Electronic Supplementary Information

Fabrication of Well-Defined Crystalline Azacalixarene Nanosheets Assisted by Se···N Non-Covalent Interaction

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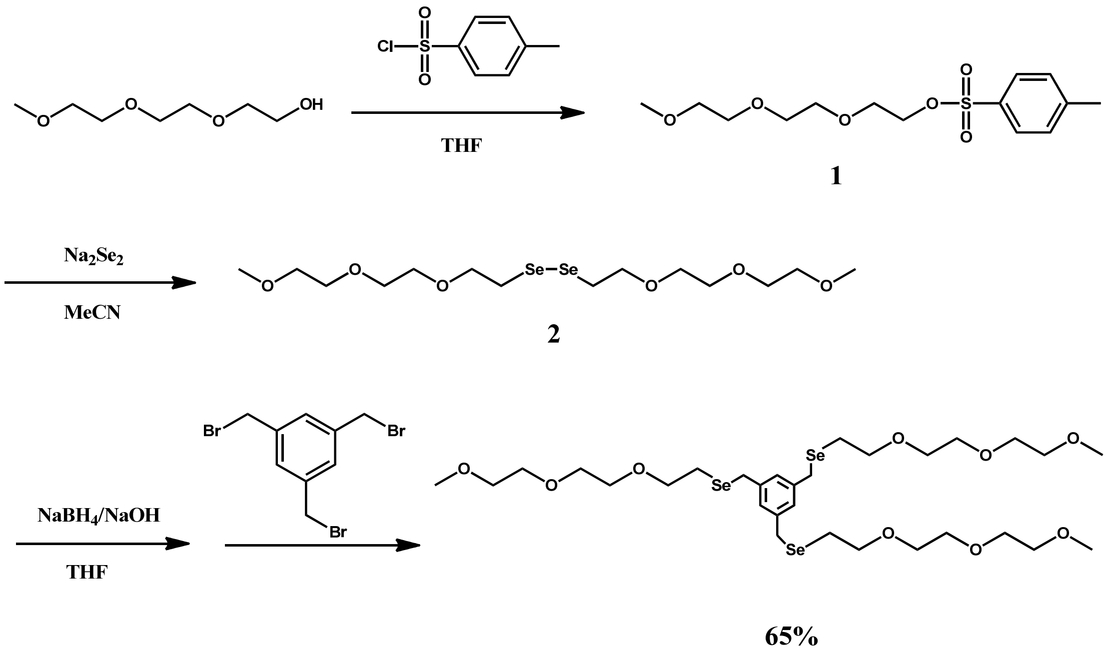
Synthesis Details

Materials. Triethylene glycol monomethyl ether was purchased from Sigma Aldrich. Selenium powder was from Aladdin Chemical Reagent Co. Ltd. 1,3,5-tris(bromomethyl)benzene was purchased from Creasyn Finechem (Tianjin) Co. Ltd. Sodium borohydride, p-toluenesulfonyl chloride, Et_3N, NaOH, NaH, other organic solvents and chemicals used in this work were analytical grade products from Beijing Chemical Reagent Company. Tetrahydrofuran (THF) was dried by CaH_2 to remove the moisture and oxidative impurity. N_2 saturated acetonitrile and THF were prepared by continuously bubbling nitrogen through them for 10 min. Other solvents and chemicals were used as received unless stated.

Instruments. ^{1}H, ^{13}C and ^{77}Se NMR spectra were recorded on a JEOL JNM-ECA 300, a JEOL JNM-ECA 400 and a JEOL JNM-ECA 600 spectrometer at 25°C. ESI-MS was carried out on a PE Sciex API 3000 spectrometer.

Synthesis of 1,3,5-tri(2,5,8-trioxa-11-selenadodecan-12-yl)benzene (SeG).

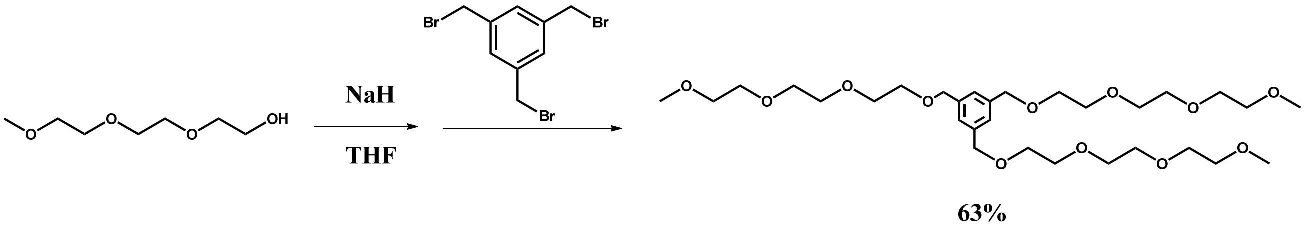


Scheme S1 The synthesis route of SeG

a) Compound 1 was synthesized according to the previous literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.80 (d, *J* = 8.2, 2H), 7.34 (t, *J* = 7.9, 2H), 4.16 (t, *J* = 4.8, 2H), 3.69 (t, *J*= 4.8, 2H), 3.63~3.52 (m, 8H), 3.37 (s, 3H), 2.45 (s, 3H).

b) Synthesis of SeG: To a solution of 0.2270 g (6.0 mmol) $NaBH_4$ in 10 mL water, 0.4738 g (6.0 mmol) Se powder was added in room temperature (RT). The resulting solution was then moved to 50°C and stirred for 20 min in a nitrogen environment. Then a solution of 1.9103 g (6.0 mmol) compound 1 in 10 mL N_2 saturated acetonitrile was added and the solution was stirred for 5 h at 50°C in a nitrogen environment. After evaporating the acetonitrile under reduced pressure and extracting with CH_2Cl_2, the organic layer was collected and concentrated. Yellow oil (compound 2) was obtained. Without further purification, to the compound 2, a solution of 0.6780 g (1.9 mmol) 1,3,5-tris(bromomethyl)benzene in 10 mL N_2 saturated THF was added. Then a solution of 0.4540 g (12.0 mmol) $NaBH_4$ and 0.0240 g (0.6 mmol) NaOH in 5mL water was added in a nitrogen environment, and the solution was allowed to stir at RT for 5h. After evaporating the THF, the resulting solution was subsequently extracted with CH_2Cl_2 and dried over Na_2SO_4. Then the product was purified by column chromatography (silica gel, first CH_2Cl_2/MeOH, 50:1, then CH_2Cl_2/MeOH, 20:1), to afford 0.9879 g (1.2 mmol) product as yellow oil (yield: 65%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.07 (s, 3H), 3.77 (s, 6H), 3.68~3.53 (m, 30H), 3.37 (s, 9H), 2.67 (t, J = 7.1, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 139.84, 127.83, 71.91, 71.39, 70.60, 70.53, 70.11, 59.01, 27.13, 22.98. ^{77}Se NMR (114 MHz, $CDCl_3$, diphenyldiselenide as reference (δ 464.1 ppm)): δ 233.87. ESI-MS: m/z (%) 817.9 (66), 821.6 (93), 819.7 $[M+Na]^+$ (100).

Synthesis of 1,3,5-tri(2,5,8,11-tetraoxadodecyl)benzene (OG).



Scheme S2 The synthesis route of OG

To 3.05 mL (18 mmol) triethylene glycol monomethyl ether in 10 mL dried THF, 0.6857 g (20 mmol) 70% NaH was added in a nitrogen environment. After stirring for 1h at 50°C, a solution of 1.9650 g (5.5 mmol) 1,3,5-tris(bromomethyl)benzene in 40 mL dried THF was added and the resulting solution was refluxed for 1 day at 70°C in a nitrogen environment. Then after evaporating the THF under reduced pressure, the mixture was subsequently extracted with CH_2Cl_2 and dried over Na_2SO_4. The product was purified by column chromatography (silica gel, first EtOAc, then EtOAc/MeOH, 20:1), to afford 2.0965 g (3.46 mmol) product as colorless oil (yield: 63%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.23 (s, 3H), 4.55 (s, 6H), 3.66~3.53 (m, 36H), 3.38 (s, 9H). ^{13}C NMR (101 MHz MHz, $CDCl_3$, ppm): δ 138.56, 126.29, 73.06, 71.90, 70.59, 70.51, 69.49, 59.02. MS (ESI): *m*/*z* (%) 631.4 (6), 630.1 (32), 629.6 $[M+Na]^+$ (100).

Synthesis of Azacalix[6]pyridine (APy6).

The compound was synthesized according to the previous literature.[2] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ7.37 (t, J = 8.0 Hz, 6H), 6.64 (d, J = 8.0 Hz, 12H), 3.46 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ156.1, 138.2, 107.0, 36.0.

Physical and Spectroscopic Measurements

Transmission Electron Microscopy (TEM) Images

TEM images were obtained from a JEM-2010 Microscope with an accelerating voltage of 120 kV and H-7650B Microscope with an accelerating voltage of 80 kV. The TEM samples were prepared by drop-coating the aqueous solution on the carbon-coated copper grid and staining by 1.2% uranium acetate before observation. Various complex ratios of SeG and APy6 were tried, and we found the proper situations were that the concentration of SeG molecule was 2mM or higher and the amount of APy6 molecule was 5×10^{-7}~1×10^{-6} mmol in 1mL water.

Cryo-TEM Images

Cryo-TEM samples were prepared in a controlled environment vitrification system (CEVS) at 28°C. The vitrified samples were then stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined by a JEM 2200FS TEM (200 kV) at about –174°C. The phase contrast was enhanced by underfocus. Similar results are obtained as TEM and AFM measurements, indicating that the formation of the nanosheets is in solution instead of on substrates during the drying process.

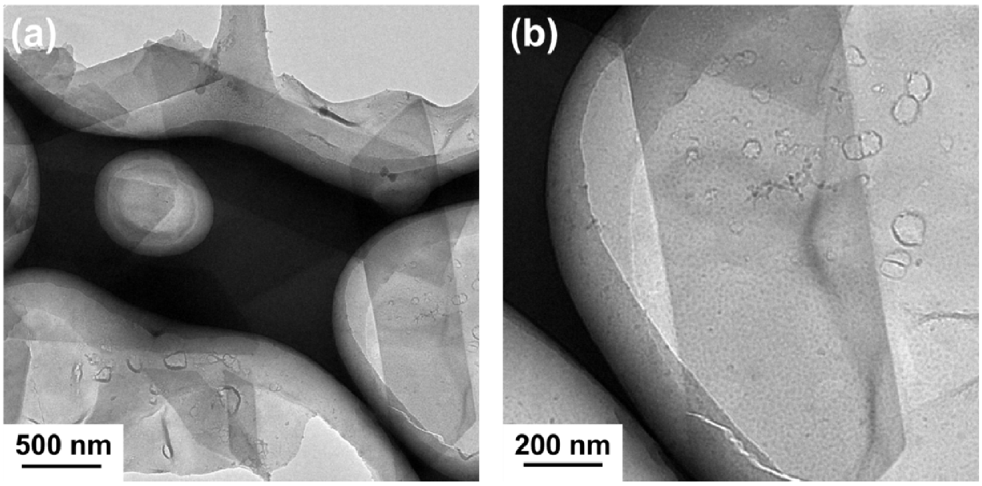


Fig. S1 Cryo-TEM images of the nanosheets. Results indicate that the formation of the nanosheets is in solution instead of on substrates during the drying process.

Dynamic Light Scattering (DLS) and Critical Micelle Concentration (CMC)

The size distribution of the aggregates was analyzed by a Malvern 3000HS Zetasizer using a monochromatic coherent He–Ne laser (633 nm) as the light source and a detector that detected the scattered light at an angle of 90°. 2mM SeG was prepared in water with the typical procedure and was stood for 2 h before characterization. As shown in Fig. S2a, the diameter of the micelles is 141.8 nm.

Fluorescence spectra were recorded on a HITACHI F-7000 apparatus at 20°C. The critical micelle concentration (CMC) of SeG was measured by the fluorescent probe method. A series of solutions with different concentrations were prepared with the typical procedure using saturated pyrene water solution. As shown in Fig. S2b, the CMC of SeG in water is 1.2 mM. (The CMC was chosen as the concentration when pyrene exhibited an apparent decrease in the I_1/I_3 ratio with an increasing concentration of the SeG, indicating that the aggregation of the amphiphile occurred.)

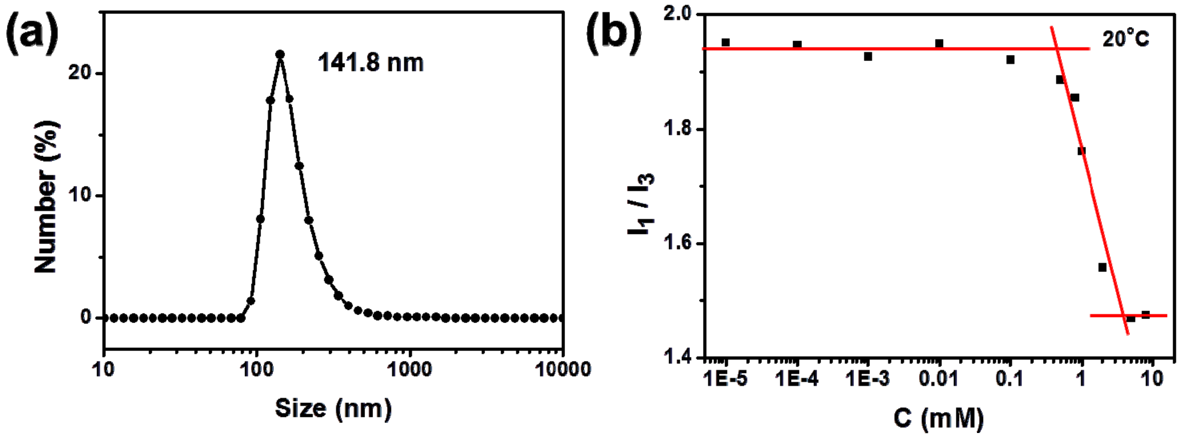


Fig. S2 Size distribution (a) and CMC (b) of the SeG micelles in water. The CMC of SeG in water is 1.2 mM and the diameter of the micelles is 141.8 nm.

X-Ray Diffraction (XRD)

The XRD data were recorded on a Rigaku D/max 2500 diffratometer. The Bragg peak λ was extracted from the XRD data and the layer thickness d could be obtained according to the Bragg equation $d=\lambda/2\sin\theta$, $\lambda=0.15405$ nm. The sample was prepared by casting the solution on a clean glass substrate for several times.

The result shows the 001 and 002 peaks are 9.48° and 19.0° respectively, indicating that the distance between layers of the nanosheets is 0.93 nm ($d=\lambda/2\sin\theta$). According to the literature,[3] the information of the APy6 single crystal is listed below: $a=12.886$ Å, $b=13.548$ Å, $c=10.889$ Å; $\alpha=111.54$, $\beta=105.45$, $\gamma=102.90$, $V=1591.307$. The vertical distance of the face packing dimension is calculated as 9.35 Å ($d=V/(a\ b\ \sin\gamma)$), which agrees well with the XRD data of the nanosheets.

Atomic Force Microscope (AFM) Measurement

AFM was performed by using tapping-mode in air on a commercial multimode Nanoscope IVAFM. The samples were prepared by casting the solution on mica substrates. As shown in Fig. S3, the thickness of the nanosheets ranges from 24~35 nm with an average value of 27.66 nm, indicating that the nanosheet is composed of multi layers.

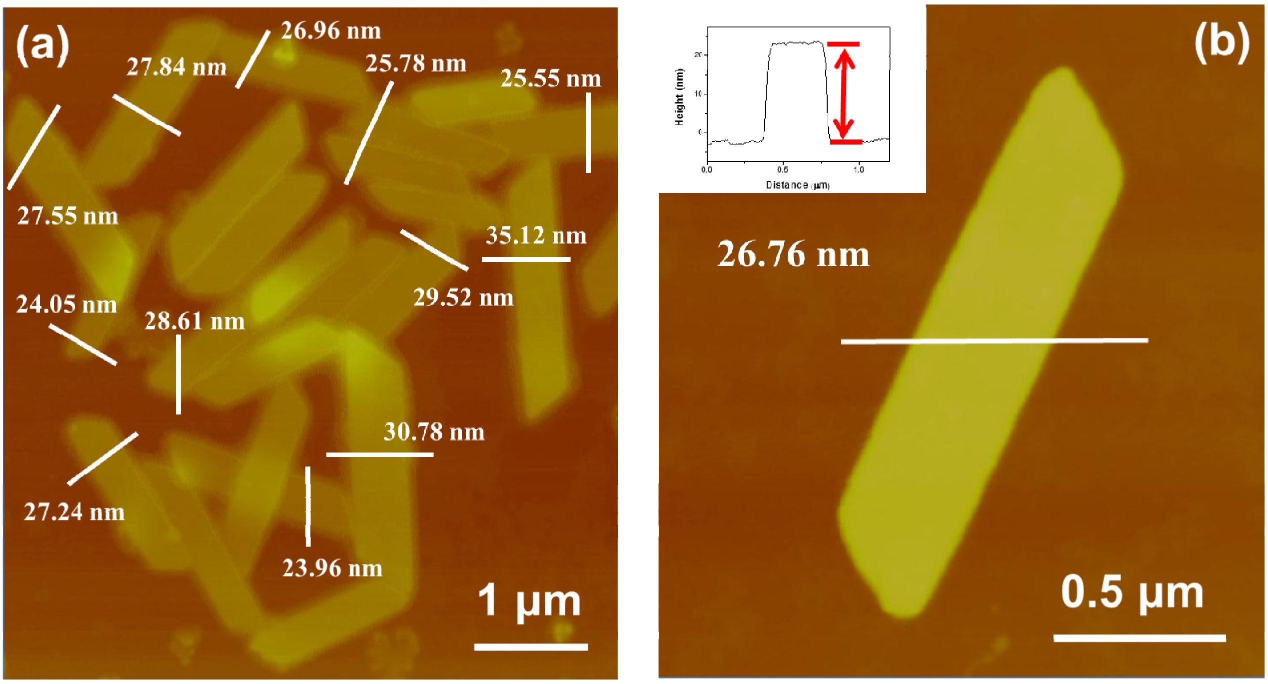


Fig. S3 Height characterizations of the nanosheets. The thickness of the nanosheets ranges from 24~35 nm with an average value of 27.66 nm.

TEM Electron Diffraction and Energy Dispersive Spectroscopy (EDS)

The electron diffraction and EDS were obtained on a JEM-2010 TEM Microscope. The samples were prepared by casting solution onto the copper grid. Then water was dropped on the grid and adsorbed away. This rinse procedure was repeated for five times to fully wash away the physical adsorbing SeG molecules. As shown in Fig. S4, Se atoms are found in the nanosheets, while in the blank area on the same grid no Se element is found.

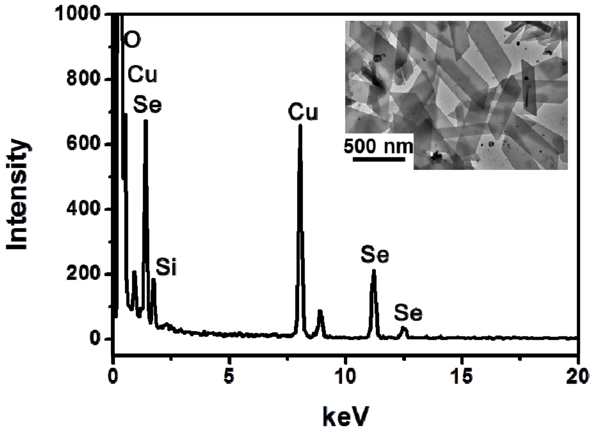


Fig. S4 TEM-EDS of the nanosheets. Results show Se atoms are existed in the nanosheets. (The TEM image on the upper right is the detected area.)

X-Ray Photoelectron Spectroscopy (XPS) Analysis

The XPS analysis was carried on an ESCA Lab220i-XL scanning X-ray microprobe. All solution samples were prepared with the typical procedure. The testing samples were prepared by casting sample solutions on clean Si substrates which were washed by piranha solution. Then water was dropped on the substrates and adsorbed away for three times to wash away the physical adsorbing SeG molecules before analysing (no rinse for the SeG and APy6 samples).

Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectrum was obtained from a Bruker IFS 66v/S. The samples were prepared the same way as the XPS samples.

ESI-Q-TOF Measurement

ESI-Q-TOF measurement was performed on a Bruker micrOTOF-Q mass spectrometer. As shown in Fig. S5, SeG/APy6 1:1 complex (plus K^+, m/z: 1471.1684, calcd: 1471.4107) is found. In addition, the isotope peaks indicate that three Se atoms are contained.

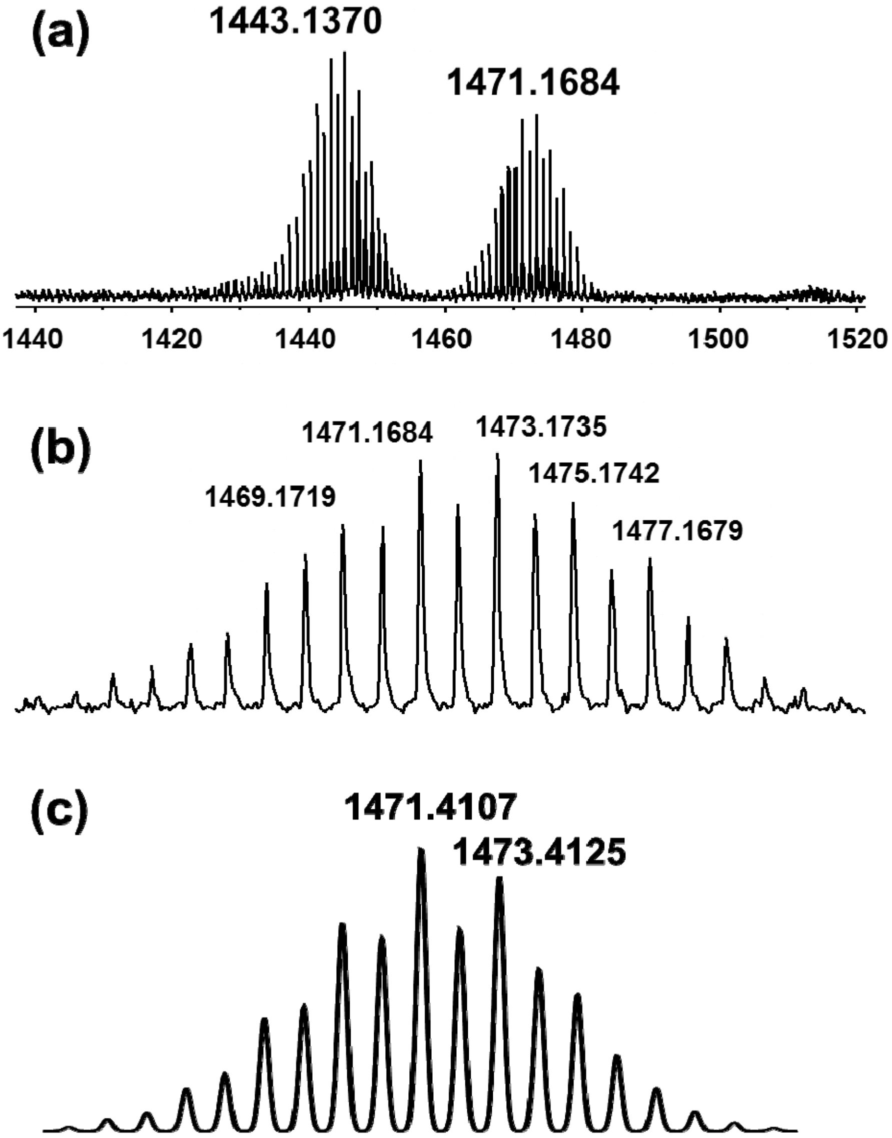


Fig. S5 ESI-Q-TOF MS of the sample solution. (a) The spectrum from 1440~1520 (m/z). (b) The enlargement spectrum of the 1471.1684 (m/z) peaks and (c) calculated spectrum. SeG/APy6 1:1 complex (plus K^+, m/z: 1471.1684, calcd: 1471.4107) is found and the isotope peaks indicate that three Se atoms are contained.

Gaussian Calculation

The frequency was calculated on Gaussian 09 program.[4] The geometry of model compound (Fig. S6) is optimized using B3LYP energy. 6-311G basis set for C, H, O atoms and LANL2DZ for Se atoms are used and the calculated frequency corresponding to C-Se (Ar-H_2*C*-*Se*-CH_2-) bond stretching mode is 571.86 cm^{-1}, basically coinciding with the experimental value (561 cm^{-1}) since the calculated value is usually a little higher than the experimental data.

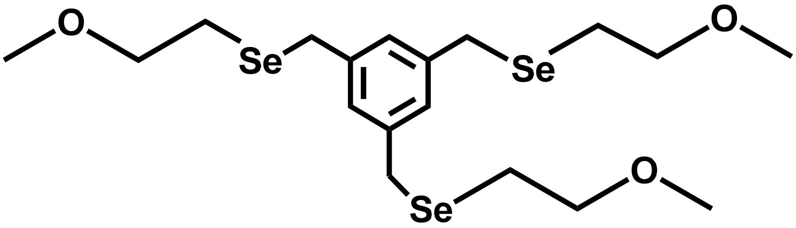


Fig. S6 The model molecule.

Reference

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3. Y. Miyazaki, T. Kanbara and T. Yamamoto, *Tetrahedron Lett.*, 2002, **43**, 7945-7948.
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