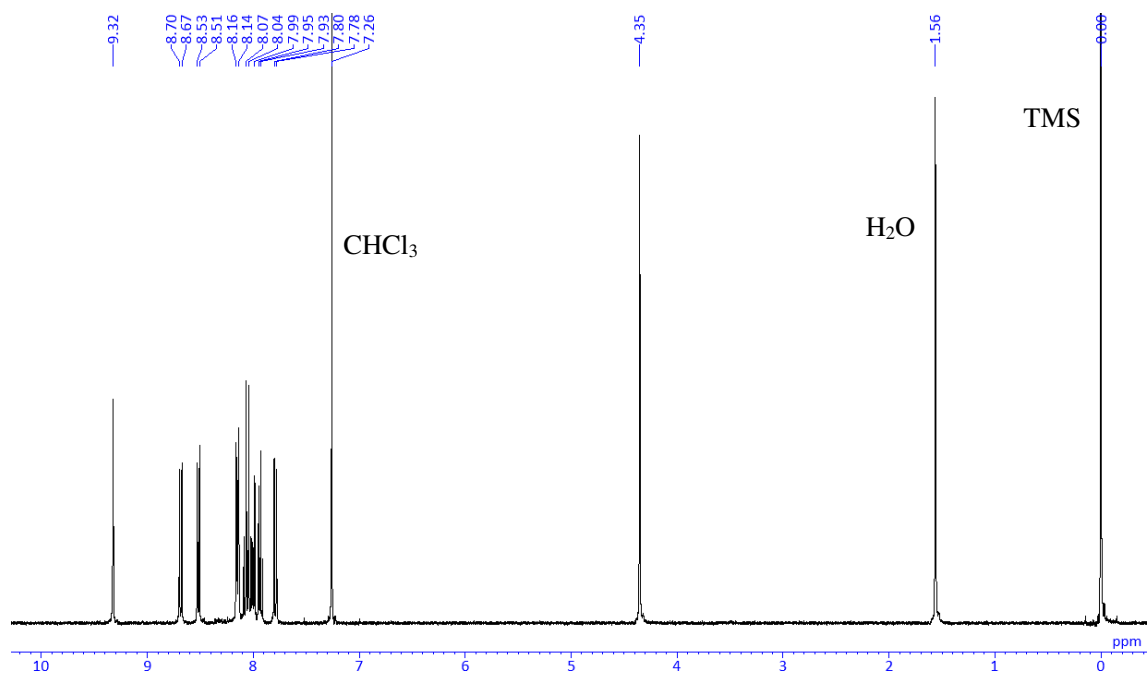


Chart S8. ¹H NMR spectrum of **PIEDA** in CDCl_3 .

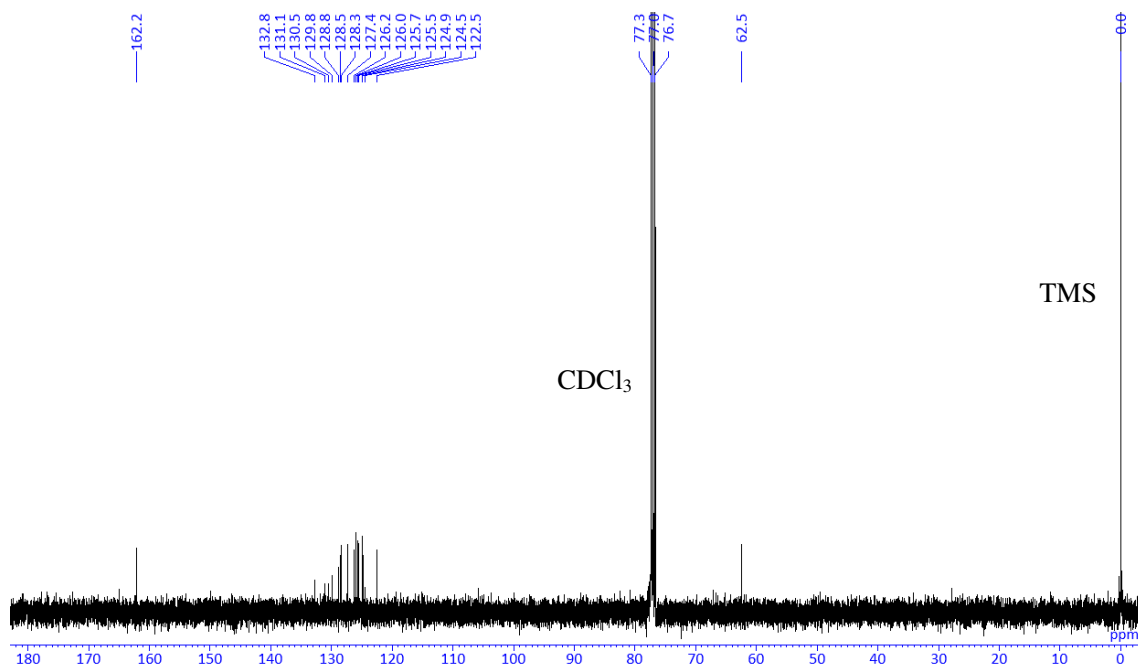


Chart S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **PIEDA** in CDCl_3 .

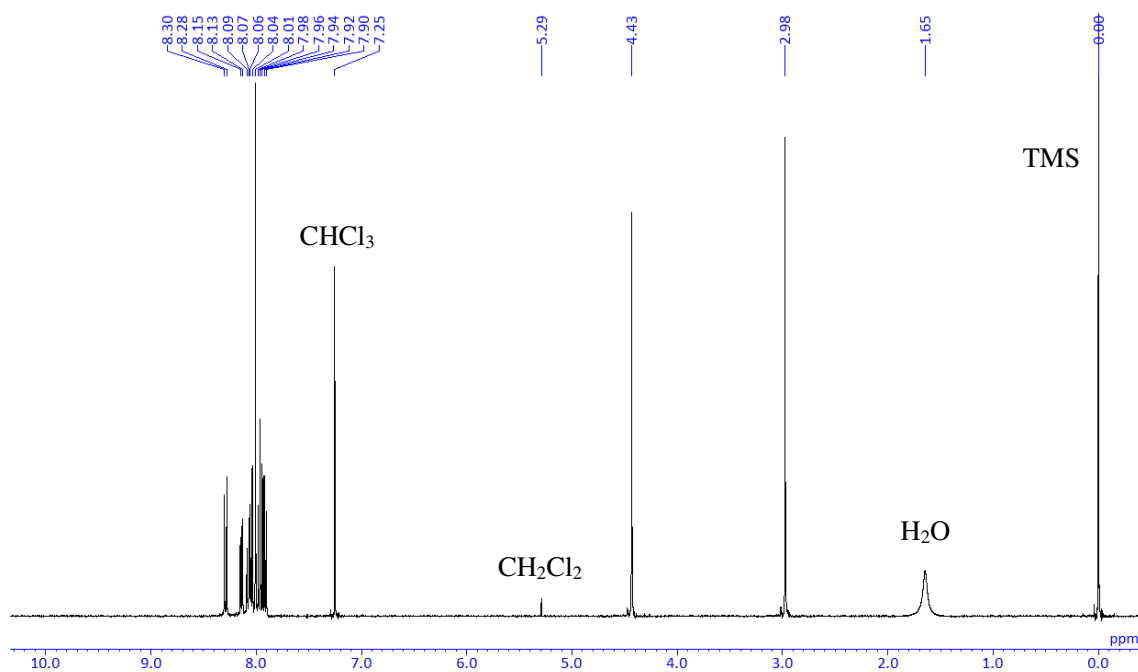


Chart S10. ^1H NMR spectrum of **PEDA** in CDCl_3 .

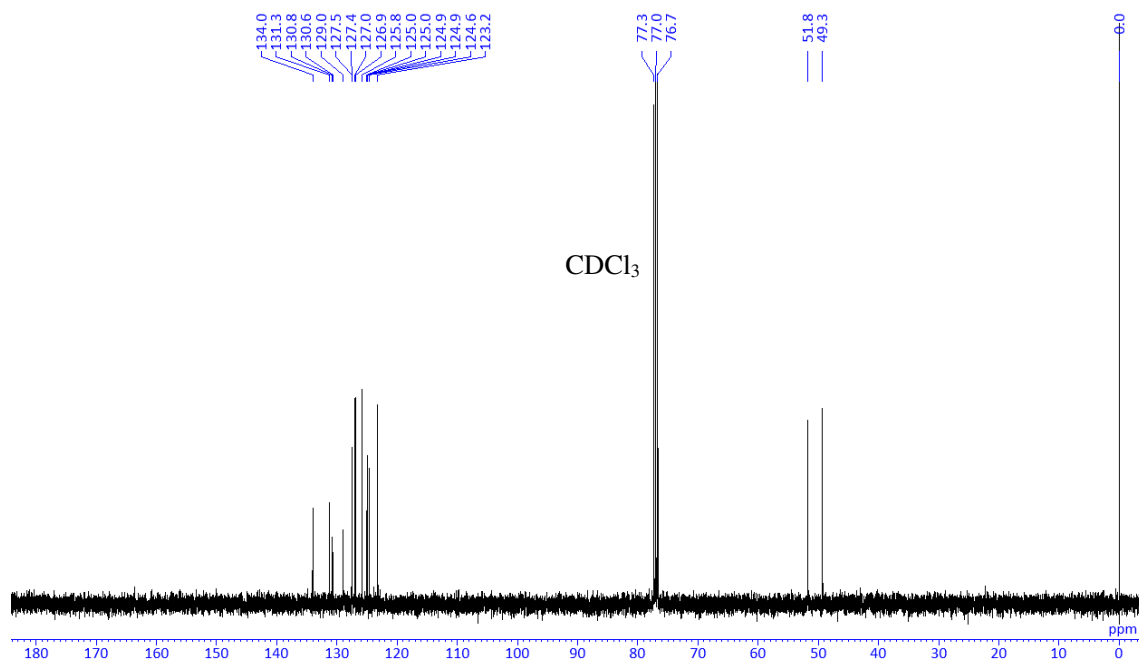


Chart S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of PEDA in CDCl_3 .

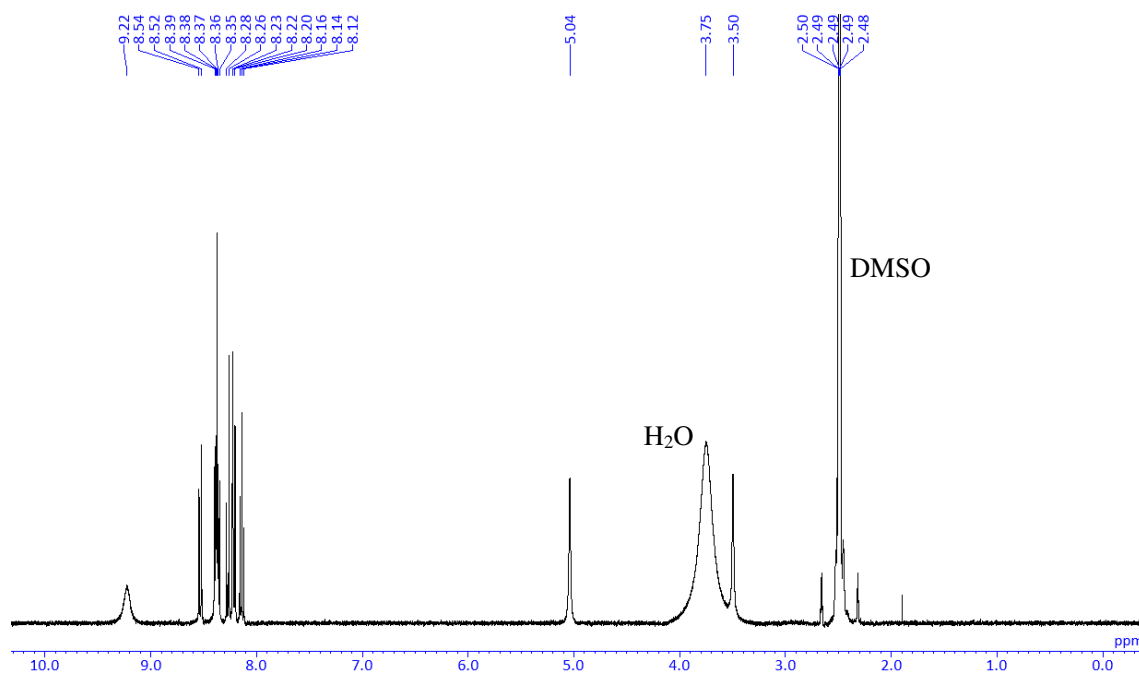


Chart S12. ^1H NMR spectrum of PEDA-TFA in $\text{DMSO}-d_6$.

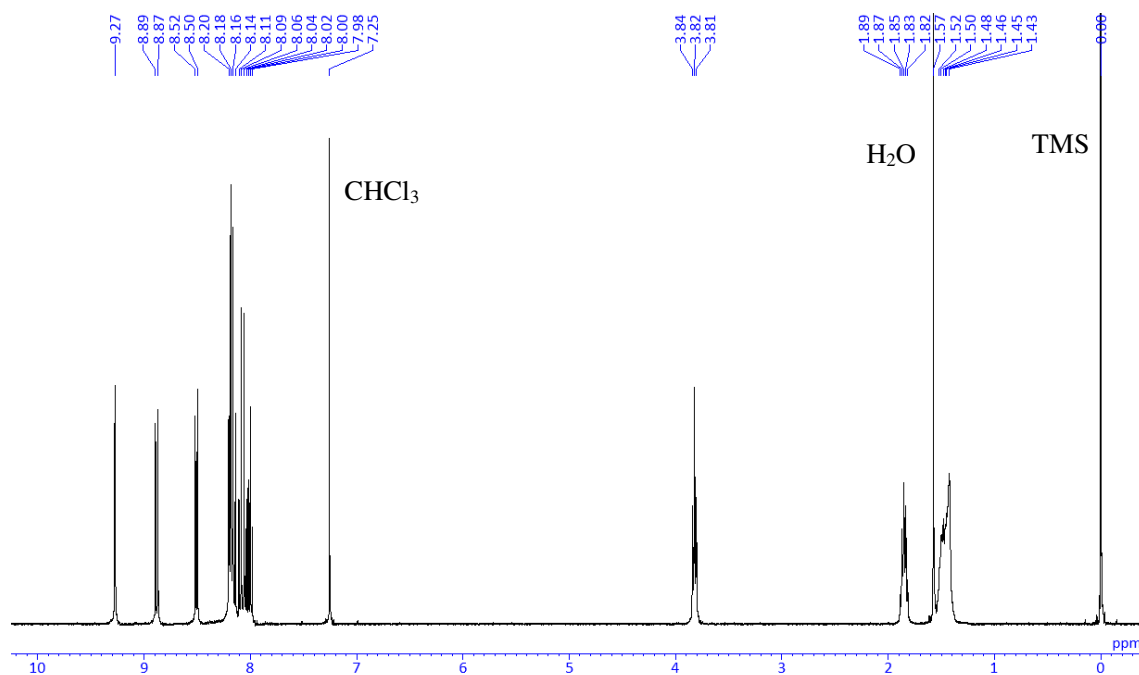


Chart S13. ¹H NMR spectrum of PINDA in CDCl₃.

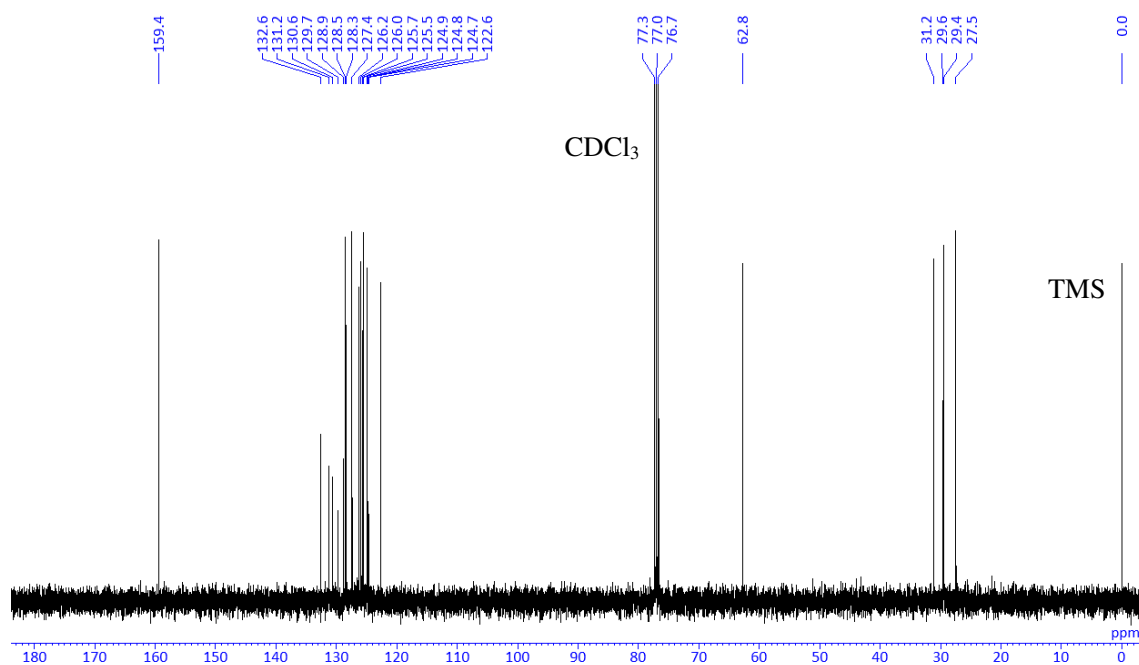


Chart S14. ¹³C{¹H} NMR spectrum of PINDA in CDCl₃.

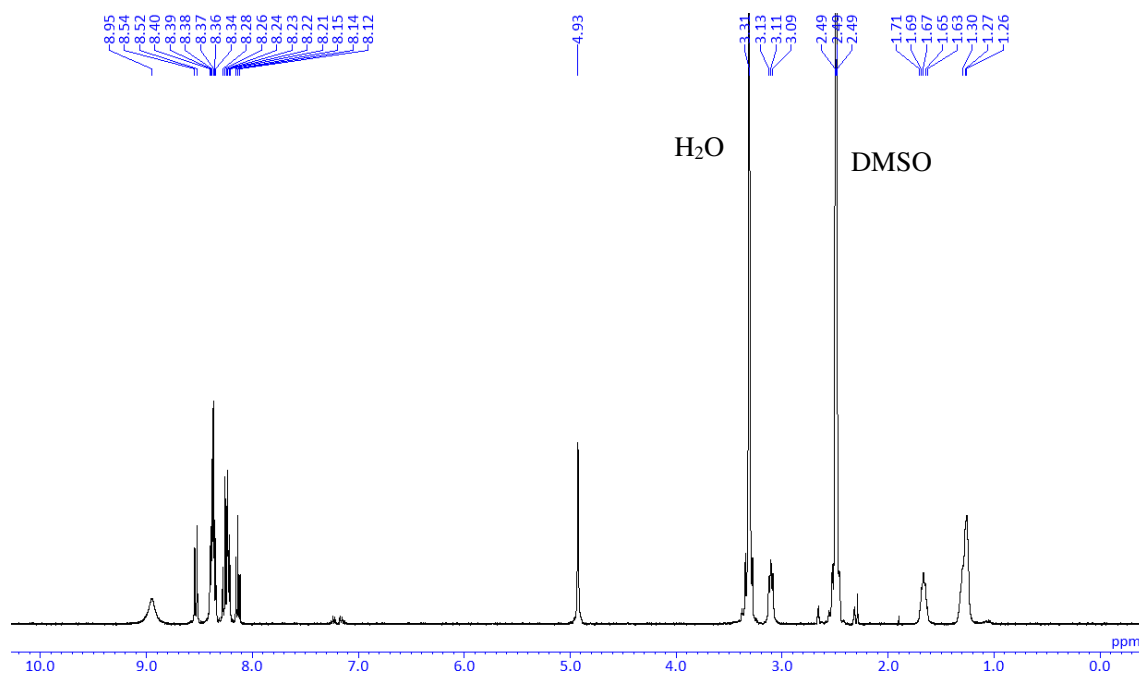


Chart S15. ¹H NMR spectrum of **PNDA-TFA** in DMSO-*d*₆.

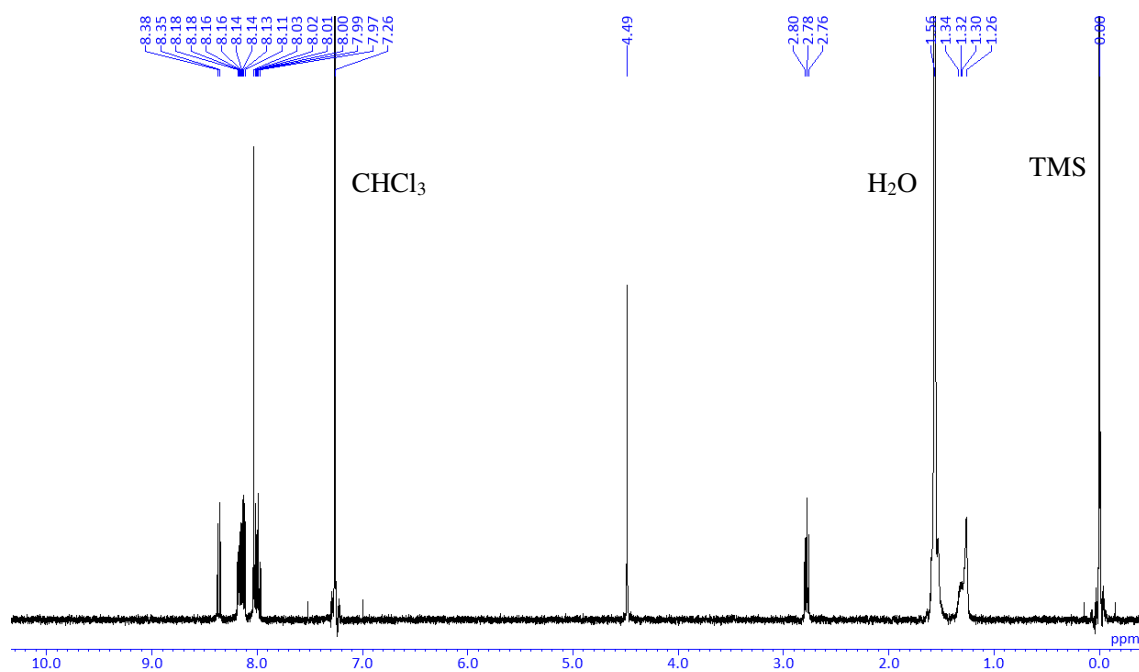


Chart S16. ¹H NMR spectrum of **PNDA** in CDCl₃.

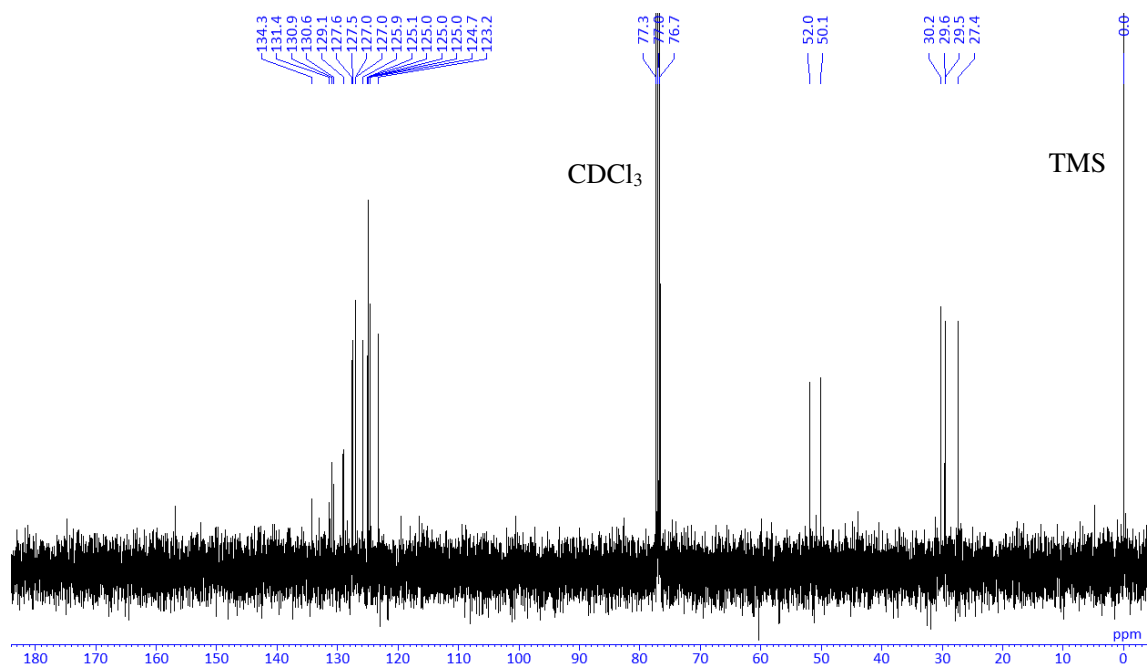


Chart S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **PNDA** in CDCl_3 .

Reference

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