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Organically templated zinc selenite compounds: synthesis, structural chemistry and DFT calculations

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EXPERIMENTAL PART

All analytical grade reagents and solvents were obtained commercially (Sigma-Aldrich) and used without prior treatment. Reactions were performed with open atmosphere. Solid-state ^{77}Se NMR spectra were recorded at room temperature on a Bruker Avance III HD 600 MHz operating at 114.45 MHz with 4 mm MAS BB/1H probe spinning at 12 kHz. The acquisition time approximately 35 ms, 5 sec recycle delay and 8 ms contact time. ^{77}Se NMR chemical shifts are given with respect to the signals of H_2SeO_3. ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technologies). All MS results are given in the form: m/z, assignment. Elemental analyses (CHN) were determined using a VARIO EL (Elementar Analysen systeme GmbH). FT-IR spectra were recorded using the ATR sampling mode on a Bruker VERTEX 70 spectrophotometer with Platinum ATR accessory (diamond crystal) in the 4000–30 cm^{-1} region. Confocal FT-Raman spectra were recorded on a Bruker Senterra spectrophotometer using a 785 nm laser line, in the 3500–50 cm^{-1} region. Single-crystal data were collected with a Bruker D8 Venture diffractometer operating with an Incoatec X-ray source with Montel two-dimensional optics, Mo-Kα radiation (λ = 0.71073 Å) and a Photon 100 detector. The structures were solved by dual space methods using Bruker XT and refined with Bruker XL on F^2 using anisotropic temperature parameters for all non-hydrogen atoms.[1] The hydrogen atoms positions were calculated starting from the idealized positions. Crystal data and further details regarding the data collection and refinement for **1** and **2** are shown in Table S1. CCDC 1977087 and 1977088 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk; from the Cambridge Crystallographic Data Centre at 12 Union Road, Cambridge CB2 1EZ, UK; via fax: (+44) 1223-336-033; or via e-mail: deposit@ccdc.cam.ac.uk. X-ray powder diffraction data were collected at 298 K with a Bruker D8 Advance diffractometer operated using Cu K α radiation (λ = 1.5418 nm). PXRD patterns were obtained by scanning samples from 4 to 60°, with a step size of 0.2° and 600 ms dwell time. Chemical composition was analyzed by Energy-dispersive X-Ray Spectroscopy (EDS) using a Quantax 75 (Bruker Nano GmbH, Germany) device accomplished to JEOL 55 M6360 microscopy. The particulate material was deposited on stubs covered with double-sided carbon adhesive tape. The stubs were then tapped on gently to remove any excess of material not adhered to the tape. Subsequently, particles remaining on the stub were gold coated on an ion sputter. Diffuse reflectance spectra of **1** and **2** were performed using a UV-Vis 1650-PC Shimadzu spectrometer, fitted with a diffuse reflectance accessory, over the UV-Vis wavelength range of 200 to 800 nm. The optical band gap energy (E_g) for **1** and **2** was estimated following methodology described by Lang and coworkers.[2,3] The E_g value was obtained by extrapolating the steep absorption edge to the crossing with the energy axis.[4]

Preparation of [$Zn_4(\mu$-$SeO_3)_2(\mu_4$-$SeO_3)_2$(bipy)$_4$]·$11H_2O$ (1): In a test tube, 0.022 g (0.10 mmol) of $Zn(CH_3COO)_2·2H_2O$, 0.053 g (0.20 mmol) of $Na_2SeO_3·5H_2O$ and 0.016 g (0.10 mmol) of 2,2'-bipy were suspended in 5 mL of a 1:5 mixture of deionized water and methanol. The test tube was placed in a stainless-steel reactor (Figure S10) and the reactor was closed. The system was heated in an Oxylab OXY-E – 1 oven equipped with a NOVUS N1200 temperature controller, according to the parameters described in Table S3. When the oven temperature was lower than 40 °C, the reactor was opened, and the transparent solution was transferred to a beaker. After twenty days of slow evaporation, colorless crystals (blocks) were obtained. Yield: 22%, based on $Zn(CH_3COO)_2·2H_2O$ taken. *Properties*: air stable, colorless crystalline solid. Elemental analysis: Calcd. for $C_{40}H_{54}N_8O_{23}Se_4Zn_4$ (1592.23 g mol^{-1}): C = 30.17% N = 7.04% H = 3.42%. Found: C = 30.00% N = 6.93% H = 3.26%. FT-IR (ATR, cm^{-1})$^{5-9}$: 3331 [ν(O-H)]; 3114, 3079 [ν_s(C-H)$_{Ar.}$]; 1596, 1576, 1493, 1474, 1442, 1412 [ν_s(C=C/C=N)]; 1316, 1252 [ν_s(C-N)]; 1161, 1056, 1043, 1012 [δ_{ip}(C=C-H)]; 923, 857, 825 [$\nu_s(SeO_3)^{2-}$]; 766, 734, 701 [$\nu_{as}(SeO_3)^{2-}$]; 647, 619 [δ_{op}(C=C-H)]; 461 [δ_{op}(C=C-C)$_{Ar.}$]; 360 [ν(Zn-O)]; 230 [ν(Zn-N)]. FT-Raman (cm^{-1})$^{5-9}$: 1598, 1567, 1494, 1475, 1434 [ν_s(C=C/C=N)]; 1318, 1286, 1269, 1250 [ν_s(C-N)]; 1163, 1060, 1023 [δ_{ip}(C=C-H)]; 855, 830, 814 [$\nu_s(SeO_3)^{2-}$.]; 768 [$\nu_{as}(SeO_3)^{2-}$]; 652, 629 [δ_{op}(C=C-H)]; 463 [δ_{op}(C=C-C)$_{Ar.}$]; 360 [ν(Zn-O)]; 231 [ν(Zn-N)] (ν_s = symmetric stretching; ν_{as} = asymmetric stretching; δ_{ip} = in-plane deformation; δ_{op} = out-of-plane deformation). ^{77}Se NMR (solid-state, 114.45 MHz) δ (ppm) = 1291.47 and 1285.97. ESI$^+$ MS (*m/z*): [$Zn_4Se_3O_9C_{40}H_{32}N_8$ + K]$^{3+}$ 435.0761 (found), 435.4297 (calcd.). Crystal data and further details of the data collection and refinement are shown in Table S1. Molecular structure of **1** in 50% probability ellipsoids is depicted in Figure S11.

Preparation of [$Zn_4(\mu$-$SeO_3)_2(\mu_4$-$SeO_3)_2$(phen)$_4$]·$9H_2O$ (2): In a test tube, 0.022 g (0.10 mmol) of $Zn(CH_3COO)_2·2H_2O$, 0.053 g (0.20 mmol) of $Na_2SeO_3·5H_2O$ and 0.018 g (0.10 mmol) of 1,10-phenathroline were suspended in 5 mL of a 1:5 mixture of deionized water and methanol. The next step in the procedure is the same as reported for compound **1**. After twenty days colorless crystals (blocks) were obtained. Yield: 24%, based on $Zn(CH_3COO)_2·2H_2O$ taken. *Properties*: air stable, colorless crystalline solid. Elemental analysis: Calcd. for $C_{48}H_{50}N_8O_{21}Se_4Zn_4$ (1652.28 g mol^{-1}): C = 34.89% N = 6.78% H = 3.05%. Found: C = 34.28% N = 6.38% H = 2.58%. FT-IR (ATR, cm^{-1})$^{5-9}$: 3333 [ν(O-H)]; 3074 [ν_s(C-H)$_{Ar.}$]; 1622, 1602, 1578, 1515, 1492, 1423 [ν_s(C=C/C=N)]; 1338, 1308, 1222 [ν_s(C-N)]; 1101, 1052, 1038, [δ_{ip}(C=C-H)]; 978, 853, 817 [$\nu_s(SeO_3)^{2-}$]; 790, 758, 706 [$\nu_{as}(SeO_3)^{2-}$]; 638 [δ_{op}(C=C-H)]; 360 [ν(Zn-O)]; 290, 232 [ν(Zn-N)]. FT-Raman (cm^{-1})$^{5-9}$: 3058 [ν_s(C-H)$_{Ar.}$]; 1599, 1567, 1494, 1434 [ν_s(C=C/C=N)]; 1321, 1285, 1270 [ν_s(C-N)]; 1161, 1058, 1023, [δ_{ip}(C=C-H)]; 856, 817 [$\nu_s(SeO_3)^{2-}$]; 769 [$\nu_{as}(SeO_3)^{2-}$.]; 653, 629 [δ_{op}(C=C-H)]; 466 [δ_{op}(C=C-C)$_{Ar.}$]; 363 [ν(Zn-O)]. ^{77}Se NMR (solid-state, 114.45 MHz) δ (ppm) = 1311.97 and 1280.41. ESI$^+$ MS (*m/z*): [$Zn_2Se_2O_6$ + K]$^+$ 423.0685 (found), 423,8041 (calcd.); [$C_{12}H_8N_2$ + K]$^+$ 203,0592 (found), 203,1951 (calcd.). Crystal data and further details of the data collection and refinement are shown in Table S1. Molecular structure of **2** in 50% probability ellipsoids is depicted in Figure S12.

Density functional theory (DFT): DFT calculations were carried out on the fixed atomic positions of molecular units determined by X–ray diffraction for the compounds **1** and **2**. The total energy calculation was performed at the wB97XD/LANL2DZ ECP[10,11] level of theory applying Gaussian09[12].

Table S1. Crystallographic and structure refinement data for the compounds **1**-**2**.

	1	**2**
Formula	$C_{40}H_{54}N_8O_{23}Se_4Zn_4$	$C_{48}H_{50}N_8O_{21}Se_4Zn_4$
F.W. (g.mol^{-1})	1592.23	1652.28
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6069(6)	8.4181(5)
b (Å)	12.3824(8)	13.0306(7)
c (Å)	12.6845(8)	13.70108)
α (°)	100.648(2)	102.147(2)
β (°)	107.253(2)	103.589(2)
γ (°)	107.393(2)	91.969(2)
T (K)	100(2)	294(2)
V (Å^3)	1311.77(15)	1422.56(14)
Z	1	1
$\rho_{calc.}$ (g·cm^{-3})	2.016	1.929
μ (mm^{-1})	4.671	4.309
F(000)	790	818
Refl. collected	15888	45989
Refl. unique (R_{int})	8071 [0.0484]	8744 [0.0754]
R_1 [$I > 2\sigma(I)$]	$R_1 = 0.0401$	$R_1 = 0.0462$
wR_2 [$I > 2\sigma(I)$]	$wR_2 = 0.0865$	$wR_2 = 0.0716$
R_1 (all data)[a]	$R_1 = 0.0696$	$R_1 = 0.1108$
wR_2 (all data)[b]	$wR_2 = 0.0940$	$wR_2 = 0.0845$
Goodness-of-fit on F^2	1.015	1.003
Largest diff. peak and hole (e.Å^{-3})	1.227 and -1.020	0.662 and -0.837

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; [b]$wR_2 = \{\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for compounds **1**-**2**.

Bond lengths (Å)		**Bond angles (°)**	
1			
Zn(1)–O(1)	1.9781(16)	O(1)–Zn(1)–O(5)’	98.18(7)
Zn(1)–O(5)’	2.0651(18)	N(1)–Zn(1)–O(4)	87.50(8)
Zn(1)–O(4)	2.028(2)	O(1)–Zn(1)–O(4)	108.26(8)
Zn(1)–N(1)	2.127(2)	O(1)–Zn(1)–N(2)	105.58(8)
Se(1)–O(2)	1.658(2)	O(2)–Se(1)–O(3)	101.87(12)
Se(1)–O(3)	1.696(2)	O(2)–Se(1)–O(1)	102.48(13)
Se(1)–O(1)	1.7013(19)	O(3)–Se(1)–O(1)	103.45(9)
Se(2)–O(5)	1.7316(15)		
Zn(2)’···O(4)	2.6255(14)		
Zn(2)···O(4)’	2.6255(14)		
Cp···Cp	3.6032(2)		
2			
Zn(1)–O(1)	1.9765(15)	O(1)–Zn(1)–O(5)’	98.01(7)
Zn(1)–O(5)’	2.0894(17)	N(1)–Zn(1)–O(4)	86.67(8)
Zn(1)–O(4)	2.0347(17)	O(1)–Zn(1)–N(1)	105.72(10)
Zn(1)–N(1)	2.126(2)	O(1)–Zn(1)–O(4)	100.74(10)
Se1–O(1)	1.7002(18)	O(5)–Se(2)–O(4)	102.87(8)
Se1–O(2)	1.6575(18)	O(6)–Se(2)–O(5)	97.95(8)
Se2–O(5)	1.7209(15)	O(6)–Se(2)–O(4)	108.83(9)
Zn(1)···O(6)’	2.6799(1)		
Zn(1)’···O(6)	2.6799(1)		
Cp···Cp	3.6352(2)		

1 (’): -x+1,-y+1,-z
2 (’): -x+1,-y+1,-z+1

Table S3. Time (t) and temperature (T) used to obtain **1** and **2**.

n	t_n (minutes)[a]	T_n (°C)[b]
0	–	90
1	60	110
2	60	130
3	60	140
4	240	140
5	120	130
6	120	120
7	120	100
8	120	80
9	300	40
Total time: 20 h, with 4 h at 140 °C.		

a) time required for the oven to reach T_n; b) temperature in the reactor.

Table S4. Topological parameters for compound **1** (top) and **2** (bottom).

Contact	CP	Density	Laplacian	Ellipticity	G(r)	V(r)	H(r)	V/G	Einter (KJ)
Zn1−O	A	0.0722	0.3961	0.0387	0.0898	-0.103	-0.013	1.1468	-135.202
		0.0766	0.4326	0.0430	0.0972	-0.1113	-0.0141	1.1451	-146.130
Zn1−O	B	0.0603	0.3239	0.0502	0.0752	-0.085	-0.010	1.1412	-112.676
		0.0579	0.3033	0.0488	0.0711	-0.0814	-0.0103	1.1452	-106.9008
Zn1−O	C	0.0616	0.3504	0.0317	0.0796	-0.089	-0.009	1.1236	-117.444
		0.0624	0.3566	0.0363	0.0808	-0.0908	-0.0100	1.1232	-119.1418
Zn1−N	D	0.0543	0.2361	0.0331	0.0592	-0.071	-0.012	1.2111	-94.2488
		0.0537	0.2324	0.0291	0.0584	-0.0707	-0.0124	1.2116	-92.8701
Zn1−N	E	0.0648	0.3130	0.0453	0.0746	-0.088	-0.014	1.1910	-116.812
		0.0605	0.2805	0,0473	0.0680	-0.0816	-0.0136	1.1995	-107.1517
Zn1···O'	F	0.0190	0.0677	0.1926	0.0174	-0.018	-0.001	1.0756	-24.6982
		0.0172	0.0619	0.3354	0.0156	-0.0163	-0.0007	1.0437	-21.3394
Zn2−O	A’	0.0761	0.4295	0.0504	0.0965	-0.110	-0.013	1.1444	-144.9842
		0.0800	0.4627	0.0524	0.1033	-0.1181	-0.0148	1.1435	-155.05
Zn2−O	B’	0.0604	0.3301	0.0383	0.0761	-0.086	-0.010	1.1346	-113.2964
		0.0564	0.2970	0.0373	0.0696	-0.0793	-0.0098	1.1402	-104.12
Zn2−O	C’	0.0638	0.3679	0.0398	0.0831	-0.093	-0.010	1.1234	-122.4728
		0.0683	0.4072	0.0430	0.0908	-0.1017	-0.0109	1.1197	-133.50
Zn2−N	D’	0.0549	0.2405	0.0443	0.0600	-0.072	-0.012	1.2098	-95.3067
		0.0600	0.2765	0.0495	0.0674	-0.0809	-0.0135	1.2008	-106.18
Zn2−N	E’	0.0603	0.2789	0.0448	0.0677	-0.081	-0.013	1.1995	-106.648
		0.0547	0.2411	0.0403	0.0600	-0.0725	-0.0124	1.2074	-95.12

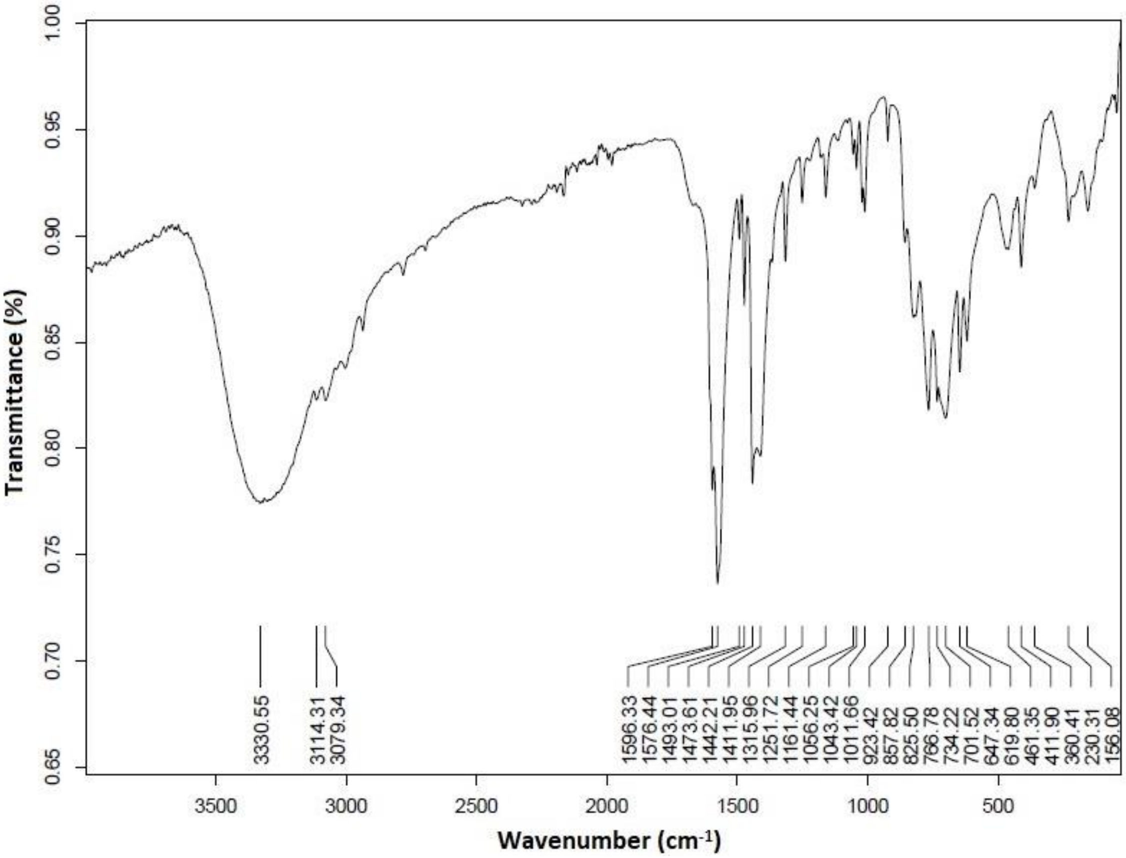

Figure S1. FT-IR spectrum for compound **1**.

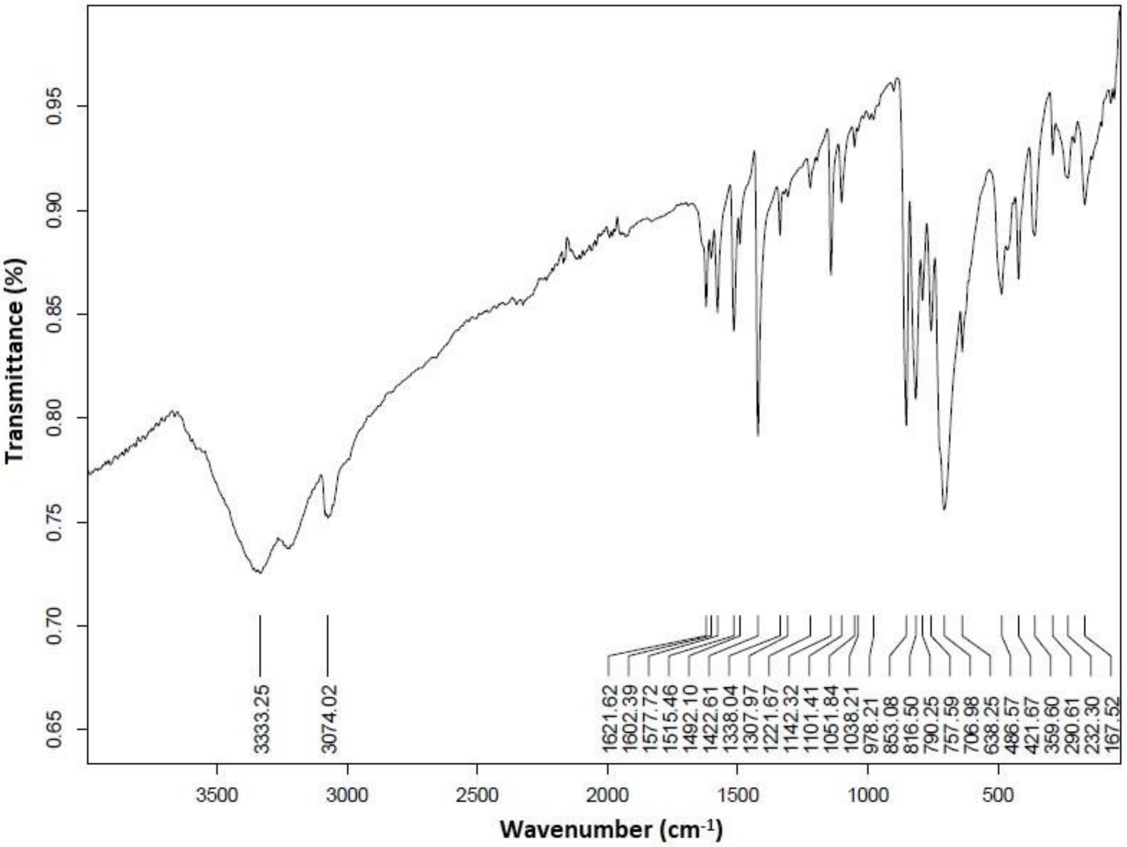

Figure S2. FT-IR spectrum for compound **2**.

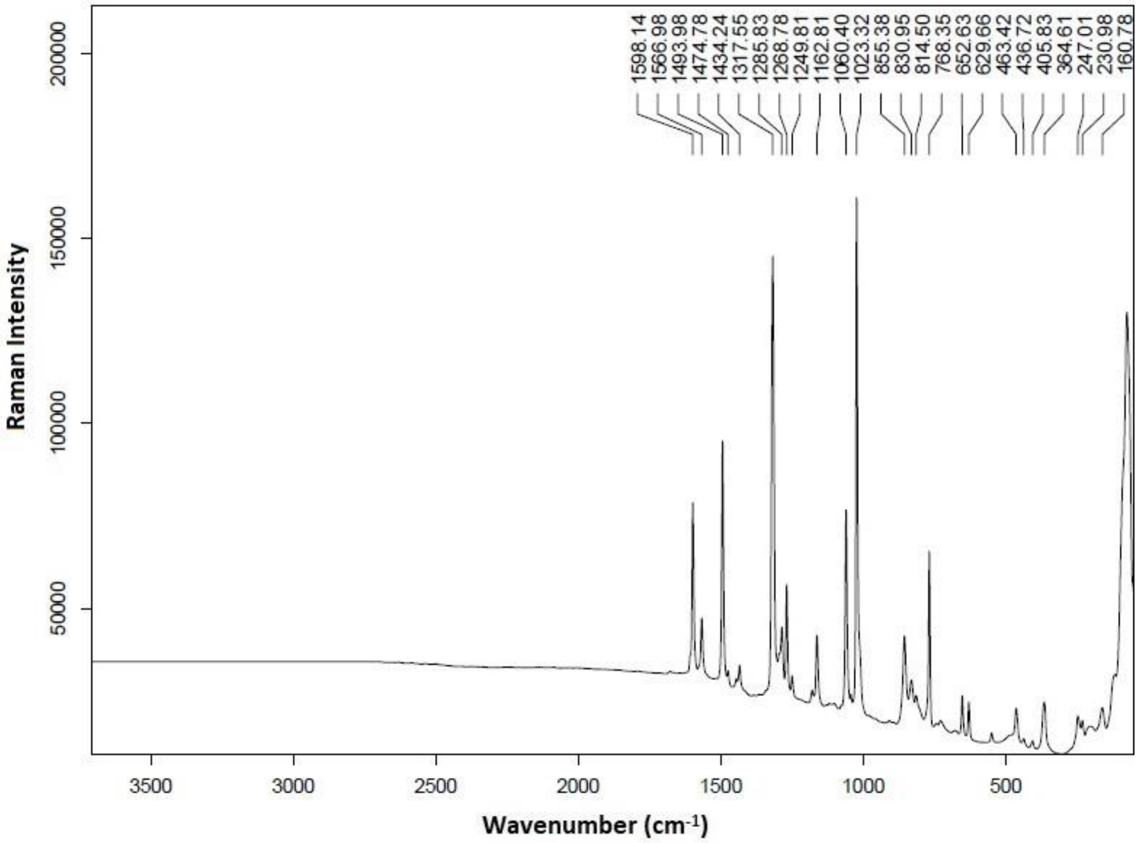

Figure S3. FT-Raman spectrum for compound **1**.

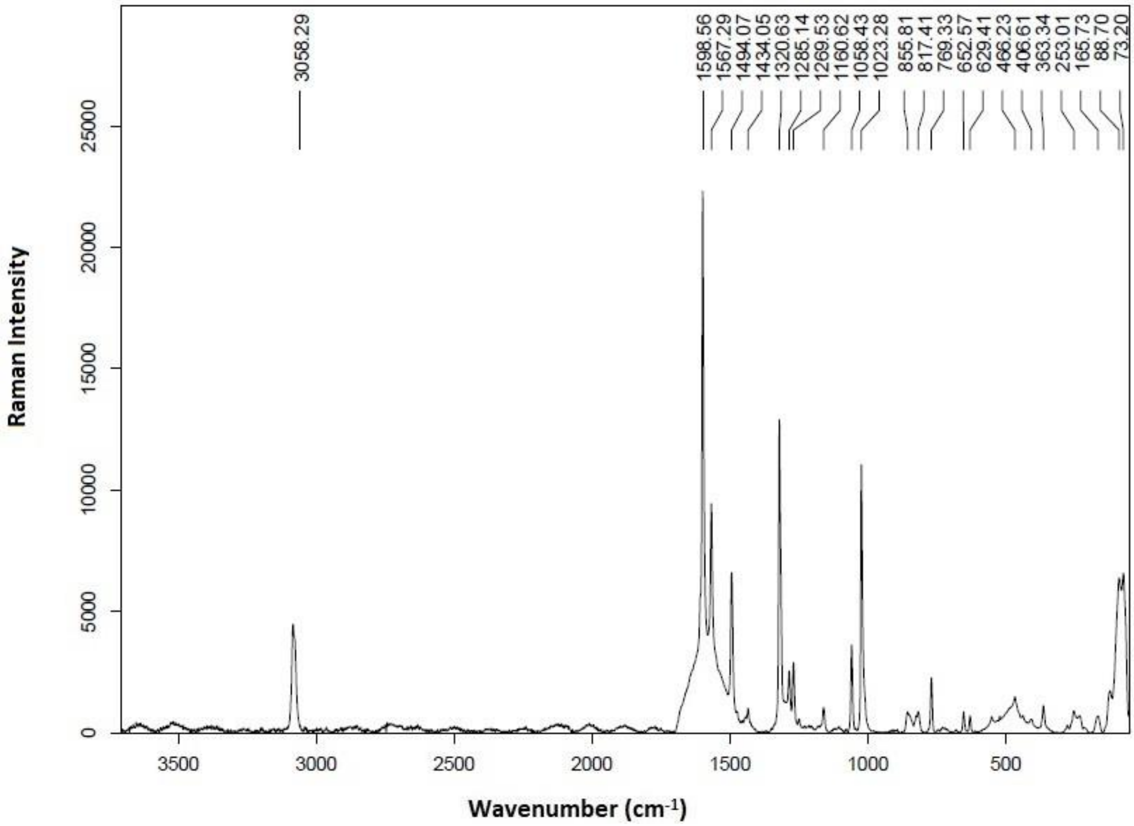

Figure S4. FT-Raman spectrum for compound **2**.

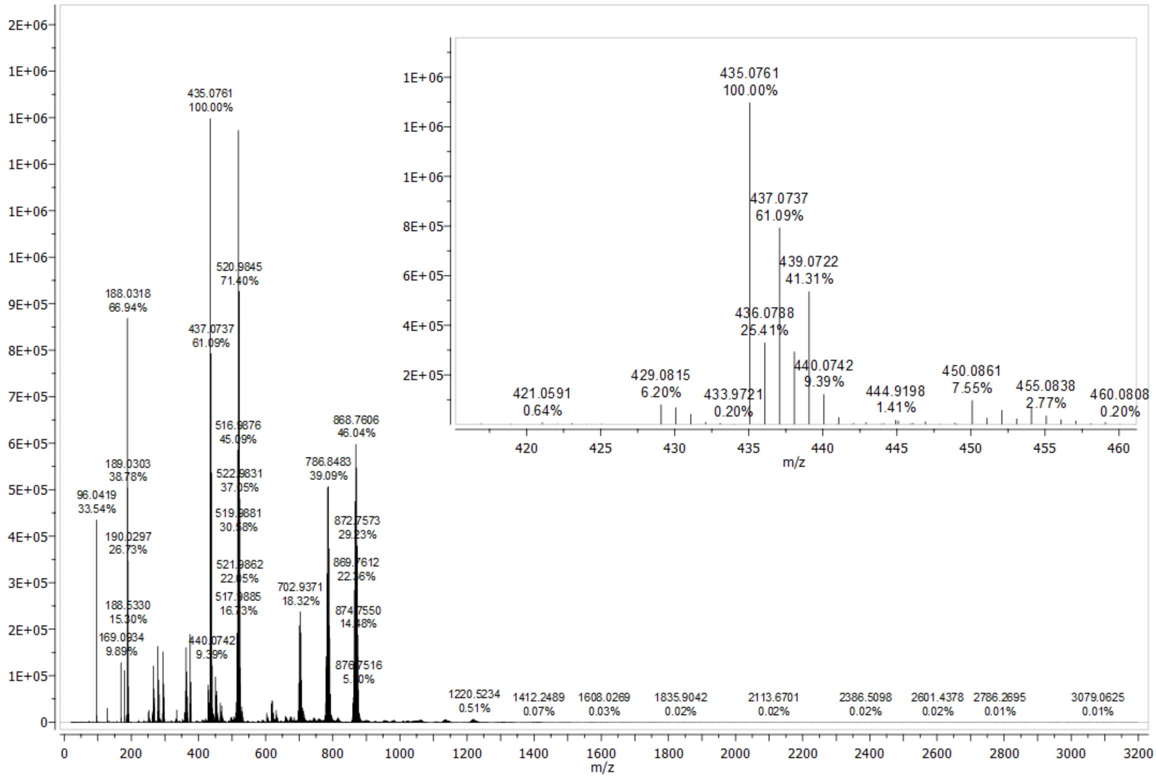

Figure S5. ESI$^+$ MS spectrum for compound **1**.

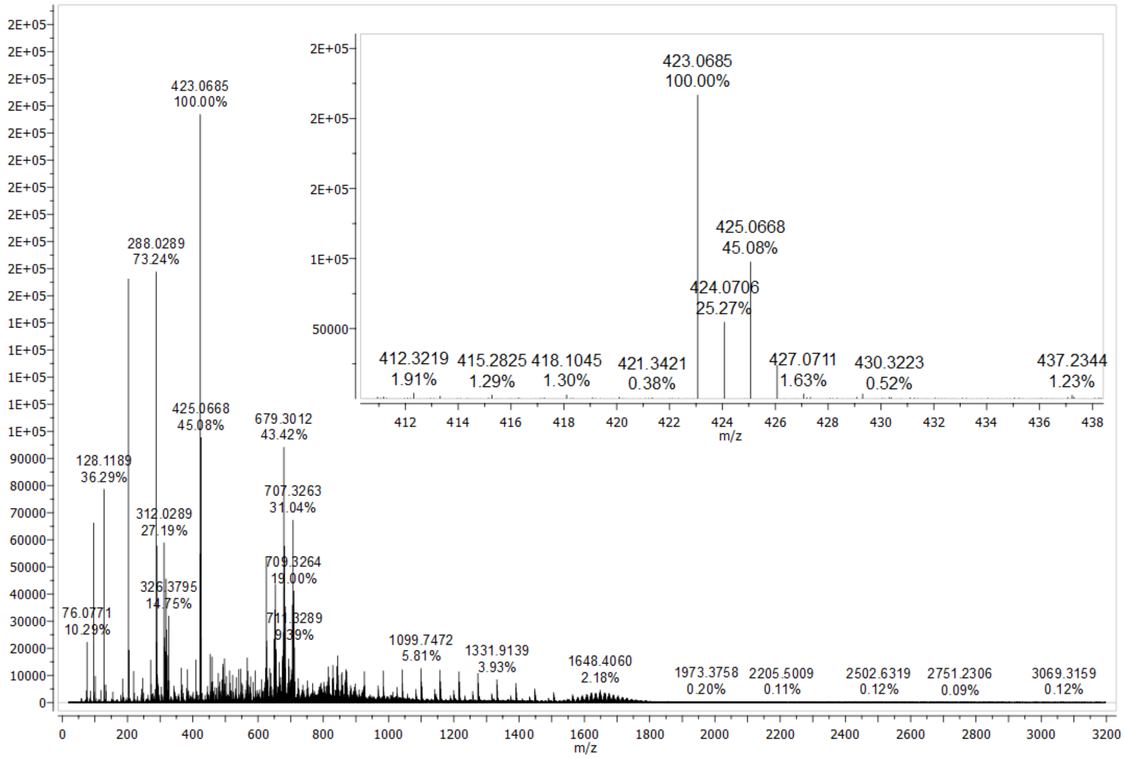

Figure S6. ESI$^+$ MS spectrum for compound **2**.

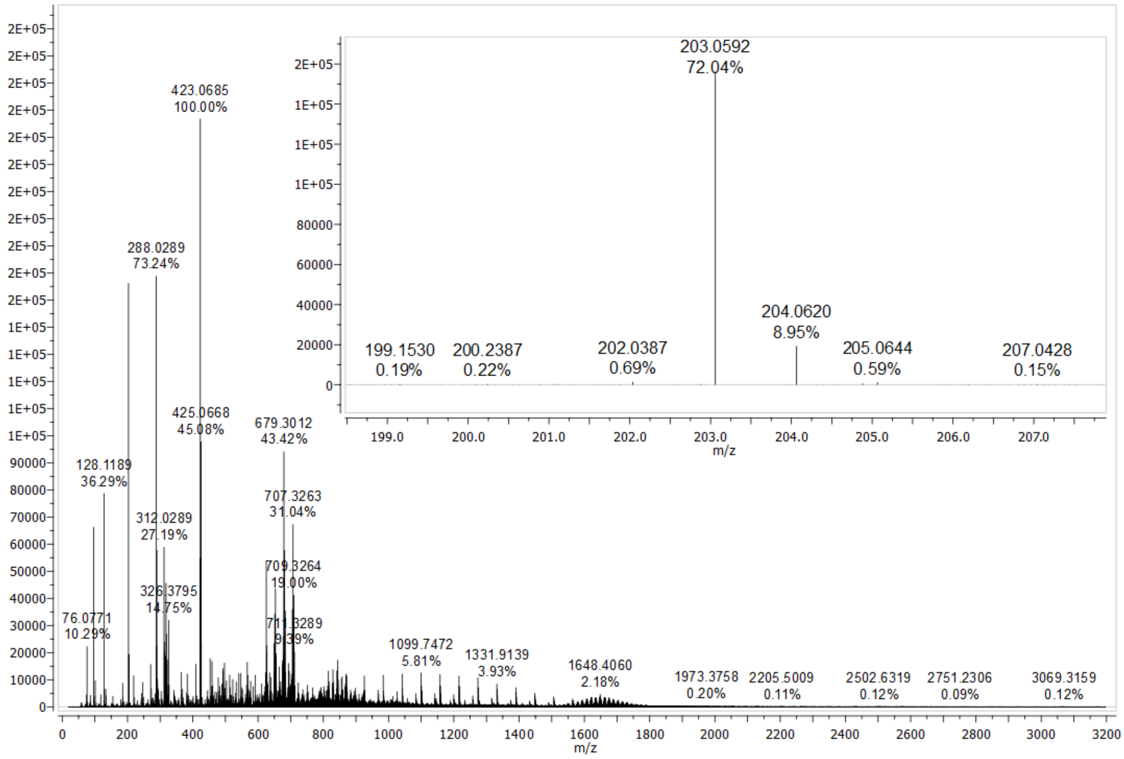

Figure S7. ESI$^+$ MS spectrum for compound **2**.

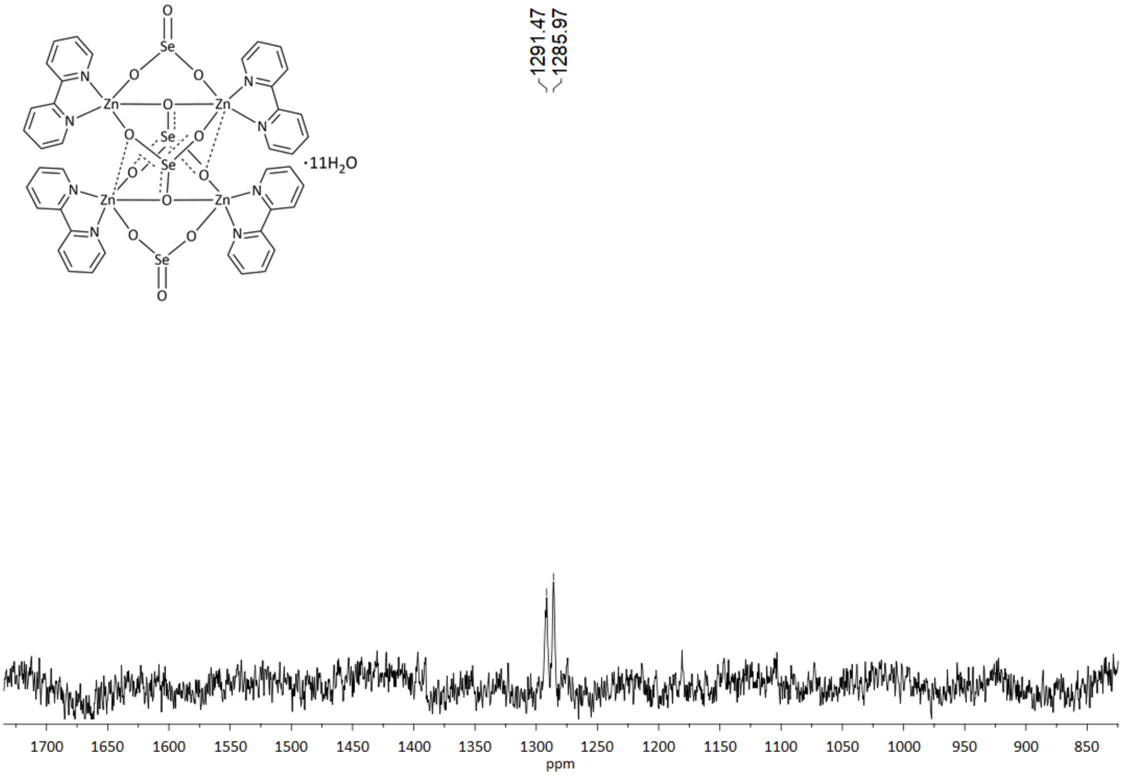

Figure S8. ^{77}Se NMR spectrum for compound **1**.

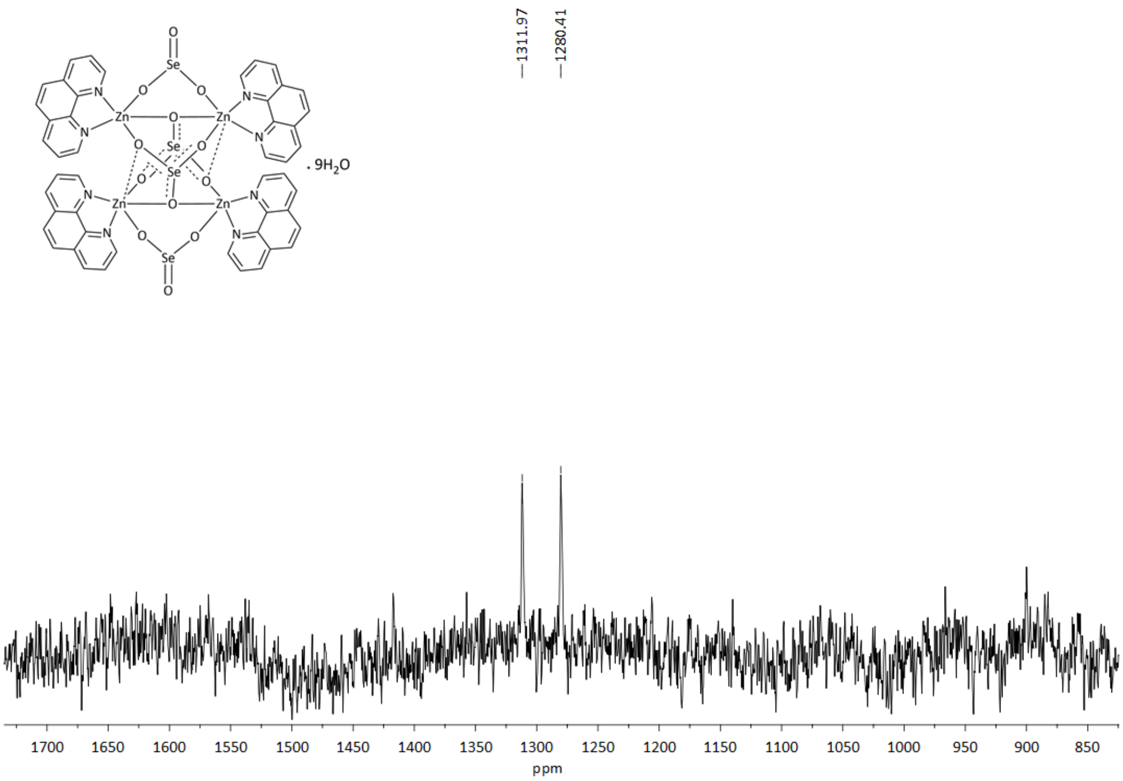

Figure S9. ^{77}Se NMR spectrum for compound **2**.

Figure S10. Reactor used in syntheses of **1** and **2.**

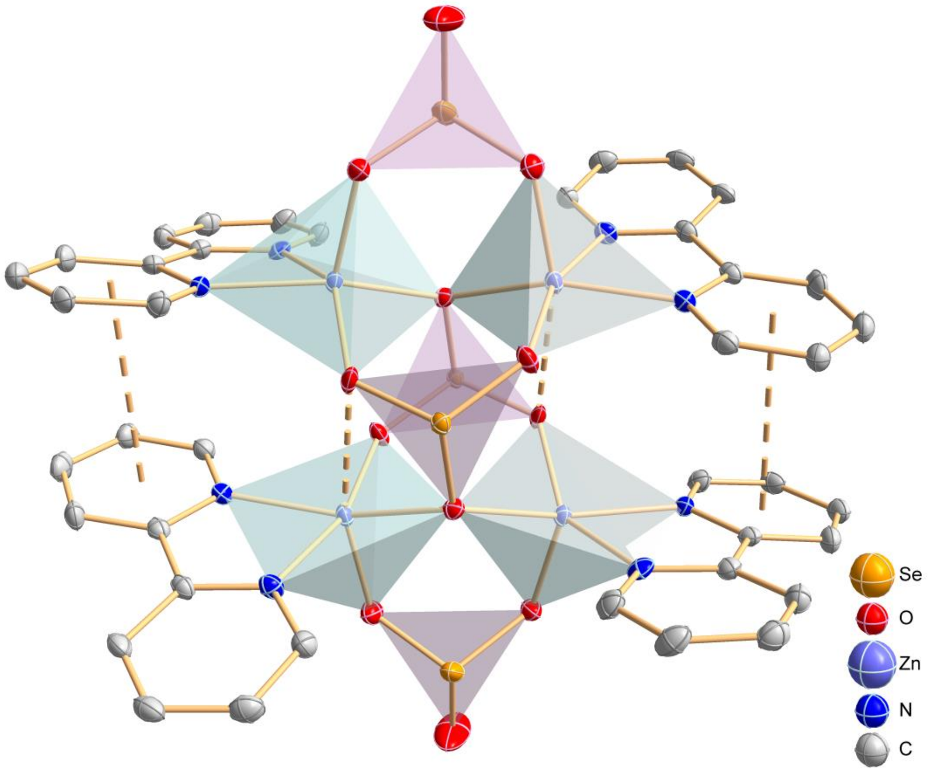

Figure S11. ORTEP[13] representation of the molecular structure of **1**. The thermal ellipsoids indicate the 50% probability level. For clarity, the hydrogen atoms were omitted.

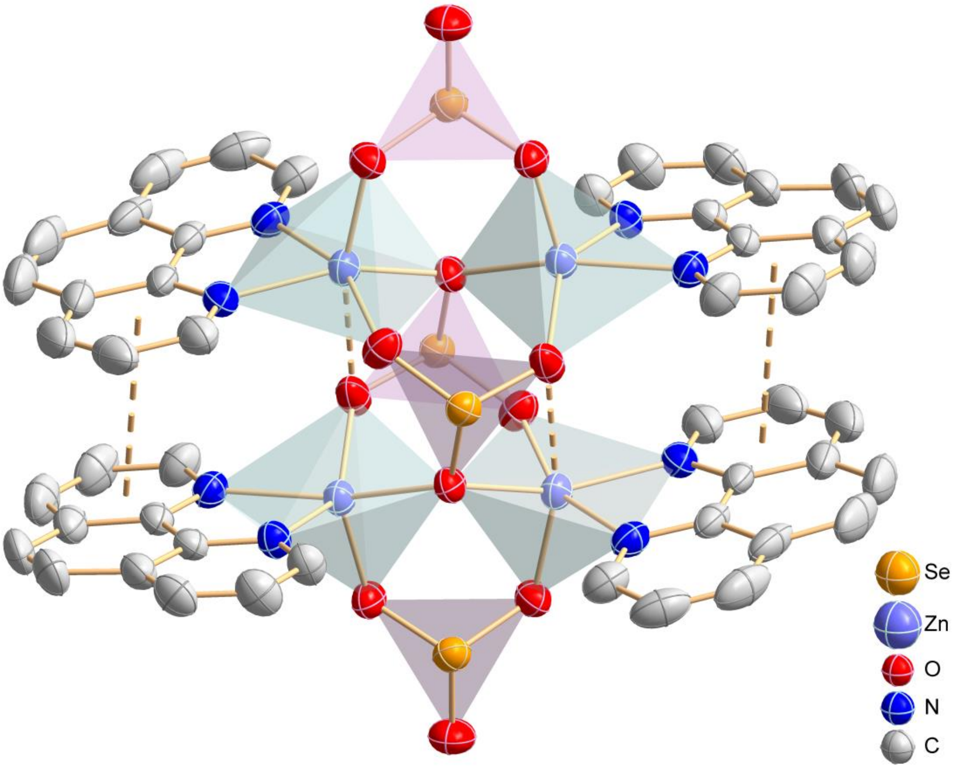

Figure S12. ORTEP[13] representation of the molecular structure of **2**. The thermal ellipsoids indicate the 50% probability level. For clarity, the hydrogen atoms were omitted.

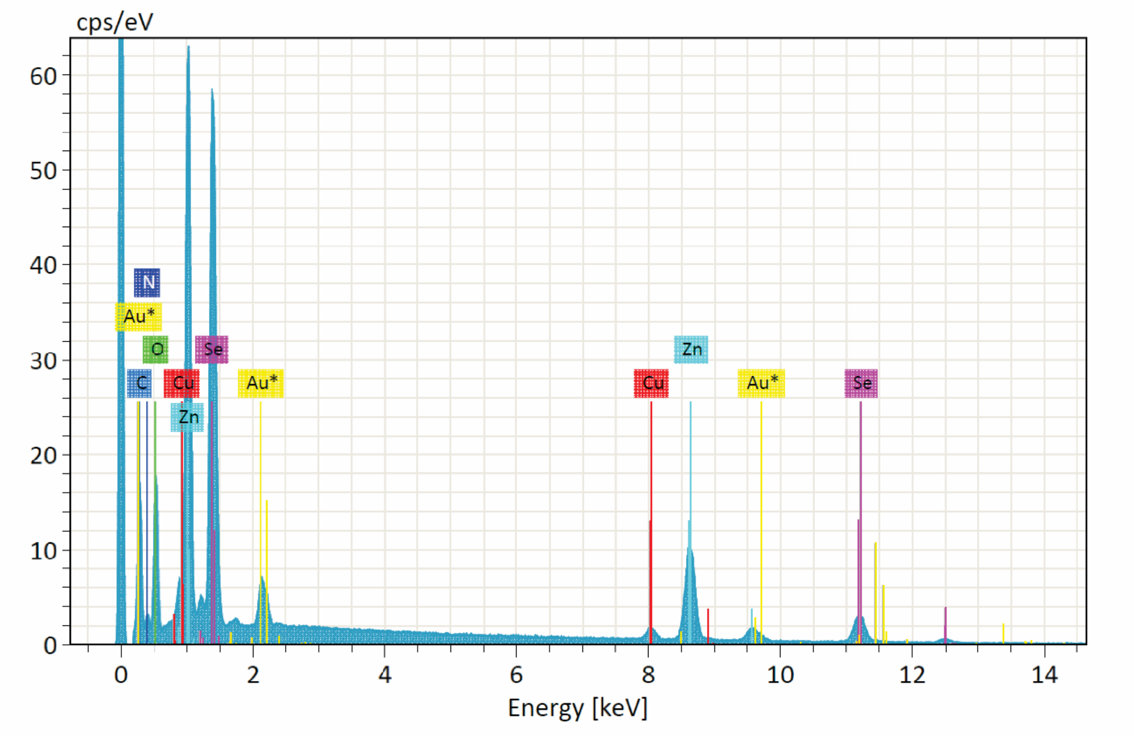

Figure S13. EDX analysis for compound **1**.

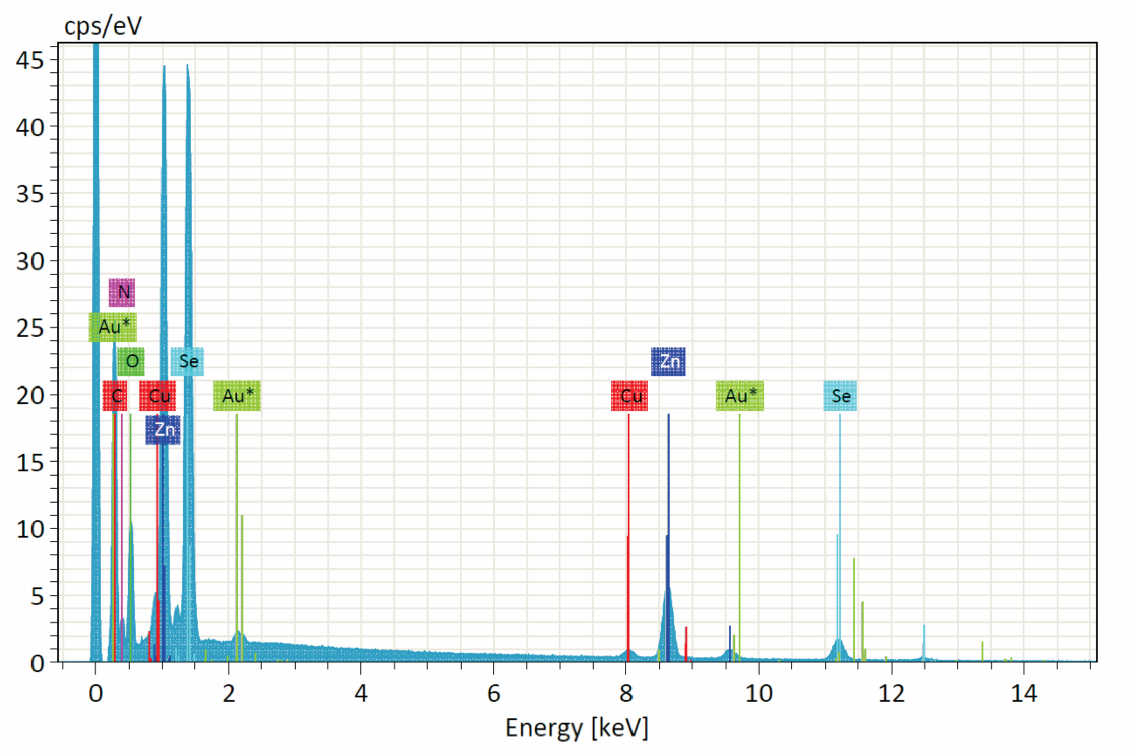

Figure S14. EDX analysis for compound **2**.

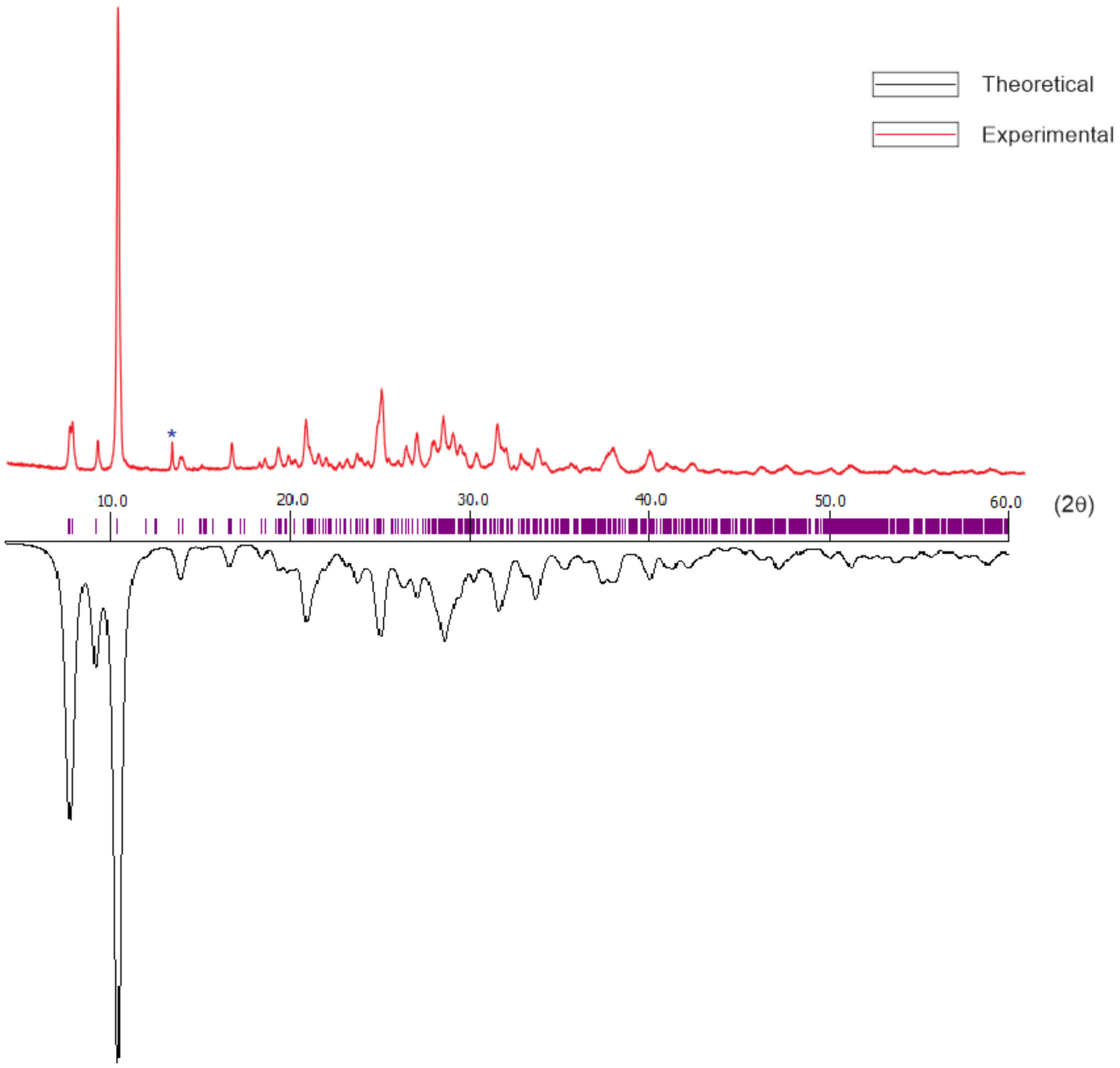

Figure S15. Simulated and experimental XRD pattern for compound **1**.
*is attributed to zinc acetate dihydrate.

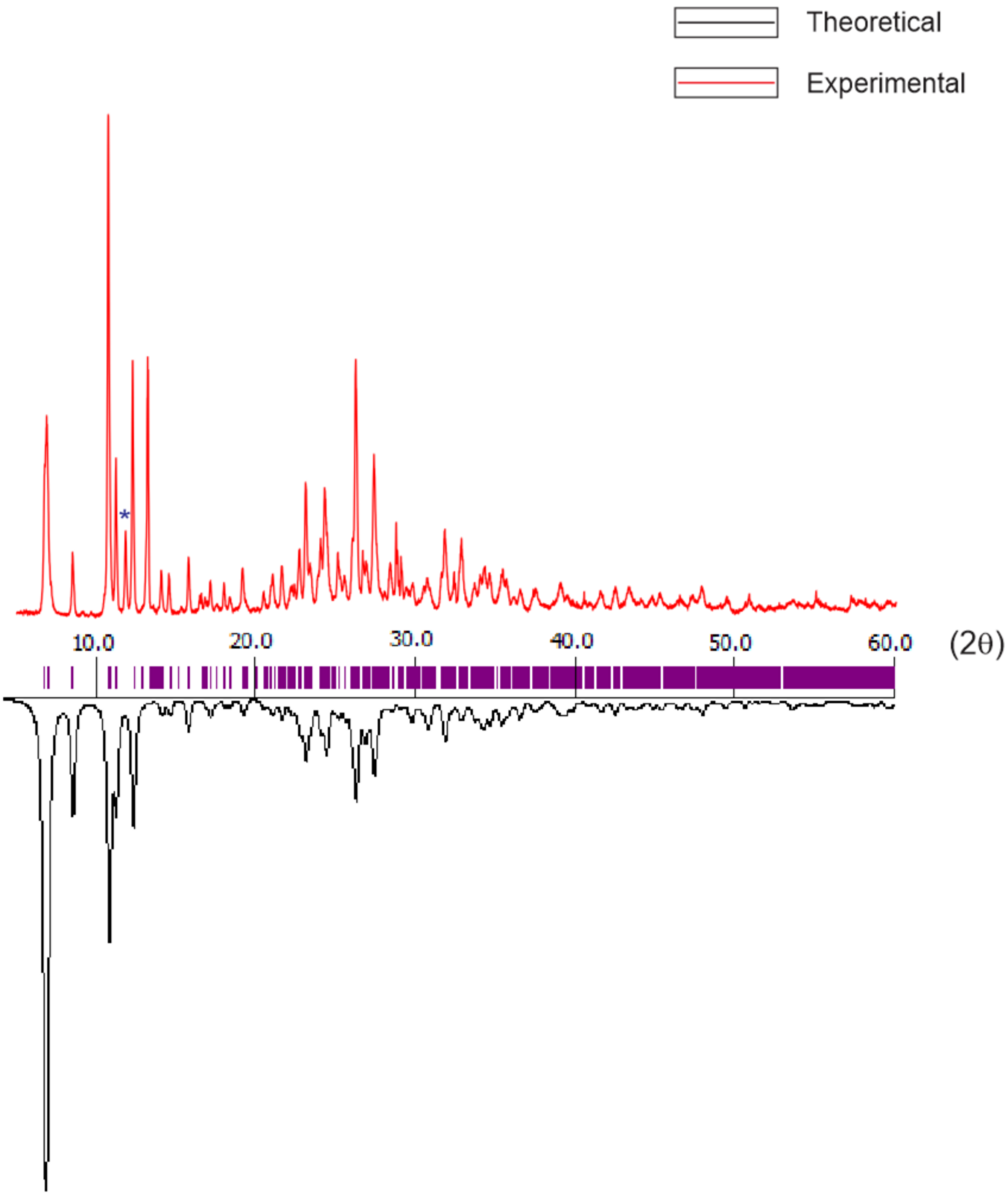

Figure S16. Simulated and experimental XRD pattern for compound **2**.
*is attributed to zinc acetate dihydrate.

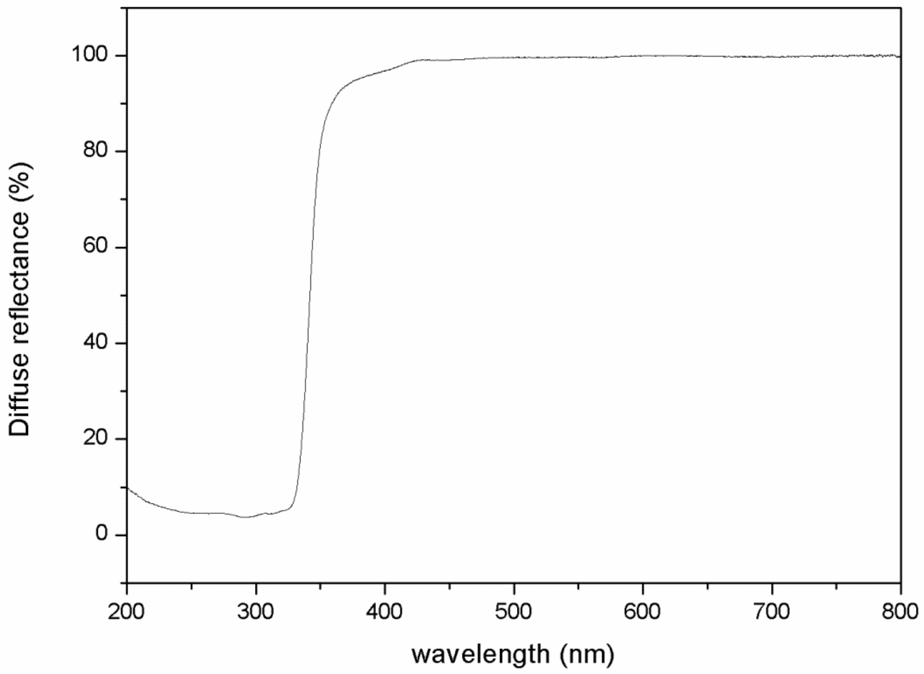

Figure S17. UV-vis diffuse reflectance spectrum for compound **1**.

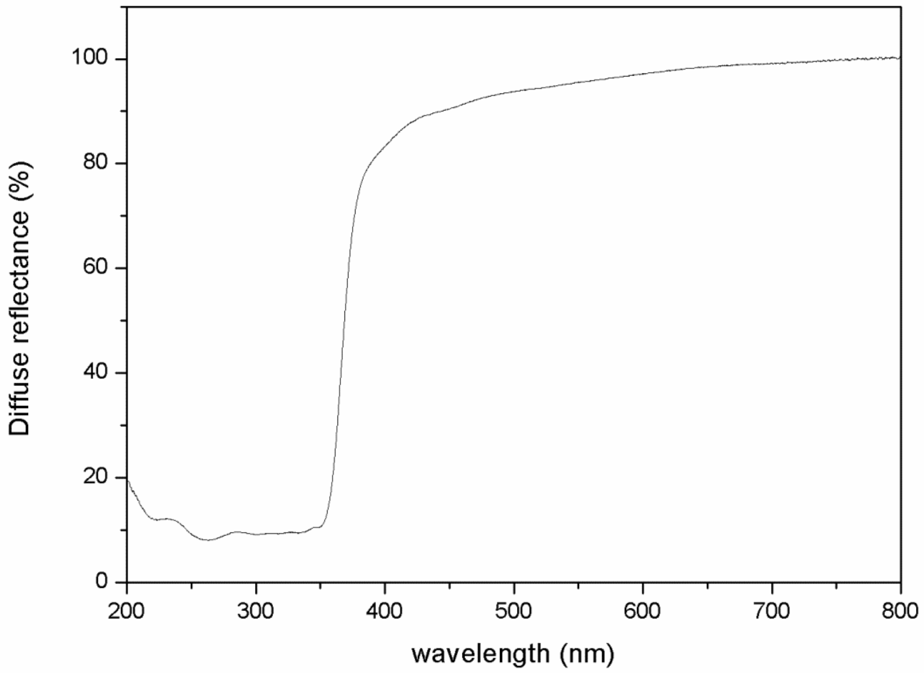

Figure S18. UV-vis diffuse reflectance spectrum for compound **2**.

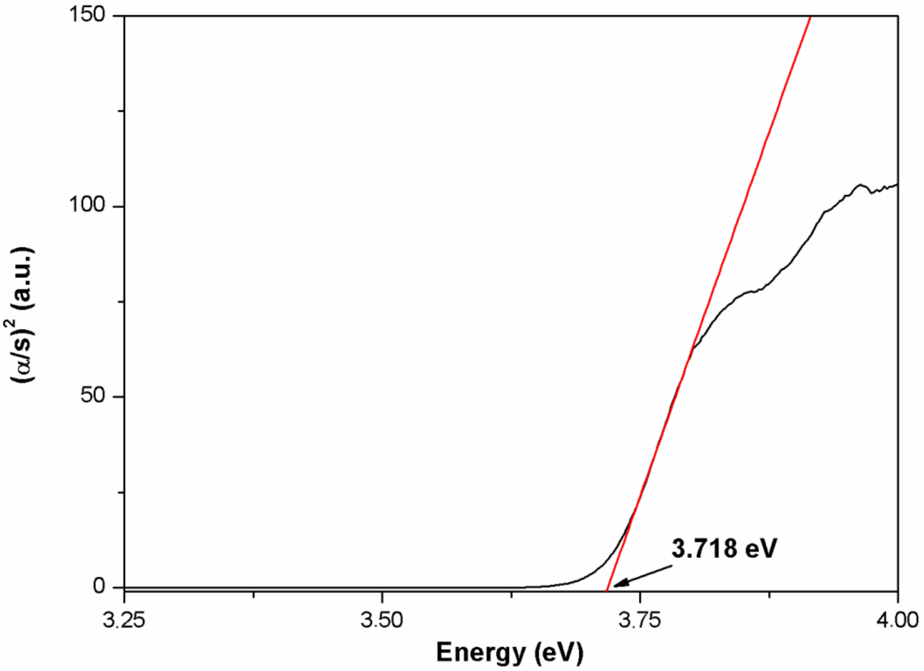

Figure S19. Graphical determination of the E_g value for compound **1**.

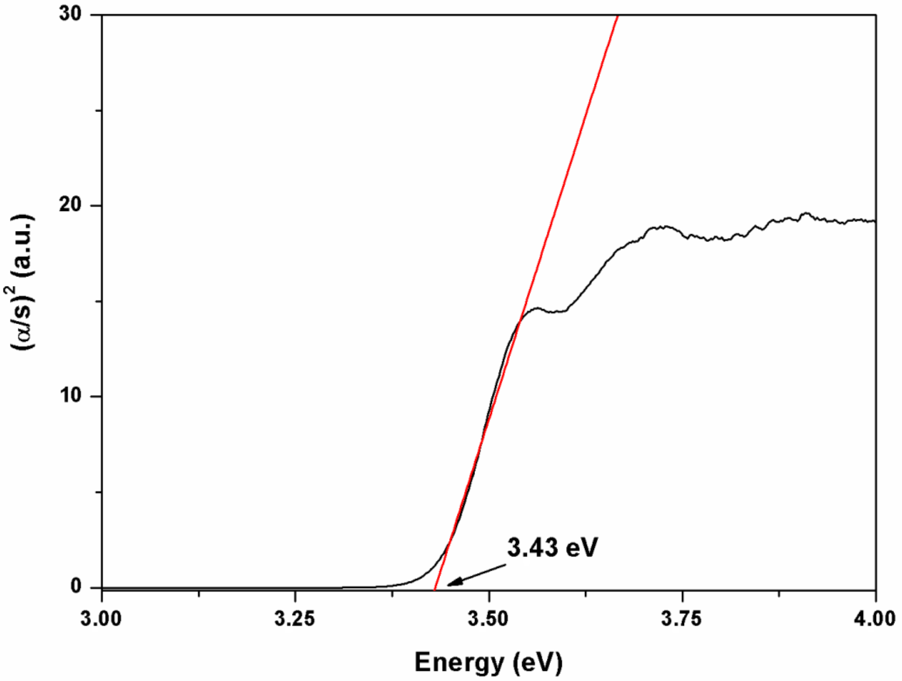

Figure S20. Graphical determination of the E_g value for compound **2**.

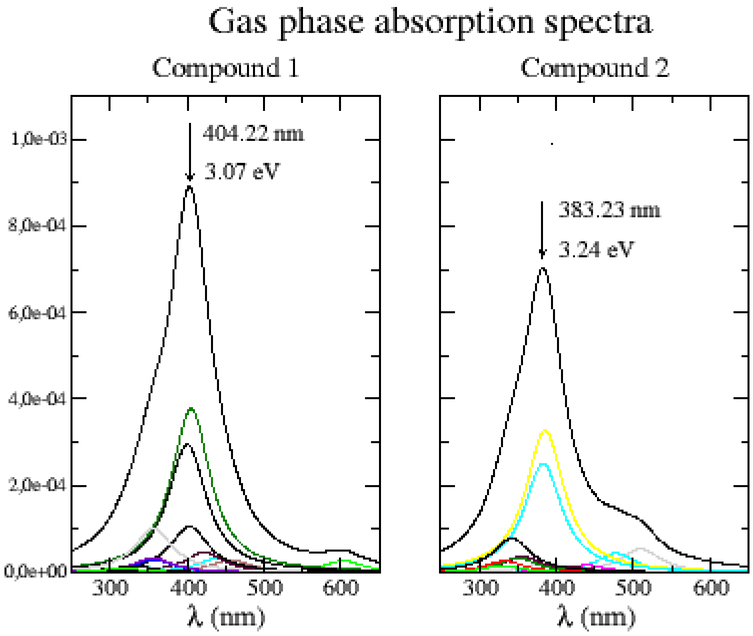

Figure S21. Theoretical absorption spectra for compounds **1** and **2.** The curves were built using a Lorentzian fit, with a width at half height of 60.0 nm. The values of the wavelength and energy of the most intense peaks are showed.

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