Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

FOR:

In situ formation and solid state-state oxidation of a triselenane NSeN-pincer MOF†

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Experimental Section

A. General

Materials. Ligand syntheses were peformed under a N_2 atmosphere using standard Schlenk techniques. Sodium (99%; sticks, in mineral oil, Alfa Aesar), sodium borohydride (98%; Alfa Aesar), 2-chloronicotinic acid (98%; Combi-Blocks), selenium (99.5%; Aldrich), sodium hydroxide (98.9%, Fisher Chemicals), hydrazine monohydrate (98%; Alfa Aesar), hydrochloric acid (36%; Fisher Chemicals), and metal salts (Sigma-Aldrich) were used as received. Triphenylphosphine selenide was prepared by reaction of Se with triphenylphosphine in Tetrahydrofuran at room temperature overnight. All solvents (Fisher Scientific) were pre-dried and degassed using an Innovative Technologies Solvent Purification System or dried using known literature procedures and stored over 4 Å molecular sieves.

FT-IR. FT-IR data were collected using a Thermo Scientific Nicolet iS50 spectrometer equipped with an ATR apparatus.

TGA Analysis. TGA analyses were performed on a TA Instruments Q50 analyzer using high purity N_2 as the carrier gas in the range of 25–800 °C. A ramp rate of 3.50 °C s^{-1} was applied between 25–500 °C and 5.00 °C s^{-1} between 500–800 °C.

NMR Studies. Solution ^1H and ^{13}C NMR were collected in-house using an Agilent Technologies 400-MR NMR Spectrometer or a Bruker AVANCE III 500 NMR spectrometer fitted with a BBFO Prodigy liquid nitrogen CryoProbe. Data was analyzed using Mestrelab MNOVA NMR data processing software.

Elemental microanalyses. Elemental analyses were performed by Midwest Microlab LLC (Indianapolis).

X-ray Diffraction. Powder X-ray diffraction (PXRD) experiments were performed in borosilicate capillaries in a Rigaku R-Axis Spider diffractometer using CuK_α radiation with data collected in the range 4–40° 2θ. Simulated PXRD patterns were generated using single crystal reflection data via the SimPowPatt facility in PLATON.

For all single crystal studies, a suitable crystal was mounted on a thin glass fiber loop using perfluoropolyether oil, which was frozen in situ by a nitrogen gas Cryostream flow. Data was collected at 100 K using CuK_α radiation (1.7902 Å) on an Agilent Super Nova diffractometer equipped with an AtlasS2 CCD, and Oxford 700 low-temperature attachment. The initial structure was solved by direct methods and structural refinements were made using the SHELXL-97 software suite.

Gas sorption studies. Samples were activated under reduced pressure at 75 °C prior to gas uptake experiments. Gas adsorption isotherms were recorded on a Quantachrome Autosorb-1 system; all gases (99.995+%) were purchased from Praxair. Gas sorption studies on Ni-SeCM-1 were carried out using a volumetric sorption analyzer (Quantachrome). Gas adsorption-desorption isotherms for these samples were collected at 77 K (N_2, H_2, O_2) and 196 K (CO_2, CH_4) after dehydration under vacuum ($< 10^{-5}$ Torr).

Solid UV-vis spectrophotometry. Solid-state UV-Vis-NIR spectra were collected on a Cary 5000UV-VIS NIR spectrophotometer, equipped with an equipped with an DRA-2500 integrating sphere at room temperature (298K). Samples were prepared by sticking to a black conductive tape.

B. Synthesis

*Procedure for 2,2′-Diselanediyldinicotinic Acid (**2**).* The compound was synthesized using a modified literature procedure.[1] A 250 cm^3 Schlenk flask fitted with reflux apparatus and magnettic stirrer was charged with sodium metal (0.38 g, 16.5 mmol) and dry ethanol (20 cm^3), which was cooled to 0 °C using an ice water bath. Next, $NaBH_4$ (0.062 g, 1.66 mmol) was directly added. After stirring for 5 min, selenium powder (0.9 g, 11.4 mmol) was introduced and the mixture was stirred at room temperature for 1 h, followed by another 0.5 h upon slow warming to 70 °C. The resulting dark reddish reaction mixture was cooled to room temperature, and 2-chloronicotinic acid (**1**; 1.82 g, 11.56 mmol) was added in small portions over 20 min, followed by addition of a further 20 cm^3 of dry ethanol. The reaction mixture was stirred at 70 °C for 3 h, and the resulting greenish yellow slurry was concentrated and subsequently acidified by the addition of 10% HCl. The yellow precipitate was collected by centrifugation (6000 rpm, 5 min). After decanting away the supernatant, the solids were washed three times with water followed by further centrifugation and allowed to air-dry. The crude product was purified by column chromatography (silica gel, 70:30 dichloromethane/methanol) to give the title compound as yellow powder. Yield: 28%. ^{1}H-NMR (400 MHz, DMSO-d_6): $\delta = 7.30$ (dd, 1H), 8.21 (dd, 1H), 8.55 (dd, 1H). HRMS (ESI$^+$): Calcd. for $C_{12}H_9N_2O_4Se_2$([M+H]$^+$), 404.8890, found, 404.8898. ν_{max} (solid/cm^{-1}): 2957 w, 2870 w, 2800 w, 2702 w, 2651 w, 2556 w, 2100 w, 1963 w, 1659 s, 1569 s, 1547 s, 1496 w, 1472 w, 1445 s, 1420 s, 1383 s, 1299 s, 1238 s, 1225 s, 1181 w, 1151 s, 1120 s, 1063 s, 1053 s, 991 w, 967 w, 888 s, 818 s, 758 s, 705 s, 641 m, 555 s, 476 s, 446 w, 424 w, 413 m.

*Procedure for 2-selenonicotinic acid (**3**).* **2** (1.0 g, 2.47 mmol) was suspended in degassed H_2O (20 cm^3) in a 100 cm^3 schlenk flask and aqueous NaOH (1.0 M, 5.5 mmol) was added to give a clear yellow solution. Hydrazine monohydrate (362 µL, 7.43 mmol) was added and the reaction mixture was stirred at 60 °C for 4 h. After cooling to room temperature, the reaction solution was precipitated with excess degassed aqueous HCl (5.0 M). The yellow precipitate was isolated by centrifuge, washed three times with a small amount of degassed H_2O, followed by centrifugation (6000 rpm, 5 min). After decanting away the supernatant, the solid was dried under flowing N_2. The resulting yellow powder was dispersed in H_2O and heated at 60 °C under N_2 for 2h, then subjected to hot filtration through a medium porosity frit under N_2. The filtrate was freeze-dried to afford pure product as yellow solid. Yield: 60%. ^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 7.20 (dd, 1H), 8.06 (dd, 1H), 8.23 (dd, 1H). ^{13}C-NMR (DMSO-*d*$_6$, 100 MHz): δ = 116.8, 136.0, 141.7, 143.7, 166.3, 168.3. HRMS (ESI$^-$): Calcd. for $C_6H_4NO_2Se([M-H]^-)$, 201.9413, found, 201.9417. ν_{max}(solid/cm^{-1}): 3178 w, 3084 w, 3014 w, 2947 w, 2878 w, 2792 w, 2680 w, 2351 br m, 2135 w, 2088 w, 2004 w, 1926 w, 1868 w, 1665 s, 1593 s, 1574 s, 1523 w, 1491 s, 1436 s, 1387 s, 1323 m, 1311 m, 1223 s, 1187 s, 1131 m, 1100 m, 1068 m, 1053 m, 1087 m, 984 w, 931 m, 821 m, 790 w, 749 s, 698 m, 633 s, 533 s, 492 s, 427 m, 409 w.

Procedure for Ni-SeCM-1. **3** (5.0 mg, 0.025 mmol) and $Ni(BF_4)_2 \cdot 6H_2O$ (17mg, 0.05mmol) were co-dissolved in a DMF/H_2O mixture (v/v 1:2, 5 cm^3; degassed by bubbling N_2 prior to use) under an inert (N_2) atmosphere. The clear yellow solution was sonicated briefly, before heating in a 20 cm^3 scintillation vial at 75 °C for 4-5 d in a graphite thermal bath. The green crystalline solid was isolated by decantation of the mother liquor, and washed with methanol followed by decanting away any impurities. The isolated crystals were dried in air. Ni-SeCM-1 could also be obtained by the same procedure except using **2** (10 mg, 0.025 mmol) in place of **3** in a DMF/H_2O mixture (v/v 2:3, 5 cm^3). Average yield: 65%. Ni-SeCM-1 could also be synthesized by co-dissolving $Se{=}PPh_3$ (4.3 mg0.0125 mmol) with **3** (5.0 mg, 0.025 mmol) and $Ni(BF_4)_2 \cdot 6H_2O$ (17mg, 0.05mmol) in a DMF/MeOH/H_2O mixture (v/v 1:1:2, 5 cm^3). The mixture was heated in a 20 cm^3 scintillation vial at 75 °C for 4-5 d in a graphite thermal bath. Under this condition, the crystals obtained were larger in size as long rods. Average yield: 80%. Anal. calcd. for $C_{12}H_8N_2O_5Se_3Ni$: C, 25.93; H, 1.45; N, 5.04. Found: C, 25.79; H 1.72; N, 4.72; ν_{max} (solid/cm^{-1}): 3087 w, 2917 br s, 2240 br w, 1590 s, 1561 s, 1547 s, 1456 m, 1401 m, 1379 s, 1248 w, 1222 w, 1176 m, 1114 w, 1082 s, 1058 m, 1024 w, 980 w, 953 br m, 831 s, 775 s, 718 s, 672 m, 575 m, 487 m, 451 s.

Procedure for Co-SeCM-1. Synthesis and isolation of Co-SeCM-1 followed the procedure for Ni-SeCM-1, except using $CoCl_2 \cdot 6H_2O$ and degassed solvent mixture DMF/Dioxane/H_2O (v/v = 1:1.5:1.5, 5cm^3). Average yield: 43%. Anal. calcd. for $[C_{12}H_8N_2O_5Se_3Co] \cdot 2CH_3OH$: C, 27.12; H, 2.60; N, 4.52. Found: C, 27.65; H, 2.00; N, 4.60. ν_{max} (solid/cm^{-1}): 3090 w, 2953 br s, 2841 w, 1588 s, 1558 s, 1543 s, 1456 m, 1400 m, 1372 s, 1287 w, 1245 m, 1228 w, 1174 m, 1115 m, 1074 s, 1056 m, 976 w, 921 br m, 886 w, 872 m, 825 s, 773 s, 711 s, 666 m, 613 m, 574 m, 482 m, 445 s.

Procedure for SeCM-1 post-synthetic oxidation: Ni-SeCM-1 (30 mg) was treated with an aqueous H_2O_2 solution (5% w/w, 15 cm^3) in a 20 cm^3 scintillation vial and left at room temperature for 3 h. The crystals turned from green to almost colorless. The resulting crystals were isolated by washing and decanting with deionized water and allowed to dry in air. When treated with less concentrated H_2O_2 (20 eq., 1% w/w), the green crystals visibly evolved a red amorphous by-product, which became off-white/pale green after being left at room temperature for 1-5 d, or further addition of H_2O_2. Yield: 50%. Anal. calcd. for $C_{12}H_{16}N_2O_{12}Se_2Ni$: C, 24.15; H, 2.70; N, 4.69. Found: C, 24.31; H, 2.63; N, 4.64. ν_{max} (solid/cm^{-1}): 3547 w, 3426 w, 3272 w, 2943 br w, 2354 br w, 1599 s, 1558 s, 1460 w, 1446 w, 1410 w, 1371 s, 1330 m, 1259 w, 1227 m, 1170 m, 1111 m, 1087 m, 1051 w, 1015 w, 979 w, 899 w, 814 s, 770 s, 713 m, 654 s, 557 s, 501 m, 456 m, 415 s.

References:

1. L. Sancineto, A. Mariotti, L. Bagnoli, F. Marini, J. Desantis, N. Iraci, C. Santi, C. Pannecouque, O. Tabarrini, *J. Med. Chem.* **2015**, 58, 9609.

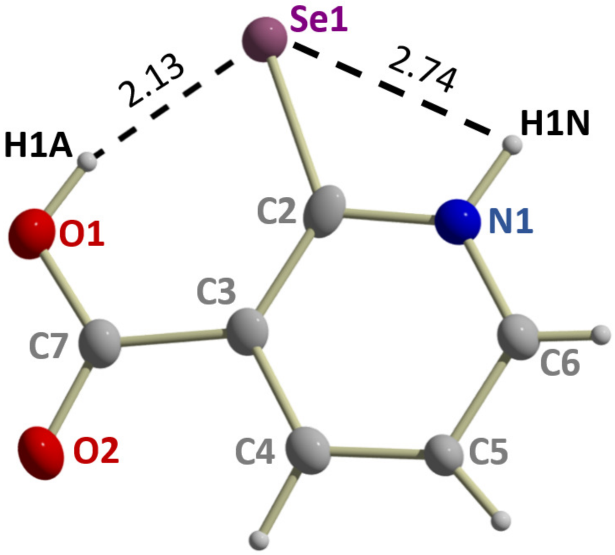

Figure S1. X-ray crystal structure of the ligand **3**, drawn with thermal ellipsoids at the 50% probability level; H-atoms were located in the difference map and H···Se contact distances are shown in Å.

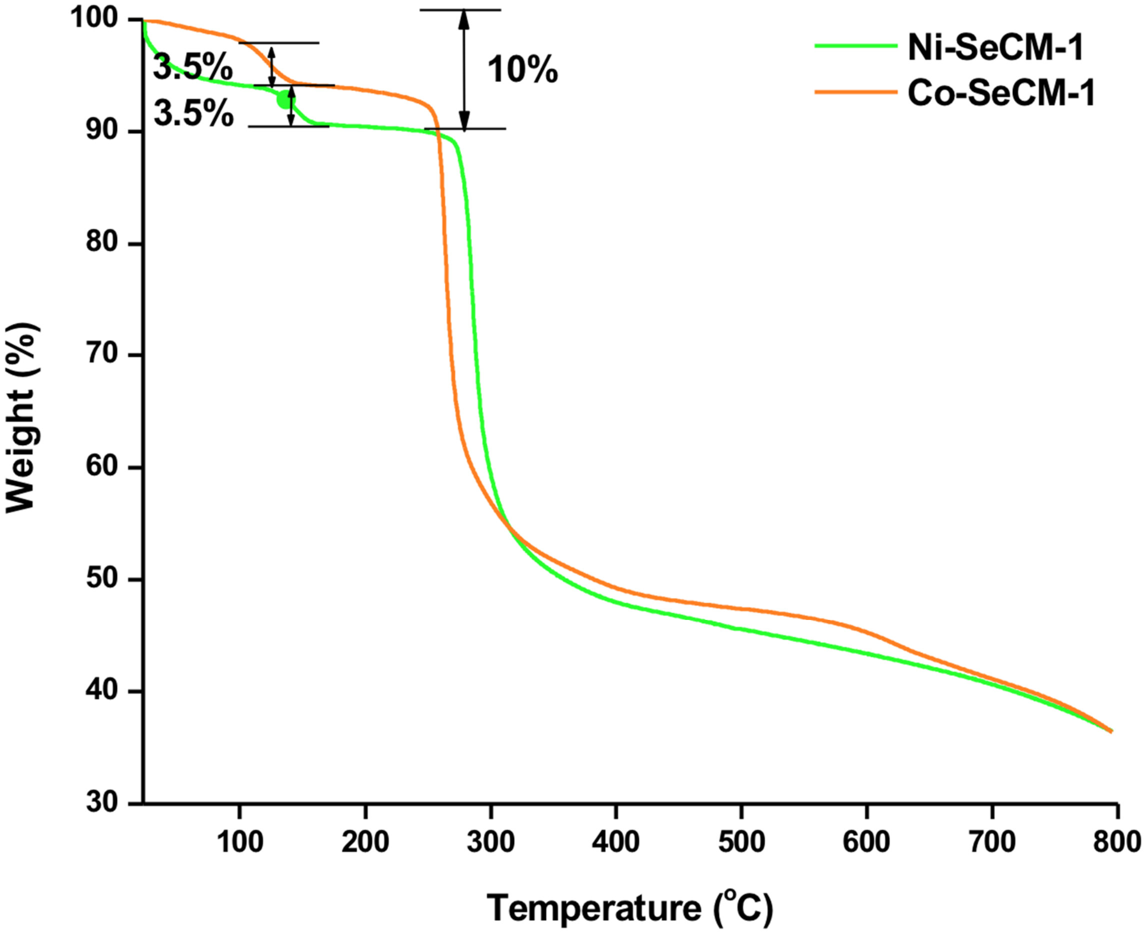

Figure S2. Thermogravimetric Analysis (TGA) data for Ni-SeCM-1 and Co-SeCM-1.

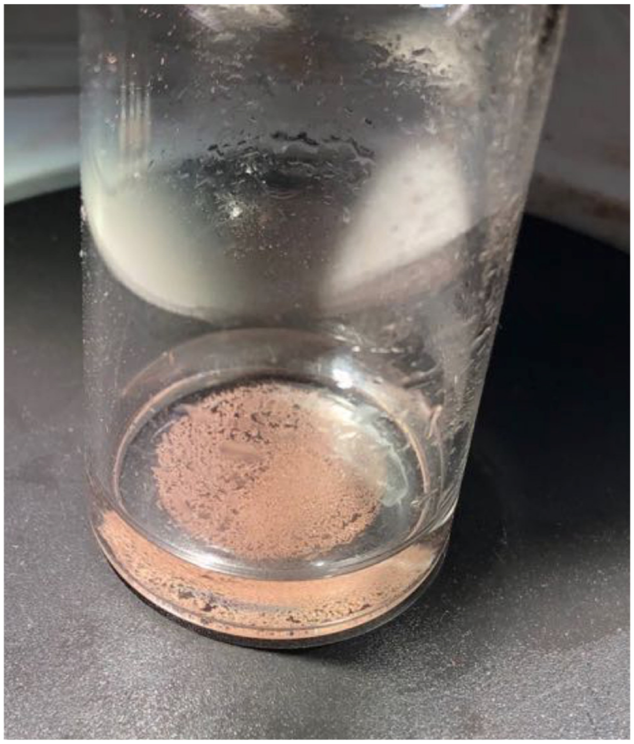

Figure S3. Picture of Ni-SeCM-1 upon initial treatment with H_2O_2 showing bulk evolution of amorphous Se.

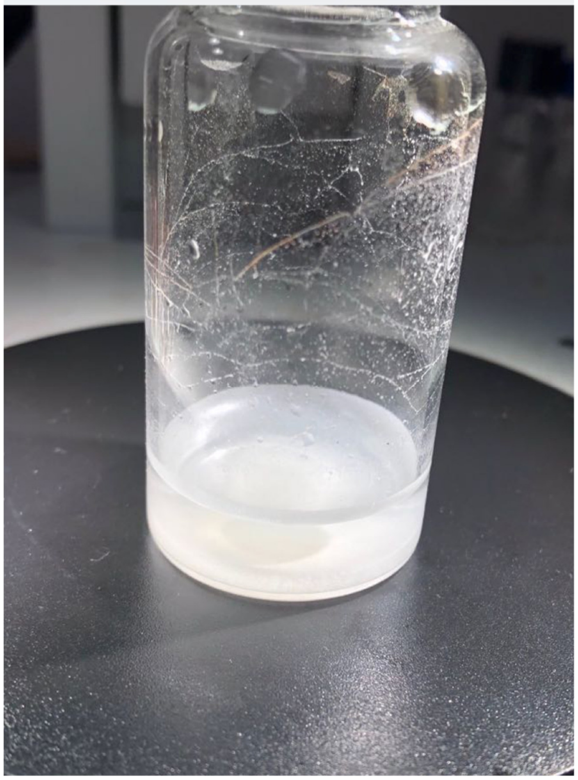

Figure S4. Picture of the final post-oxidation product after prolonged exposure to H_2O_2.

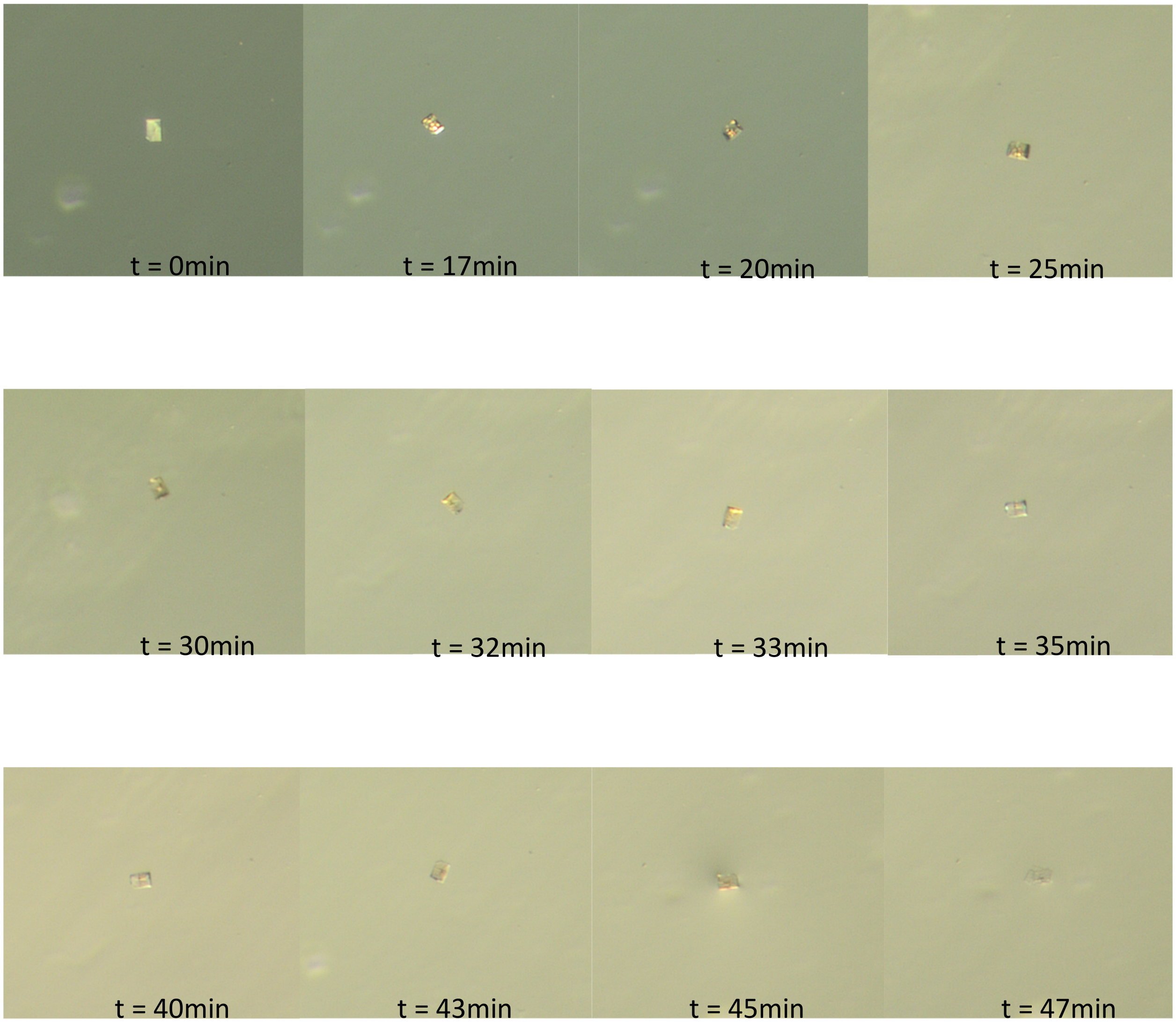

Figure S5. Microscopic images of Ni-SeCM-1 single crystal in 3% H_2O_2 in excess.

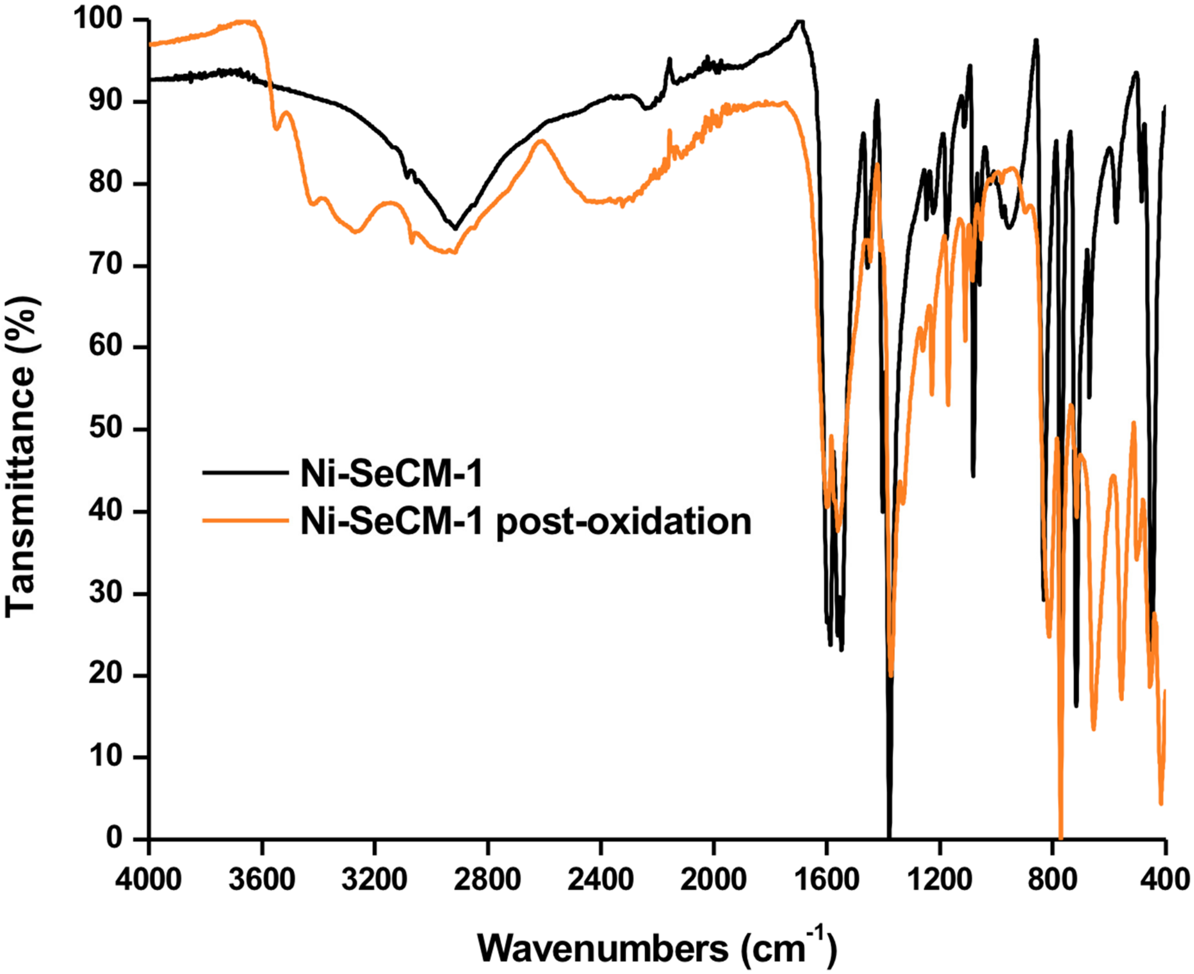

Figure S6. Infrared spectral comparison of Ni-SeCM-1 (black) and Ni-SeCM-1 (orange) post-oxidation with H_2O_2.

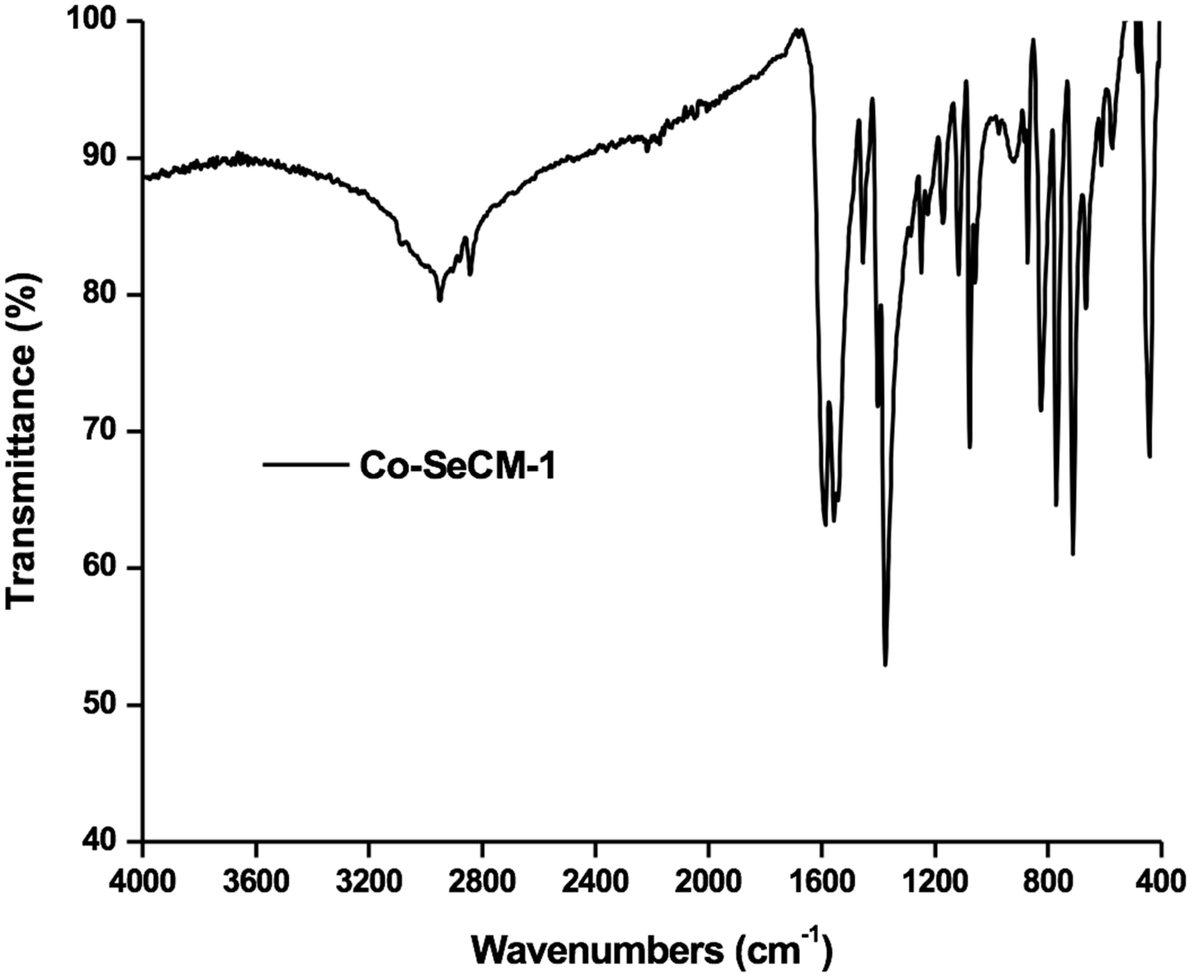

Figure S7. Infrared spectral comparison of Co-SeCM-1.

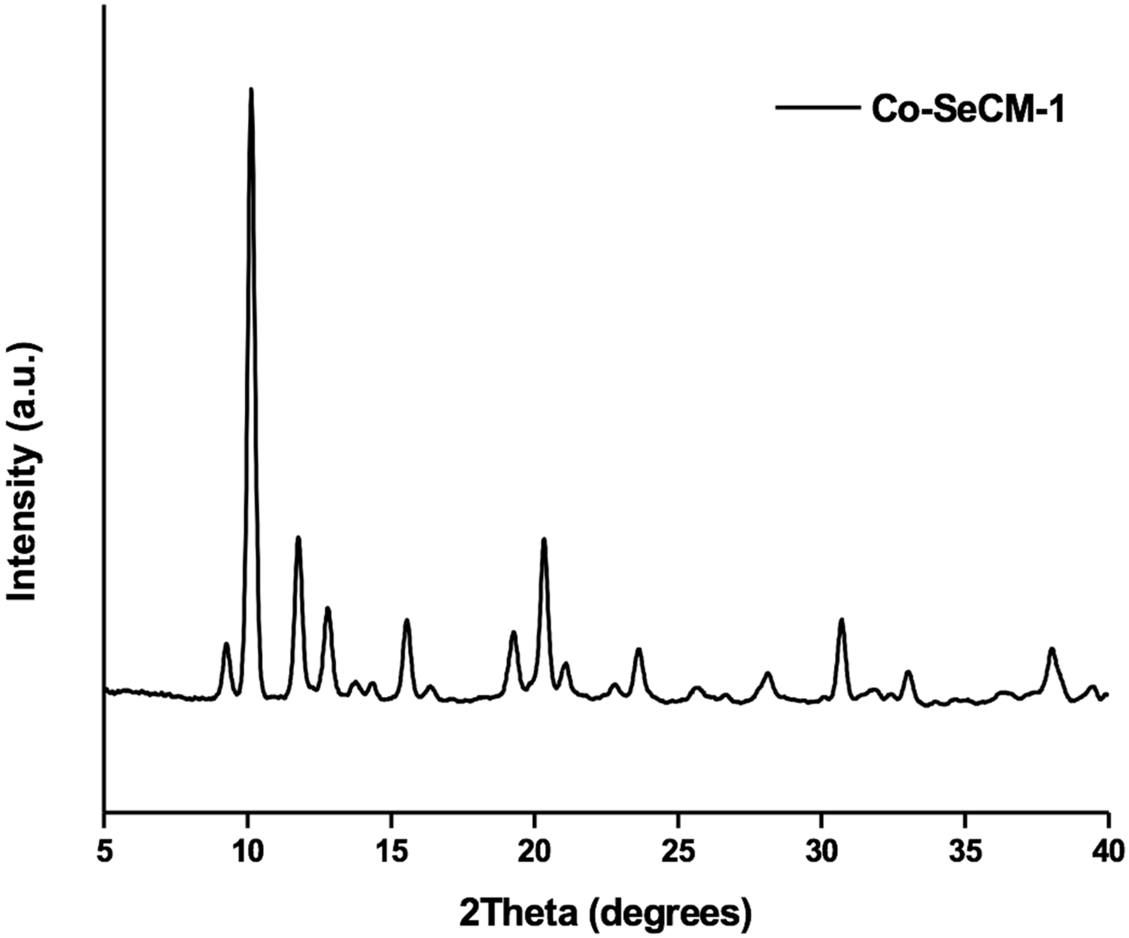

Figure S8. PXRD pattern of Co-SeCM-1.

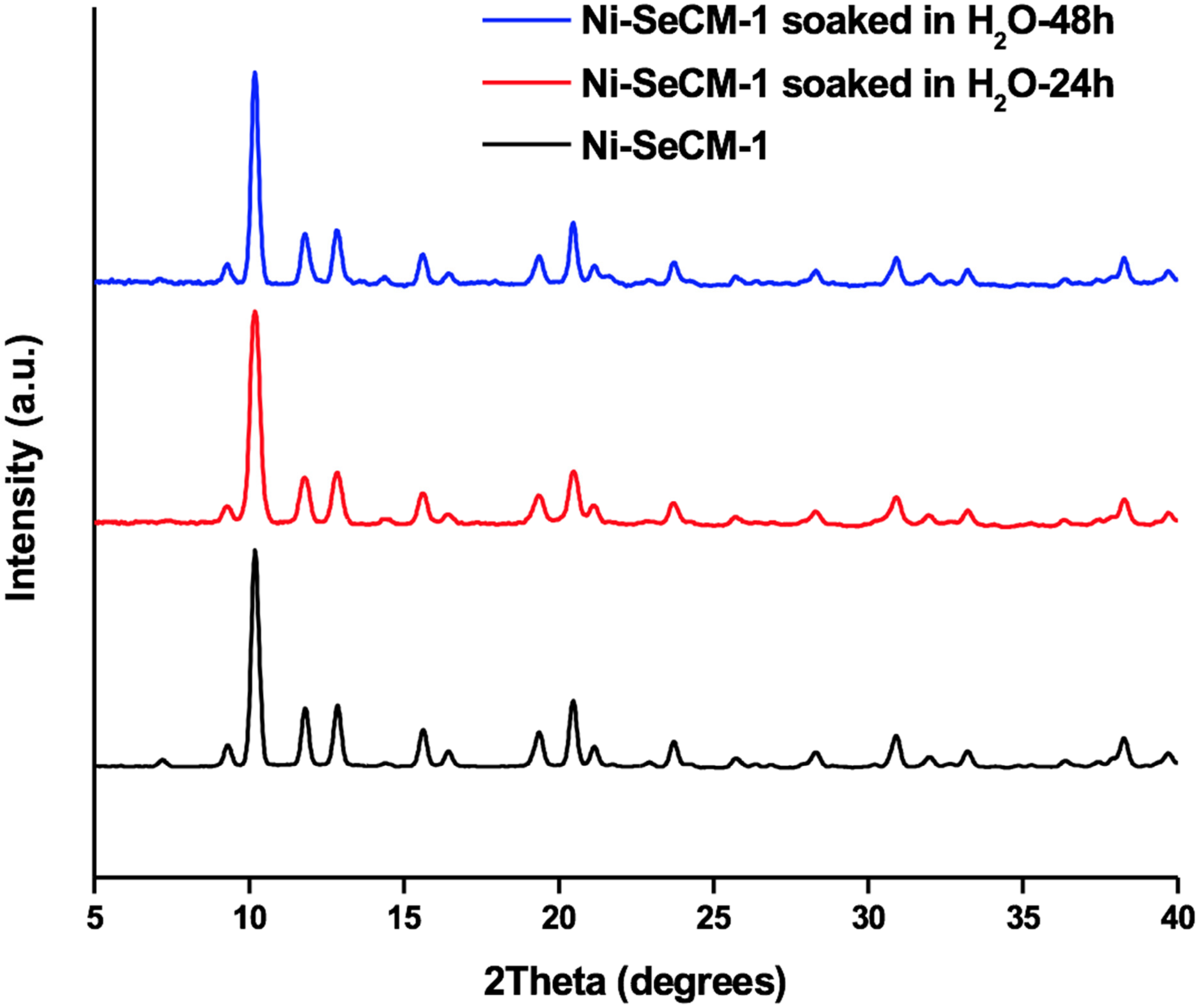

Figure S9. PXRD patterns of Ni-SeCM-1 in H_2O.

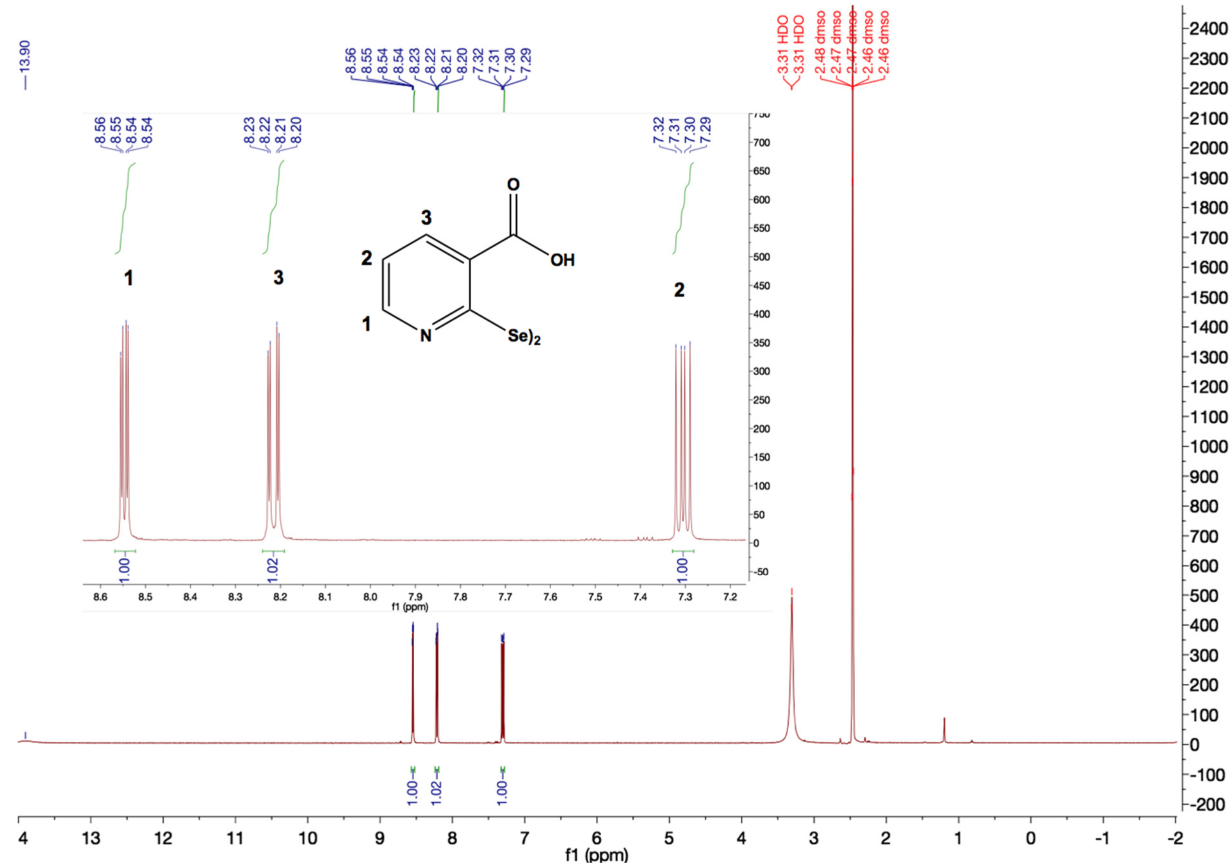

Figure S10. ^{1}H NMR spectrum of *2,2'-diselanediyldinicotinic acid* **1**.

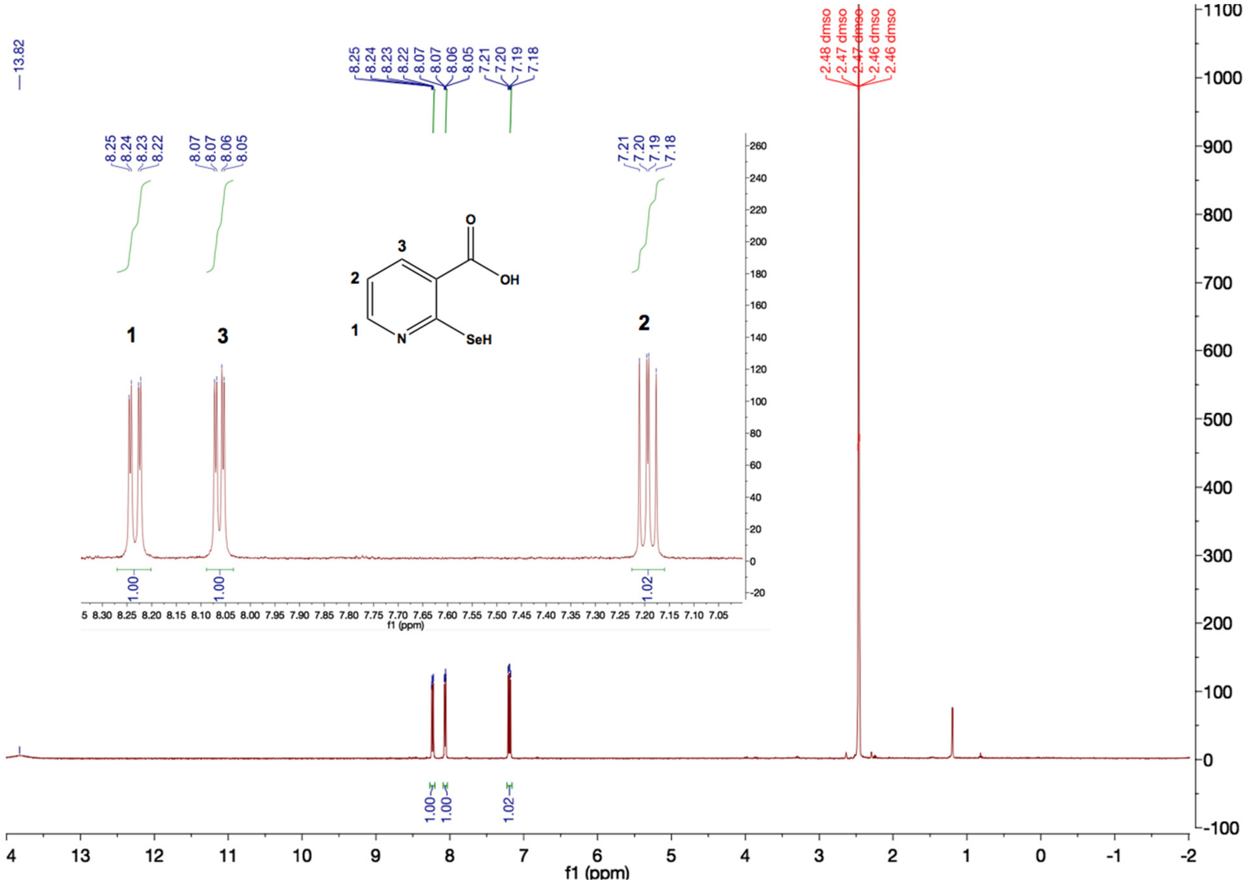

Figure S11. ^{1}H NMR spectrum of *2-selenonicotinic acid* **2**.

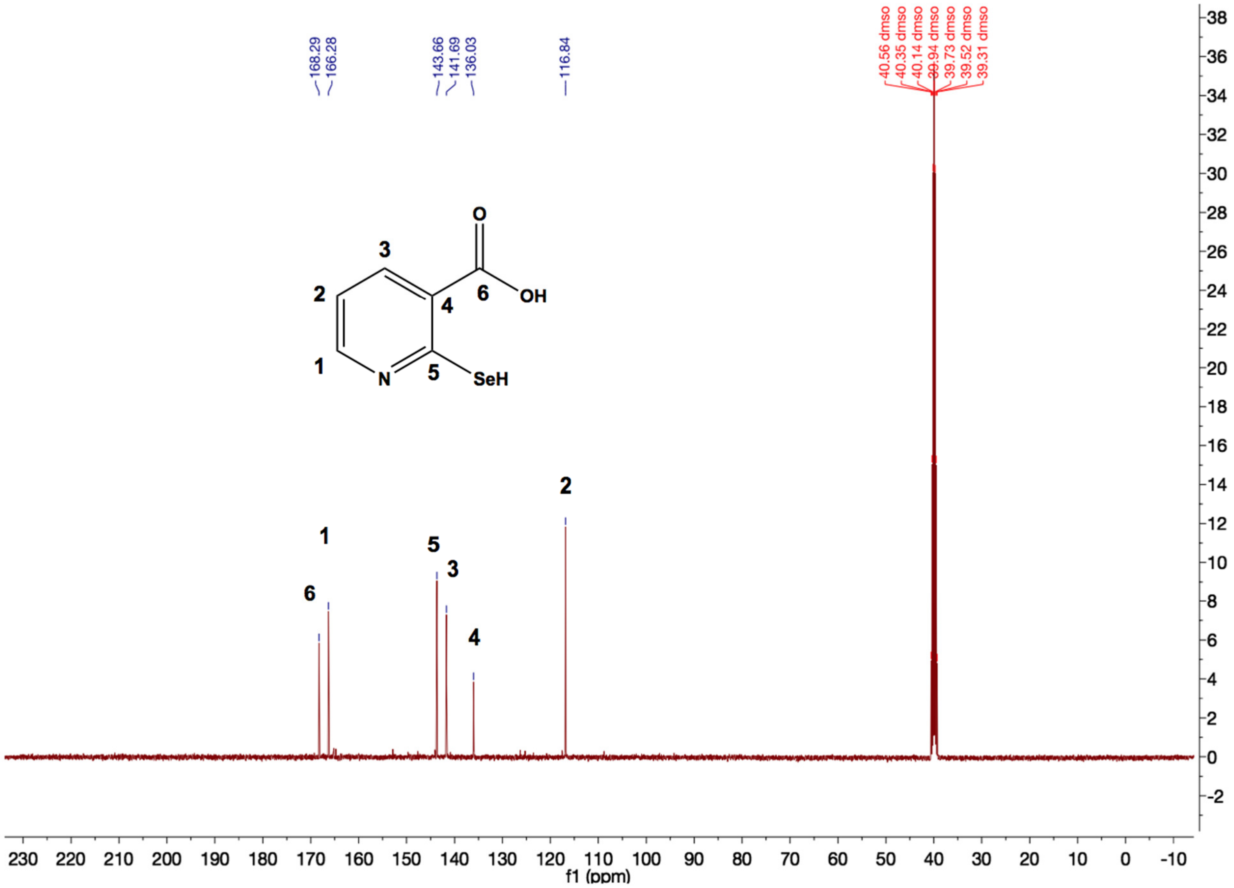

Figure S12: ^{13}C NMR spectrum of *2-selenonicotinic acid* **2**.

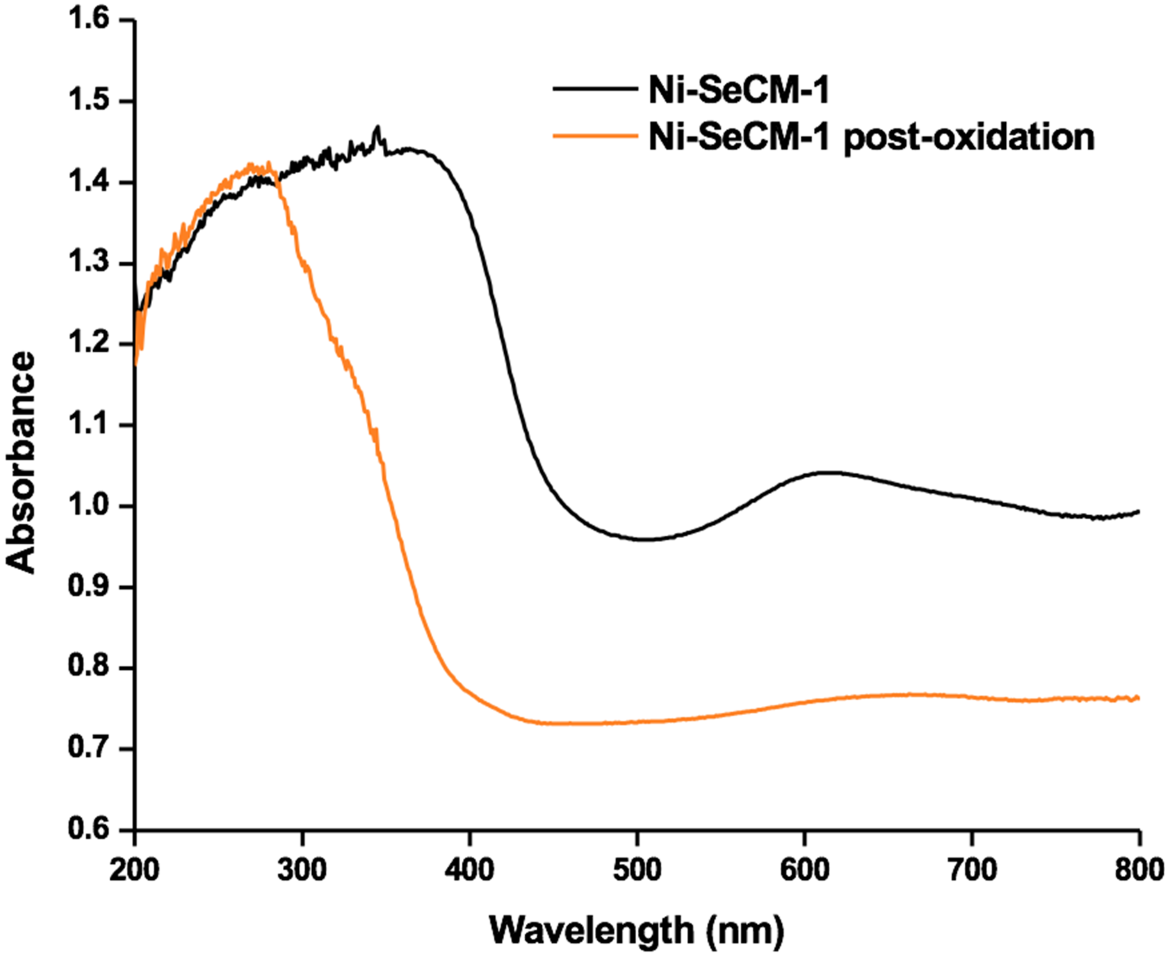

Figure S13: Solid UV-vis spectra for Ni-SeCM-1 (black) and the post-oxidation material (orange), showing loss of the d-d band *ca*. 620 nm and a marked shift in the L/M-CT band.