Electronic Supplementary Information

Chalcogen bonded metal-organic frameworks: insights from X-ray analysis and theoretical calculations

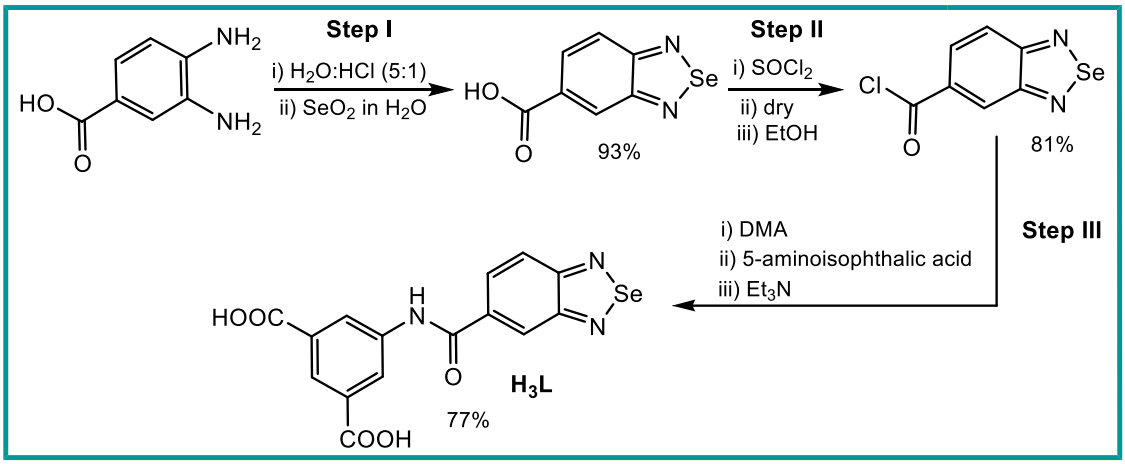
Vusala A. Aliyeva,[a,b,c] Vânia André,[a,b,c] Luísa M. D. R. S. Martins,[a,c] Atash V. Gurbanov,[d] Rosa M. Gomila,[e] Antonio Frontera,*[e] Tiago F. C. Cruz[a,c] and Kamran T. Mahmudov*[d]

[a] *Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisboa, Portugal*
[b] *Associação do Instituto Superior Técnico para a Investigação e Desenvolvimento (IST-ID), Avenida António José de Almeida, 12, 1000-043 Lisboa, Portugal*
[c] *Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisboa, Portugal*
[d] *Excellence Center, Baku State University, Z. Xalilov Str. 23, Az 1148 Baku, Azerbaijan. E-mail: mahmudov.kt@gmail.com*
[e] *Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km7.5, Palma, Baleares, Spain. E-mail: toni.frontera@uib.es*

1. Materials and instrumentation

All the chemicals were obtained from commercial sources and used as received. The IR spectra (4000−400 cm^{-1}) were recorded on a Bruker Alpha-P ATR-IR Spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained at room temperature on a Bruker 400.13 MHz spectrometer using $Si(CH_3)_4$ as the internal reference. Elemental analyses (C, H, and N) were performed on a Finnigan EA 1112 instrument.

2. Synthesis and characterization of H_3L



Scheme S1. Synthetic steps for the synthesis of **H_3L**.

Step I (Scheme S1):[s1] 3,4-Diaminobenzoic acid (10 mmol) was dissolved in 250 mL hydrochloric acid solution (HCl : H_2O = 1 : 5, v/v) in a 500 mL flask. 10 mmol of SeO_2 which dissolved in 20 mL of hot distilled water, was dropping into the flask through a constant pressure funnel stirred for 2 h. Next, the reacted mixture was filtrated and the obtained solids were washed with distilled water for several times until the pH value reached to 7. Then the products were dried at room temperature to afford the pure benzo[*c*][1,2,5]selenadiazole-5-carboxylic acid.

Yield: 93%. IR (KBr, selected bands, cm^{-1}): 2808 *ν*(OH), 1676 *ν*(C=O), 1606 *ν*(C=N). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 7.87-7.89 (d, J_{HH} = 8 Hz, 1H), 7.93-7.95 (d, J_{HH} = 8 Hz, 1H), 8.39 (s, 1H) and 13.35 (s, 1H, COOH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 123.24, 125.42, 127.87, 131.20, 159.18, 160.73, 166.90.

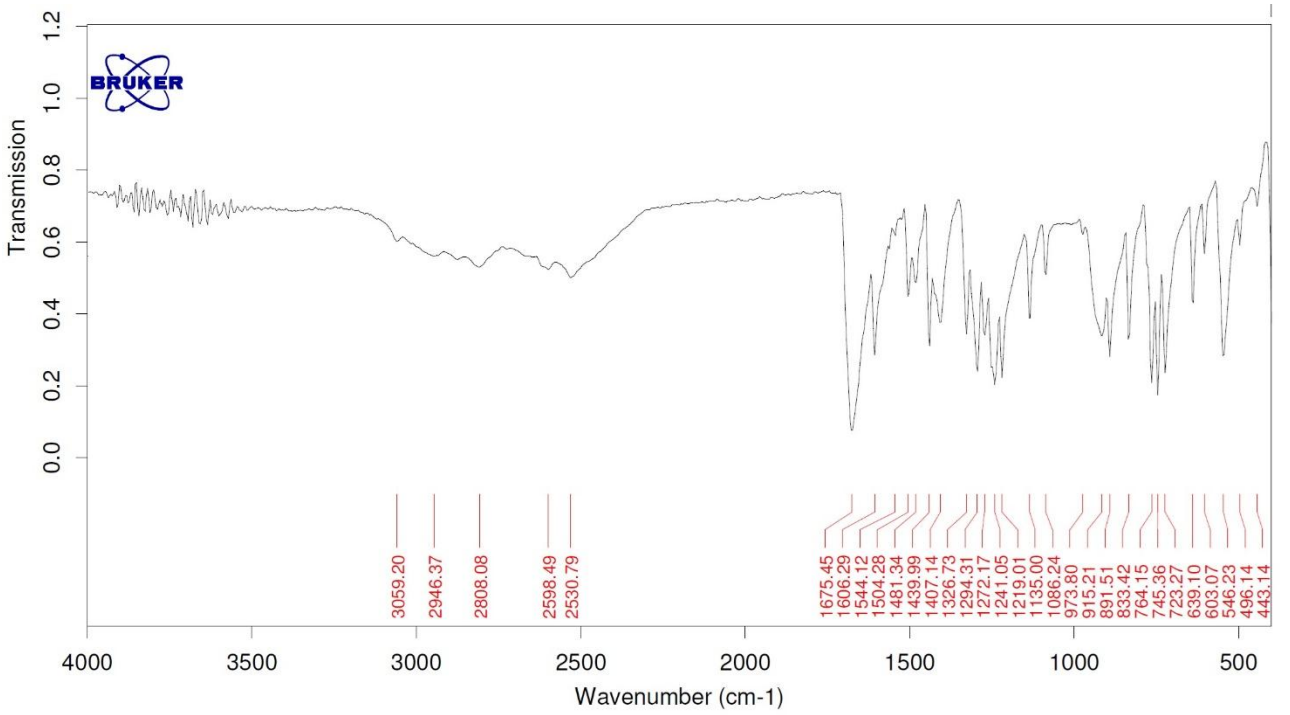
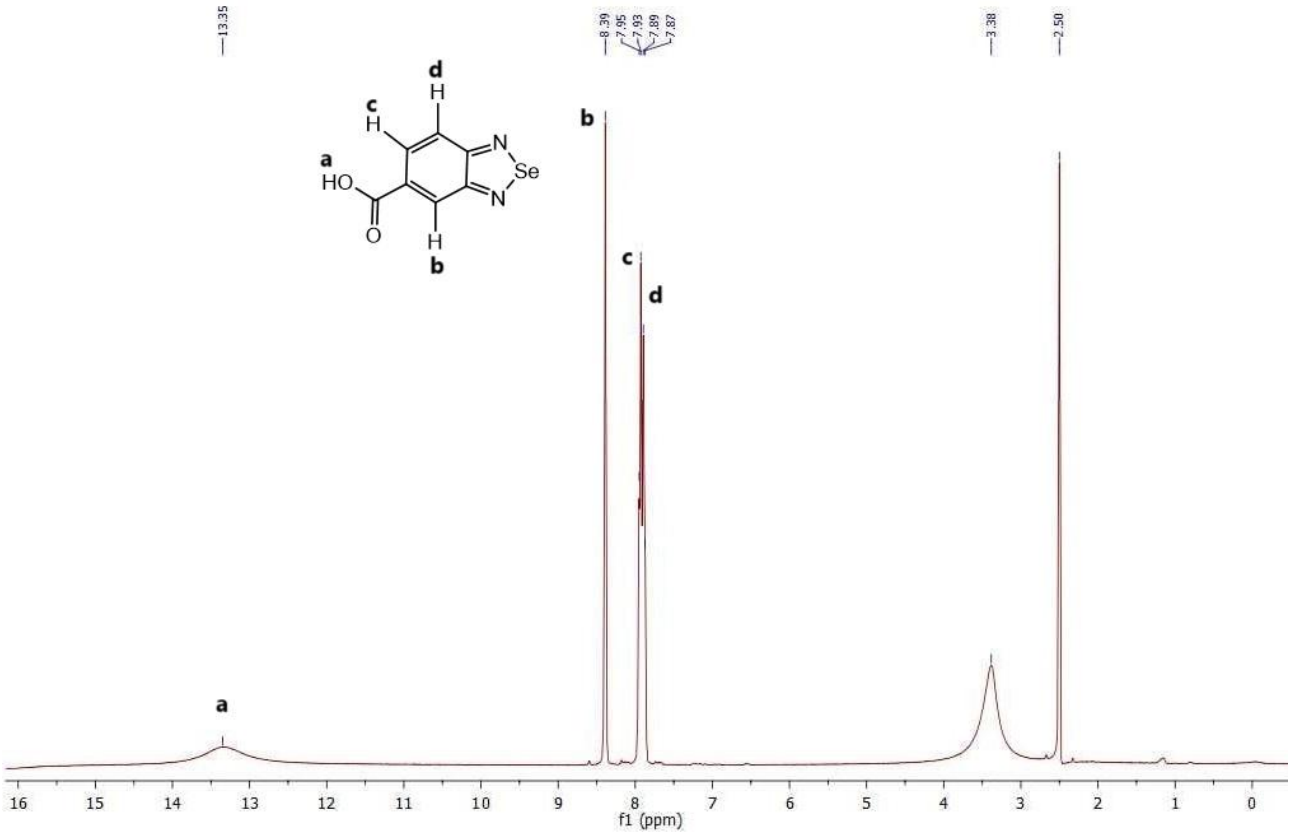


Fig. S1. IR spectrum of benzo[*c*][1,2,5]selenadiazole-5-carboxylic acid.



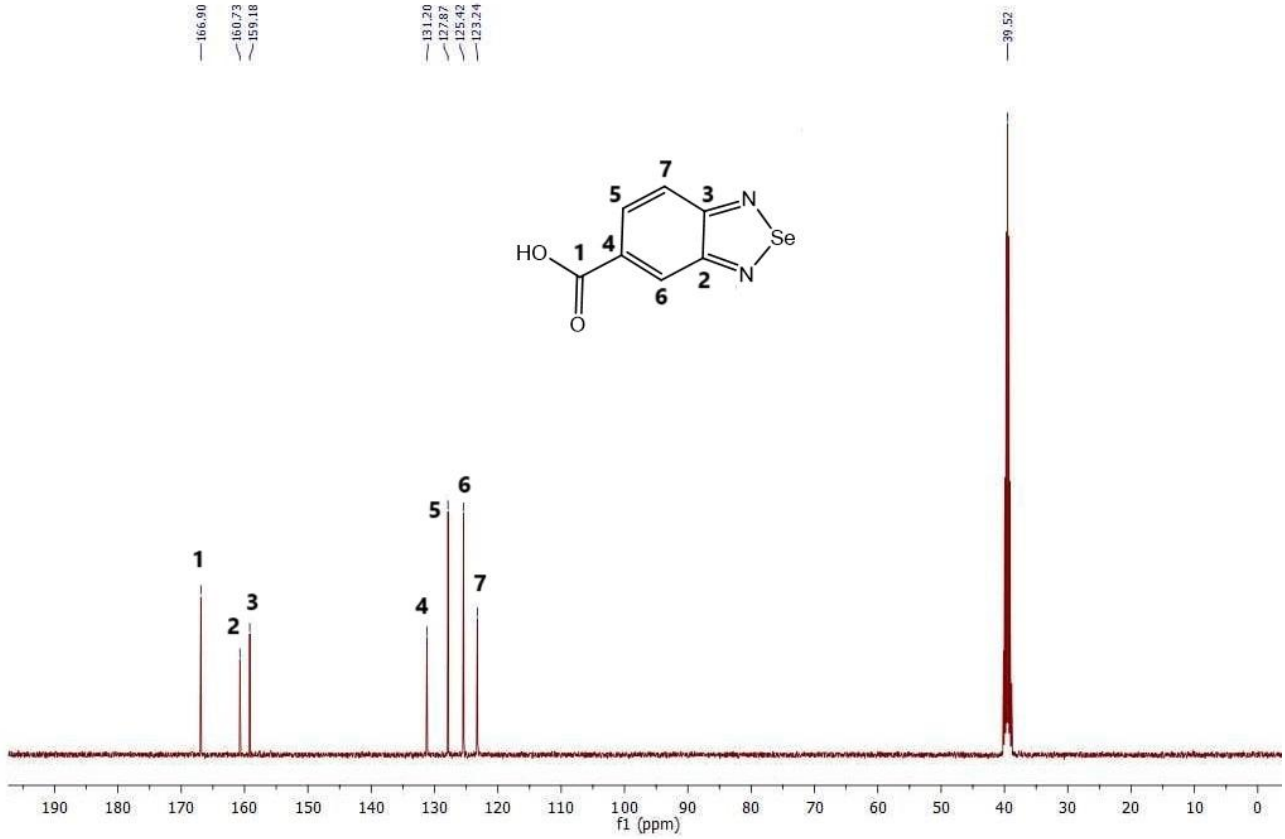


Fig. S2. ^{1}H (top)/^{13}C (bottom) NMR spectra of benzo[*c*][1,2,5]selenadiazole-5-carboxylic acid.

Step II (Scheme S1):[s2] A mixture of benzo[*c*][1,2,5]selenadiazole-5-carboxylic acid (10 mmol) and thionyl chloride (50 mL) was stirred at 80 ºC for 2 h. The reaction was monitored by IR spectroscopy. Formation of the acyl chloride was confirmed following the wavenumber position in IR peaks: carbonyl group of benzo[*c*][1,2,5]selenadiazole-5-carboxylic acid showed up at *ca.* 1675 cm^{-1}, but the carbonyl in the benzo[*c*][1,2,5]selenadiazole-5-carbonyl chloride at *ca.* 1749 cm^{-1}. The resulting benzo[*c*][1,2,5]selenadiazole-5-carbonyl chloride was isolated by evaporation of the thionyl chloride under reduced pressure in a well-ventilated hood, quenched with ethanol and then distilled water, and appropriately disposed.

Yield: 81%. IR (KBr, selected bands, cm^{-1}): 2992 *ν*(OH), 1749 *ν*(C=O), 1606 *ν*(C=N). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 7.90-7.92 (d, J_{HH} = 8 Hz, 1H), 7.94-7.97 (d, J_{HH} = 12 Hz, 1H), and 8.40 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 123.45, 125.60, 128.12, 131.44, 159.37, 160.93, 167.10.

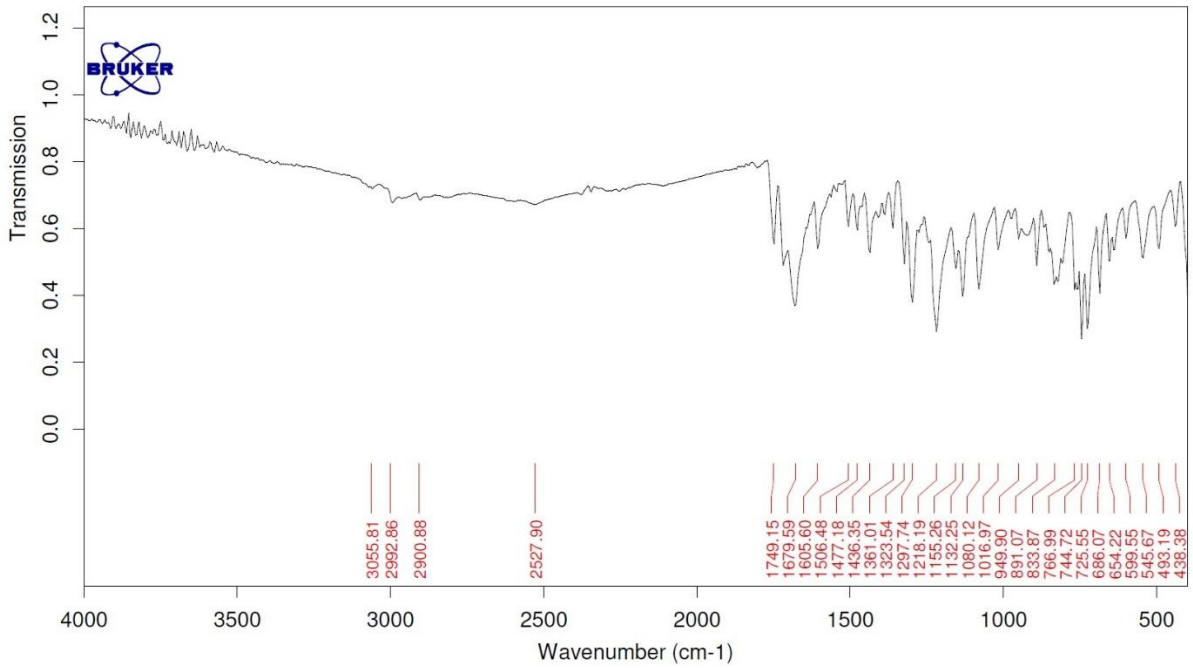
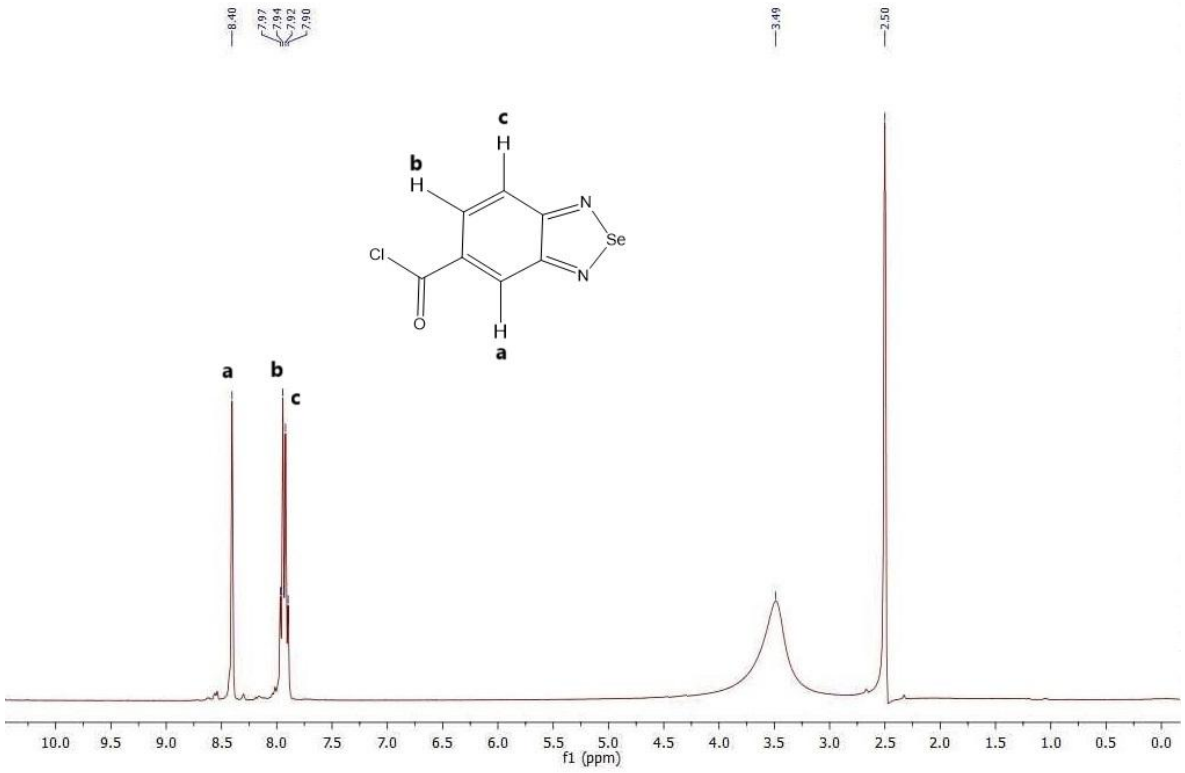


Fig. S3. IR spectrum of benzo[*c*][1,2,5]selenadiazole-5-carbonyl chloride.



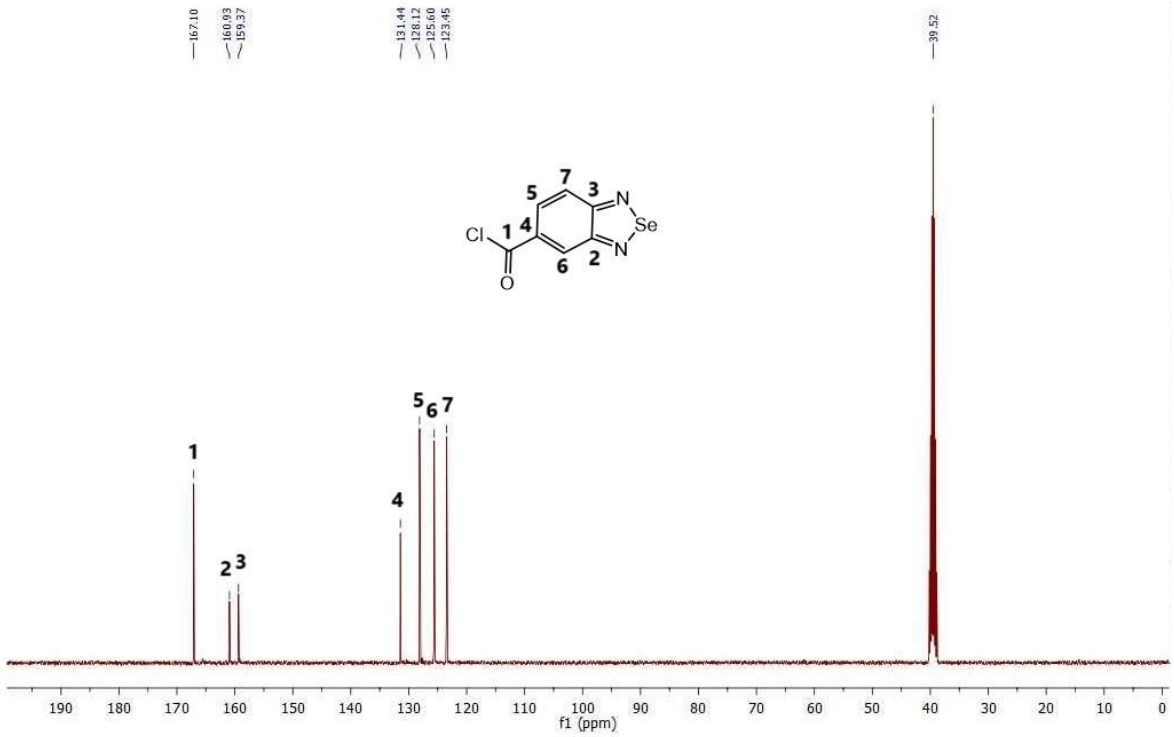


Fig. S4. ^{1}H (top)/^{13}C (bottom) NMR spectra of benzo[*c*][1,2,5]selenadiazole-5-carbonyl chloride.

Step III (Scheme S1): Benzo[*c*][1,2,5]selenadiazole-5-carbonyl chloride (10 mmol) was dissolved in dimethylacetamide (20 mL) and added to the solution of 5-aminoisophthalic acid (11 mmol) in dimethylacetamide (20 mL). Triethylamine (20 mmol, 2.8 mL) was added to the resulting mixture and stirred overnight at ambient temperature. Then 150 mL of hydrochloric acid solution (pH = 5) was added to the flask. The light yellow precipitated was isolated by filtration and washed with distilled water to obtain 5-(benzo[*c*][1,2,5]selenadiazole-5-carboxamido)isophthalic acid (**H_3L**).
Yield: 77%. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 13.28 (s, 2H, 2COOH), 10.89 (s, 1H, NH), 8.71 (s, 2H, 2CH), 8.61 (s, 1H, CH), 8.24 (s, 1H, CH), 8.02-8.05 (d, J_{HH} = 12 Hz, 1H, CH) and 7.96-7.98 (d, J_{HH} = 8 Hz, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 123.06, 123.29, 124.73, 125.25, 127.85, 131.84, 134.41, 139.72, 159.15, 160.42, 165.11, 166.58. IR (KBr, selected bands, cm^{-1}): 3344 *v*(OH), 2994 *v*(NH), 1711 and 1677 *v*(C=O), 1606 *v*(C=N).

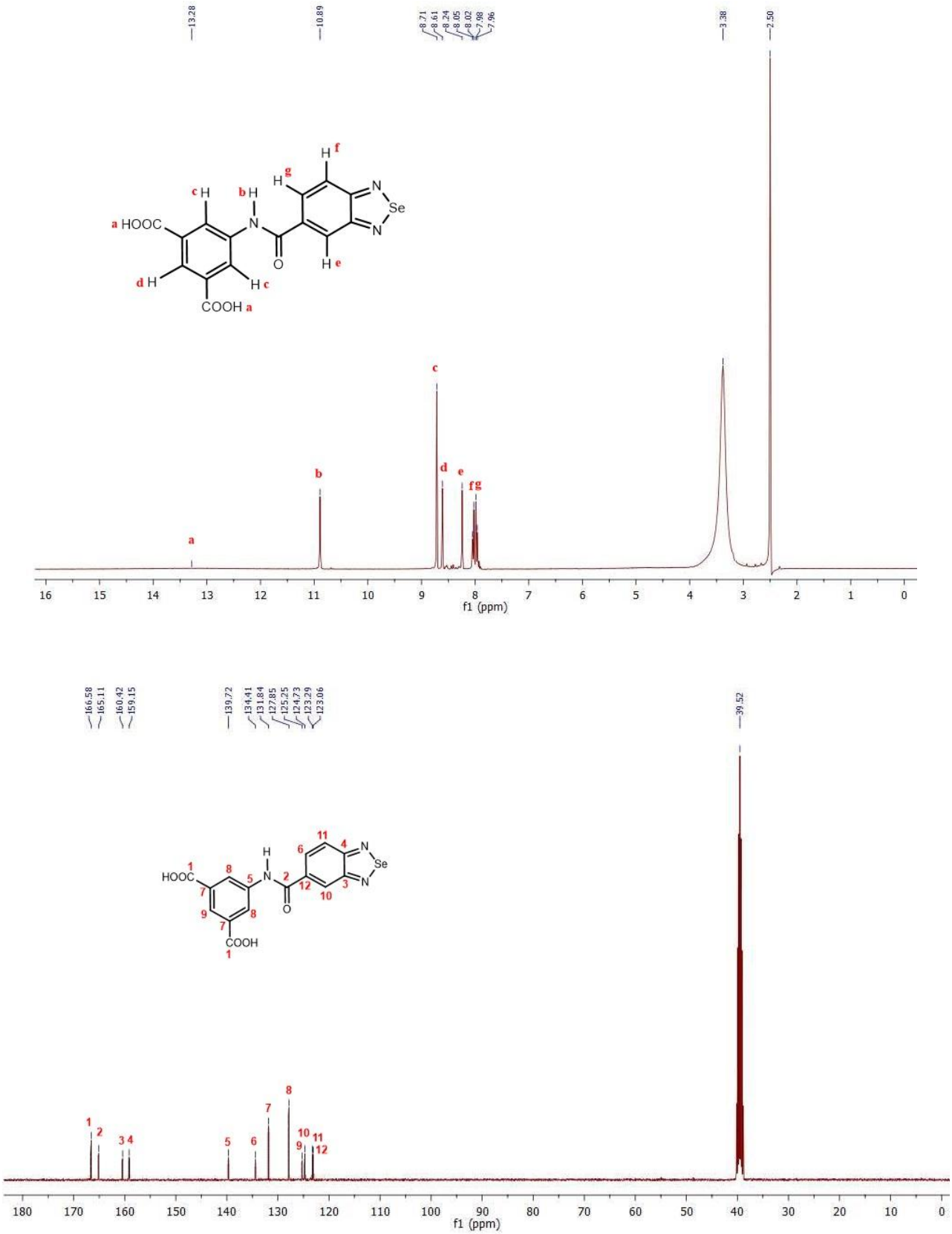


Fig. S5. ^{1}H (top)/^{13}C (bottom) NMR spectra of **H_3L**.

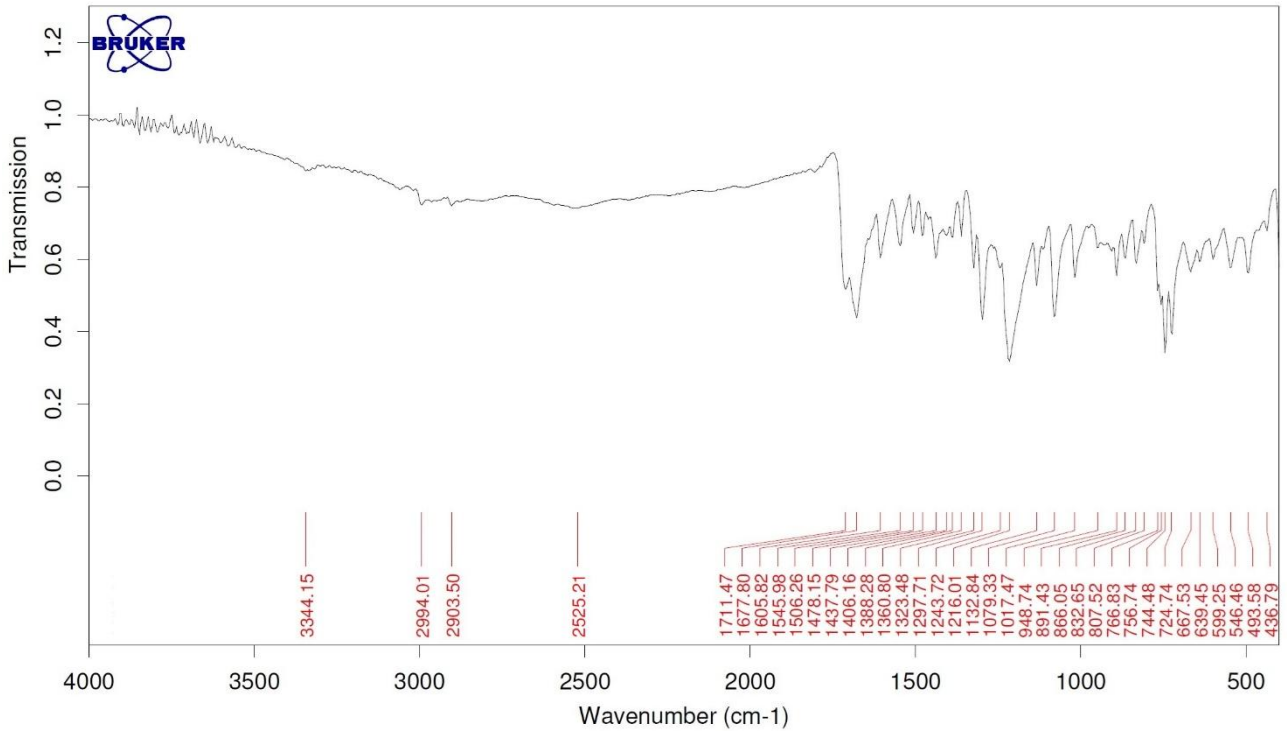


Fig. S6. IR spectrum of **H_3L**.

3. Synthesis and characterization of 1 and 2

*Synthesis of **1***. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.1 mmol) and H_3L (39 mg, 0.1 mmol) was dissolved in 2 mL of DMF. The resulting mixture was sealed in an 8 mL glass vessel and heated at 75 °C for 48 h, and yellow powder was formed. Then, gradually cooled to room temperature (0.2 °C min^{-1}), filtered and left for slow evaporation; the yellow crystals of **1** is started to form after *ca*. 5 d at room temperature. For the elemental analysis, IR, X-ray and XRPD we used the yellow crystals of **1**.

1: Yield: 31% (based on Zn). Calcd. for $C_{21}H_{21}N_5O_7SeZn$ (*Mr* = 599.78): C 42.05, H 3.53, N 11.68; found C 42.01, H 3.50, N 11.66. IR (ATR, 298 K): 2929 *ν*(N−H), 1646 *ν*(C=O) and 1573 *ν*(C=N) cm^{-1}.

*Synthesis of **2***. A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (31 mg, 0.1 mmol) and H_3L (39 mg, 0.1 mmol) was dissolved in 2 mL of DMA. The resulting mixture was sealed in an 8 mL glass vessel and heated at 75 °C for 48 h, and orange crystals were formed. Then, gradually cooled to room temperature (0.2 °C min^{-1}), and orange crystals were used for the elemental analysis, IR, X-ray and XRPD.

2: Yield: 83% (based on Cd). Calcd. for $C_{46}H_{50}Cd_2N_{10}O_{14}Se_2$ (*Mr* = 1349.73): C 40.93, H 3.73, N 10.38; found C 40.90, H 3.71, N 10.35. IR (ATR, 298 K): 2930 and 3062 *ν*(N−H), 1667 and 1621 *ν*(C=O) and 1594 *ν*(C=N) cm^{-1}.

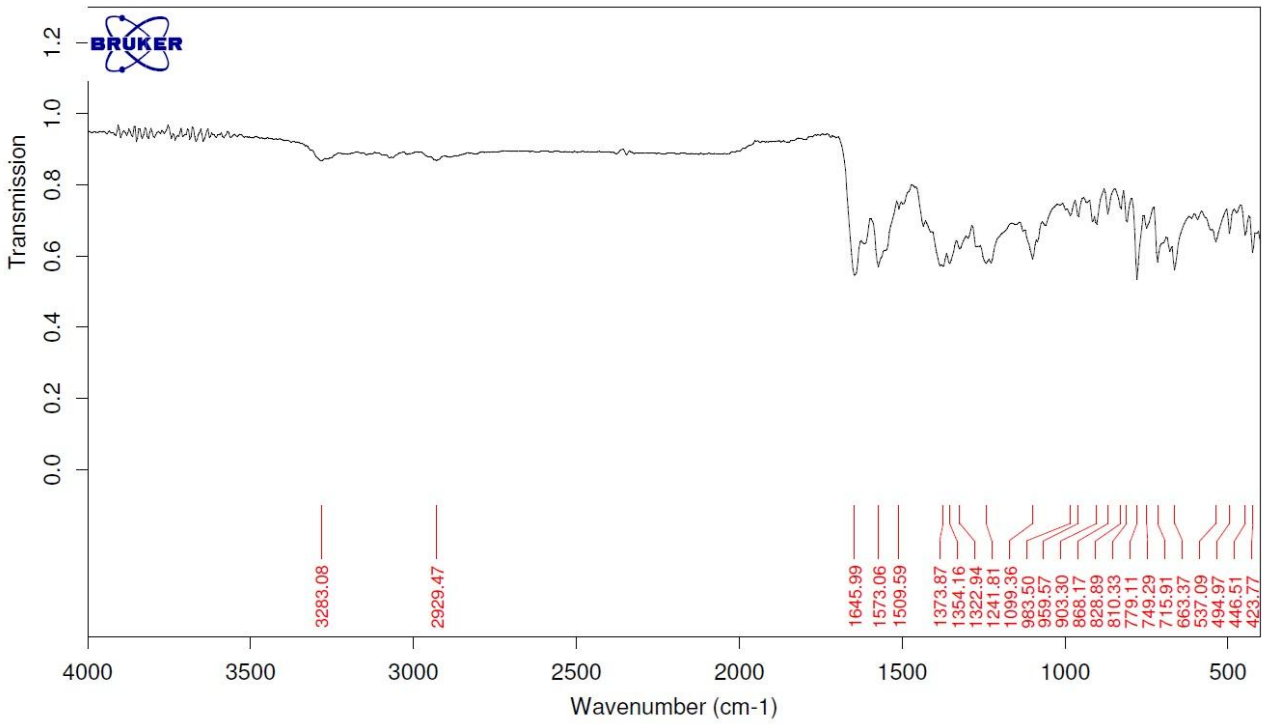


Fig. S7. IR spectrum of **1.**

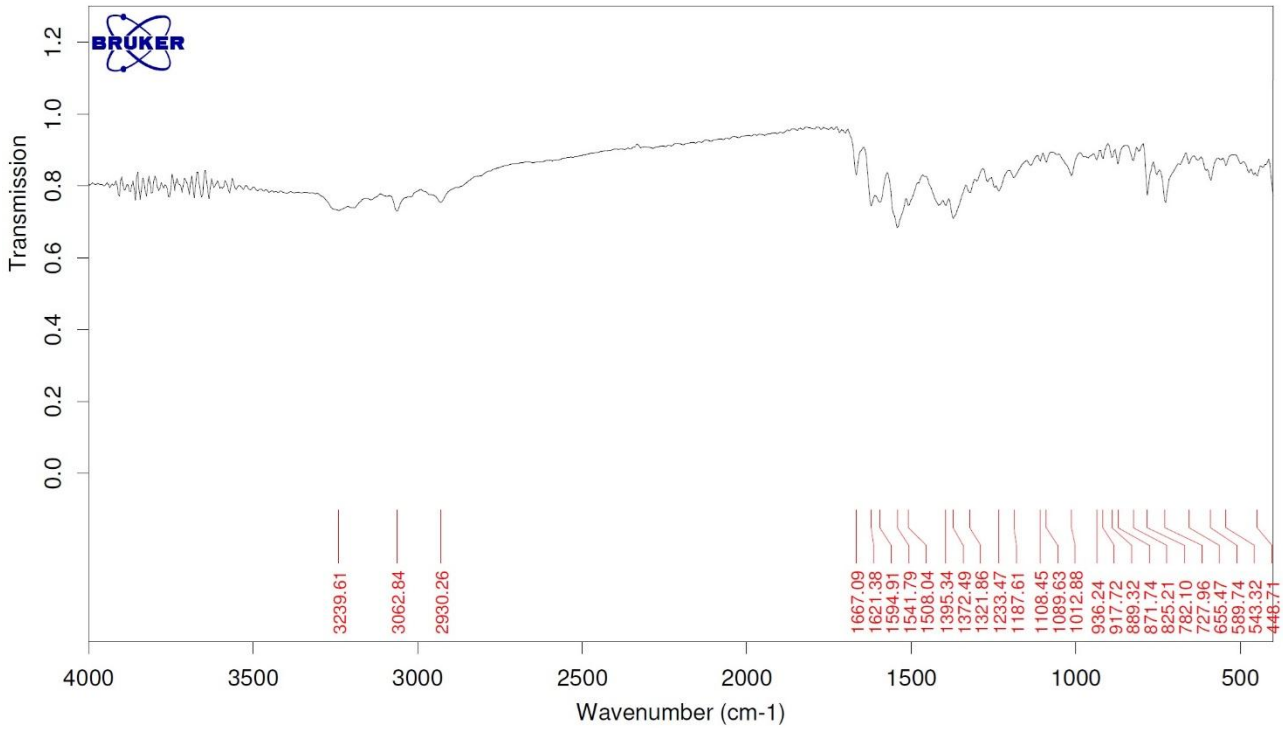


Fig. S8. IR spectrum of **2.**

4. XRPD of 1 and 2

Powder X-Ray Diffraction (PXRD) data were collected in a D8 Advance Bruker AXS θ-θ diffractometer, equipped with a LYNXEYE-XE detector, copper radiation source (Cu K_α, λ =1.5406 Å), operated at 40 kV and 30 mA, with the following data collection parameters: 3-60° 2θ range, step size of 0.02° and 0.6 s per step. The diffractograms were used to ascertain bulk material purity of the synthesised compounds, by comparing the calculated (from SCXRD data) and experimental PXRD patterns. MERCURY[s3] was used to obtain the calculated patterns from single-crystal data. There are

splitting patterns in the experimental diffraction peaks of **1** in Figure S9, which can be explained with the phase transformation from a distorted trigonal bipyramidal to a distorted trigonal monopyramidal geometry of Zn centre. In fact, the Zn(1)-O(5)$_{DMF}$ (2.230 Å) distance is longer than Zn(1)-O(4)$_{DMF}$ (2.095 Å) in **1**, leading to the elimination of a weak coordinated DMF molecule in the grinding process.

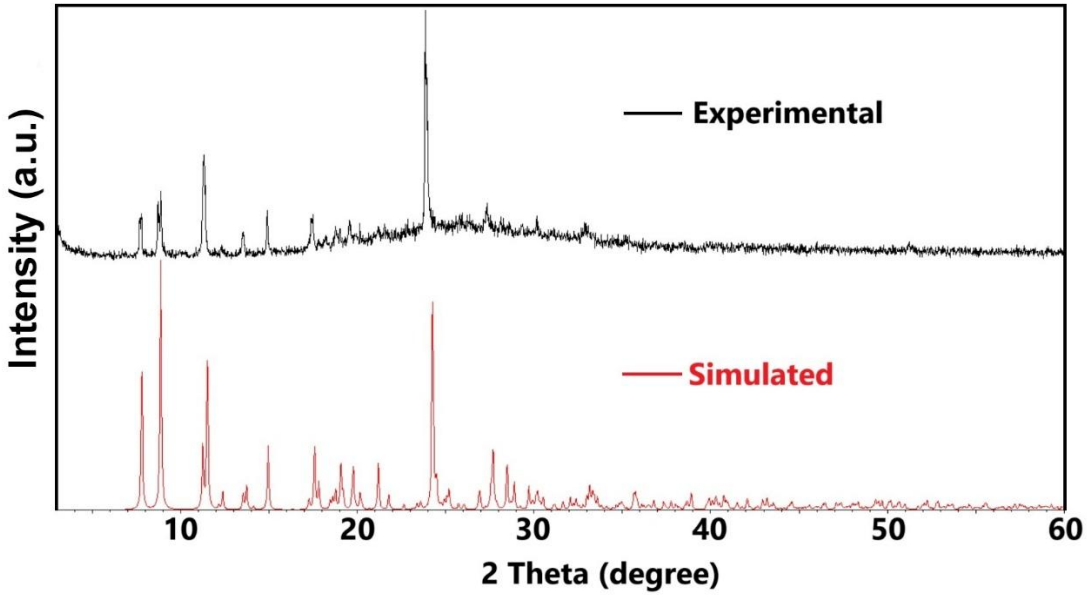


Fig. S9. The experimental and simulated PXRD patterns of **1.**

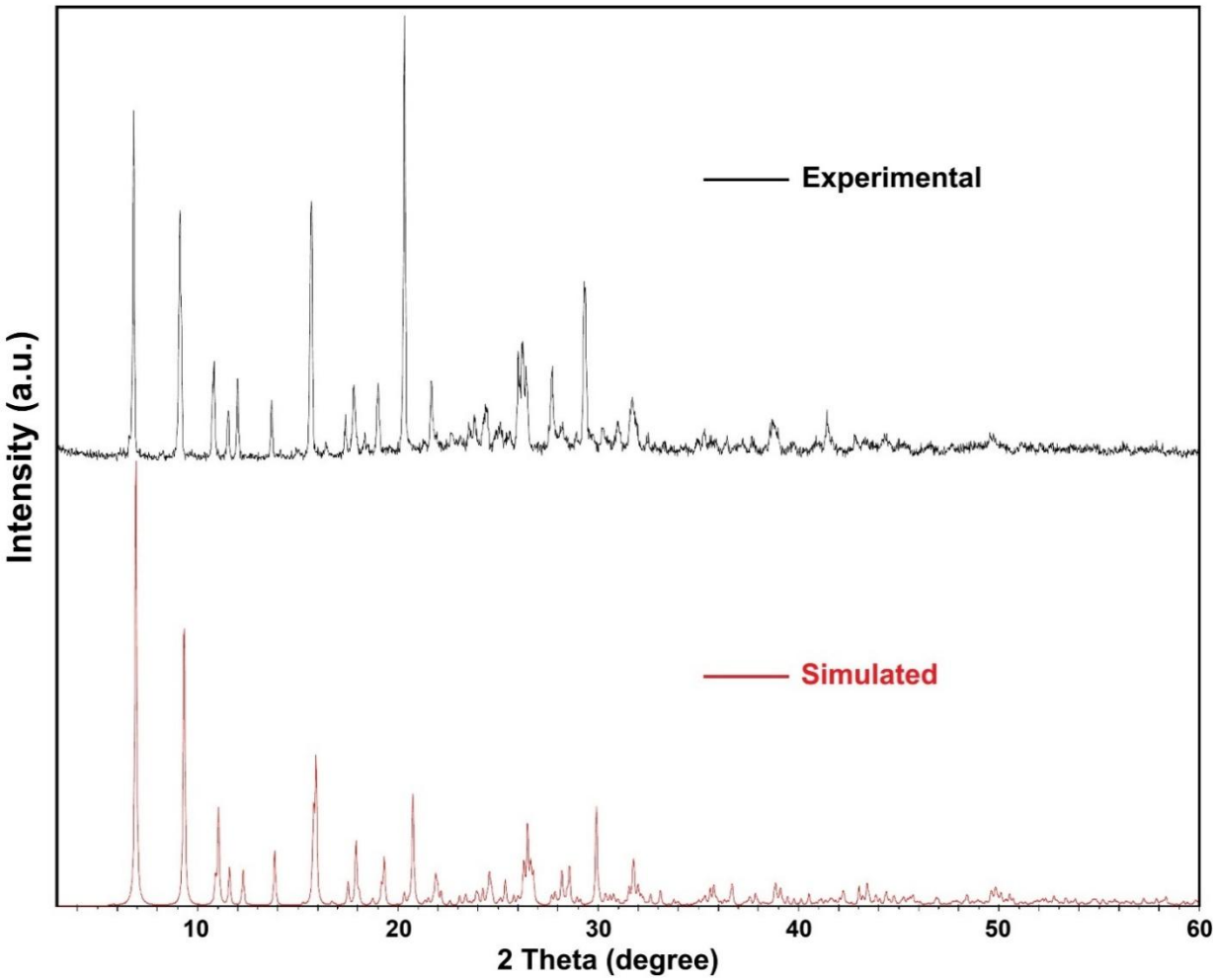


Fig. S10. The experimental and simulated PXRD patterns of **2.**

5. Single crystal X-ray analysis

Data for single crystals of **1** and **2** were collected using a Bruker SMART APEX-II CCD area detector equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 150 K. Cell parameters were retrieved using Bruker SMART[s4] software and refined using Bruker SAINT[s4] on all the observed reflections. Absorption corrections were applied using SADABS.[s5] Structures were solved by direct methods by using the SHELXS-2014 package[s5] and refined with SHELXL-2014/6.[s6] Calculations were performed using the WinGX System-Version 2014.1.[s7] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at calculated positions. Crystallographic and selected structural details are listed in Table S1. Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Center [CCDC 2416236 (for **1**) and 2416237 (for **2**)]. Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif). MERCURY[s3] was used for packing diagrams.

Table S1. Crystallographic data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{21}H_{21}N_5O_7SeZn$	$C_{46}H_{50}Cd_2N_{10}O_{14}Se_2$
Formula weight	599.76	1349.68
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	10.0822(7)	11.5930(4)
b (Å)	10.1131(7)	15.1366(5)
c (Å)	11.3662(7)	16.7568(6)
α (°)	95.063(2)	67.2510(10)
β (°)	92.398(2)	89.6440(10)
γ (°)	98.918(3)	68.0130(10)
V (Å^3)	1138.63(13)	2481.26(15)
Z	2	2
D_{calc} (g/cm^3)	1.749	1.806
F000	604	1344
μ (mm^{-1})	2.731	2.401
R_{int}	0.0436	0.0317
$R(F)$ ($I \geq 2\sigma$)	0.0379	0.0392
wR (F^2) (all data)	0.1039	0.1038
GOF (F^2)	1.026	1.032

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

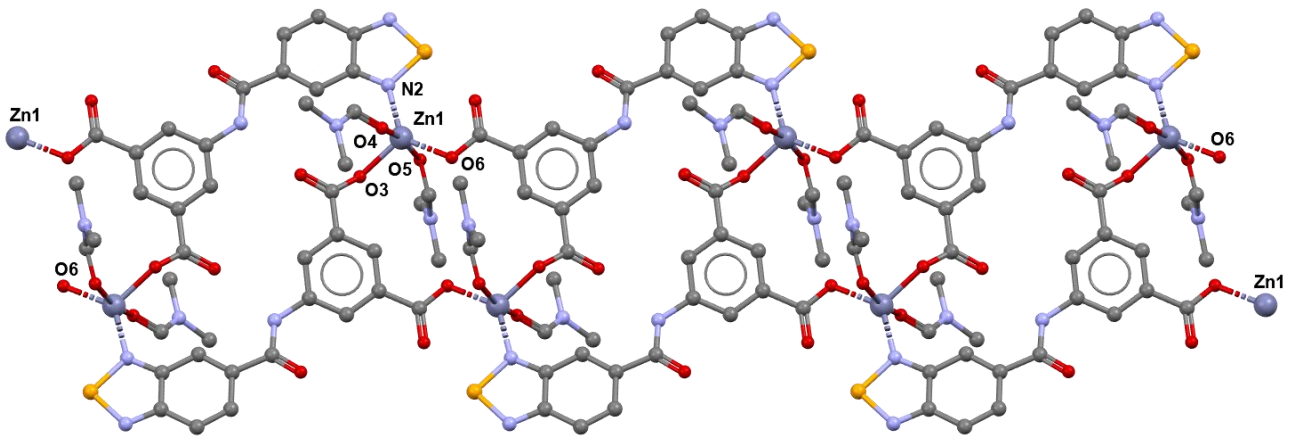


Fig. S11. Perspective view of a section of the polymeric chain of **1**. Hydrogen atoms were omitted for clarity purposes.

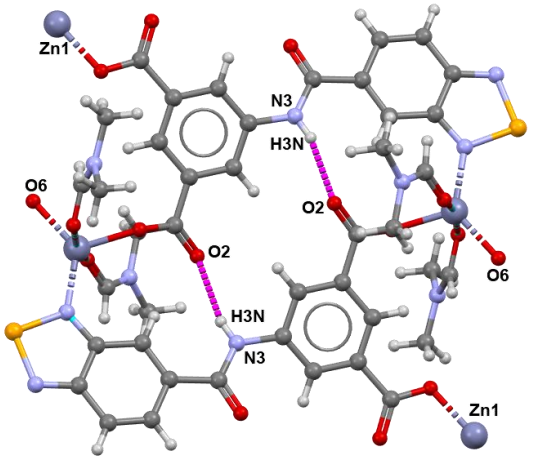


Fig. S12. Hydrogen bonding interactions in **1.**

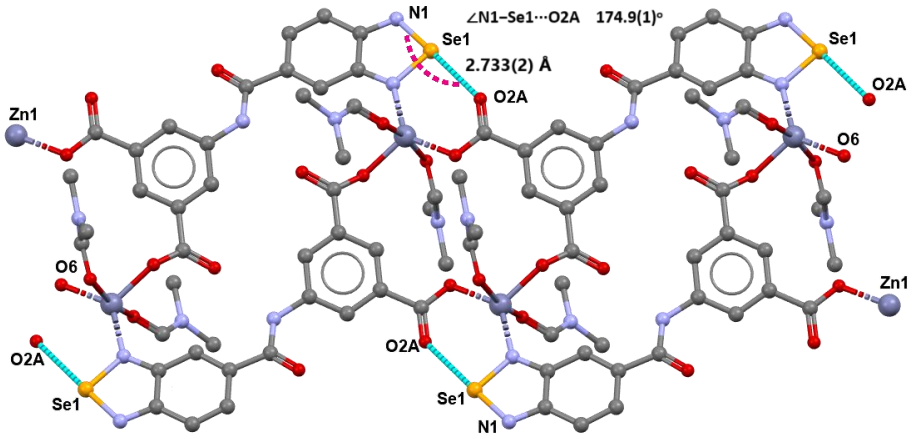


Fig. S13. Chalcogen bonding in 1D supramolecular chain of **1.** Hydrogen atoms were omitted for clarity purposes.

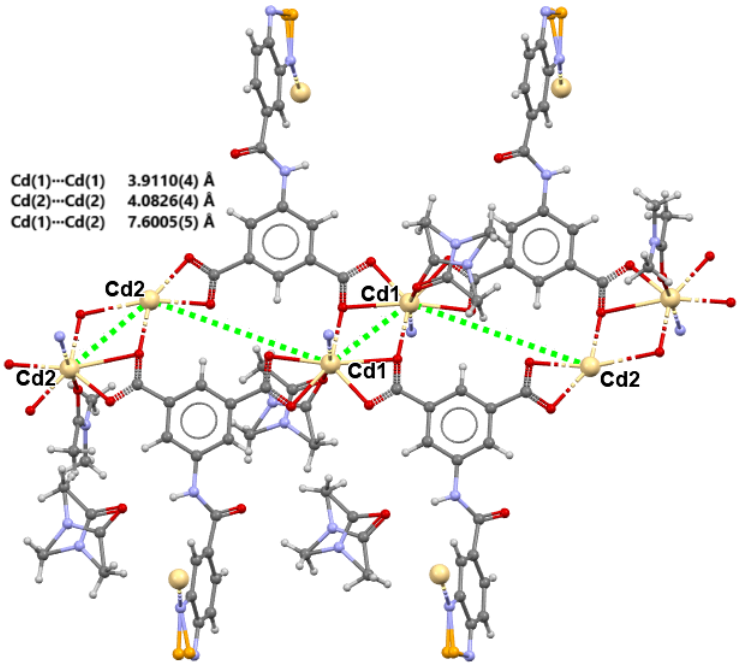


Fig. S14. Molecular structure of **2.**

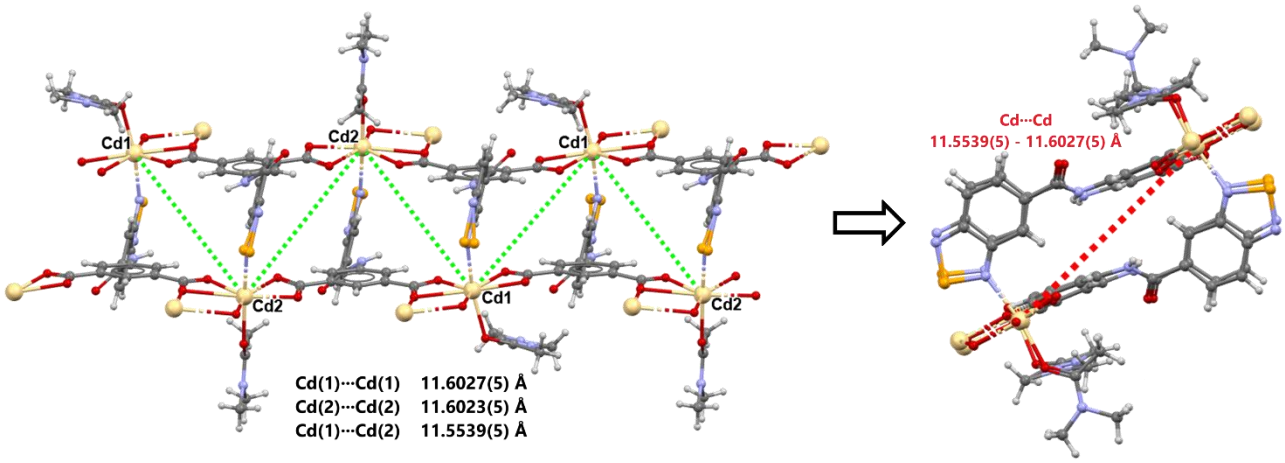


Fig. S15. The Cd···Cd separations in crystal packing of **2**. Uncoordinated DMA moleculaes were omitted for clarity purposes.

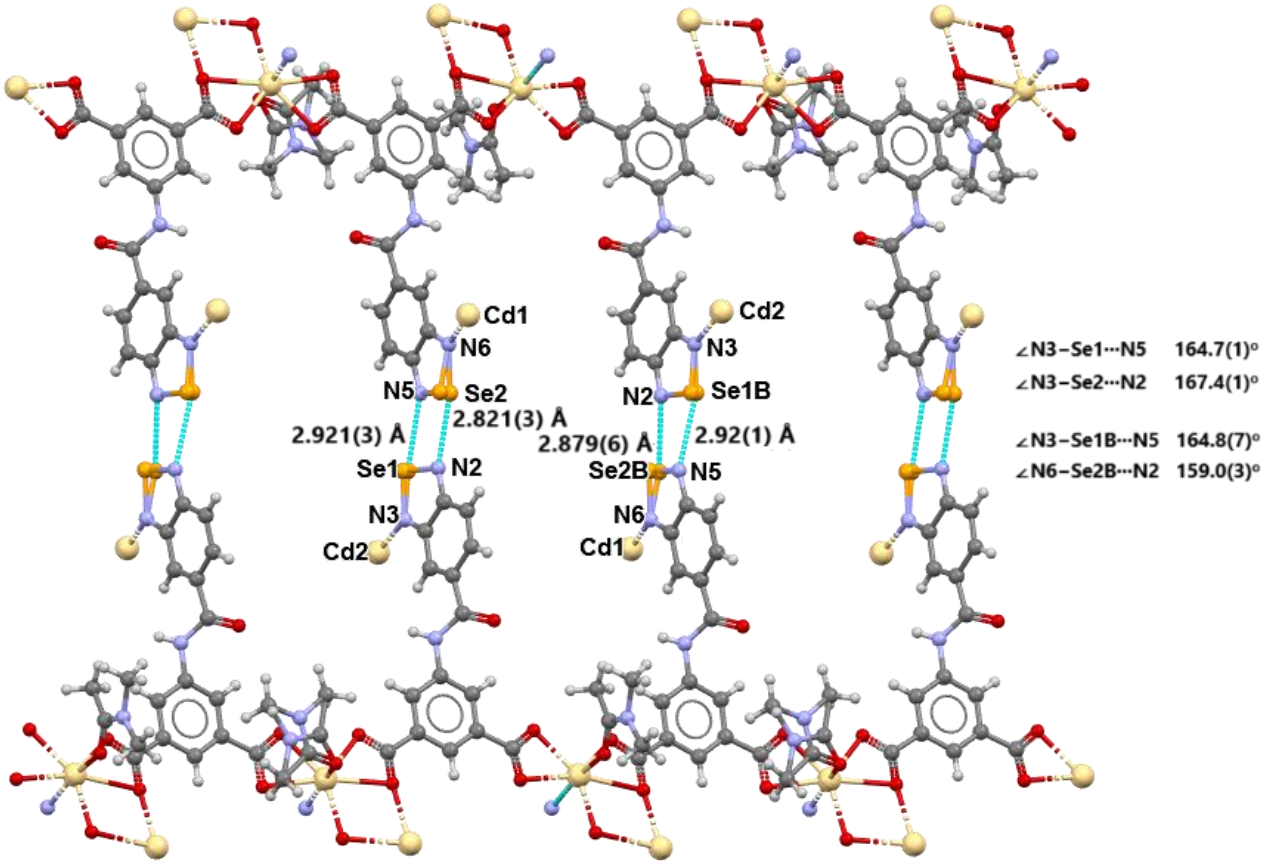


Fig. S16. Chalcogen bonding interactions between building blocks of **2.** Uncoordinated DMA moleculaes were omitted for clarity purposes.

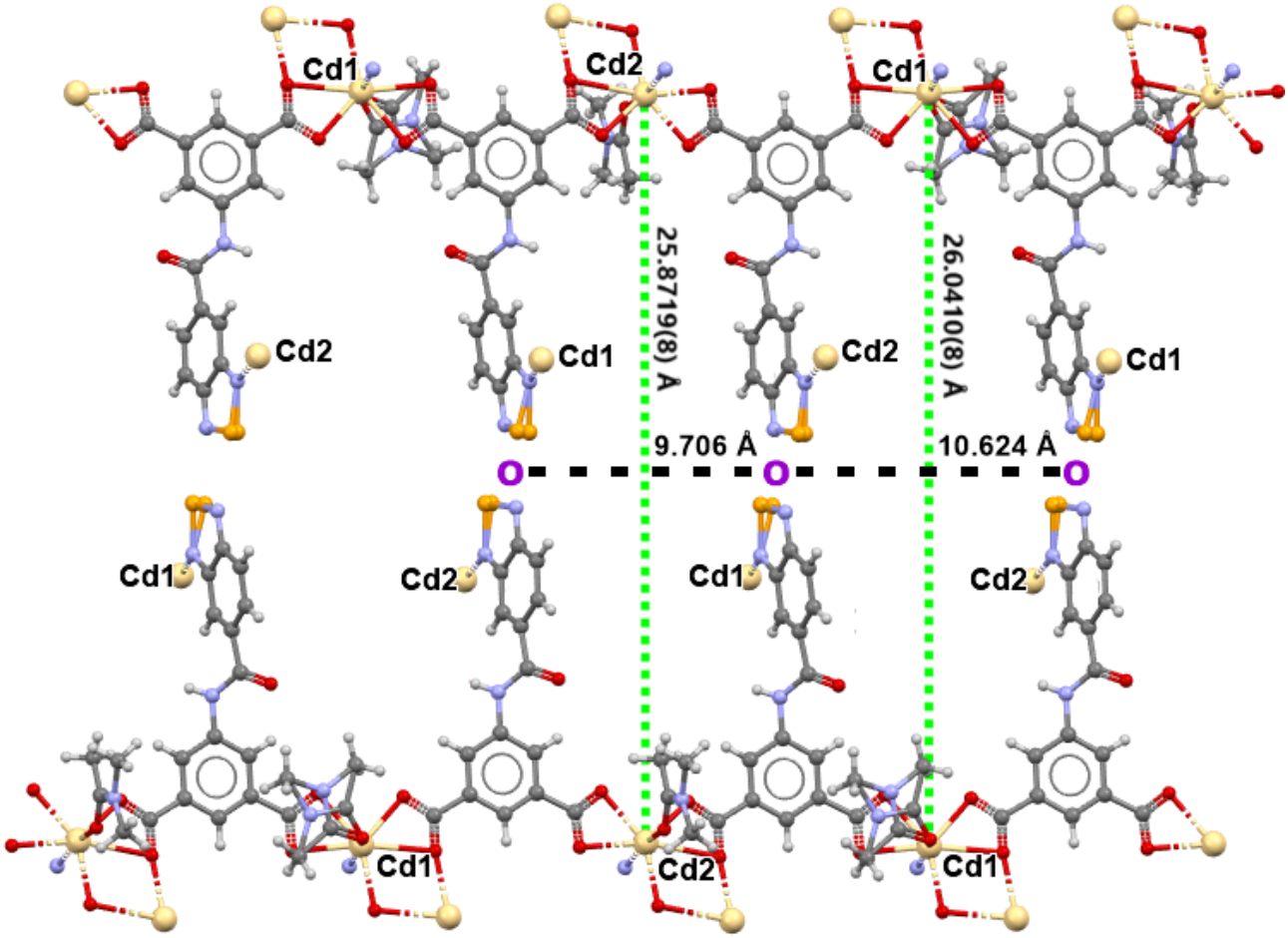


Fig. S17. The Cd···Cd separations and *centroid-centroid* distances between the Se_2N_2 synthons in crystal packing of **2.** Uncoordinated DMA moleculaes were omitted for clarity purposes.

6. Theoretical methods

The energetic calculations were carried out using the Turbomole 7.7 program[s8] at the PBE0-D4/def2-TZVP level of theory.[s9-s12] The molecular electrostatic potential (MEP) were plotted using a 0.001 a.u. isosurface. The quantum theory of atoms in molecules (QTAIM)[S13] and NCIPlot[S14] analyses were performed at the same level of theoryusing the Multiwfn program[s15] program. The natural bond orbital (NBO) analysis[s16] was conducted using the NBO7 program.[s17]

7. References

s1 S. Deng, D. Zeng, Y. Luo, J. Zhao, X. Li, Z. Zhao and T. Chen, *RSC Adv.*, 2017, **7**, 16721.

s2 A. C. Ruberte, D. Plano, I. Encío, C. Aydillo, A. K. Sharma and C. Sanmartín, *Eur. J. Med. Chem.*, 2018, **157**, 14.

s3 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466.

s4 Bruker, APEX2. Bruker AXS Inc., Madison, Wisconsin, USA, 2012.

s5 G. M. Sheldrick, SADABS Software for Empirical Absorption Correction; University of Göttingen: Germany, 2000.

s6 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

s7 L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849.

s8 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.

s9 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.

s10 E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth and S. Grimme, *J. Chem. Phys.*, 2019, **150**, 154122.

s11 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.

s12 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

s13 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893.

s14 E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498.

s15 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.

s16 E. D. Glendening, C. R. Landis and F. Weinhold, 2012, *WIREs Comput. Mol. Sci.*, **2**, 1–42.

s17 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis and F. Weinhold, *NBO 7.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2018.