Supporting Information

Synthesis, Self-Assembly and Nonlinear Optical Activity of Selenium-Annulated Perylene Diimide

Guo-Bin Huang,‡[a] Lei Shen,‡[b] Jie Liu,[a] Wen-Fa Zhou,[b] Kaspars Traskovskis,[c] Ying-Lin Song,*[b] Wei Jiang,*[d] Zhao-Hui Wang[e] and Xiang-Kui Ren*[a]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.

[b] School of Physical Science and Technology, Soochow University, Suzhou 215006, P. R. China.

[c] Faculty of Materials Science and Applied Chemistry, Riga Technical University, Riga LV-1048, Latvia.

[d] Beijing National Laboratory for Molecular Science, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

[e] Key Laboratory of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.

‡ These authors contributed equally to this work.

Section 1. Materials and Methods

Perylene-3,4,9,10-tetracarboxylic acid dianhydride (PDA, 98 %, Beijing HWRK company), p-aminopropylisobutyl POSS (AM0292, ≥97 %) and Selenium (99.5 %, J&K Scientific Company) were used as received. All the other chemicals and solvents were purchased from Jiangtian Chemical Reagents Co. Ltd. and used without further purification unless otherwise specified.

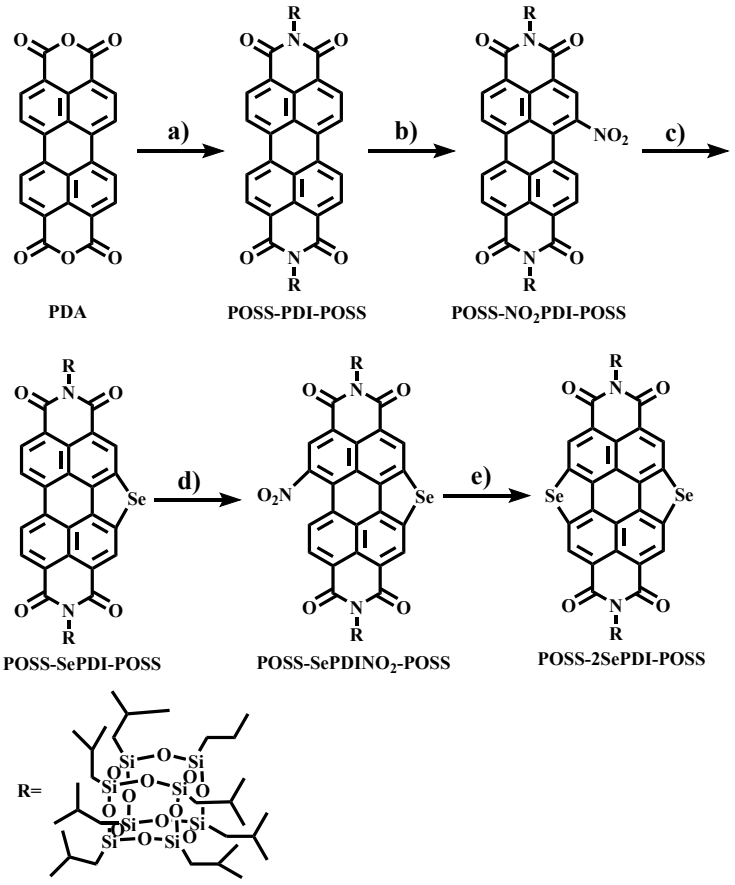
^{1}H NMR spectra were obtained using a Bruker Avance 400 spectrometer with deuterated chloroform ($CDCl_3$) as solvent at room temperature. UV/Vis absorption spectra

were performed on a Mapada UV-3200 spectrophotometer. Fluorescence spectra were determined on a Hitachi FL-2500 luminesence spectrometer. The quantum yields of the samples in chloroform solution were estimated using Rhodamine B (QY = 97 % in ethanol) as standard. The absolute photoluminescence quantum yields of the crystalline powder samples were measured on an Edinburgh FLS 920 fluorescence spectrometer with a calibrated integrating sphere. Phosphorescence spectra and fluorescence lifetimes were obtained on Edinburgh FLS980 fluorescence spectrophotometer. The 2D XRD pattern of the oriented crystal was recorded in the transmission mode on a Bruker D8 Discover diffractometer with a Vantec500 as the 2D detector. The back-ground scattering was recorded and subtracted from the sample pattern. The oriented POSS-2SePDI-POSS crystals were obtained via surface-supported self-assembly by dipping a quartz glass sheet in the POSS-2SePDI-POSS/$CHCl_3$ solution and allowing slow evaporation to utilize the quartz substrate as a template for orientation.

The nonlinear optical response was recorded by nanosecond Z-scan technology at 532 nm. The incident pulse laser consists of two parts, one for detecting the energy fluctuation of the incident pulse laser and the other for focusing the lens. The samples were dissolved in chloroform at a concentration of 1 mg/mL. The samples were placed on a precision moving platform and moved along the Z-axis direction and two energy probes were used to record changes in laser energy. Transient absorption spectra were obtained under excitation of 400 nm pulses, which generated by an optical parametric amplifier (OPA, Light Conversion ORPHEUS) with a Yb:KGW-doped fiber laser. The laser pulse width

and repetition rate are 190 fs and 20 Hz, respectively. The samples for testing the femtosecond transient absorption spectra were dissolved in chloroform with concentration 1 mg/mL.

Section 2. Synthesis



Scheme S1. Synthetic routes of POSS-2SePDI-POSS. (a) NH_2-R, imidazole, 140 °C; (b) nitrosonitric acid, dichloromethane, 0 °C; (c) Se powder, NMP, N_2 atmosphere, 190 °C; (d) nitrosonitric acid, dichloromethane, 0 °C; (e) Se powder, NMP, N_2 atmosphere, 190 °C.

Compound POSS-PDI-POSS

PDA (1.00 g, 2.55 mmol), p-aminopropylisobutyl POSS (5.36 g, 6.12 mmol) and 30.00 g imidazole were heated up to 140 °C with stirring for 4 h. After cooling down, methanol

was added and then the mixture was filtered to remove the imidazole. Next, the crude product was dried at 40 °C under vacuum oven and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1:6, V/V) to give an orange solid (95 %). ^{1}H NMR (400MHz, $CDCl_3$) δ (TMS, ppm): 8.66 (s, 4H, ArH), 8.60 (s, 4H, ArH), 4.21 (t, 4H, -N-CH_2-), 1.84 (m, 18H, -CH- and -CH_2-), 0.94 (m, 84H, -CH_3), 0.74 (t, 4H, -CH_2-), 0.59 (m, 28H, -CH_2-).

Compound POSS-NO_2PDI-POSS

POSS-PDI-POSS (1.00 g, 0.48 mmol) dissolved in dichloromethane (CH_2Cl_2) at 0 °C and stirred. Then, a diluted solution of fuming nitric acid in CH_2Cl_2 was added dropwise. The mixture was stirred at 0 °C for 1 h. The reaction mixture was poured into methanol and filtered. The crude product was washed by methanol, and then dried at 40 °C under vacuum oven. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1:1, V/V) to give a red solid (96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm): 8.83 (s, 5H, ArH), 8.67 (s, 1H, ArH), 8.31 (s, 1H, ArH), 4.24 (t, 4H, -N-CH_2-), 1.88 (m, 18H, -CH- and -CH_2-), 0.97 (m, 84H, -CH_3), 0.76 (t, 4H, -CH_2-), 0.63 (m, 28H, -CH_2-).

Compound PDI-SePDI-POSS

POSS-NO_2PDI-POSS (0.50 g, 0.23 mmol), Se (0.18 mg, 2.32 mmol) and 50 mL NMP were added in a 100 mL round-bottom flask under Argon. The mixture was heated to 190 °C with vigorous stirring for 3 h. Upon cooling, the mixture was poured into 1 L of 2 M HCl, and the precipitate was washed by methanol. The crude product was purified by

column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1:1, V/V) to give an orange solid (60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm): 9.27 (s, 2H, ArH), 8.84 (s, 4H, ArH), 4.24 (t, 4H, -N-CH_2-), 1.80 (m, 18H, -CH- and -CH_2-), 0.96 (m, 84H, -CH_3), 0.78 (t, 4H, -CH_2-), 0.61 (m, 28H, -CH_2-).

Compound POSS-SePDINO$_2$-POSS

PDI-SePDI-POSS dissolved in CH_2Cl_2 at 0 °C and stirred. Then, a diluted solution of fuming nitric acid in CH_2Cl_2 was added dropwise. After stirred at 0 °C for 1 h, the reaction mixture was poured into methanol and filtered. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1:1, V/V) to give an orange solid (85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm): 9.48 (s, 1H, ArH), 9.41 (s, 1H, ArH), 8.88 (t, 2H, ArH), 8.66 (s, 1H, ArH), 4.24 (t, 4H, -N-CH_2-), 1.83 (m, 18H, -CH- and -CH_2-), 0.94 (m, 84H, -CH_3), 0.77 (t, 4H, -CH_2-), 0.59 (m, 28H, -CH_2-).

Compound POSS-2SePDI-POSS

POSS-SePDINO$_2$-POSS (0.18 g, 0.08 mmol), Se (0.06 g, 0.80 mmol) and 50 mL NMP were added in a 100 mL round-bottom flask under Argon. The mixture was heated to 190 °C with vigorous stirring for 3 h. Upon cooling, the mixture was poured into 1 L of 2 M HCl, and the precipitate was washed by methanol. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1:1, V/V) to give a yellow solid (40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm): 9.51 (s, 4H), 4.24 (t, 4H, -N-CH_2-), 1.86 (m, 18H, -CH- and -CH_2-), 0.93-0.72 (t, 88H, -CH_3- and -CH_2-), 0.59 (m, 28H,

-CH_2-).

Section 3. Photophysical properties of POSS-PDI-POSS and POSS-2SePDI-POSS in solution and solid state

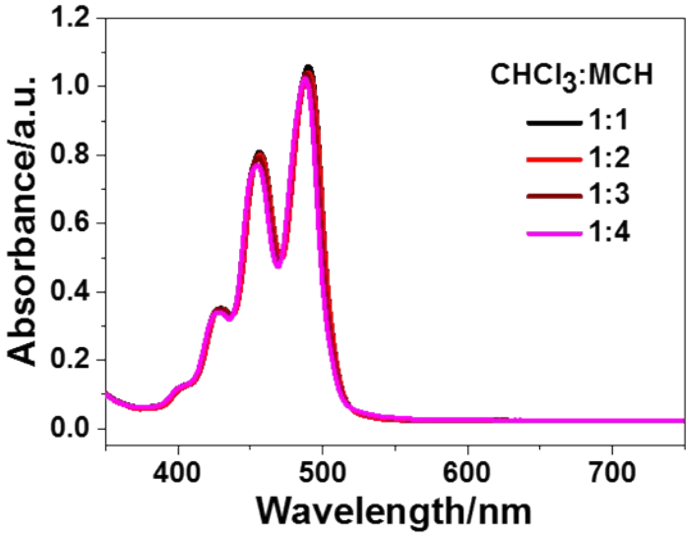


Fig. S1 Absorption spectra of POSS-2SePDI-POSS in $CHCl_3$/MCH mixture at a concentration of 5×10^{-5} mol L^{-1}.

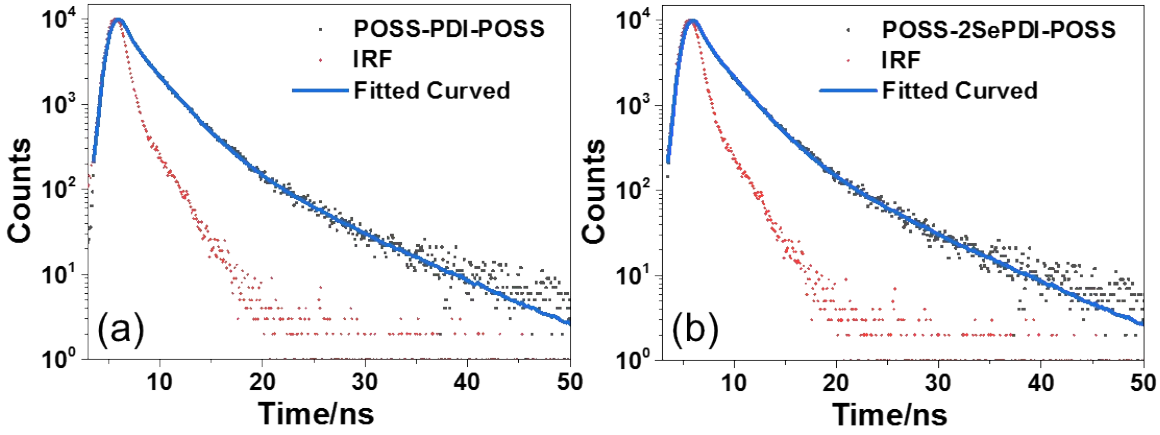


Fig. S2 (a) The fluorescence decay curve of POSS-PDI-POSS were fitted and the lifetime τ was calculated as an amplitude-averaged decay time (τ = 5.33 ns, monitored at λ_{max} = 541

nm); (b) Curve of POSS-2SePDI-POSS were fitted (τ = 2.32 ns, monitored at λ_{max} = 516 nm).

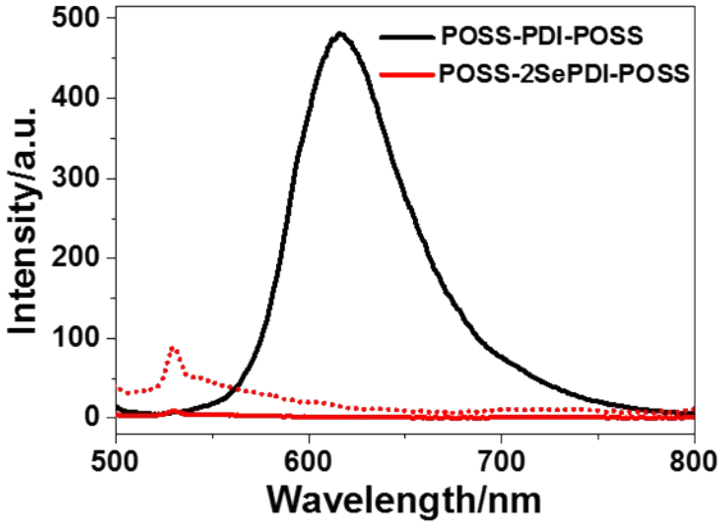


Fig. S3 Fluorescence spectra of POSS-PDI-POSS and POSS-2SePDI-POSS in solid state, the dash-dot represents 10 times the intensity of POSS-2SePDI-POSS.

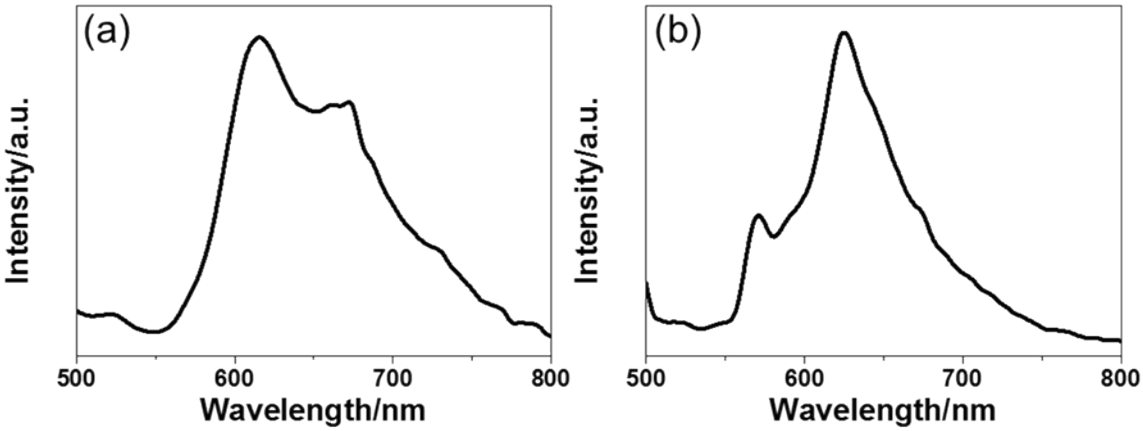


Fig. S4 Phosphorescence spectra of POSS-2SePDI-POSS in solution and in solid state at 77 K.

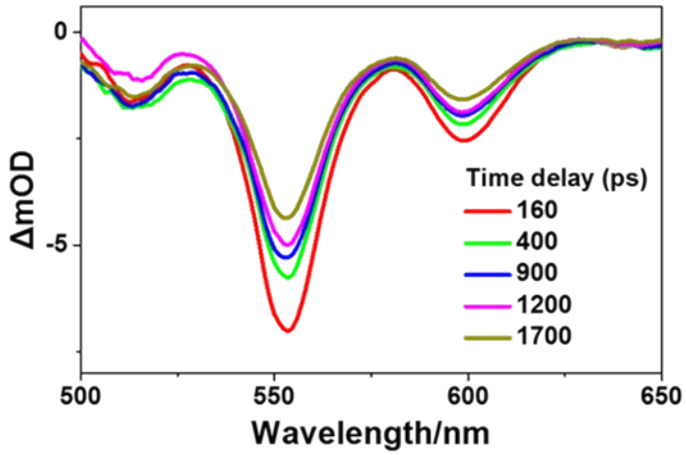


Fig. S5 Femtosecond transient absorption spectra of POSS-PDI-POSS at various time delays.

Section 4. The Value of Nonlinear Absorption Coefficient

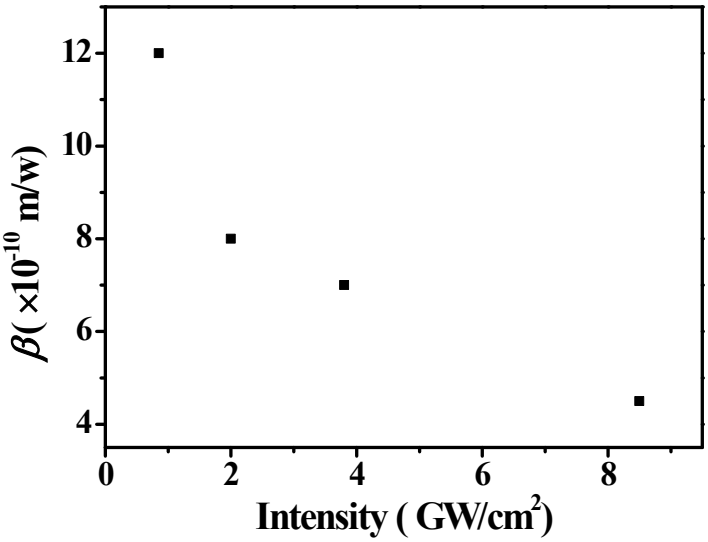


Fig. S6 Nonlinear absorption coefficient β of POSS-2SePDI-POSS as a function of input fluence.

Section 5. ^{1}H NMR Spectra

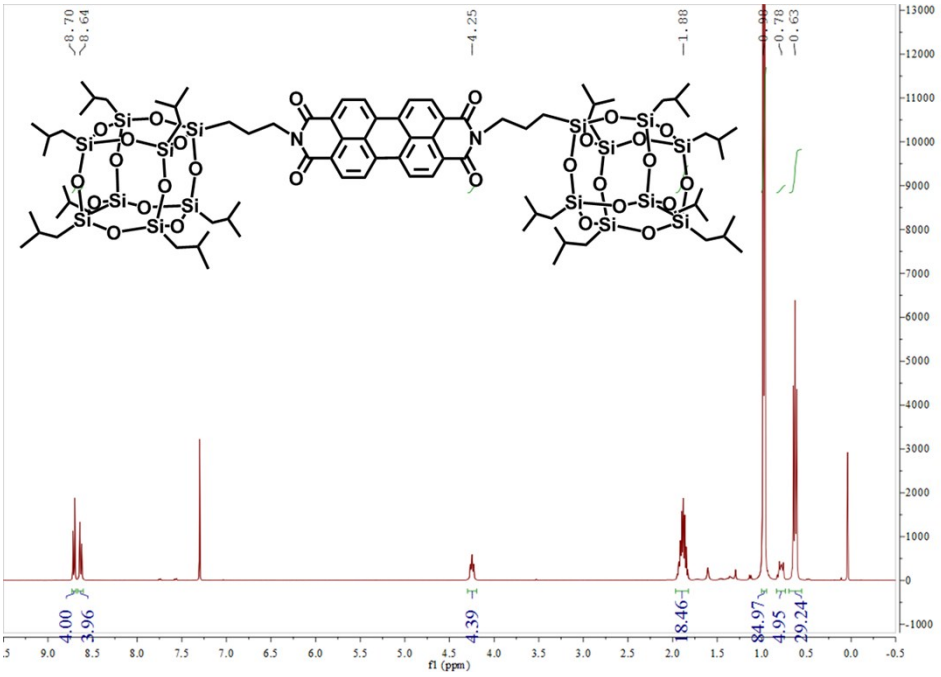


Fig. S7 ^{1}H NMR spectrum of POSS-PDI-POSS recorded in $CDCl_3$.

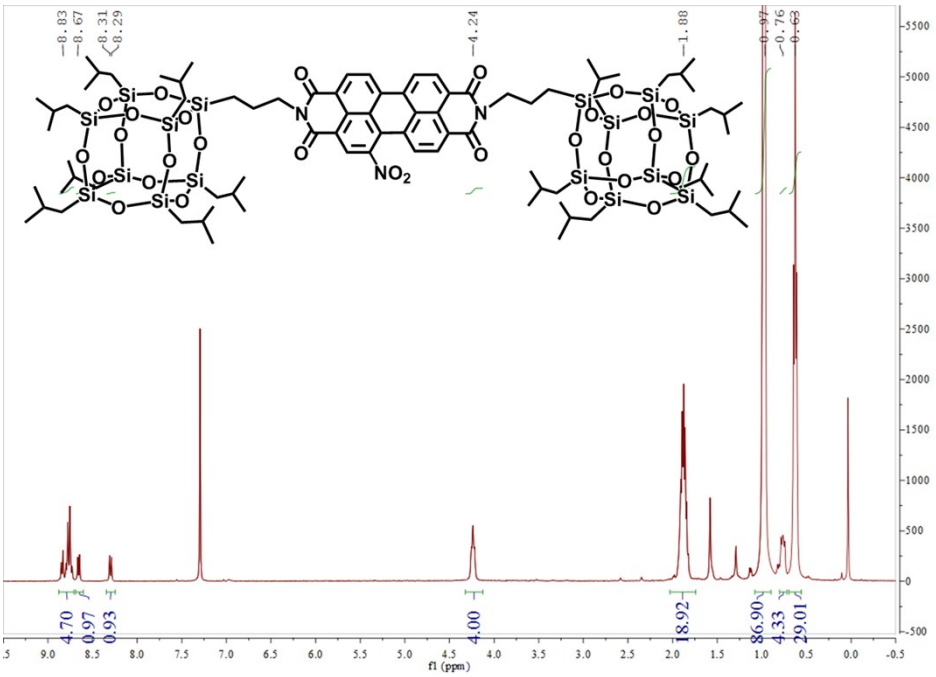


Fig. S8 ^{1}H NMR spectrum of POSS-NO_2PDI-POSS recorded in $CDCl_3$.

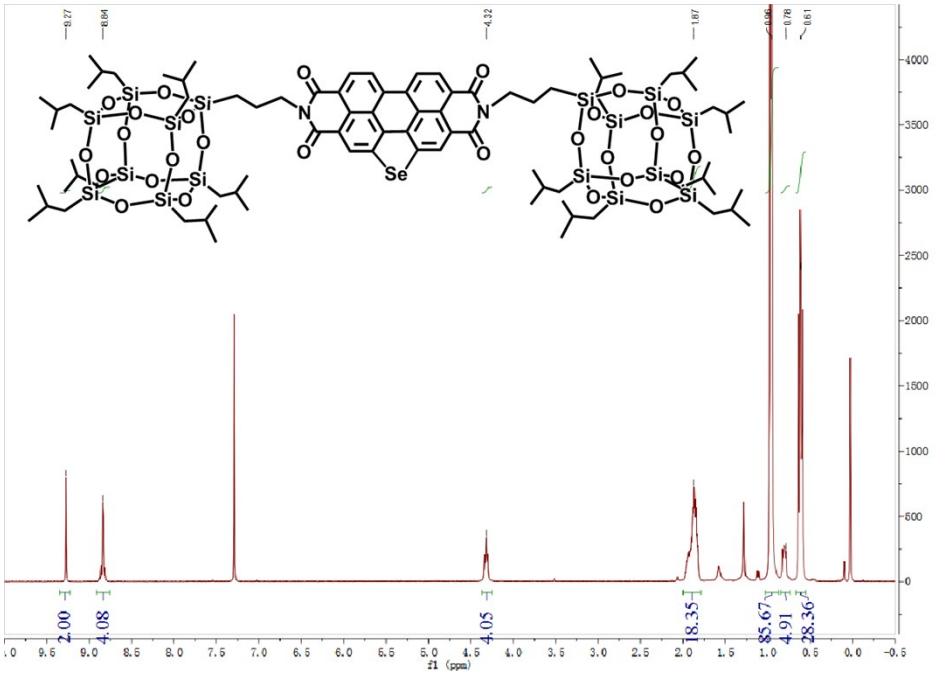


Fig. S9 ^{1}H NMR spectrum of POSS-SePDI-POSS recorded in $CDCl_3$.

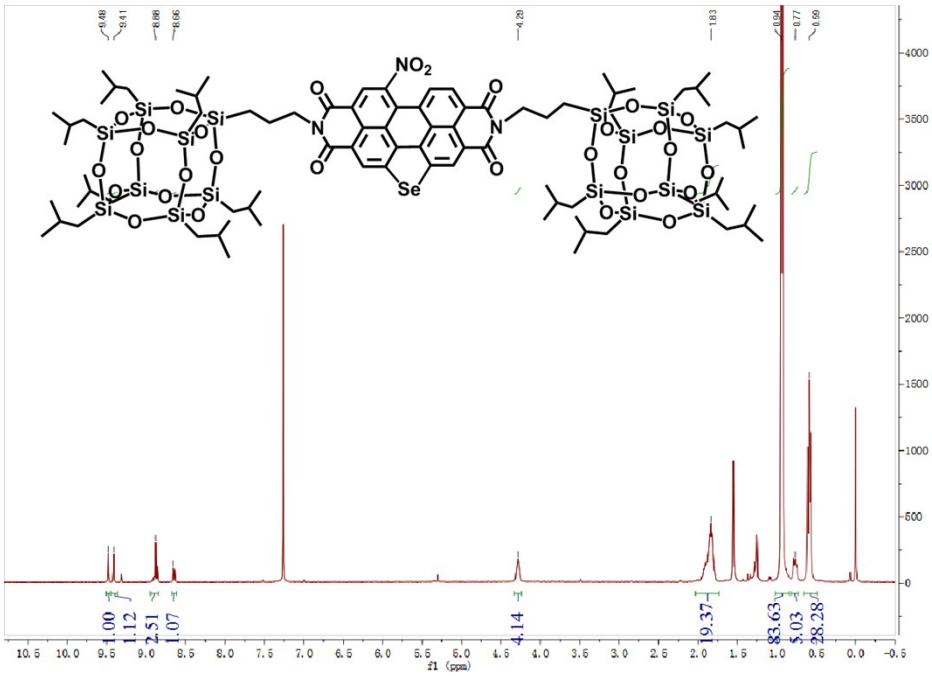


Fig. S10 ^{1}H NMR spectrum of POSS-SePDINO$_2$-POSS recorded in $CDCl_3$.

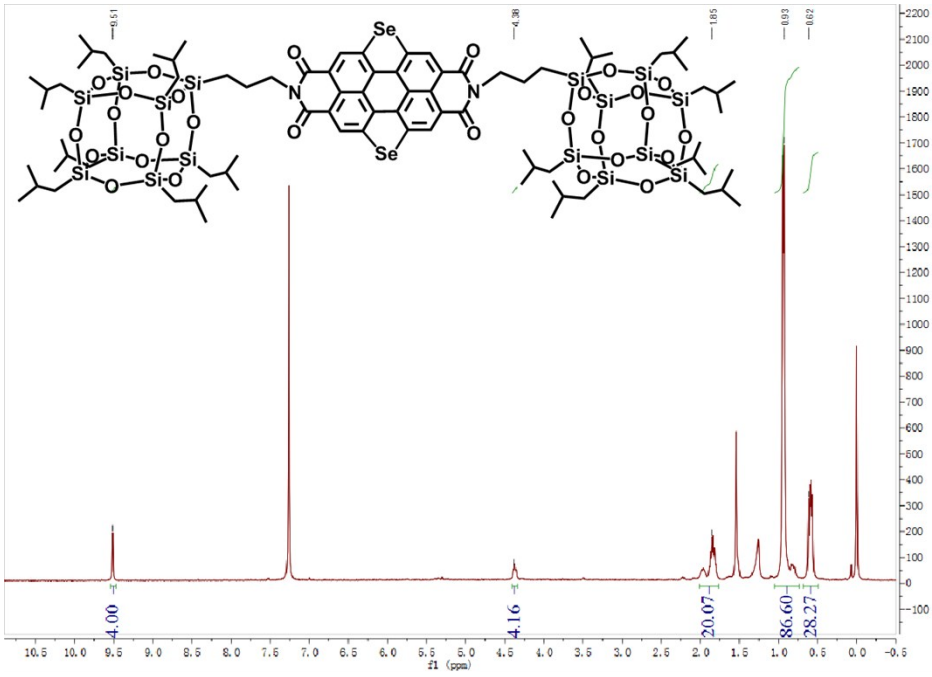


Fig. S11 ^{1}H NMR spectrum of POSS-2SePDI-POSS recorded in $CDCl_3$.