Supplementary Information

Polymetallic Titanium Chalcogenide Clusters Comprising $\{E_n\}^{2-}$ Ligands (E = S, Se; n = 1–3)

Subhash Bairagi,[‡] Soumen Giri,[‡] Debipada Chatterjee, Soham Chowdhury, and Sundargopal Ghosh[*]

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India, E-mail: sghosh@iitm.ac.in

[‡]These authors contributed equally to this work.

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I Supplementary Data

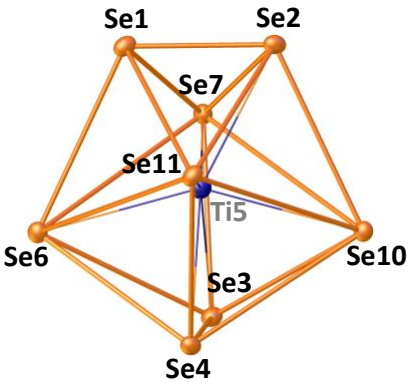


Figure S1. Dodecahedron core in **1**.

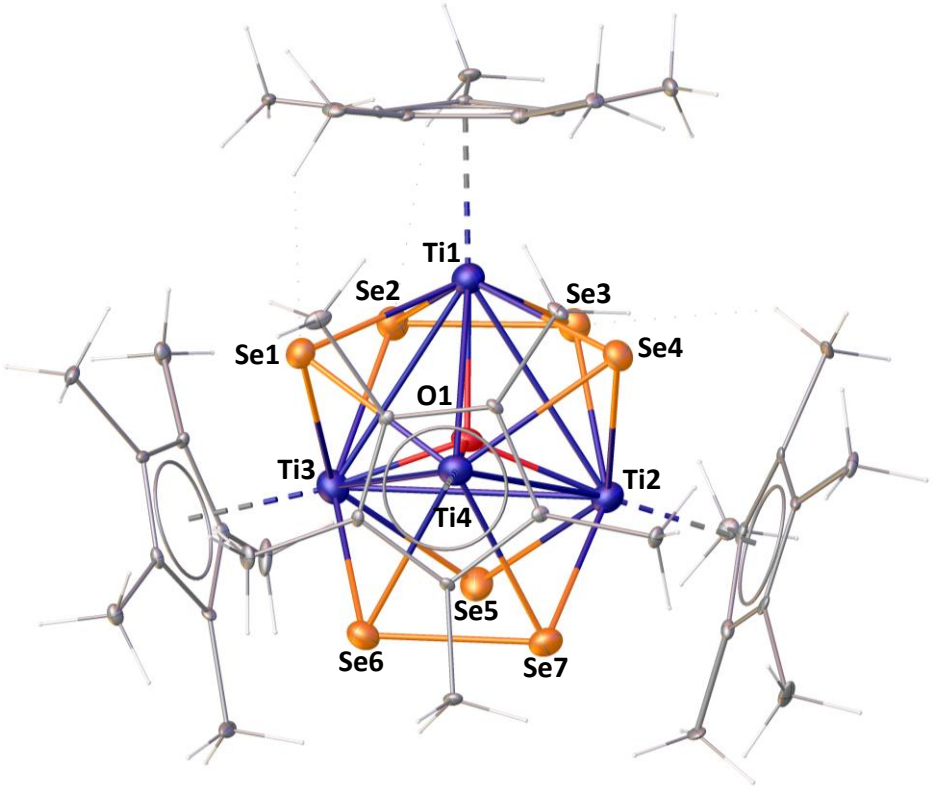


Figure S2. Molecular structure and labelling diagram of **2**. Selected bond lengths (Å) and bond angles (˚): Ti1−Ti4 3.1504(16), Ti1−Ti3 3.3008(11), Ti3−Se5 2.5259(9), Ti3−Se6 2.6881(13), Ti1−O1 2.0757(18), Se6−Se7 2.3185(8), Ti3−Ti1−Ti2 63.388, Ti1−O1−Ti2 110.21(3).

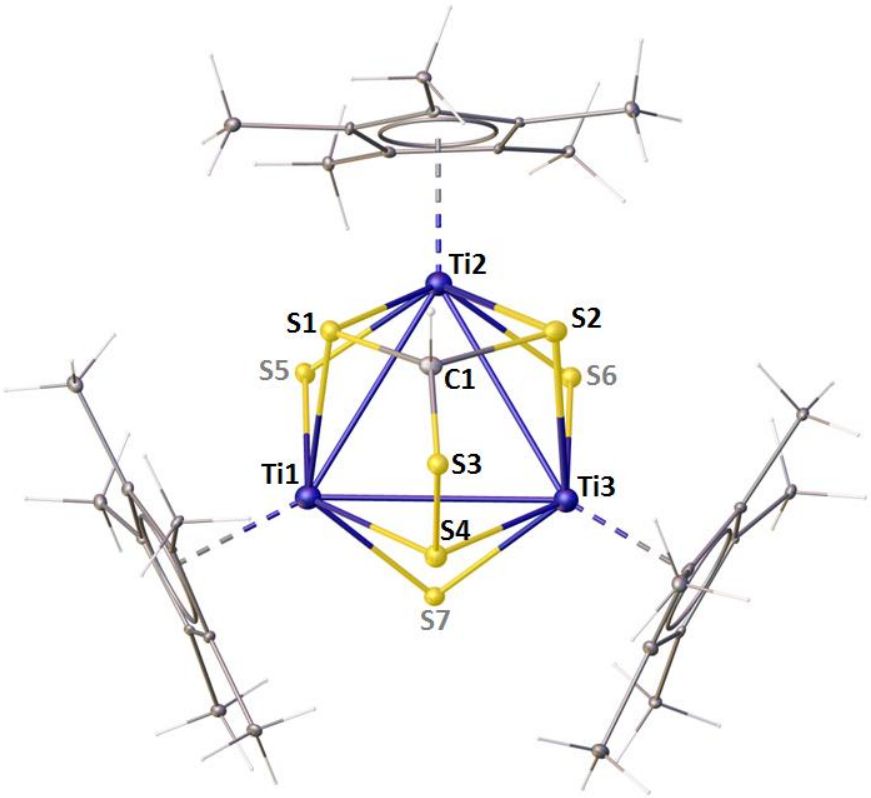


Figure S3. Molecular structure and labeling diagram of **5**. Selected bond lengths (Å) and bond angles (˚): Ti1−Ti2 3.366, Ti1−S1 2.5302(18), S3−S4 2.083(2), C1−S3 1.769(6), Ti1−S1−Ti2 83.90(6), S1−C1−S2 102.4(3).

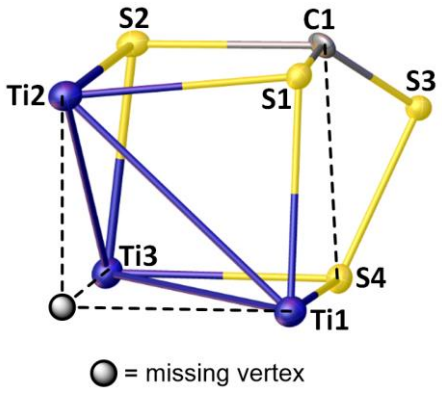


Figure S4. Missing vertex homocubane core in **5**.

II Spectroscopic Details

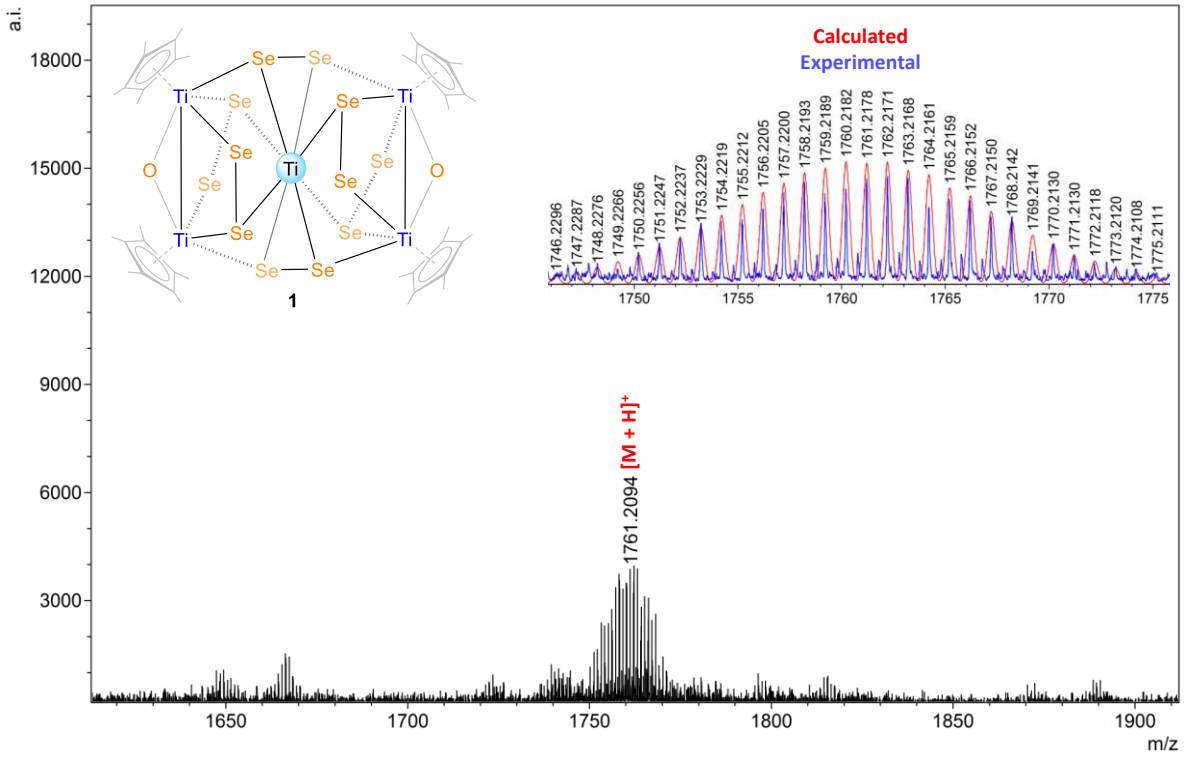


Figure S5. ESI-MS spectrum of **1**.

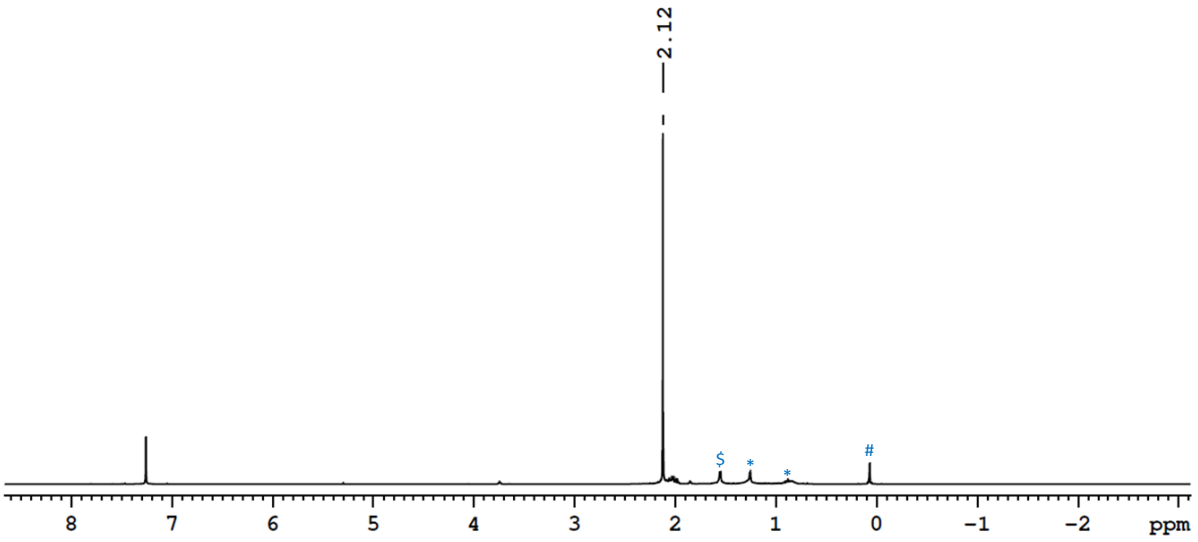


Figure S6. ^{1}H NMR spectrum of **1** in $CDCl_3$ ($H_2O, *Grease, #Silicon grease).

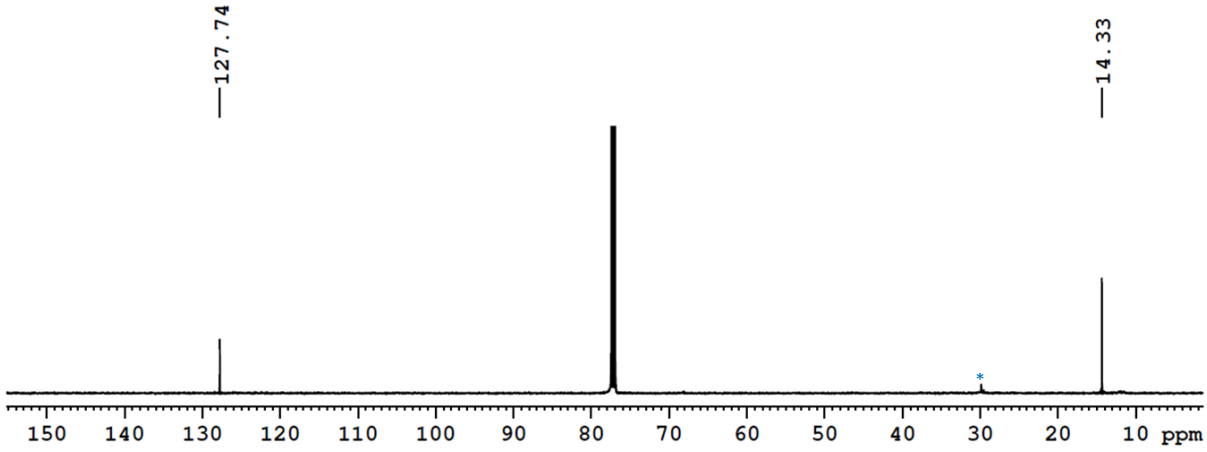


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ (*Grease).

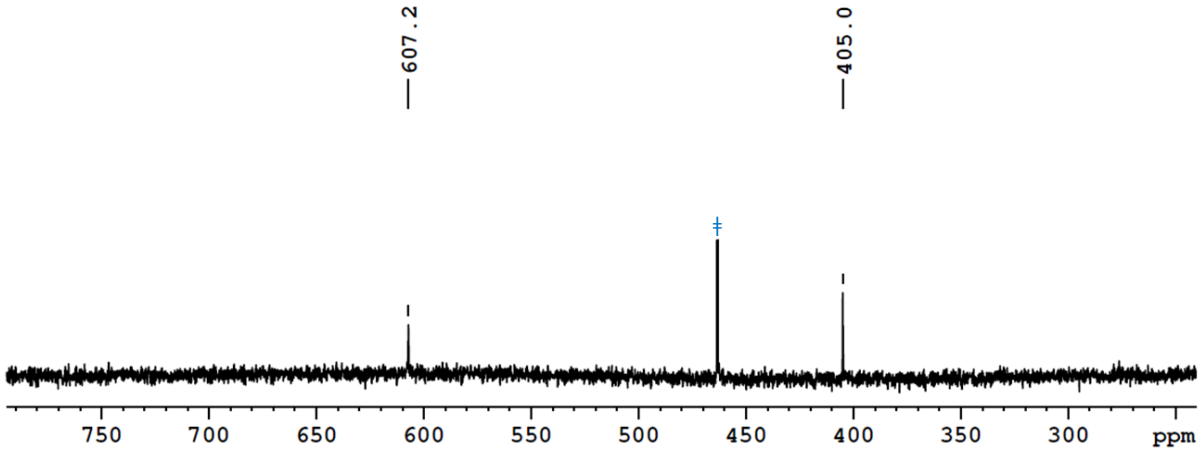


Figure S8. ^{77}Se NMR spectrum of **1** in $CDCl_3$ (‡ Peak at δ = 463 ppm is due to the presence of Se_2Ph_2 as external reference).

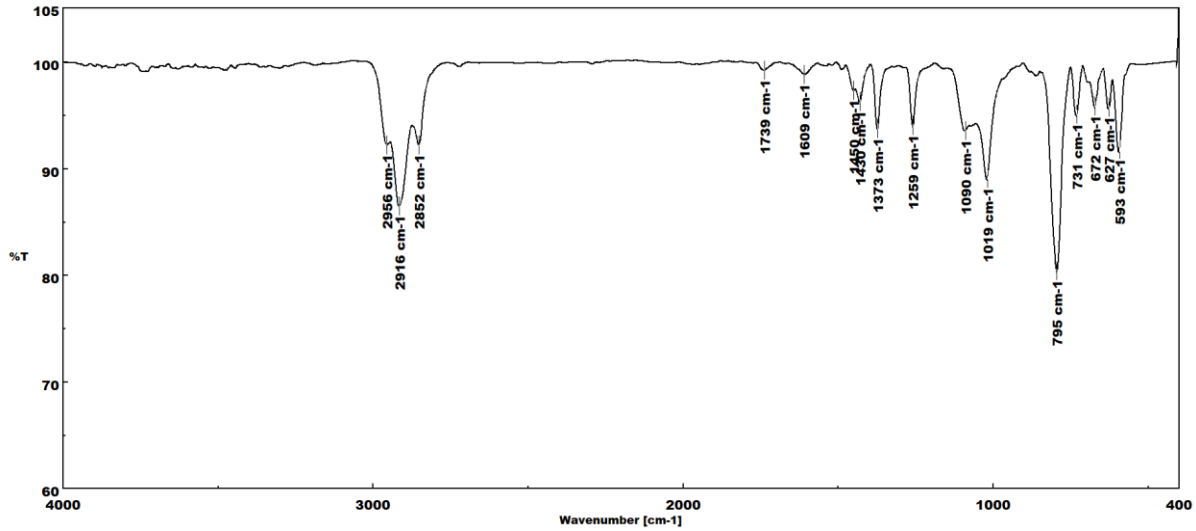


Figure S9. IR spectrum of **1**.

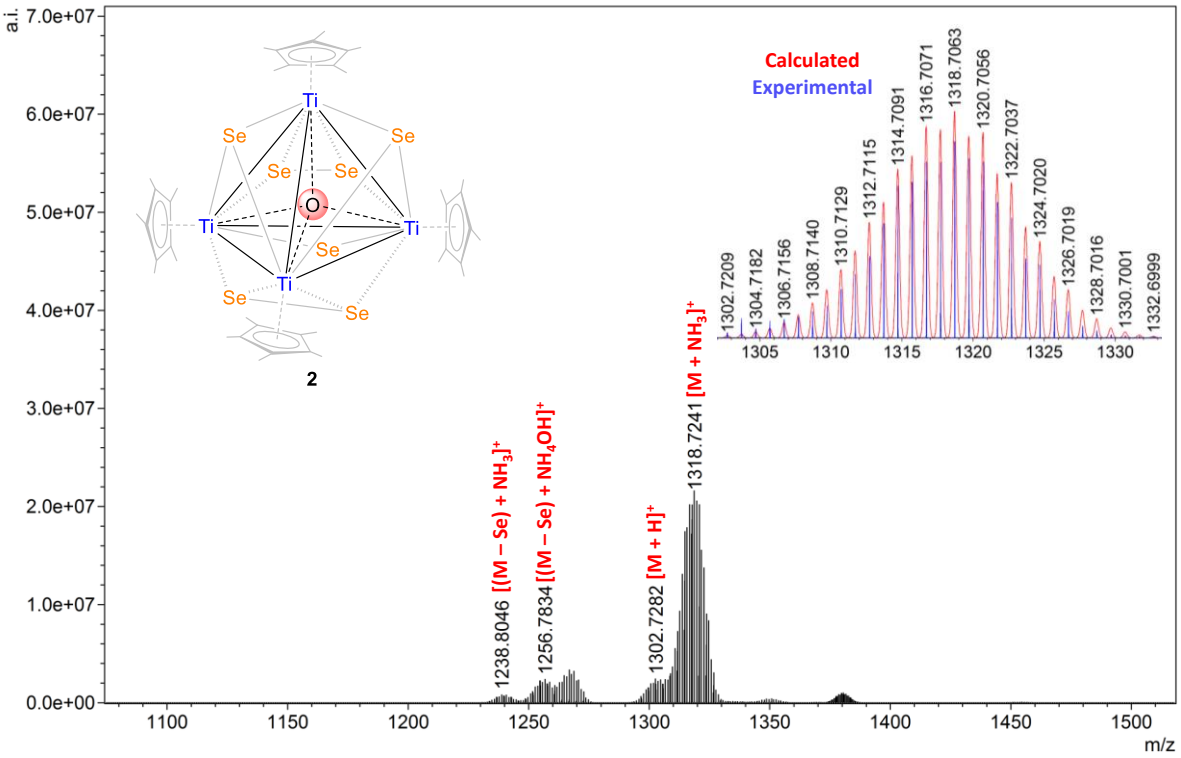


Figure S10. ESI-MS spectrum of **2**.

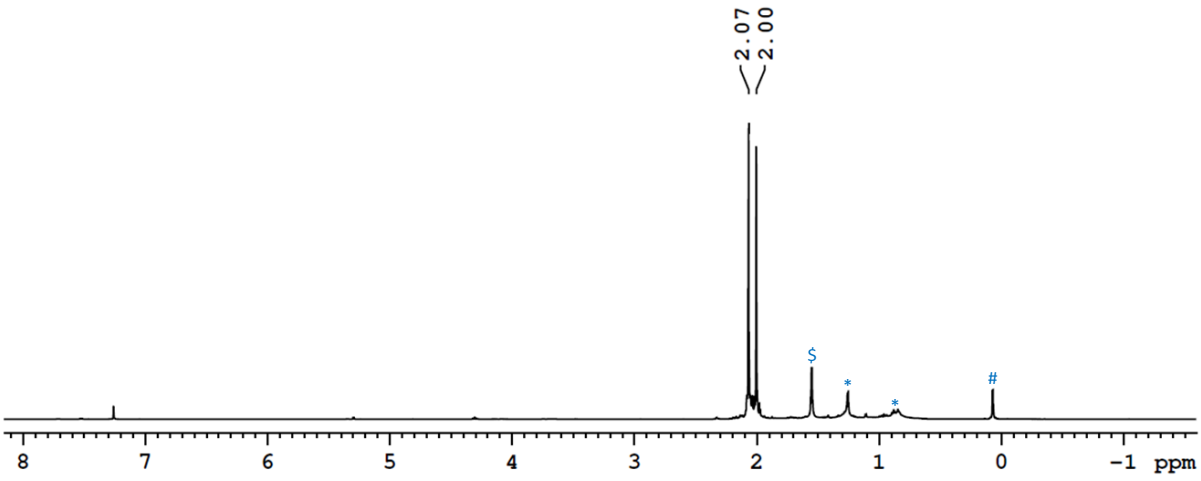


Figure S11. ^{1}H NMR spectrum of **2** in $CDCl_3$ ($H_2O, *Grease, #Silicon grease).

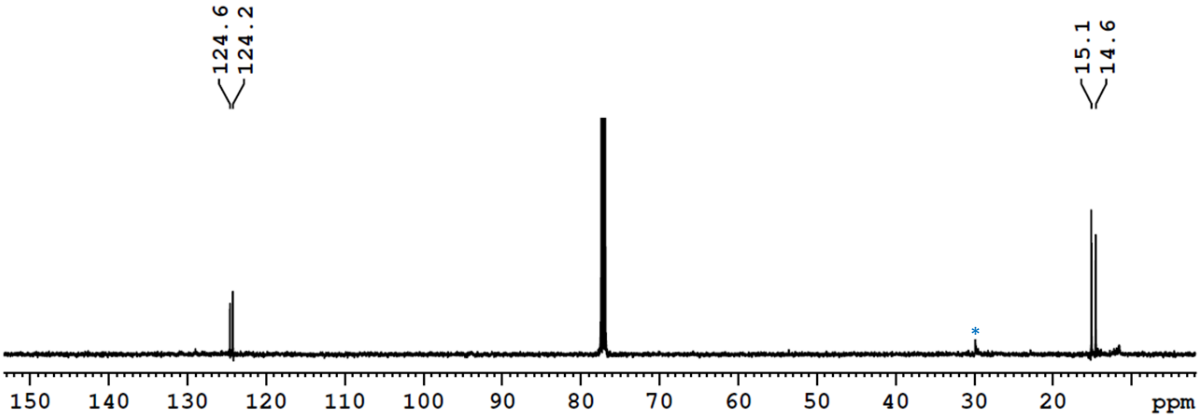


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (*Grease).

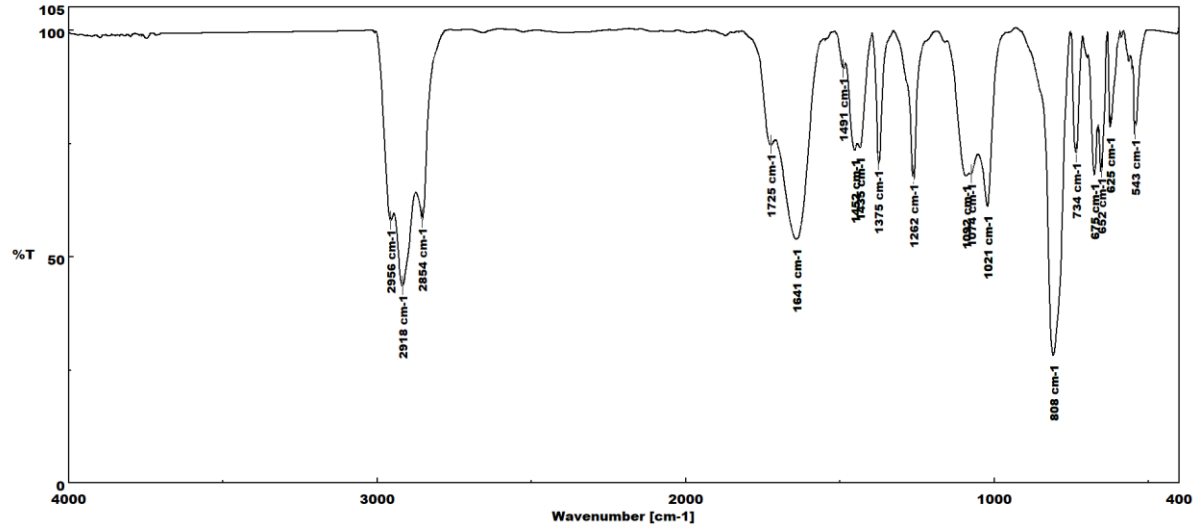


Figure S13. IR spectrum of **2**.

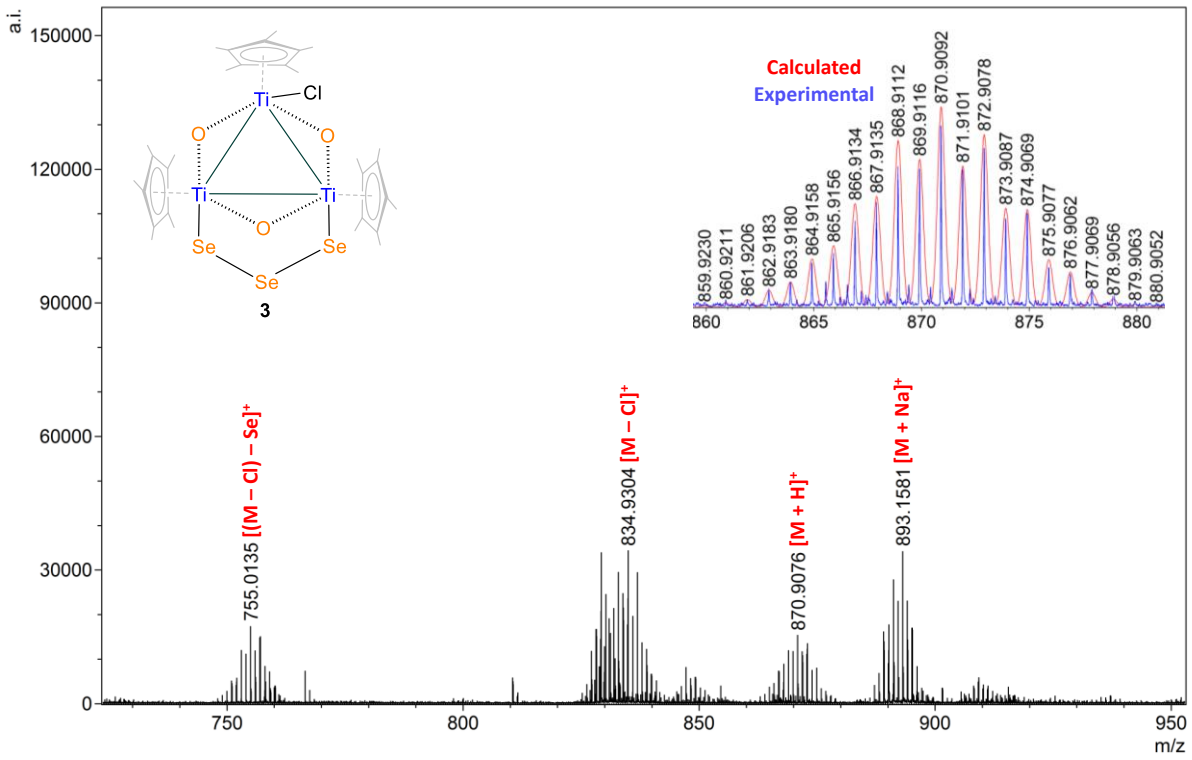


Figure S14. ESI-MS spectrum of **3**.

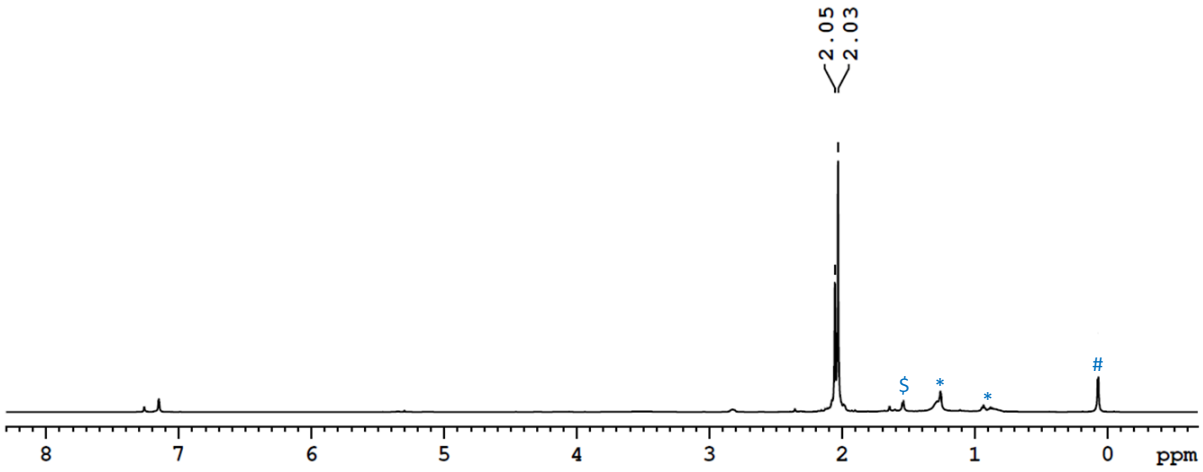


Figure S15. ^{1}H NMR spectrum of **3** in $CDCl_3$ ($H_2O, *Grease, #Silicon grease, †Inseparable impurity).

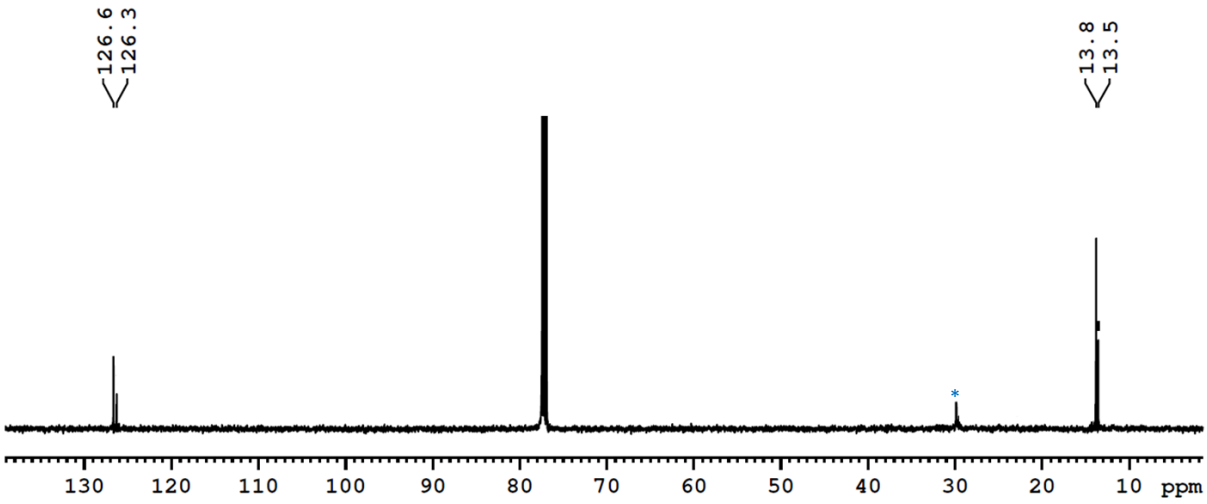


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ (*Grease).

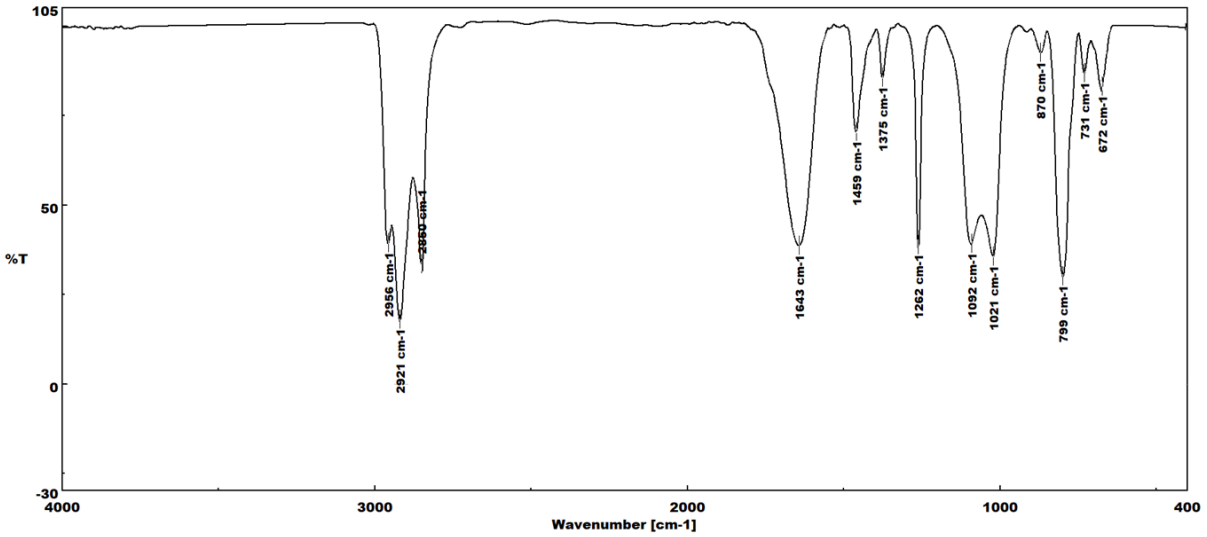


Figure S17. IR spectrum of **3**.

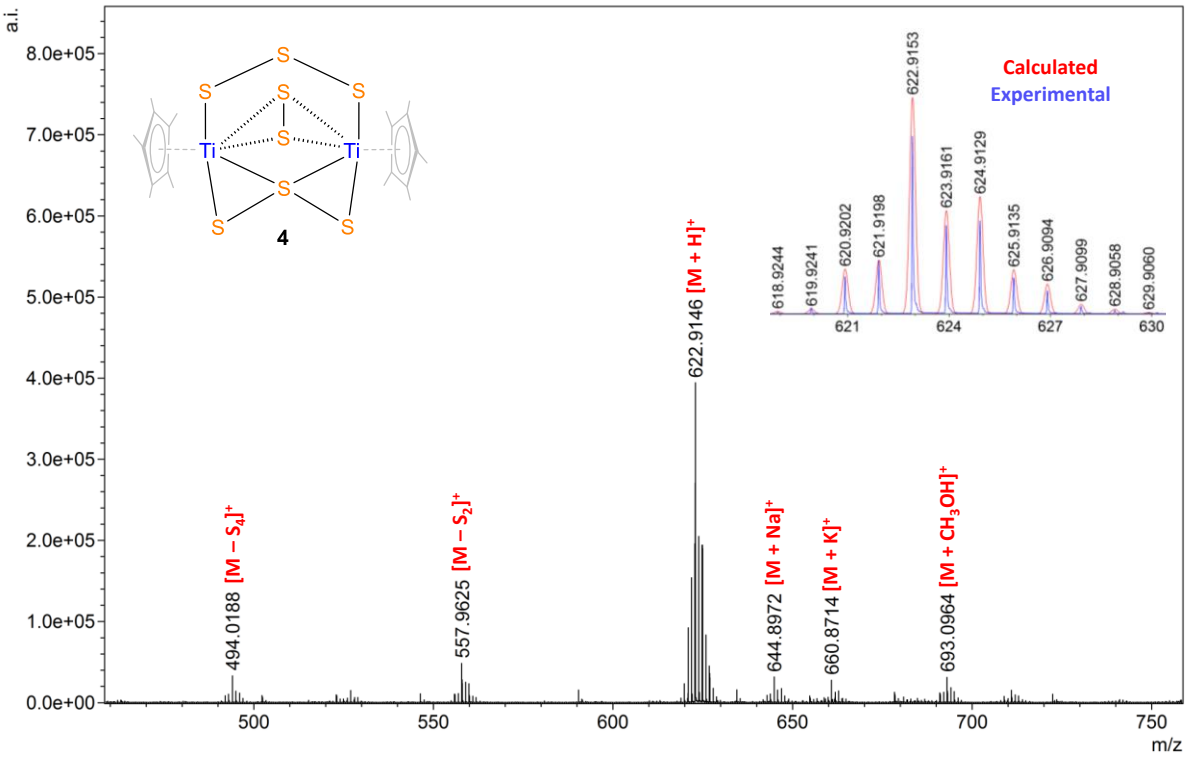


Figure S18. ESI-MS spectrum of **4**.

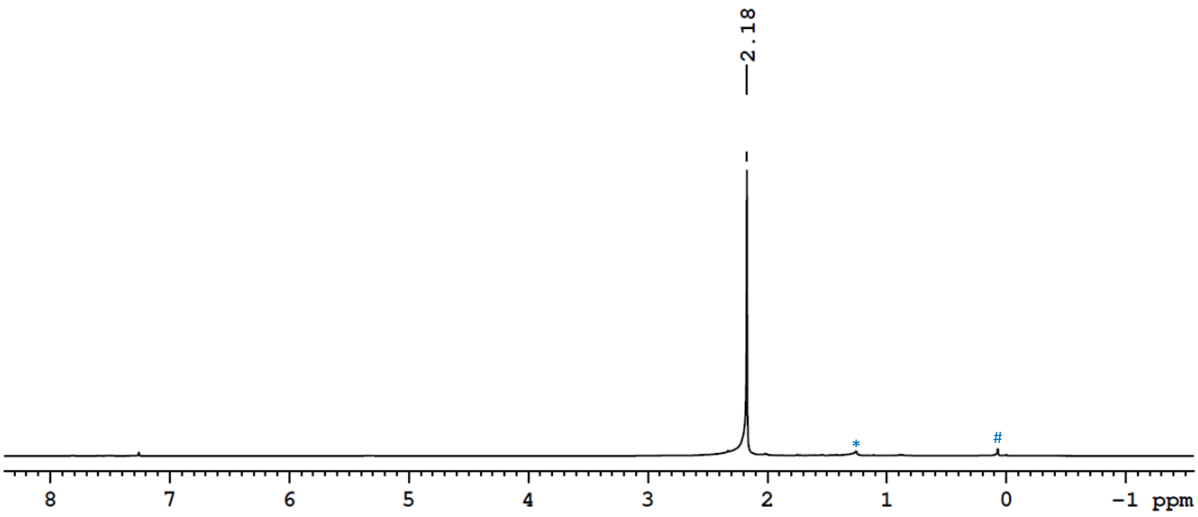


Figure S19. ^{1}H NMR spectrum of **4** in $CDCl_3$ (†Inseparable impurity, *Grease, #Silicon grease).

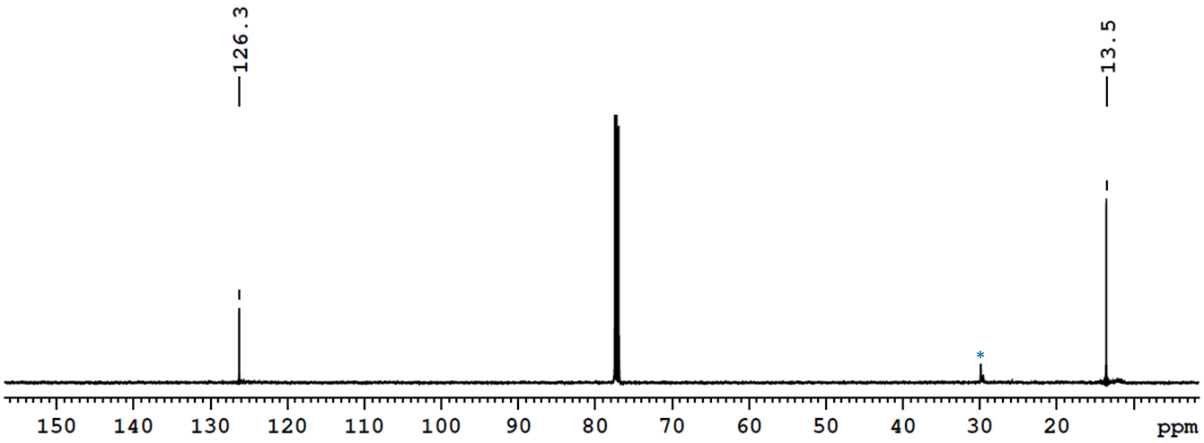


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ (*Grease).

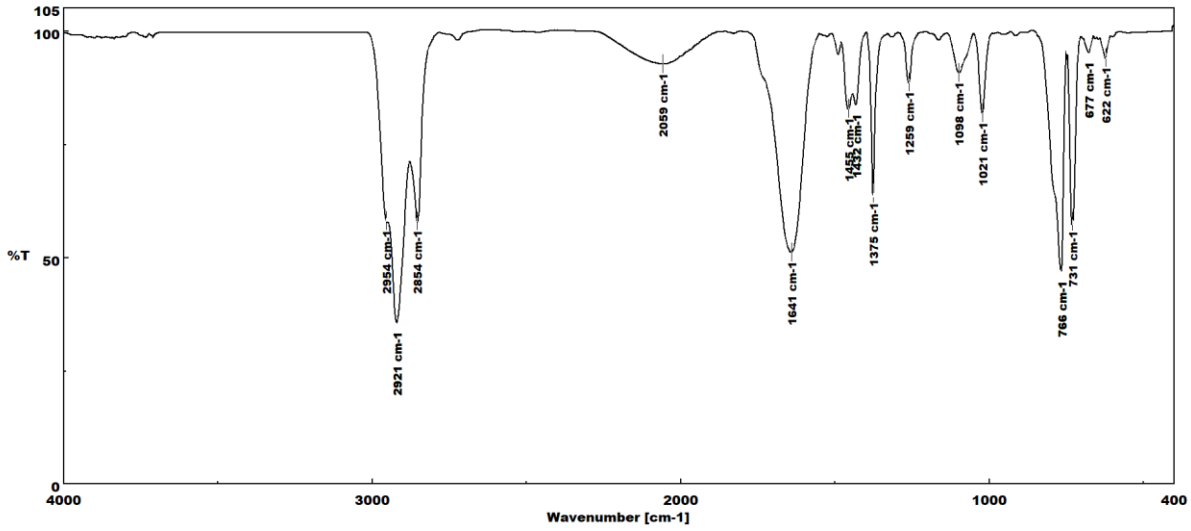


Figure S21. IR spectrum of **4**.

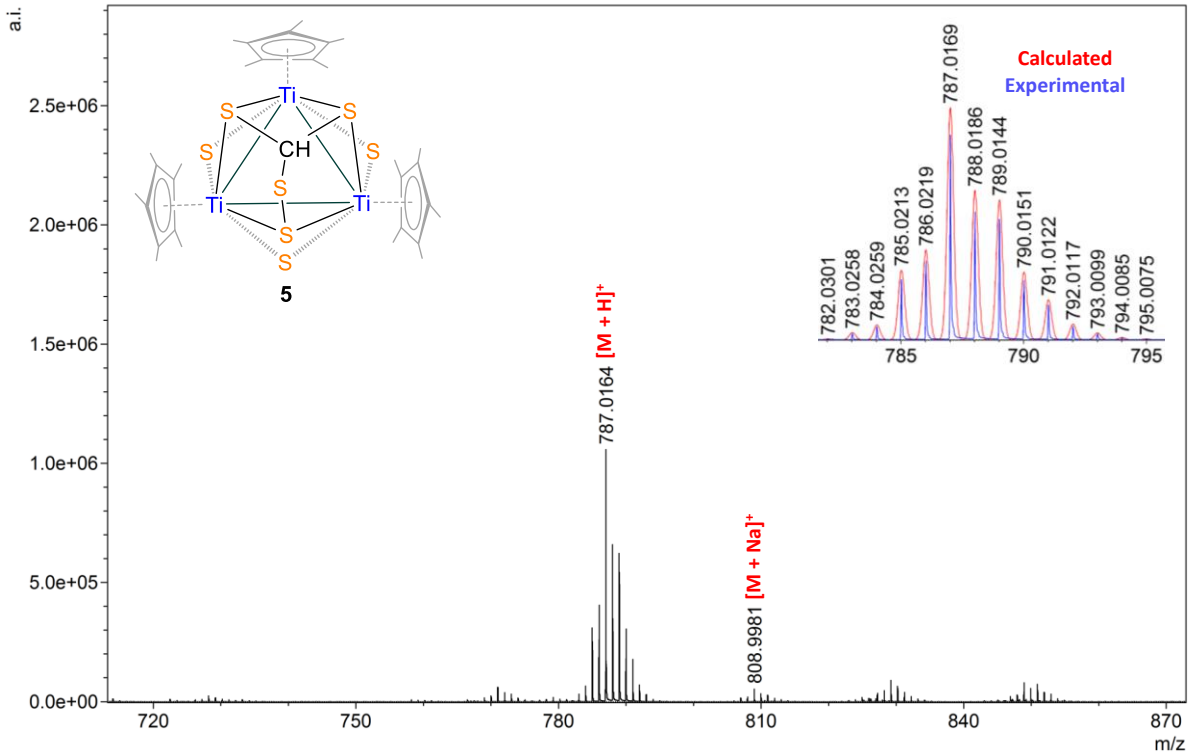


Figure S22. ESI-MS spectrum of **5**.

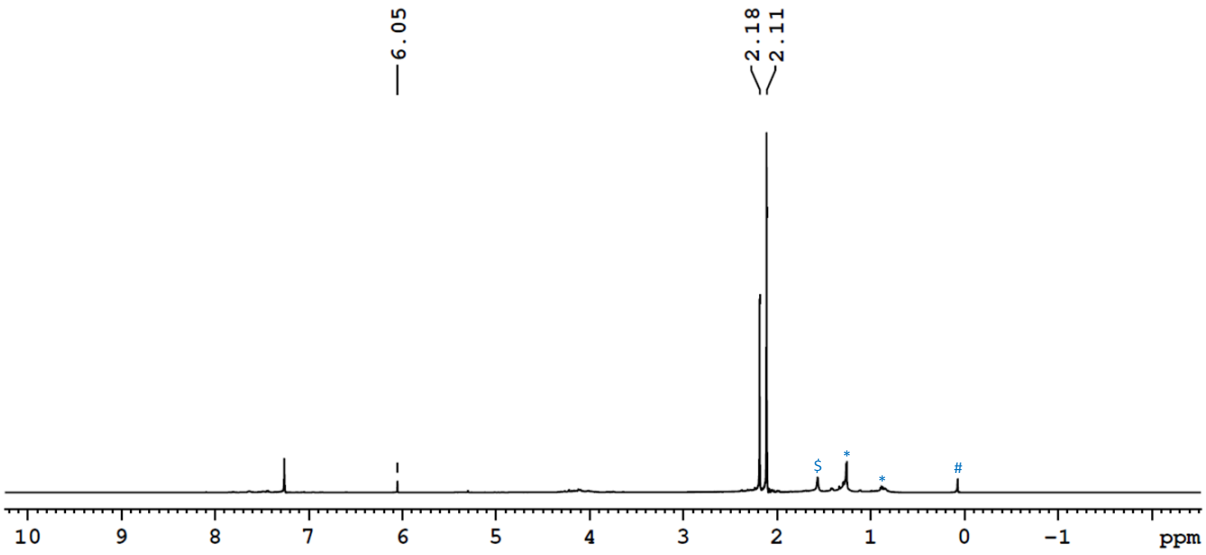


Figure S23. ^{1}H NMR spectrum of **5** in $CDCl_3$ ($H_2O, *Grease, #Silicon grease).

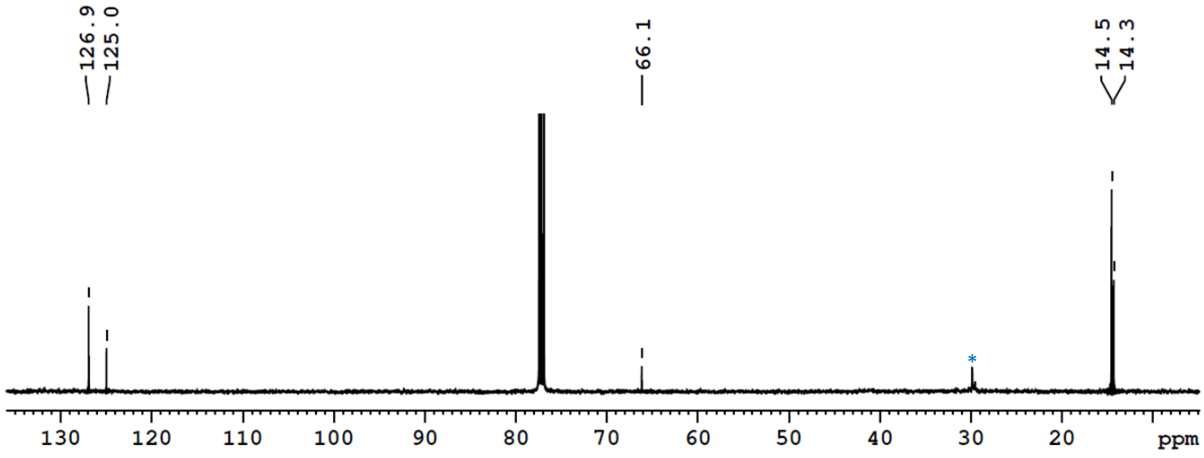


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$ (*Grease).

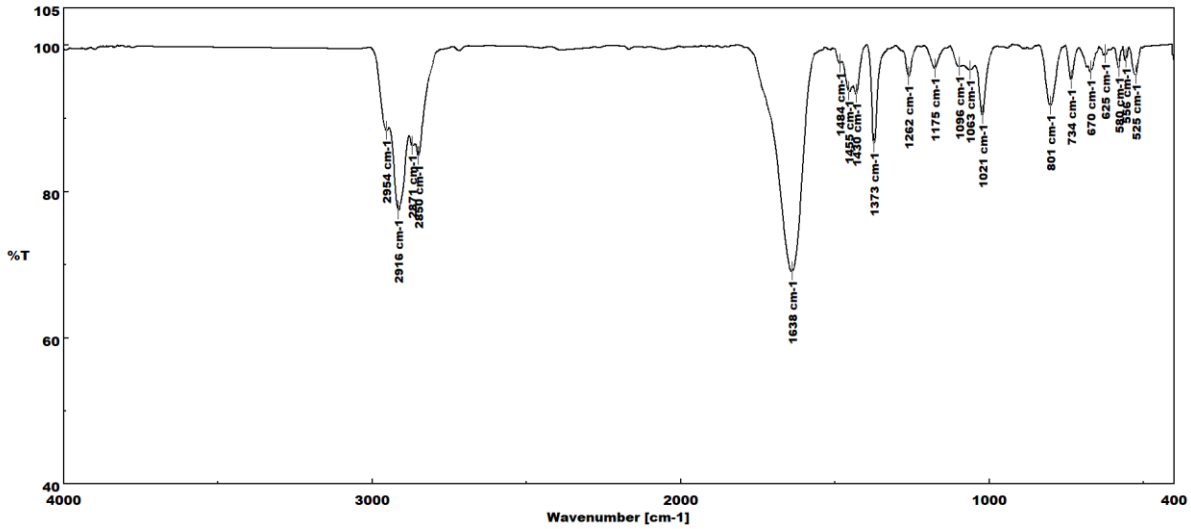


Figure S25. IR spectrum of **5**.

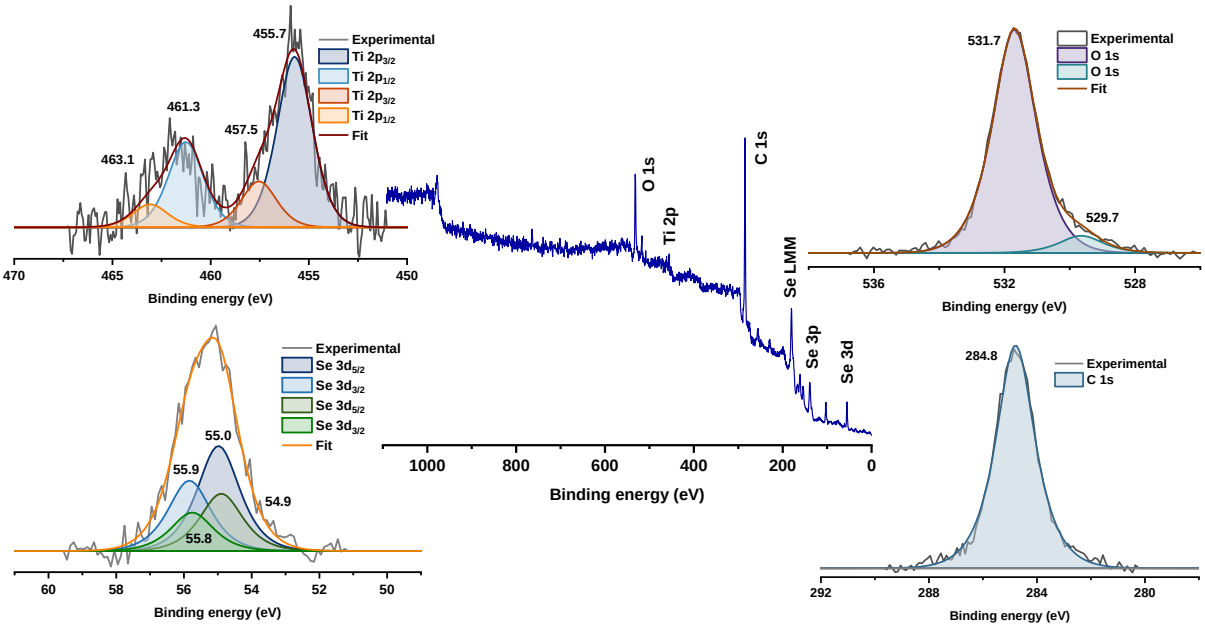


Figure S26. XPS spectra of **1**. The survey spectrum shows the presence of respective elements. The detailed spectra show deconvoluted peaks of Ti 2p, Se 3d, O 1s, and C 1s in the respective spectral regions.

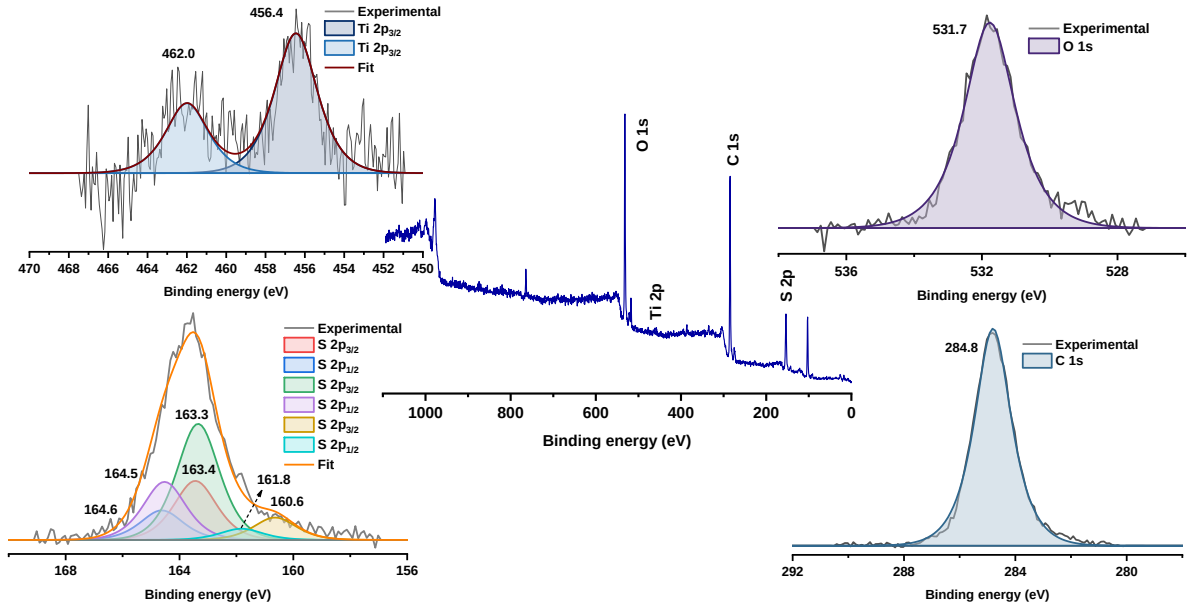


Figure S27. XPS spectra of **4**. The survey spectrum shows the presence of respective elements. The detailed spectra show deconvoluted peaks of Ti 2p, S 2p, O 1s and C 1s in the respective spectral regions.

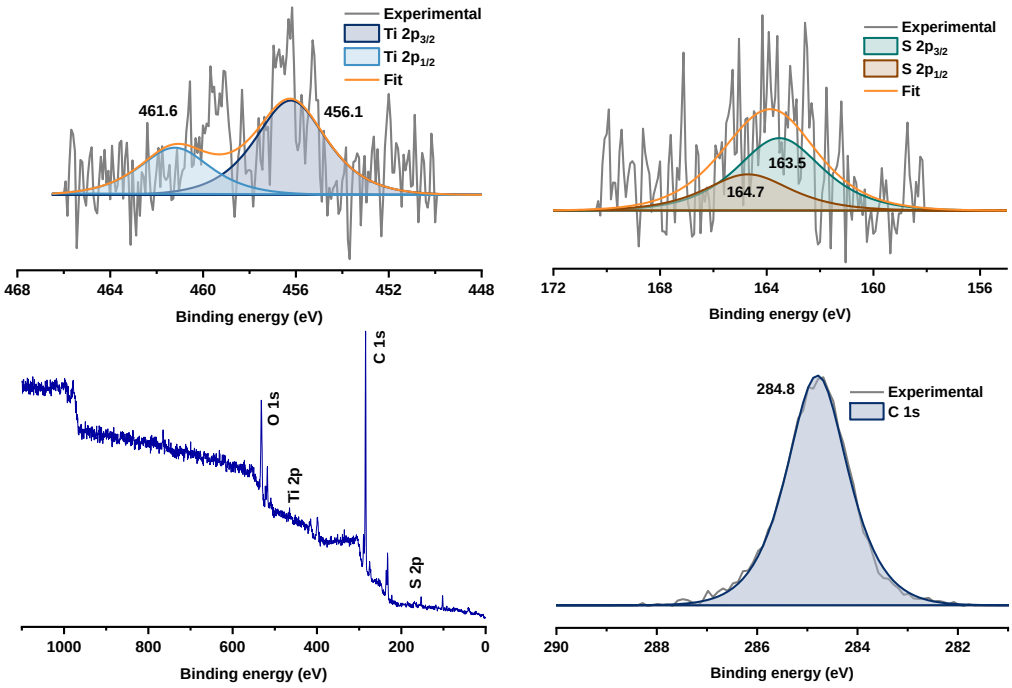


Figure S28. XPS spectra of **5**. The survey spectrum shows the presence of respective elements. The detailed spectra show deconvoluted peaks of Ti 2p, S 2p, and C 1s in the respective spectral regions.

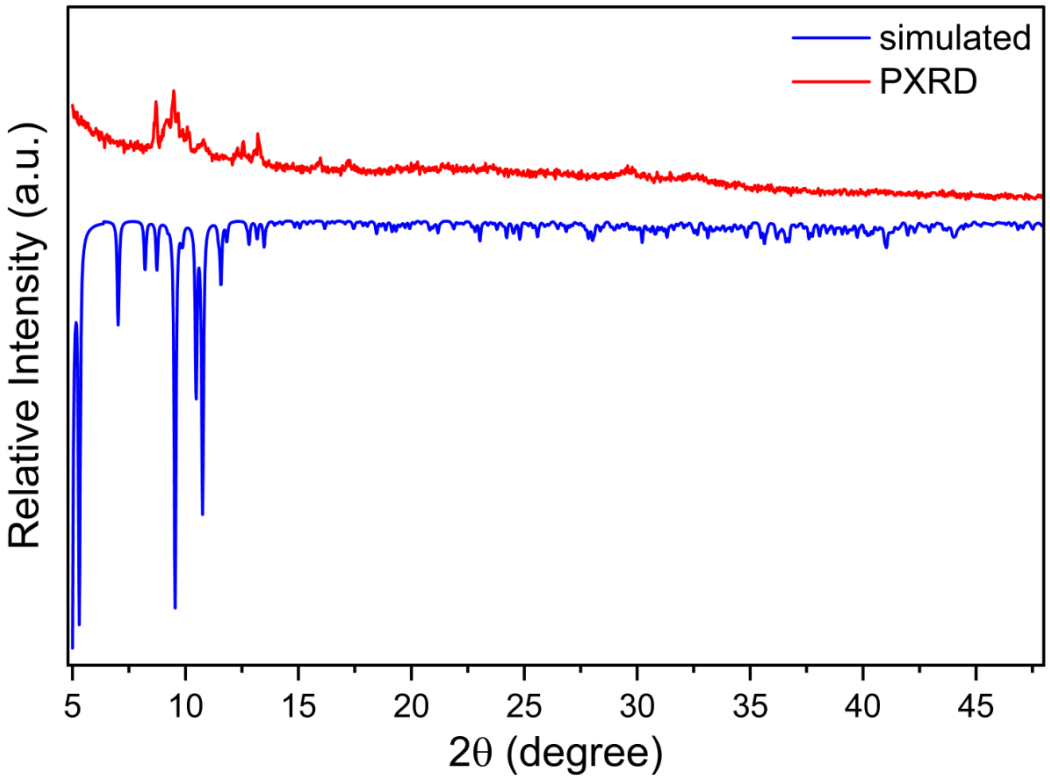


Figure S29. Comparison of powder X-ray diffraction (PXRD) patterns with the simulated patterns from single-crystal X-ray diffraction (SCXRD) for **1**.

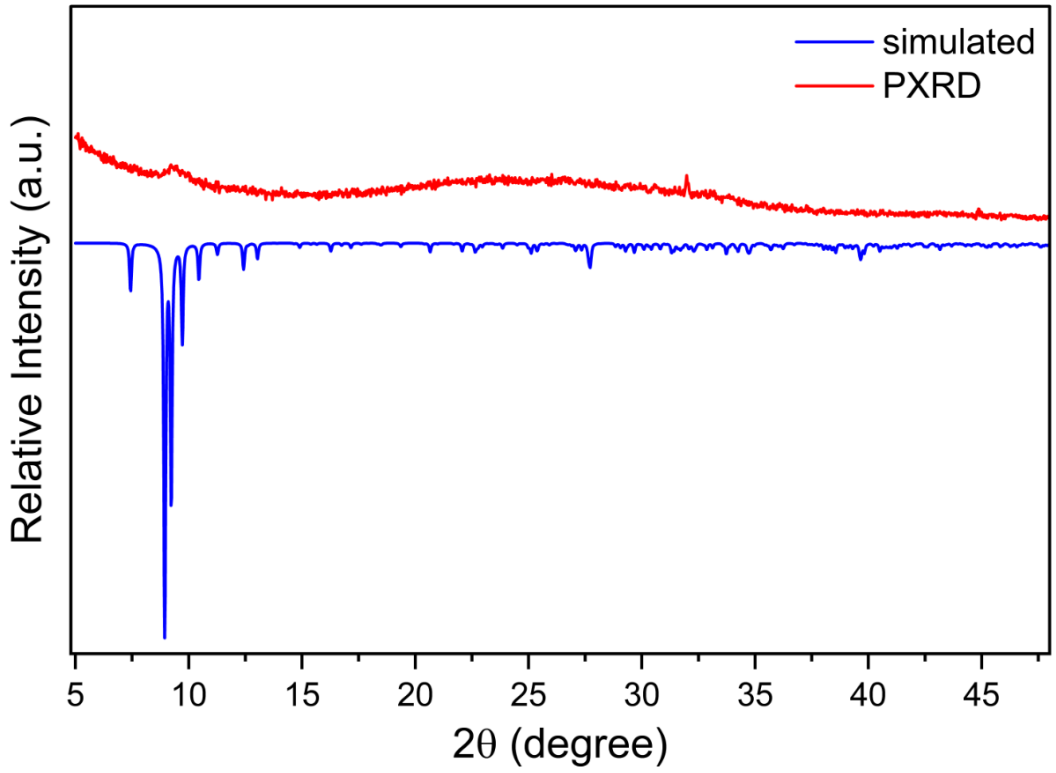


Figure S30. Comparison of powder X-ray diffraction (PXRD) patterns with the simulated patterns from single-crystal X-ray diffraction (SCXRD) for **2**.

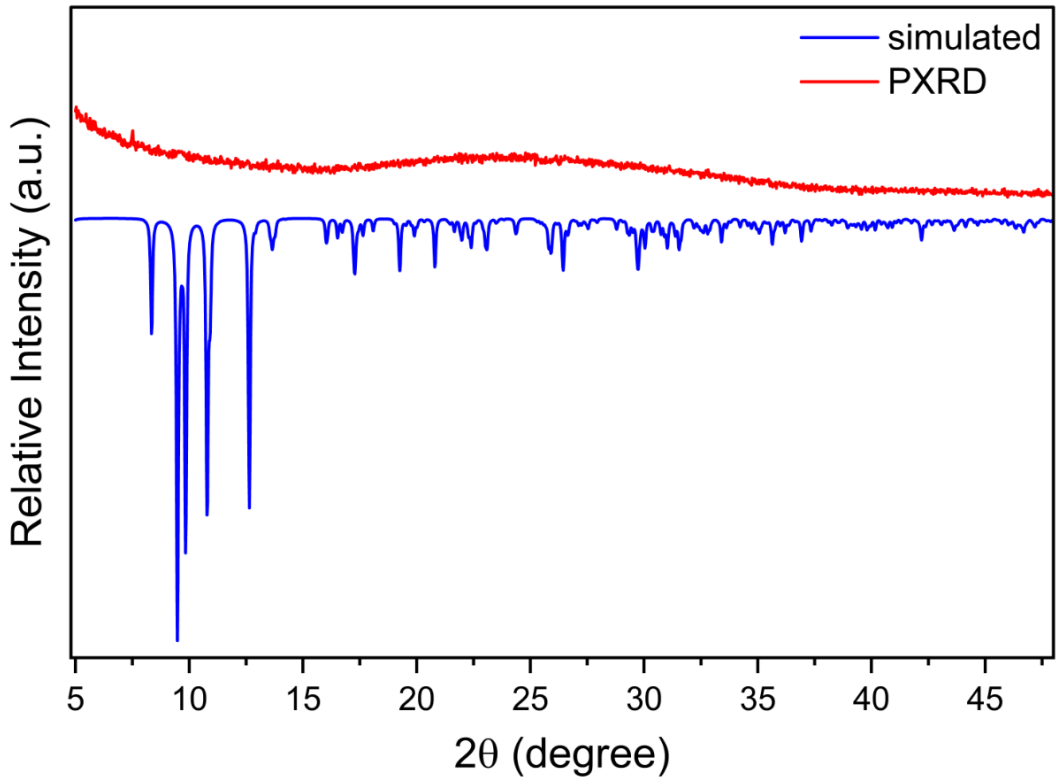


Figure S31. Comparison of powder X-ray diffraction (PXRD) patterns with the simulated patterns from single-crystal X-ray diffraction (SCXRD) for **3**.

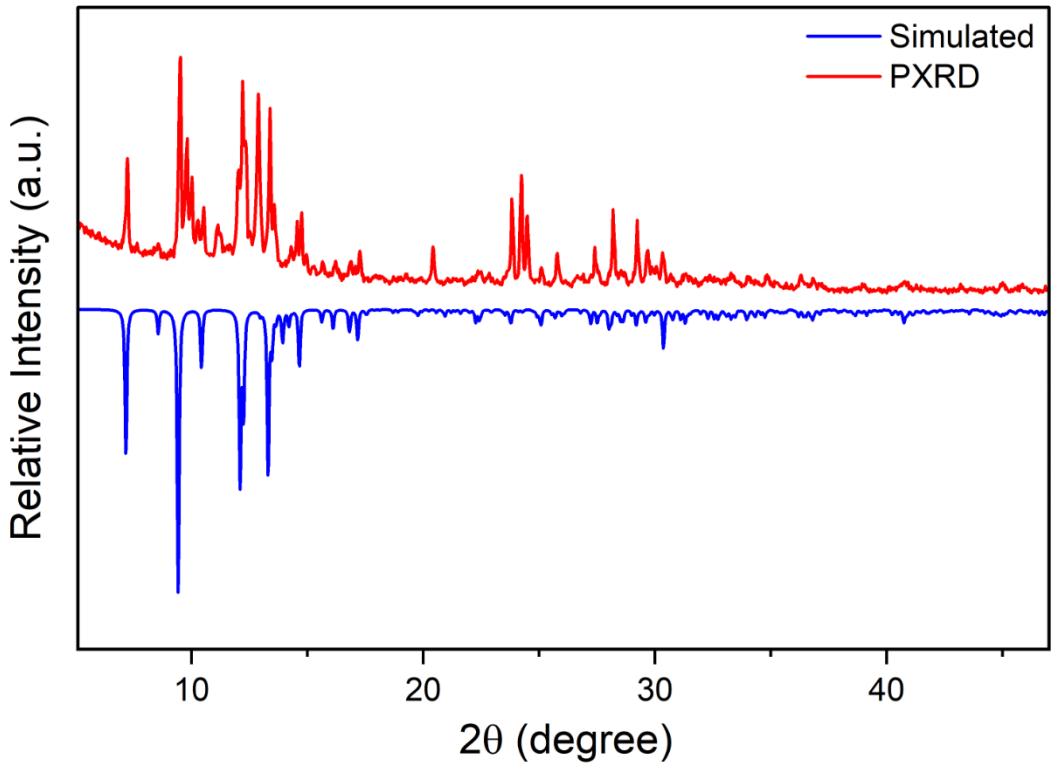


Figure S32. Comparison of powder X-ray diffraction (PXRD) patterns with the simulated patterns from single-crystal X-ray diffraction (SCXRD) for **4**.

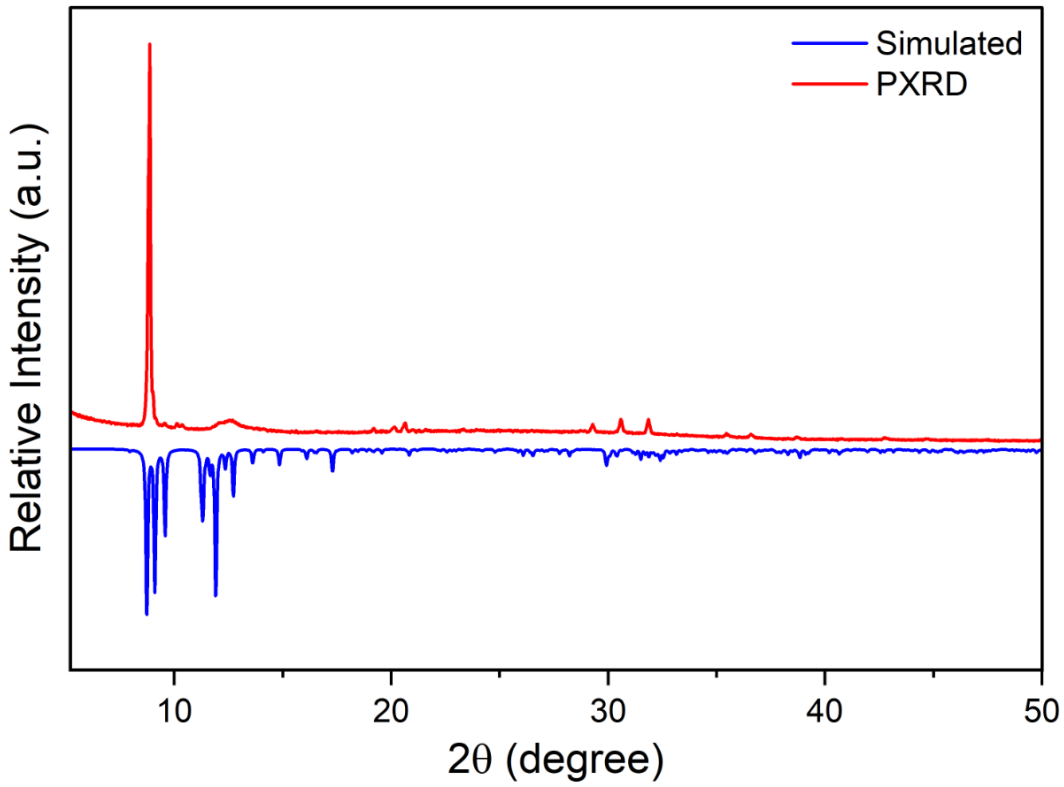


Figure S33. Comparison of powder X-ray diffraction (PXRD) patterns with the simulated patterns from single-crystal X-ray diffraction (SCXRD) for **5**.

III Computational Details

Table.S1. Selected geometrical parameters and Wiberg bond indices (WBI) of **1**-**5**.

1				**2**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ti1-Ti2	3.139	3.178	0.212	Ti1-Ti2	3.355	3.354	0.097
T3-Ti4	3.152	3.178	0.212	Se2-Se3	2.318	2.357	0.932
Ti1-Se1	2.753	2.751	0.723	Ti3-Se5	2.526	2.533	1.154
Se1-Se2	2.372	2.451	0.729	Ti2-Se4	2.764	2.774	0.632
Ti3-O2	1.844	1.834	0.882	Ti1-O1	2.075	2.079	0.539
Ti3-Se11	2.663	2.699	0.758	**3**			
Ti5-Se7	2.670	2.709	0.772		Expt.	Cal.	WBI
Se7-Se8	2.354	2.406	0.865	Ti1-Ti2	3.301	3.335	0.081
Ti5-Se2	2.600	2.633	0.860	Ti2-Cl1	2.294	2.319	1.012
Ti4-Se12	2.516	2.520	1.163	Ti2-O2	1.820	1.818	1.147
Ti5-Se10	2.678	2.701	0.774	Ti3-Se3	2.470	2.491	1.111
Se3-Se4	2.378	2.453	0.720	Se2-Se3	2.327	2.377	0.979
4				**5**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Ti1-S1	2.429	2.466	0.959	Ti1-Ti2	3.356	3.387	0.159
S1-S2	2.057	2.116	0.998	Ti1-S1	2.533	2.559	0.786
S4-S5	2.075	2.175	0.829	Ti2-S6	2.339	2.336	1.245
Ti2-S7	2.719	2.753	0.367	C1-S3	1.840	1.800	1.029
S6-S7	2.054	2.120	0.926	S3-S4	2.054	2.176	0.855

Table S2. Selected experimental and Calculated bond angles of **1**-**5**.

1			**2**		
	Expt.	Cal.		Expt.	Cal.
Ti1-Se1-Ti5	86.11	86.55	Ti1-Ti4-Ti3	60.88	61.08
Ti1-Se6-Ti2	64.90	64.80	Ti2-O1-Ti3	120.40	120.71
Se1-Ti5-Se2	54.30	55.48	Ti2-Se5-Ti3	87.62	88.47
Ti3-O2-Ti4	117.8	120.05	Se6-Ti4-Se7	52.13	52.80
Ti5-Se11-Se12	111.81	111.27	**3**		
Ti5-Se10-Ti4	85.52	86.31		Expt.	Cal.
Ti4-Se4-Ti5	85.78	86.58	Ti1-Ti2-Ti3	60.24	60.08
Ti2-Se3-Se4	113.63	113.19	Ti2-O2-Ti3	130.44	131.09
			Ti3-Se3-Se2	93.58	92.40
			Se1-Se2-Se3	105.41	106.10

4			**5**		
	Expt.	Cal.		Expt.	Cal.
Ti1-S1-S2	110.08	107.48	Ti1-Ti2-Ti3	60.41	60.95
Ti1-S4-Ti2	91.57	91.67	Ti1-S5-Ti2	91.84	93.07
Ti2-S8-S7	76.07	76.03	Ti2-S2-Ti3	84.05	82.89
S6-S7-S8	108.90	107.75	S1-C1-S2	97.0	102.60

Table S3. Calculated natural charges (q) and natural valence population (Pop) of **1**-**5**.

1			**2**		
	q	Pop(val)		q	Pop(val)
Ti1	0.206	3.505	Ti1	0.172	3.821
Ti2	0.201	3.511	Ti2	0.190	3.802
Ti3	0.206	3.505	Ti3	0.190	3.802
Ti4	0.202	3.511	Ti4	0.172	3.821
Ti5	-1.198	4.907	Se1	-0.124	6.118
Se1	0.166	5.793	Se2	0.043	5.939
Se2	0.166	5.793	Se3	0.044	5.938
Se3	0.168	5.791	Se4	-0.124	6.118
Se4	0.168	5.791	Se5	-0.109	6.104
Se5	0.307	5.935	Se6	0.044	5.938
Se6	0.307	5.654	Se7	0.043	5.939
Se7	0.302	5.660	O1	-0.546	6.541
Se8	0.032	5.933			
Se9	0.030	5.935			
Se10	0.307	5.654			
Se11	0.301	5.660			
Se12	0.032	5.933			
3			**4**		
	q	Pop(val)		q	Pop(val)
Ti1	0.661	3.334	Ti1	-0.102	4.088
Ti2	0.749	3.245	Ti2	-0.102	4.088
Ti3	0.660	3.335	S1	-0.133	6.113
Se1	-0.102	6.087	S2	0.036	5.923
Se2	-0.006	5.975	S3	-0.133	6.113
Se3	-0.101	6.086	S4	0.067	5.909
O1	-0.494	6.488	S5	0.024	5.955
O3	-0.496	6.490	S6	-0.043	6.023
Cl1	-0.283	7.279	S7	0.219	5.733
			S8	-0.043	6.023

5		
	q	Pop(val)
Ti1	-0.144	3.945
Ti2	-0.159	3.967
Ti3	-0.148	3.952
S1	0.223	5.743
S2	0.223	5.744
S3	0.125	5.843
S4	0.089	5.859
S5	-0.008	5.975
S6	-0.003	5.969
S7	-0.002	5.969
C1	-0.631	4.598

Table S4. Calculated HOMO–LUMO energy gap of **1**-**5**.

	1	**2**	**3**	**4**	**5**
$\Delta E_{H\text{-}L}$ (eV)	1.509	1.135	1.631	1.666	1.331

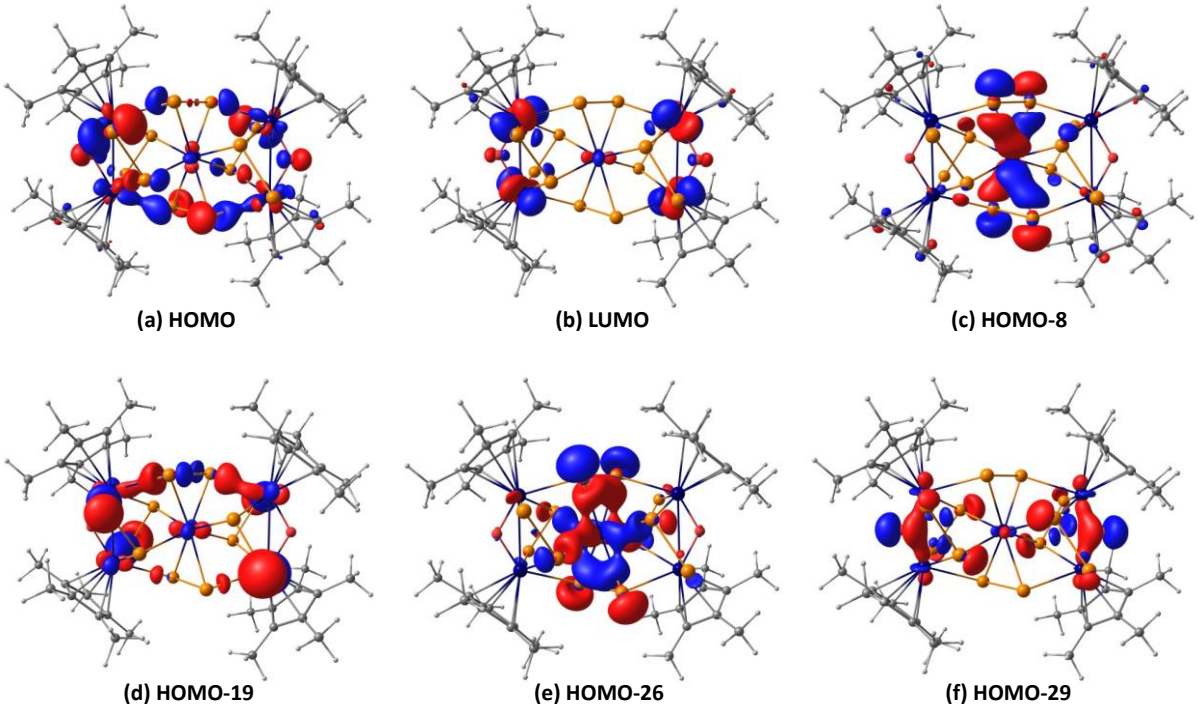


Figure S34. Selected molecular orbitals of **1** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).

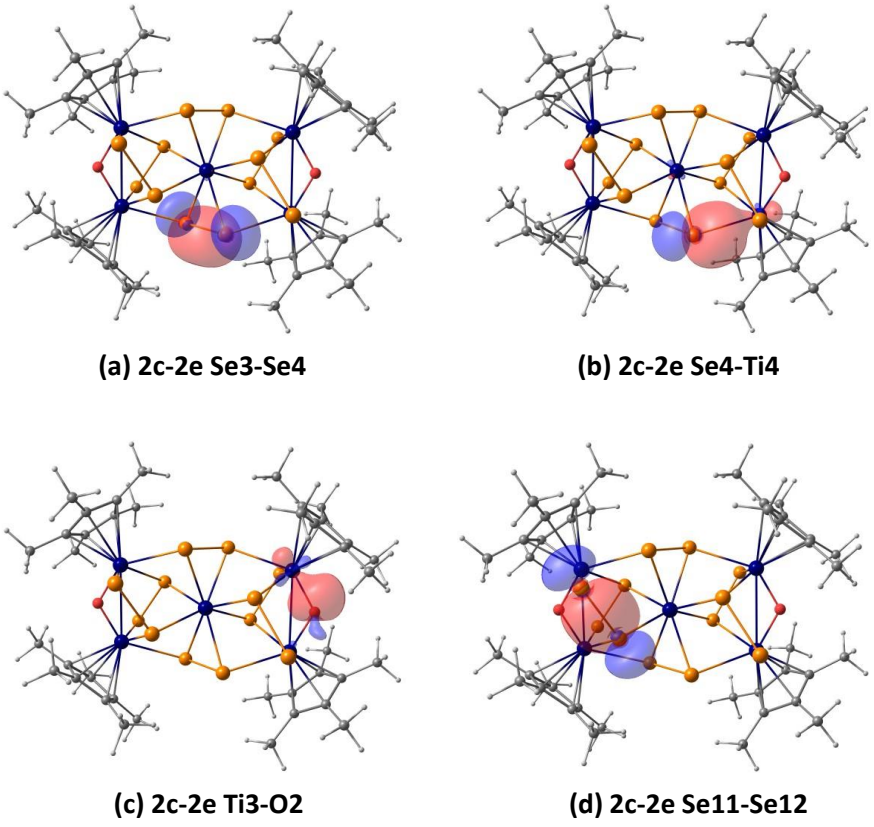


Figure S35. Selected NBO interactions of **1** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).

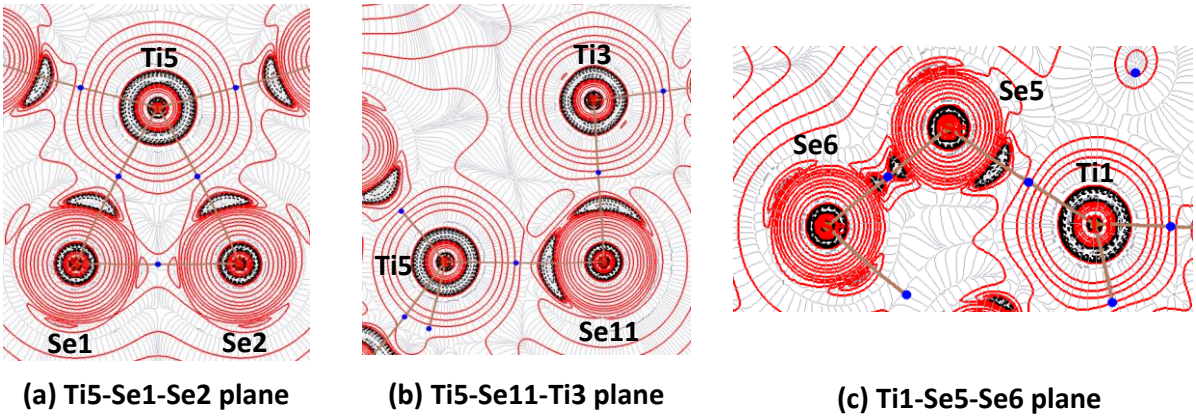


Figure S36. Contour-line diagram of the Laplacian of the electron density of **1** in selected planes. The solid brown lines are bond paths, whereas blue dots indicate the bond-critical points (BCP). Solid red lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed black lines show the areas of charge depletion ($\nabla^2\rho(r) > 0$).

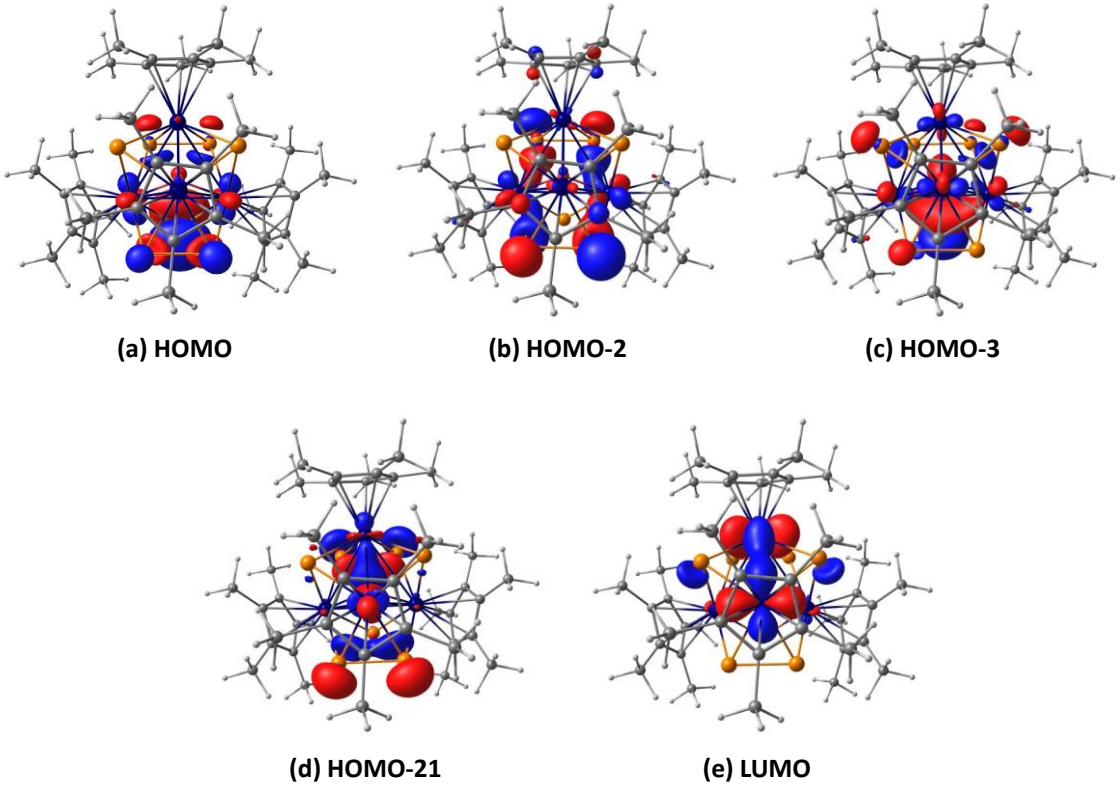


Figure S37. Selected molecular orbitals of **2** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).

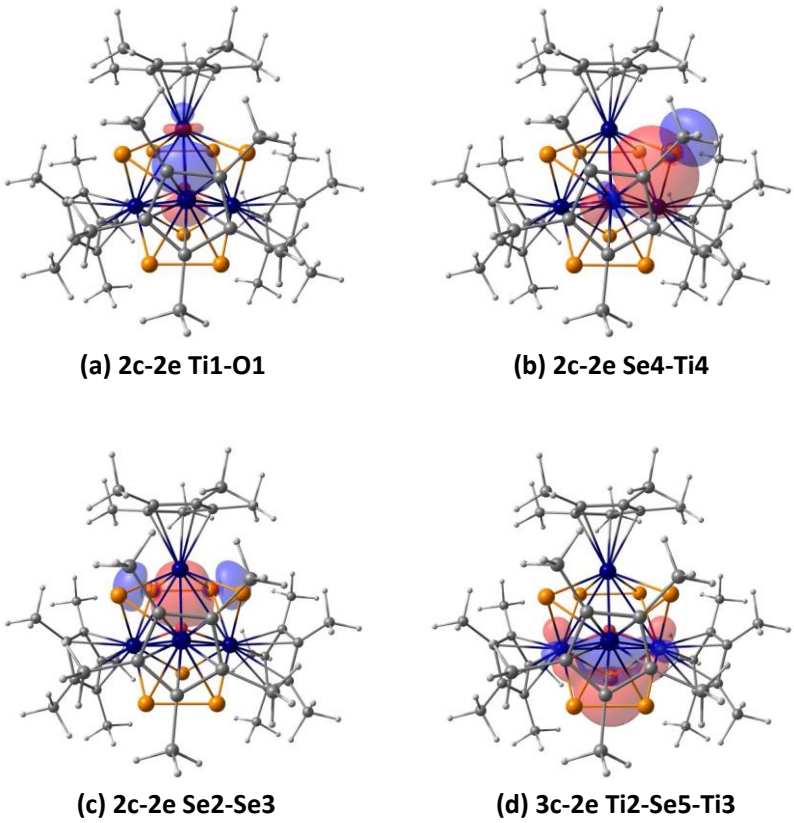
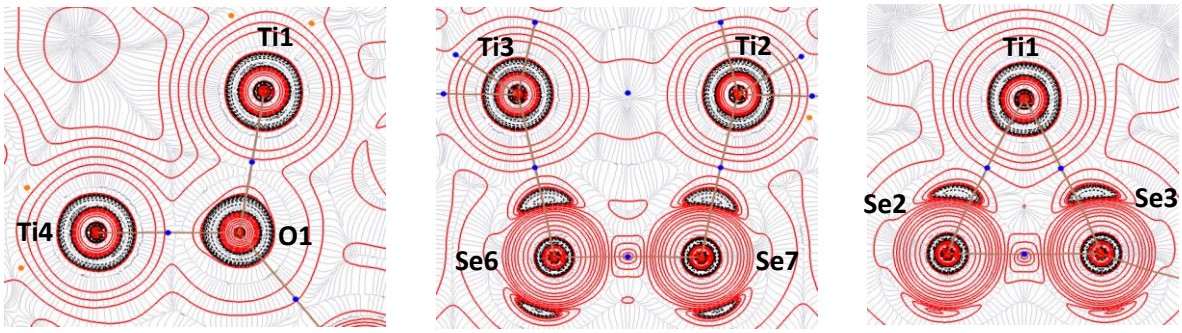
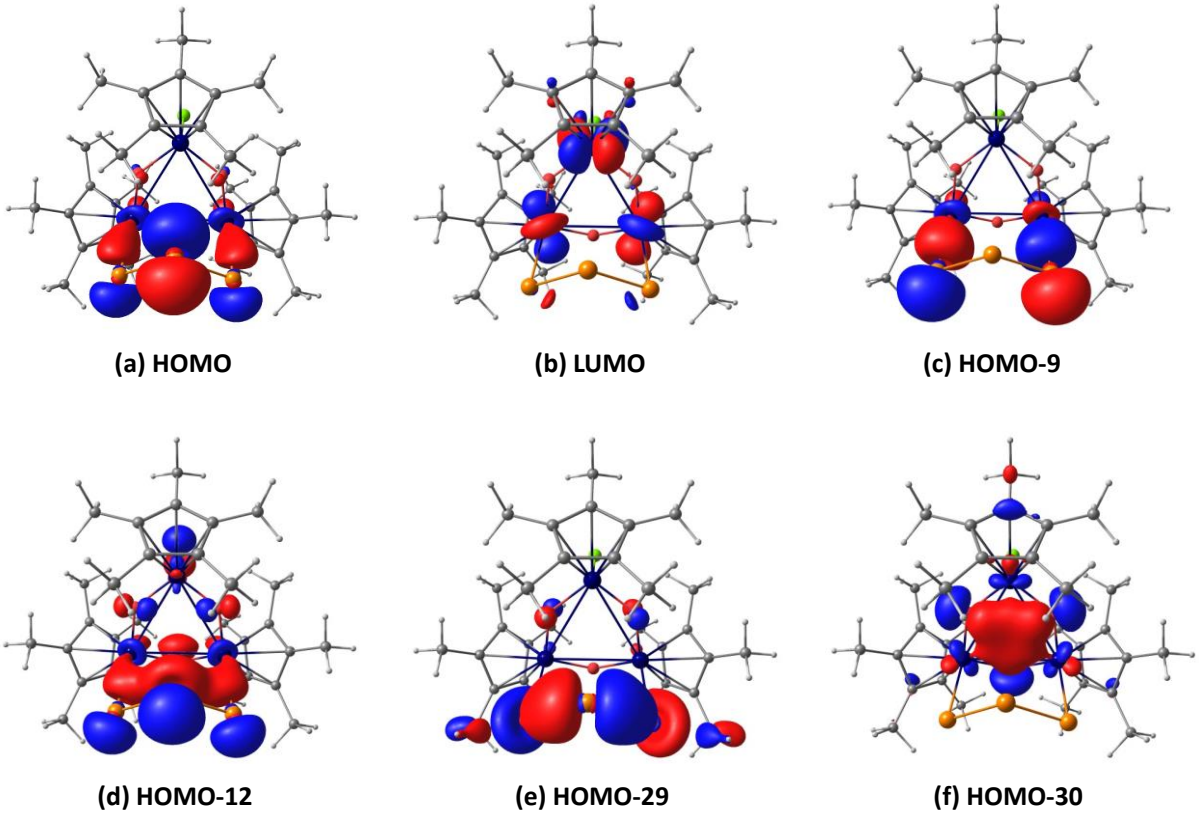


Figure S38. Selected NBO interactions of **2** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).



(a) Ti4-O1-Ti1 plane (b) Ti3-Se6-Se7 plane (c) Ti1-Se2-Se3 plane

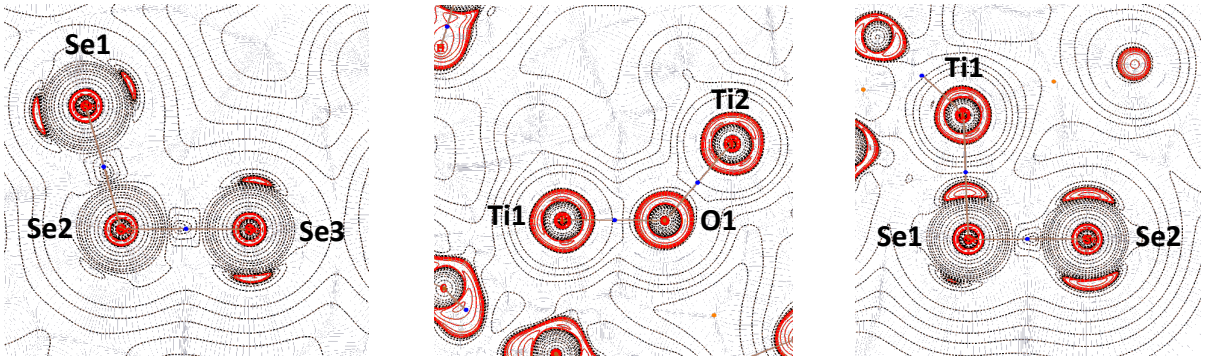
Figure S39. Contour-line diagram of the Laplacian of the electron density of **2** in selected planes. The solid brown lines are bond paths, whereas blue dots indicate the bond-critical points (BCP). Solid red lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed black lines show the areas of charge depletion ($\nabla^2\rho(r) > 0$).



(a) HOMO (b) LUMO (c) HOMO-9

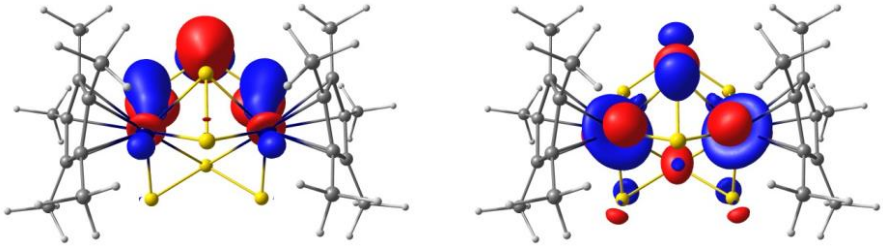
(d) HOMO-12 (e) HOMO-29 (f) HOMO-30

Figure S40. Selected molecular orbitals of **3** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).

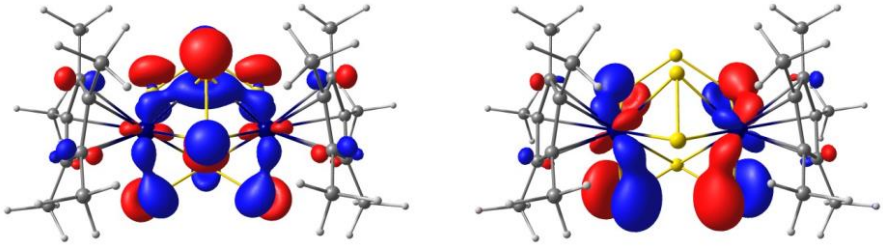


(a) Se1-Se2-Se3 plane **(b) Ti1-O1-Ti2 plane** **(c) Ti1-Se2-Se2 plane**

Figure S41. Contour-line diagram of the Laplacian of the electron density of **3** in selected planes. The solid brown lines are bond paths, whereas blue dots indicate the bond-critical points (BCP). Solid red lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed black lines show the areas of charge depletion ($\nabla^2\rho(r) > 0$).

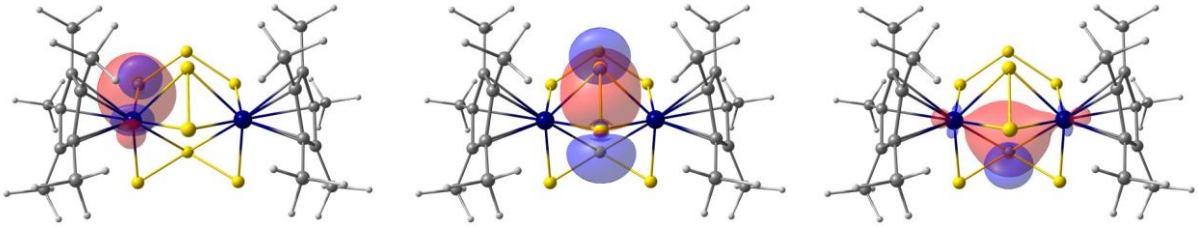


(a) HOMO **(b) LUMO**



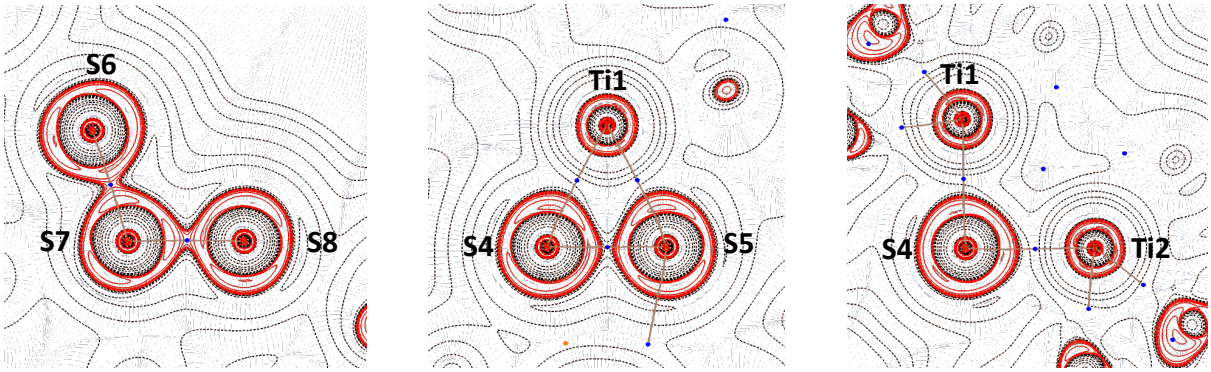
(c) HOMO-1 **(e) HOMO-10**

Figure S42. Selected molecular orbitals of **4** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).



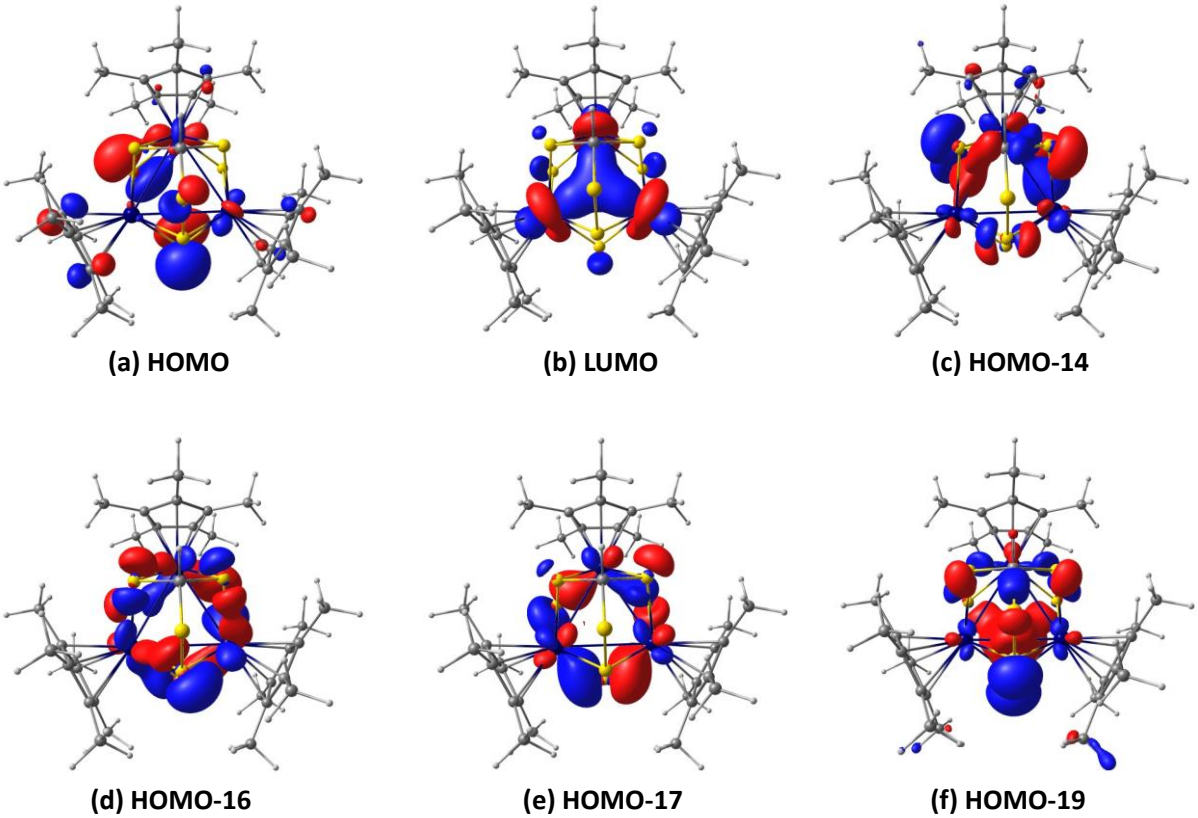
(a) 2c-2e Ti1-S1 **(c) 2c-2e S4-S5** **(c) 3c-2e Ti1-S7-Ti2**

Figure S43. Selected NBO interactions of **4** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).



(a) S6-S7-S8 plane **(b) Ti1-S4-S5 plane** **(c) Ti1-S4-Ti2 plane**

Figure S44. Contour-line diagram of the Laplacian of the electron density of **4** in selected planes. The solid brown lines are bond paths, whereas blue dots indicate the bond-critical points (BCP). Solid red lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed black lines show the areas of charge depletion ($\nabla^2\rho(r) > 0$).



(a) HOMO **(b) LUMO** **(c) HOMO-14**

(d) HOMO-16 **(e) HOMO-17** **(f) HOMO-19**

Figure S45. Selected molecular orbitals of **5** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).

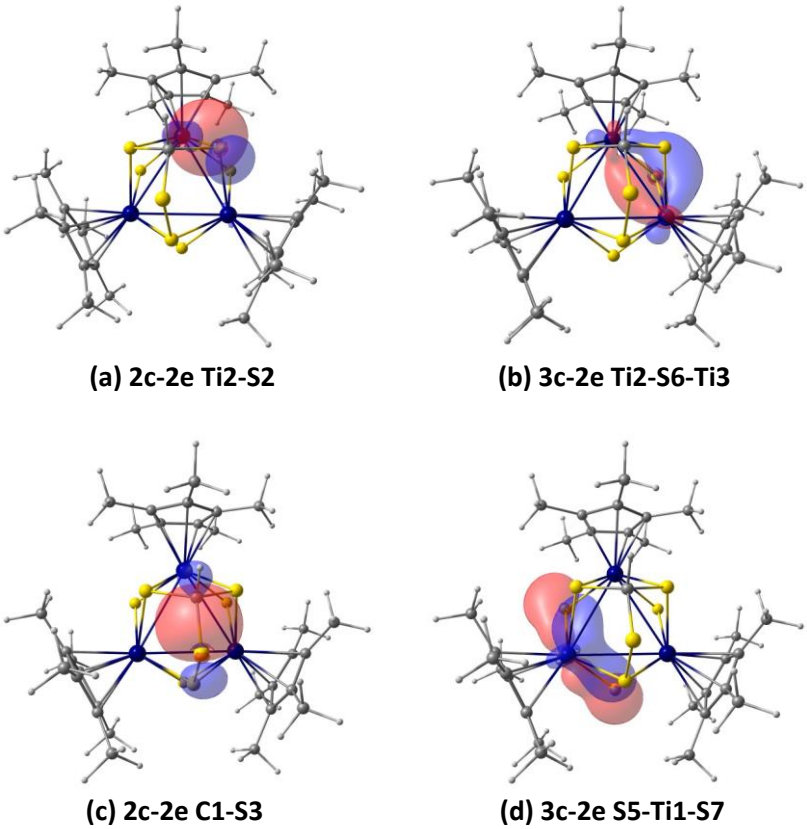


Figure S46. Selected NBO interactions of **5** (isocontour values: ±0.045 [e.bohr^{-3}]$^{1/2}$).

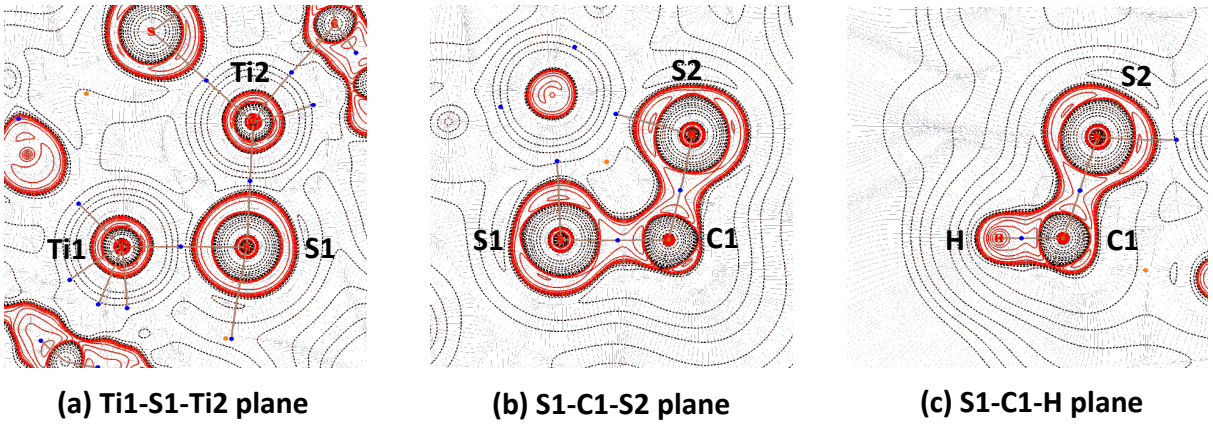


Figure S47. Contour-line diagram of the Laplacian of the electron density of **5** in selected planes. The solid brown lines are bond paths, whereas blue dots indicate the bond-critical points (BCP). Solid red lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed black lines show the areas of charge depletion ($\nabla^2\rho(r) > 0$).

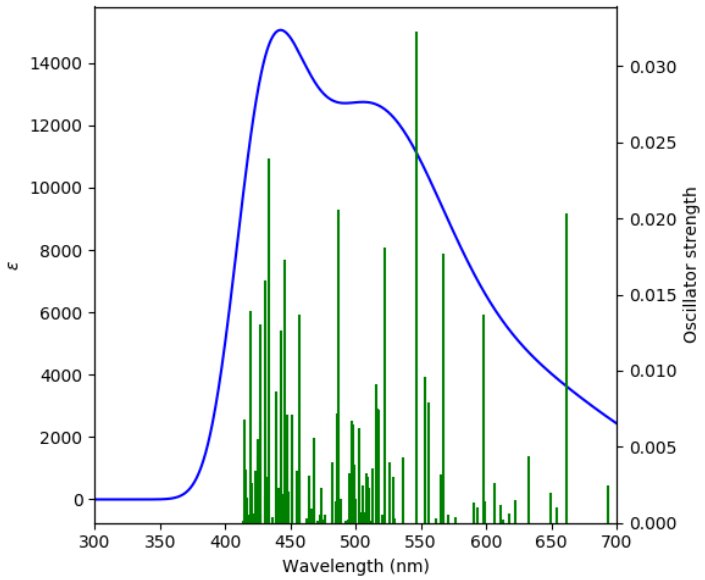


Figure S48. Absorption spectrum of **1** computed at TD-DFT-BP86/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Table S5. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (*f*), and main composition of the first UV−vis electronic excitations for **1**. Experimental absorption wavelengths (λ_{exp}, nm) of **1** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) [b]
		Calc. (*f*) [a]	Expt.	
1	1.875	661 (0.020)		HOMO-2→LUMO+2 (95)
2	2.073	598 (0.014)		HOMO-7→LUMO (13)
				HOMO-6→LUMO (15)
				HOMO-5→LUMO+1 (34)
				HOMO-1→LUMO+3 (33)
3	2.185	567 (0.018)		HOMO-4→LUMO+3 (13)
				HOMO-3→LUMO+4 (13)
				HOMO→LUMO+5 (62)
4	2.269	546 (0.032)		HOMO-4→LUMO+3 (71)
				HOMO→LUMO+7 (13)
5	2.373	522 (0.018)		HOMO→LUMO+7 (72)
6	2.545	487 (0.021)	483	HOMO→LUMO+9 (69)
				HOMO-5→LUMO+5 (14)
7	2.713	457 (0.014)		HOMO-4→LUMO+8 (70)
8	2.783	445 (0.017)		HOMO-13→LUMO+3 (14)
				HOMO-12→LUMO+3 (56)
				HOMO-6→LUMO+6 (16)
9	2.858	433 (0.024)		HOMO-9→LUMO+5 (14)
				HOMO-1→LUMO+12 (55)
10	2.881	430 (0.016)		HOMO-13→LUMO+4 (16)
				HOMO-6→LUMO+8 (60)

[a]Oscillator strength greater than 0.010 and [b]Components with greater than 10% contribution shown.

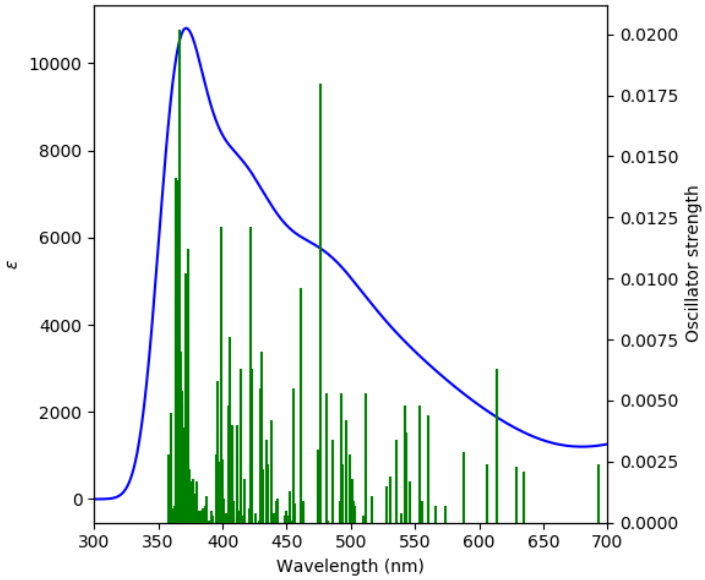


Figure S49. Absorption spectrum of **2** computed at TD-DFT-BP86/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Table S6. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (*f*), and main composition of the first UV−vis electronic excitations for **2**. Experimental absorption wavelengths (λ_{exp}, nm) of **2** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) [b]
		Calc. (*f*) [a]	Expt.	
1	2.600	477 (0.018)		HOMO-2→LUMO+3 (21)
				HOMO-2→LUMO+4 (28)
				HOMO-1→LUMO+7 (28)
2	2.937	422 (0.012)		HOMO-16→LUMO (67)
3	3.106	399 (0.012)		HOMO-10→LUMO+4 (19)
				HOMO-9→LUMO+3 (28)
				HOMO-6→LUMO+4 (14)
				HOMO-4→LUMO+6 (12)
4	3.385	366 (0.020)	366	HOMO-7→LUMO+6 (21)
				HOMO-5→LUMO+6 (11)
				HOMO-1→LUMO+16 (25)
5	3.399	365 (0.014)		HOMO-12→LUMO+3 (17)
				HOMO-12→LUMO+4 (24)
				HOMO-8→LUMO+6 (23)

[a]Oscillator strength greater than 0.010 and [b]Components with greater than 10% contribution shown.

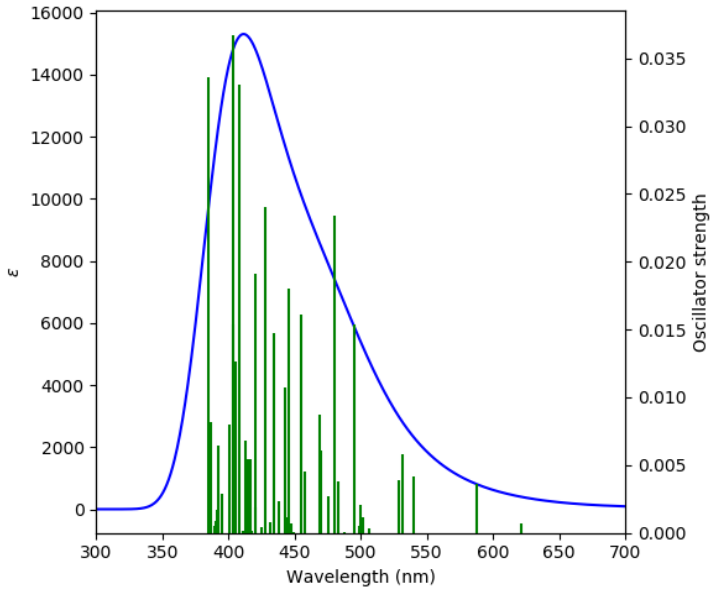


Figure S50. Absorption spectrum of **3** computed at TD-DFT-BP86/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Table S7. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (*f*), and main composition of the first UV–vis electronic excitations for **3**. Experimental absorption wavelengths (λ_{exp}, nm) of **3** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) [b]
		Calc. (*f*) [a]	Expt.	
1	2.584	480 (0.023)		HOMO-2→LUMO+1 (57)
				HOMO-1→LUMO+2 (31)
2	2.897	428 (0.024)		HOMO-5→LUMO+2 (55)
3	3.037	408 (0.033)		HOMO-2→LUMO+4 (20)
				HOMO-2→LUMO+5 (55)
4	3.074	403 (0.036)		HOMO-5→LUMO+3 (58)
5	3.220	385 (0.037)	360	HOMO-3→LUMO+6 (45)
				HOMO-5→LUMO+4 (16)

[a]Oscillator strength greater than 0.020 and [b]Components with greater than 10% contribution shown.

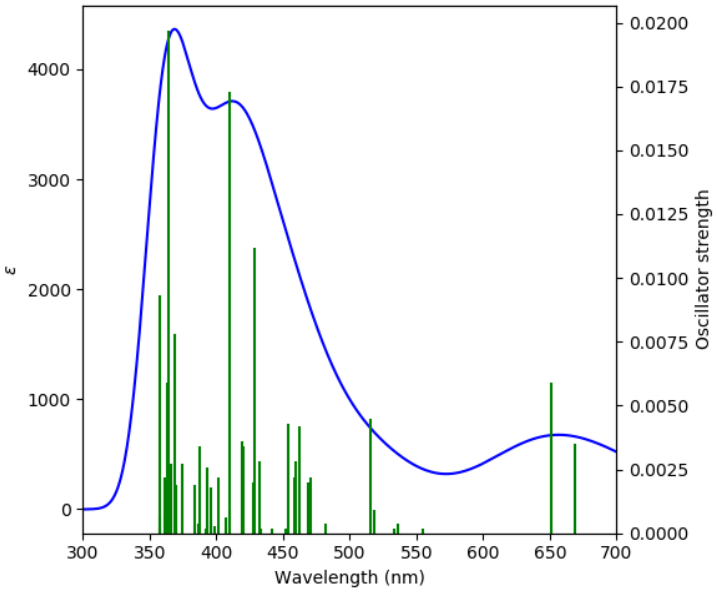


Figure S51. Absorption spectrum of **4** computed at TD-DFT-BP86/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Table S8. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (*f*), and main composition of the first UV−vis electronic excitations for **4**. Experimental absorption wavelengths (λ_{exp}, nm) of **4** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) [b]
		Calc. (*f*) [a]	Expt.	
1	2.896	428 (0.011)		HOMO-1→LUMO+3 (62)
				HOMO-6→LUMO (25)
2	3.027	409 (0.017)	391	HOMO-6→LUMO+1 (24)
				HOMO-2→LUMO+3 (15)
				HOMO→LUMO+5 (13)
				HOMO-7→LUMO (12)
3	3.406	364 (0.020)		HOMO-10→LUMO (34)
				HOMO-5→LUMO+3 (22)
				HOMO-1→LUMO+6 (14)

[a]Oscillator strength greater than 0.010 and [b]Components with greater than 10% contribution shown.

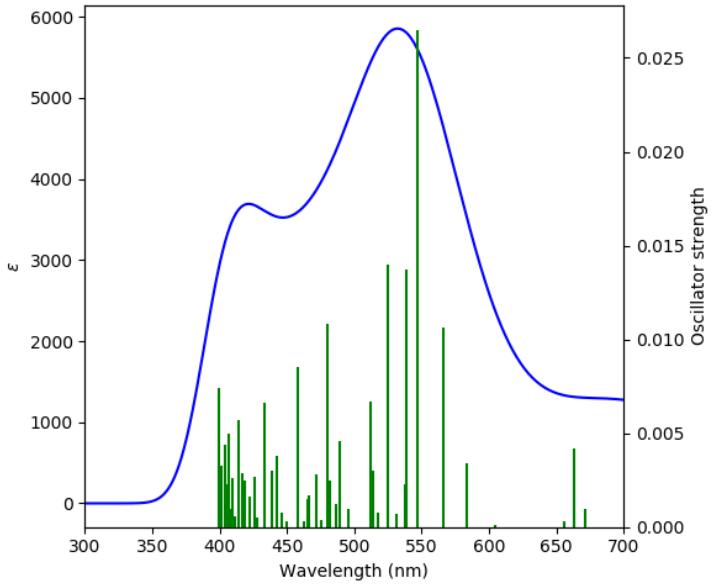


Figure S52. Absorption spectrum of **5** computed at TD-DFT-BP86/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Table S9. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (*f*), and main composition of the first UV−vis electronic excitations for **5**. Experimental absorption wavelengths (λ_{exp}, nm) of **5** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) [b]
		Calc. (*f*) [a]	Expt.	
1	2.192	566 (0.011)		HOMO-1→LUMO+1 (50)
				HOMO→LUMO+1 (33)
2	2.266	547 (0.026)		HOMO→LUMO+2 (35)
				HOMO-1→LUMO+2 (25)
				HOMO-9→LUMO (12)
3	2.302	539 (0.014)		HOMO-1→LUMO+2 (34)
				HOMO→LUMO+2 (27)
				HOMO-10→LUMO (27)
4	2.364	524 (0.014)		HOMO-2→LUMO+1 (48)
				HOMO-10→LUMO (14)
5	2.580	481 (0.011)	492	HOMO-6→LUMO+1 (40)
				HOMO-5→LUMO+1 (18)
				HOMO-7→LUMO+1 (11)

[a]Oscillator strength greater than 0.010 and [b]Components with greater than 10% contribution shown.

IV Cartesian Coordinates of all Optimized Structures

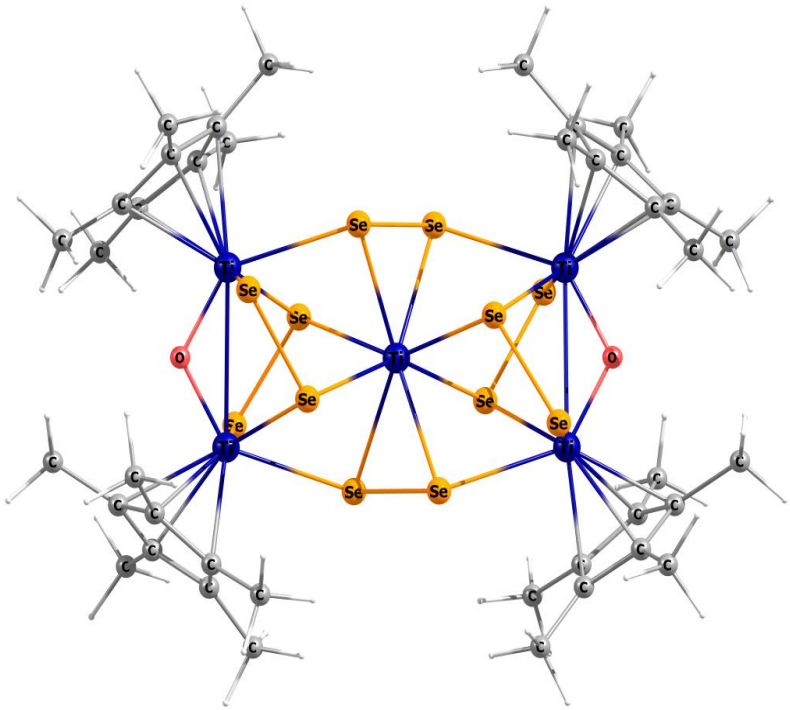


Figure S53. Optimized geometry of **1**.

Total energy = -34776.6269505 a.u.

Cartesian coordinates for the calculated structure **1** (in Å)

Se	0.793777000	-2.341336000	0.933782000
Se	-0.794022000	-2.341182000	-0.934559000
Se	3.062831000	-1.164792000	2.692011000
Se	1.832791000	0.724444000	1.842792000
Se	1.833974000	-0.741742000	-1.855774000
Se	3.027728000	1.167837000	-2.704171000
Se	-0.784865000	2.325923000	0.942525000
Se	0.784765000	2.325970000	-0.943180000
Se	-1.833270000	0.724476000	-1.843156000
Se	-3.063026000	-1.165155000	-2.691873000
Se	-3.027502000	1.167815000	2.703886000
Se	-1.833539000	-0.741841000	1.855822000
Ti	3.339010000	-1.571174000	0.226122000
Ti	3.324982000	1.573765000	-0.234046000
Ti	-3.325281000	1.574043000	0.233981000
Ti	-3.338996000	-1.571255000	-0.225764000
Ti	-0.000044000	-0.010213000	-0.000342000
O	4.248834000	0.003479000	-0.019385000
O	-4.248655000	0.003427000	0.019378000
C	3.683942000	-3.621475000	-1.030721000
C	3.666113000	-4.020659000	0.347009000
C	4.754948000	-3.362928000	1.018163000
C	5.466740000	-2.579732000	0.041803000
C	4.804333000	-2.731163000	-1.221315000
C	2.773188000	-4.157372000	-2.100022000
H	1.727328000	-4.252699000	-1.743228000
H	3.110004000	-5.166820000	-2.426689000
H	2.753783000	-3.503824000	-2.993497000
C	2.779764000	-5.067779000	0.960338000
H	2.480859000	-4.808877000	1.996400000
H	3.313588000	-6.044418000	1.004137000
H	1.852740000	-5.219856000	0.374937000
C	5.211284000	-3.643642000	2.424493000
H	5.768085000	-2.790695000	2.860652000
H	5.891001000	-4.525587000	2.440219000
H	4.364053000	-3.876297000	3.101183000
C	6.737545000	-1.819180000	0.284545000
H	6.876583000	-1.020593000	-0.468292000
H	7.618127000	-2.497463000	0.223009000
H	6.751582000	-1.346401000	1.286925000
C	5.248477000	-2.100941000	-2.511899000
H	5.388282000	-1.005000000	-2.402401000
H	4.508194000	-2.255755000	-3.320029000
H	6.214698000	-2.534560000	-2.851979000
C	5.404468000	2.689044000	-0.353835000
C	5.029889000	2.618668000	1.028220000
C	3.861169000	3.443700000	1.213167000
C	3.530721000	4.038747000	-0.050224000
C	4.465497000	3.554672000	-1.027591000
C	6.602451000	2.049028000	-0.995887000
H	7.432202000	2.783483000	-1.100038000
H	6.370034000	1.663422000	-2.009228000
H	6.980588000	1.201202000	-0.394436000
C	-5.405058000	2.688312000	0.351538000
C	-5.027731000	2.620324000	-1.029923000
C	-3.859033000	3.446150000	-1.211274000

C	-3.531413000	4.039408000	0.053689000
C	-4.467927000	3.553443000	1.028442000
C	-6.603954000	2.046277000	0.989765000
H	-6.375584000	1.666681000	2.006270000
H	-6.974631000	1.193719000	0.390386000
H	-7.437540000	2.777535000	1.085578000
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C	-4.803915000	-2.731353000	1.221963000
C	-3.683618000	-3.621756000	1.030948000
C	-3.666209000	-4.020834000	-0.346791000
C	-4.755195000	-3.362963000	-1.017539000
C	-6.737889000	-1.820025000	-0.284196000
H	-6.884847000	-1.030454000	0.476580000
H	-7.616923000	-2.501408000	-0.236687000
H	-6.746086000	-1.335946000	-1.281274000
C	5.737519000	1.864028000	2.118365000
H	6.230964000	2.565547000	2.826593000
H	6.519436000	1.198030000	1.707053000
H	5.041514000	1.228681000	2.705945000
C	3.226838000	3.787758000	2.532432000
C	2.515952000	5.125186000	-0.269181000
C	4.587135000	4.051500000	-2.442908000
H	3.599332000	4.271640000	-2.895074000
H	5.103016000	3.320569000	-3.097826000
H	5.181494000	4.992607000	-2.473890000
C	-5.733354000	1.867442000	-2.122602000
H	-6.516114000	1.200867000	-1.713812000
H	-5.036397000	1.233098000	-2.710127000
H	-6.225563000	2.570186000	-2.830469000
C	-3.221689000	3.792116000	-2.528587000
H	-3.646029000	4.744772000	-2.919702000
H	-3.397418000	3.009397000	-3.291530000
H	-2.125095000	3.928451000	-2.440885000
C	-2.517426000	5.125756000	0.276622000
H	-2.984378000	6.122789000	0.105530000
H	-1.655641000	5.038981000	-0.413574000
H	-2.118499000	5.120523000	1.310250000
C	-4.592511000	4.048103000	2.444260000
H	-5.188033000	4.988457000	2.475584000
H	-3.605710000	4.268817000	2.898338000
H	-5.108553000	3.315623000	3.097307000
C	-5.247343000	-2.101500000	2.512955000
H	-5.394972000	-1.006845000	2.401698000
H	-4.502803000	-2.249440000	3.318472000
H	-6.209175000	-2.541083000	2.857882000
C	-2.772527000	-4.157648000	2.099966000
H	-2.753588000	-3.504541000	2.993773000
H	-1.726599000	-4.252209000	1.743165000
H	-3.108772000	-5.167436000	2.426169000
C	-2.779931000	-5.067734000	-0.960602000
H	-1.853124000	-5.220424000	-0.375021000
H	-2.480644000	-4.808167000	-1.996394000
H	-3.313958000	-6.044218000	-1.005265000
C	-5.212228000	-3.643427000	-2.423696000
H	2.130085000	3.924466000	2.447456000
H	3.404187000	3.003868000	3.293808000
H	3.652285000	4.739732000	2.924005000
H	1.654658000	5.035825000	0.421315000
H	2.982454000	6.121956000	-0.095357000
H	2.116350000	5.122838000	-1.302549000
H	-5.769230000	-2.790392000	-2.859421000
H	-4.365371000	-3.876065000	-3.100861000
H	-5.892014000	-4.525334000	-2.439199000

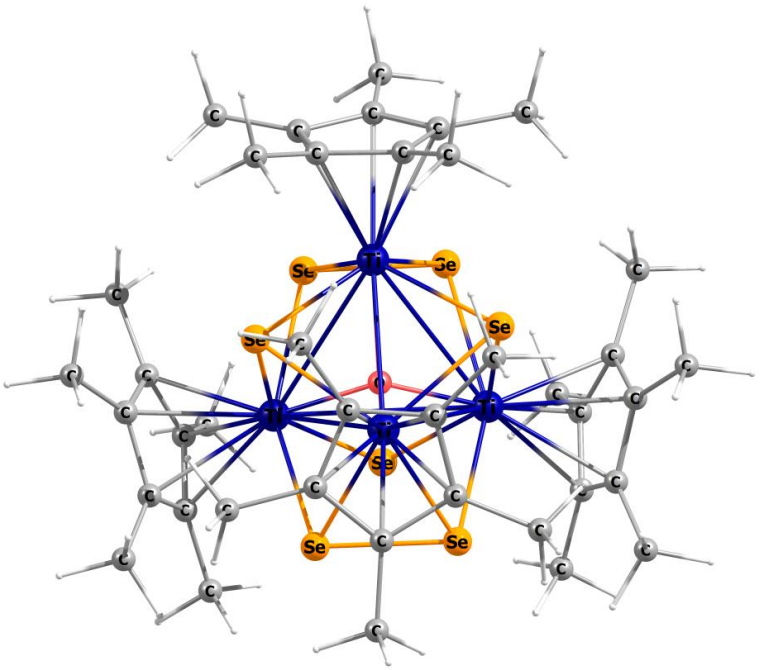

Figure S54. Optimized geometry of **2**

Total energy = -21843.9493583 a.u.

Cartesian coordinates for the calculated structure **2** (in Å)

C	0.151139000	-2.447592000	3.466785000
C	-0.158010000	-3.495187000	2.529365000
C	1.055753000	-3.864445000	1.861861000
C	2.102089000	-3.003794000	2.336911000
C	1.551937000	-2.149660000	3.351788000
C	-0.751603000	-2.007696000	4.583892000
H	-0.741917000	-2.766817000	5.399051000
H	-1.800574000	-1.881543000	4.251690000
H	-0.419515000	-1.049704000	5.028888000
C	-1.481215000	-4.198516000	2.420620000
H	-2.327225000	-3.494173000	2.555217000
H	-1.601697000	-4.689270000	1.434148000
C	1.257640000	-5.061136000	0.977833000
H	1.682304000	-5.899409000	1.575468000
H	1.964559000	-4.852199000	0.148993000
H	0.309760000	-5.413563000	0.528166000
C	3.563830000	-3.126875000	2.011843000
H	4.069796000	-3.811814000	2.729869000
H	3.724128000	-3.532273000	0.993323000
C	2.374377000	-1.355691000	4.326951000
H	2.768563000	-2.031743000	5.120081000
H	1.786385000	-0.564514000	4.826350000
H	3.240202000	-0.863329000	3.842604000
C	-2.103537000	3.003010000	2.336523000
C	-1.056402000	3.863634000	1.863128000
C	0.156514000	3.493618000	2.531742000
C	-0.153959000	2.445467000	3.468099000
C	-1.554738000	2.148047000	3.351410000
C	-3.564913000	3.127021000	2.010199000
H	-4.071112000	3.811895000	2.728124000
H	-4.082041000	2.148013000	2.072359000
H	-3.724108000	3.532977000	0.991731000
C	-3.401820000	-2.187562000	-1.621362000
C	-2.950218000	-1.666462000	-2.889322000
C	-3.327987000	-0.286752000	-2.957710000
C	-4.018940000	0.045540000	-1.735866000
C	-4.063164000	-1.129057000	-0.912842000
C	-3.463264000	-3.641030000	-1.230973000
H	-4.459918000	-4.061932000	-1.495564000
H	-3.326254000	-3.789867000	-0.141081000
H	-2.703529000	-4.253551000	-1.755566000
C	-1.257054000	5.060907000	0.979602000
H	-1.683405000	5.898500000	1.576988000
H	-1.962146000	4.852271000	0.149120000
H	-0.308414000	5.414169000	0.532212000
C	1.480006000	4.196681000	2.424731000
H	1.573388000	4.987128000	3.203530000
H	1.602191000	4.686748000	1.438120000
H	2.325680000	3.492304000	2.561177000
C	0.747238000	2.004414000	4.585977000
H	0.415080000	1.045453000	5.028809000
H	1.796860000	1.879561000	4.255378000
C	-2.378327000	1.353623000	4.325230000
H	-1.791173000	0.561573000	4.824244000
H	-2.772599000	2.029153000	5.118767000
C	-2.337604000	-2.470110000	-4.001589000
H	-3.131417000	-2.914469000	-4.643930000
H	-1.712296000	-3.299610000	-3.614826000
H	-1.688426000	-1.844626000	-4.645156000
C	-3.189948000	0.614875000	-4.151680000
H	-4.112541000	0.579916000	-4.774690000
H	-2.336027000	0.317951000	-4.790943000
H	-3.023289000	1.669418000	-3.852923000
C	-4.845843000	1.282754000	-1.502537000
H	-5.899763000	1.092009000	-1.808697000
H	-4.868351000	1.584167000	-0.436187000
C	-4.915766000	-1.298055000	0.314160000
H	-5.956756000	-1.565867000	0.018993000
H	-4.968952000	-0.371900000	0.919332000
H	-4.539649000	-2.099264000	0.979282000
O	0.000035000	0.000063000	-0.112056000
Se	1.933421000	0.594838000	1.645391000
Se	-1.934423000	-0.595488000	1.643666000
Se	0.398408000	2.823374000	-0.909387000
Se	1.864483000	-2.158752000	-0.936546000
Se	-0.397736000	-2.822961000	-0.910872000
Se	-1.863785000	2.159163000	-0.936905000
Se	0.001044000	0.000496000	-2.932848000
Ti	-0.476333000	1.517499000	1.227544000
Ti	-1.695171000	-0.498544000	-1.118431000
Ti	0.475761000	-1.517879000	1.227112000
Ti	1.695838000	0.499074000	-1.117238000
C	4.019602000	-0.045054000	-1.734693000
C	3.329211000	0.289285000	-2.956274000
C	2.952048000	1.669063000	-2.886048000
C	3.403344000	2.188137000	-1.617137000
C	4.063996000	1.128320000	-0.909920000
C	4.846145000	-1.282822000	-1.503040000
C	3.191441000	-0.610571000	-4.151608000
C	2.340173000	2.474351000	-3.997541000
H	3.134370000	2.917352000	-4.640342000
H	1.716807000	3.304959000	-3.610054000
H	1.689275000	1.850347000	-4.640828000
C	3.465009000	3.641005000	-1.224559000
H	4.461738000	4.062161000	-1.488449000
H	3.327886000	3.788248000	-0.134471000
H	2.705426000	4.254450000	-1.748304000
C	4.916226000	1.294932000	0.317668000
H	5.958006000	1.560490000	0.023258000
H	4.541487000	2.096736000	0.982841000
H	4.487704000	-2.148749000	-2.093611000
H	5.900040000	-1.092049000	-1.809278000
H	4.868868000	-1.585450000	-0.437035000
H	2.338432000	-0.311969000	-4.791298000
H	4.114670000	-0.575634000	-4.773683000
H	3.023493000	-1.665360000	-3.854434000
H	4.966939000	0.368443000	0.922548000
H	4.080377000	-2.147616000	2.074896000
H	-1.575785000	-4.988427000	3.199821000
H	-4.487848000	2.149469000	-2.092223000
H	-3.244149000	0.862305000	3.839830000
H	0.735611000	2.762185000	5.402369000

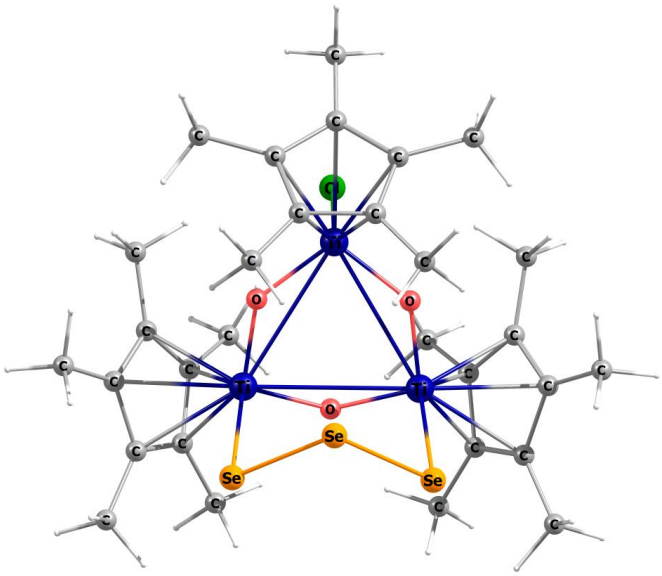

Figure S55. Optimized geometry of **3**.

Total energy = -11608.8222385 a.u.

Cartesian coordinates for the calculated structure **3** (in Å)

C	-3.473003000	-0.085008000	1.759599000
C	-2.636491000	-1.041590000	2.446808000
C	-2.774816000	-2.310376000	1.787001000
C	-3.679200000	-2.136286000	0.684292000
C	-4.105686000	-0.756095000	0.668383000
C	-3.679045000	1.340775000	2.182808000
H	-4.401675000	1.394941000	3.027638000
H	-4.086414000	1.957610000	1.358725000
H	-2.733577000	1.812020000	2.518685000
C	-1.864817000	-0.756965000	3.704162000
H	-2.554140000	-0.688121000	4.575335000
H	-1.312924000	0.202983000	3.643553000
H	-1.134502000	-1.558395000	3.924593000
C	-2.122566000	-3.602252000	2.192564000
H	-2.767911000	-4.175615000	2.895087000
H	-1.153512000	-3.425225000	2.698378000
H	-1.922534000	-4.253730000	1.318377000
C	-4.263608000	-3.239725000	-0.155974000
H	-5.181468000	-3.640849000	0.330196000
H	-3.561197000	-4.086738000	-0.285152000
H	-4.560197000	-2.891624000	-1.166439000
C	-5.086271000	-0.157721000	-0.301998000
H	-6.134688000	-0.342353000	0.023542000
H	-4.973756000	-0.586800000	-1.318160000
H	-4.958940000	0.939609000	-0.387639000
C	2.763179000	-2.318286000	1.796117000
C	2.646582000	-1.040251000	2.442058000
C	3.489633000	-0.102942000	1.735525000
C	4.103662000	-0.794707000	0.646844000
C	3.657274000	-2.168222000	0.681908000
C	2.108028000	-3.603876000	2.217499000
H	2.827799000	-4.261747000	2.753717000
H	1.720635000	-4.175413000	1.349448000
H	1.256385000	-3.420973000	2.900742000
C	1.892025000	-0.726301000	3.702802000
H	2.589792000	-0.663012000	4.567636000
H	1.144421000	-1.507289000	3.937771000
H	1.360593000	0.244726000	3.635560000
C	3.717138000	1.324810000	2.140987000
H	4.433413000	1.378343000	2.991205000
H	2.777198000	1.816859000	2.462580000
H	4.142218000	1.922970000	1.312137000
C	5.084655000	-0.221180000	-0.338041000
H	6.132858000	-0.411235000	-0.014982000
H	4.967811000	0.875913000	-0.440344000
H	4.962202000	-0.664706000	-1.346756000
C	4.214621000	-3.293142000	-0.148264000
H	5.124878000	-3.709463000	0.339677000
H	4.515964000	-2.963167000	-1.163378000
H	3.492564000	-4.125265000	-0.265400000
C	1.176319000	4.038164000	-0.655090000
C	0.022810000	4.547833000	0.034519000
C	-1.146529000	4.053923000	-0.640183000
C	-0.718180000	3.253688000	-1.754324000
C	0.722723000	3.243562000	-1.763231000
C	2.612712000	4.325610000	-0.318958000
H	3.275417000	3.495048000	-0.632464000
H	2.967998000	5.244854000	-0.837201000
H	2.760176000	4.485760000	0.768035000
C	0.036327000	5.525608000	1.174530000
H	-0.852683000	5.414064000	1.825609000
H	0.930250000	5.400597000	1.816408000
H	0.042212000	6.569122000	0.786962000
C	-2.573695000	4.361471000	-0.282764000
H	-2.707933000	4.493521000	0.809820000
H	-2.914157000	5.302411000	-0.771098000
H	-3.256612000	3.554300000	-0.613202000
C	-1.640428000	2.608525000	-2.749952000
H	-2.369825000	1.936988000	-2.251308000
H	-2.213908000	3.377443000	-3.312221000
C	1.624061000	2.587673000	-2.770954000
H	1.050842000	1.992142000	-3.507315000
H	2.205494000	3.349781000	-3.334353000
H	2.346929000	1.901128000	-2.283143000
Cl	0.012421000	2.543238000	2.509845000
O	-1.447408000	1.047986000	0.025829000
O	1.451859000	1.036883000	0.022263000
O	-0.004511000	-1.326808000	0.834258000
Se	-1.911042000	-1.922482000	-1.863437000
Se	-0.008932000	-0.821206000	-2.769411000

Se	1.889006000	-1.932668000	-1.866509000
Ti	-1.672779000	-0.758378000	0.326017000
Ti	1.666525000	-0.769904000	0.325964000
Ti	0.006565000	2.121275000	0.229262000
H	-1.084636000	1.999009000	-3.488272000

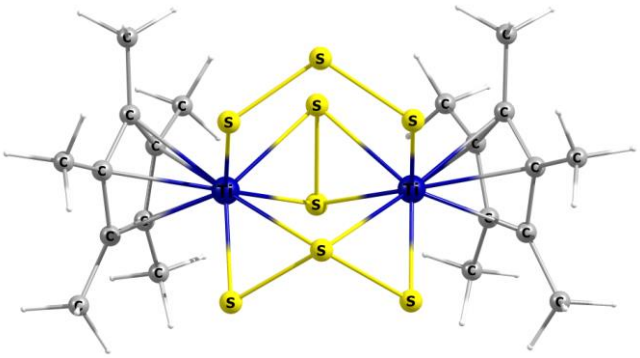

Figure S56. Optimized geometry of **4**.

Total energy = -5663.90815026 a.u.

Cartesian coordinates for the calculated structure **4** (in Å)

C	3.566882000	0.210264000	1.380111000
C	4.121132000	0.318537000	0.055308000
C	3.962669000	-0.955169000	-0.598912000
C	3.282356000	-1.837970000	0.306610000
C	3.052895000	-1.121207000	1.535617000
C	3.610302000	1.258138000	2.455826000
H	4.493105000	1.102167000	3.115743000
H	2.706107000	1.224517000	3.096616000
H	3.674289000	2.277599000	2.029859000
C	4.877303000	1.494702000	-0.498039000
H	4.511036000	2.453952000	-0.080884000
H	4.793353000	1.557294000	-1.601176000
H	5.959054000	1.413366000	-0.248542000
C	4.581809000	-1.349027000	-1.912170000
H	4.641622000	-0.498156000	-2.619207000
H	4.021540000	-2.164030000	-2.412928000
H	5.619341000	-1.717634000	-1.748154000
C	2.990517000	-3.291841000	0.058417000
H	2.115773000	-3.640594000	0.642632000
H	3.859416000	-3.923836000	0.349195000
H	2.778060000	-3.491551000	-1.010884000
C	2.511322000	-1.702755000	2.810915000
H	1.818804000	-2.546171000	2.621266000
H	1.963545000	-0.947959000	3.409269000
H	3.345235000	-2.087289000	3.439802000
C	-3.566987000	0.210337000	1.380002000
C	-3.052929000	-1.121090000	1.535657000
C	-3.282298000	-1.837985000	0.306710000
C	-3.962607000	-0.955306000	-0.598930000
C	-4.121162000	0.318459000	0.055156000
C	-2.511383000	-1.702514000	2.811023000
H	-1.964132000	-0.947512000	3.409592000
H	-1.818396000	-2.545565000	2.621452000
H	-3.345258000	-2.087538000	3.439661000
C	-2.990408000	-3.291876000	0.058691000
H	-3.859322000	-3.923853000	0.349462000
H	-2.115709000	-3.640553000	0.643018000
H	-2.777861000	-3.491695000	-1.010572000
C	-4.581658000	-1.349326000	-1.912182000
H	-4.021296000	-2.164319000	-2.412852000
H	-4.641520000	-0.498515000	-2.619288000
H	-5.619165000	-1.718011000	-1.748180000
C	-4.877321000	1.494550000	-0.498364000
H	-4.793311000	1.557013000	-1.601504000
H	-4.511084000	2.453852000	-0.081303000
H	-5.959084000	1.413233000	-0.248915000
C	-3.610531000	1.258301000	2.455625000
H	-4.493239000	1.102198000	3.115637000
H	-3.674775000	2.277709000	2.029575000
H	-2.706268000	1.224939000	3.096335000
S	1.749801000	2.423383000	-0.230129000
S	0.000012000	3.061266000	0.774862000
S	-1.749826000	2.423405000	-0.230056000
S	-0.000011000	0.316214000	1.495436000
S	0.000004000	-1.621729000	0.507501000
S	1.712894000	-0.354907000	-2.506599000
S	0.000040000	0.829302000	-2.106363000
S	-1.712864000	-0.354839000	-2.506600000
Ti	1.771723000	-0.042277000	-0.187641000
Ti	-1.771727000	-0.042264000	-0.187631000

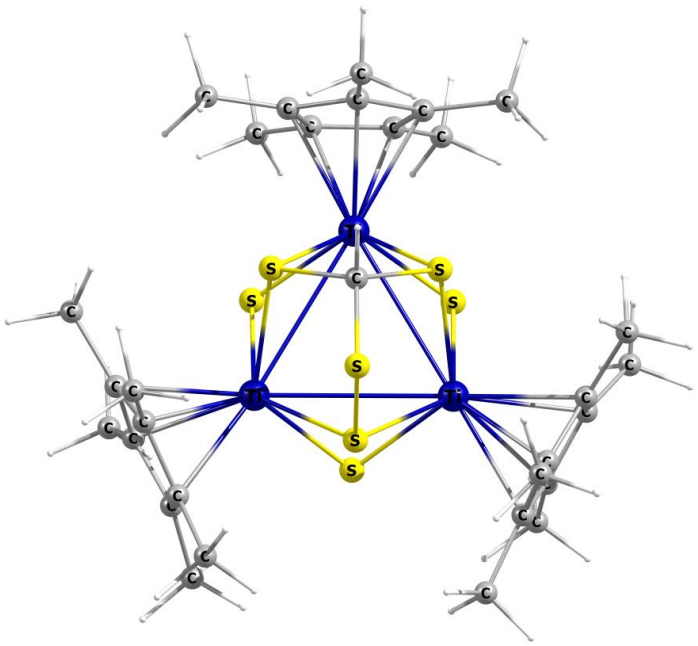

Figure S57. Optimized geometry of **5**.

Total energy = -6543.94407647 a.u.

Cartesian coordinates for the calculated structure **5** (in Å)

C	-2.895424000	2.863019000	0.802412000
C	-3.757619000	1.750221000	0.502955000
C	-3.823582000	1.608646000	-0.925707000
C	-2.982771000	2.620461000	-1.509700000
C	-2.421553000	3.406500000	-0.442724000
C	-2.653888000	3.432776000	2.172070000
H	-1.777782000	4.109669000	2.183746000
H	-3.537538000	4.019242000	2.509953000
H	-2.465507000	2.642240000	2.926847000
C	-4.573299000	0.973742000	1.498772000
H	-4.699963000	-0.084525000	1.194527000
H	-4.107965000	0.975265000	2.503404000
H	-5.590411000	1.416376000	1.596534000
C	-4.748619000	0.693073000	-1.675301000
H	-4.335903000	0.404249000	-2.661751000
H	-4.944246000	-0.242628000	-1.116023000
H	-5.726911000	1.195606000	-1.849830000
C	-2.811600000	2.873341000	-2.982452000
H	-1.829677000	3.334185000	-3.206882000
H	-2.879703000	1.936183000	-3.569571000
H	-3.602488000	3.561736000	-3.356782000
C	-1.583015000	4.643051000	-0.601247000
H	-1.004581000	4.624201000	-1.545404000
H	-2.226314000	5.551480000	-0.613673000
H	-0.858269000	4.754257000	0.229742000
C	3.454215000	2.360993000	0.247492000
C	3.492028000	2.135752000	-1.170609000
C	3.939315000	0.785157000	-1.394454000
C	4.175368000	0.176613000	-0.111761000
C	3.864437000	1.147557000	0.903665000
C	3.194038000	3.680306000	0.916843000
H	2.425861000	4.271240000	0.380014000
H	2.846630000	3.553787000	1.960561000
H	4.127476000	4.287196000	0.943543000
C	3.273214000	3.179397000	-2.229611000
H	2.506345000	3.918352000	-1.925130000
H	4.218795000	3.731883000	-2.430490000
H	2.936289000	2.733350000	-3.185880000
C	4.242862000	0.175253000	-2.734741000
H	3.580545000	0.574823000	-3.527957000
H	5.292926000	0.395241000	-3.032252000
H	4.115501000	-0.924859000	-2.723355000
C	4.740635000	-1.195824000	0.124343000
H	4.349248000	-1.646572000	1.058435000
H	4.493440000	-1.883822000	-0.707549000
H	5.849530000	-1.153289000	0.213376000
C	4.053873000	0.981382000	2.386763000
H	4.140834000	-0.085482000	2.669432000
H	4.982511000	1.496217000	2.720767000
H	3.206349000	1.405047000	2.963855000
C	-1.800307000	-3.796995000	0.291701000
C	-0.658745000	-3.934611000	1.157322000
C	0.498731000	-4.171161000	0.335502000
C	0.074331000	-4.171660000	-1.037282000
C	-1.347176000	-3.940698000	-1.064457000
C	-3.227702000	-3.626394000	0.729057000
H	-3.826486000	-3.101256000	-0.041247000
H	-3.706477000	-4.614824000	0.911332000
H	-3.301923000	-3.039721000	1.666558000
C	-0.692252000	-3.956362000	2.660721000
H	0.270191000	-3.622129000	3.097987000
H	-1.496798000	-3.308234000	3.063084000
H	-0.881961000	-4.987725000	3.034448000
C	1.890242000	-4.462136000	0.821972000
H	2.653909000	-4.096426000	0.107096000
H	2.093120000	-3.980230000	1.798802000
H	2.044090000	-5.557565000	0.947500000
C	0.928163000	-4.516343000	-2.225034000
H	1.983808000	-4.218946000	-2.071521000
H	0.906197000	-5.613528000	-2.413040000
H	0.576701000	-4.011510000	-3.146473000
C	-2.219687000	-4.000092000	-2.286757000
H	-1.683460000	-3.654751000	-3.192605000
H	-2.555798000	-5.045016000	-2.473115000
H	-3.121614000	-3.366431000	-2.178876000
C	-0.040039000	-0.363627000	2.637394000

H	-0.136127000	-0.999893000	3.543192000
S	0.292303000	1.863472000	-1.585456000
S	0.329998000	2.080259000	1.137336000
S	1.536134000	-1.356506000	-1.448421000
S	-1.895224000	-0.806596000	-1.437147000
S	1.309617000	-1.050355000	1.562372000
S	-1.553289000	-0.590939000	1.583378000
S	0.228395000	1.332626000	3.178927000
Ti	-1.556153000	1.176275000	-0.270647000
Ti	1.836538000	0.643410000	-0.282967000
Ti	-0.315585000	-1.970223000	-0.168842000