Supplementary Information

Facile Synthesis of a 2,5-Bis(silyl)selenophene-1,1-dioxide and its Photophysical Properties

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1. Copies of Spectra for All New Compounds

2. Details of Kinetic Study for the Oxidation

3. Details of DSC Analysis

4. Details of X-ray Crystallography

5. Details of Theoretical Calculations

6. Details of Solid-State Fluorescence Study

1. Copies of Spectra for All New Compounds

a. 2,5-Bis(trimethylsilyl)selenophene-1,1-dioxide (5)

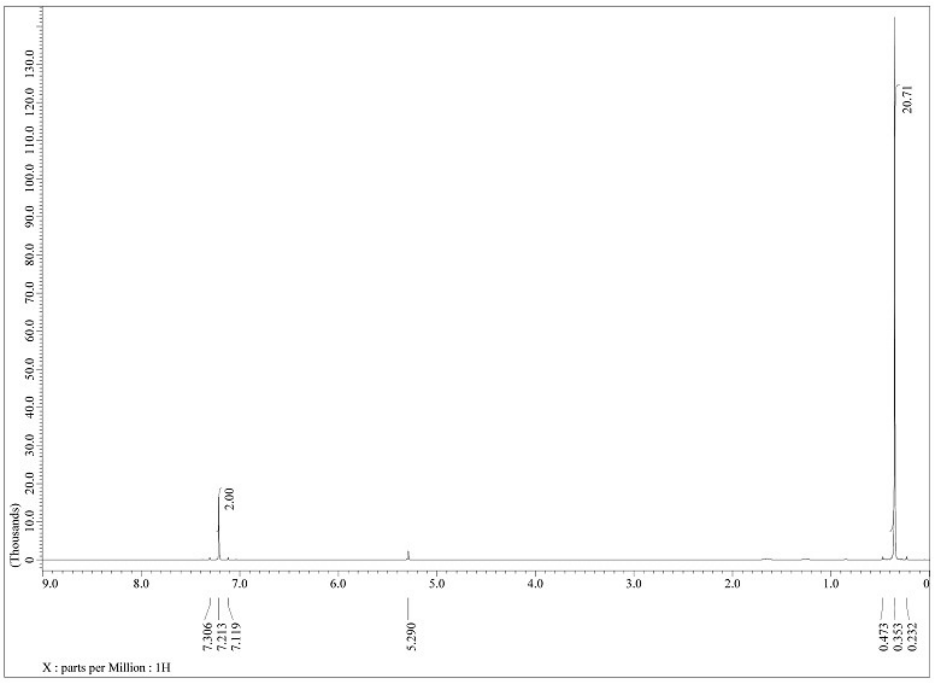


Fig. S1. ^{1}H NMR spectrum of 2,5-Bis(trimethylsilyl)selenophene-1,1-dioxide (**5**) in CD_2Cl_2.

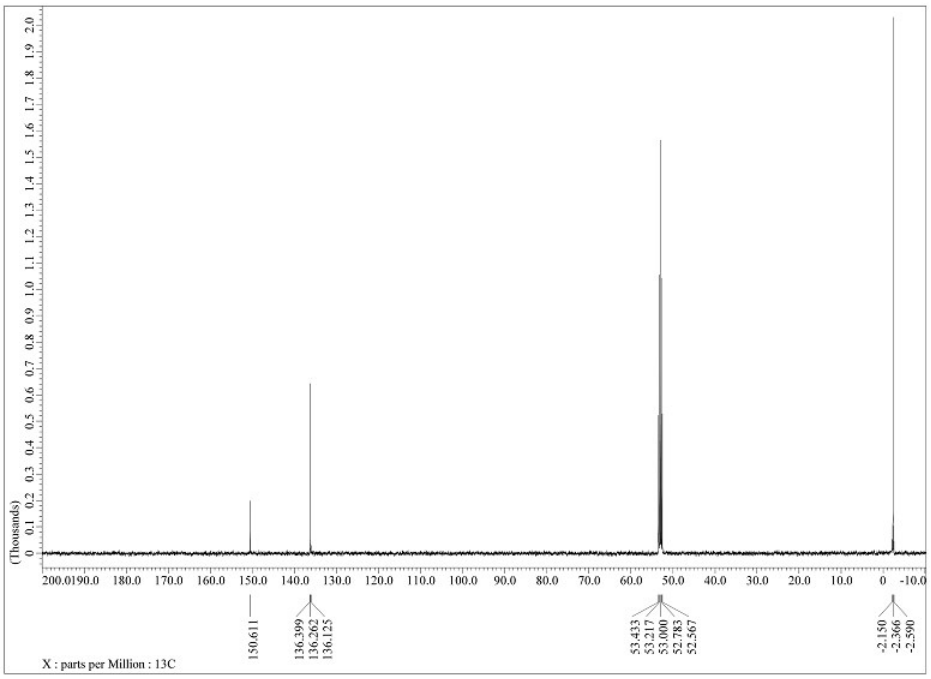


Fig. S2. ^{13}C NMR spectrum of 2,5-Bis(trimethylsilyl)selenophene-1,1-dioxide (**5**) in CD_2Cl_2.

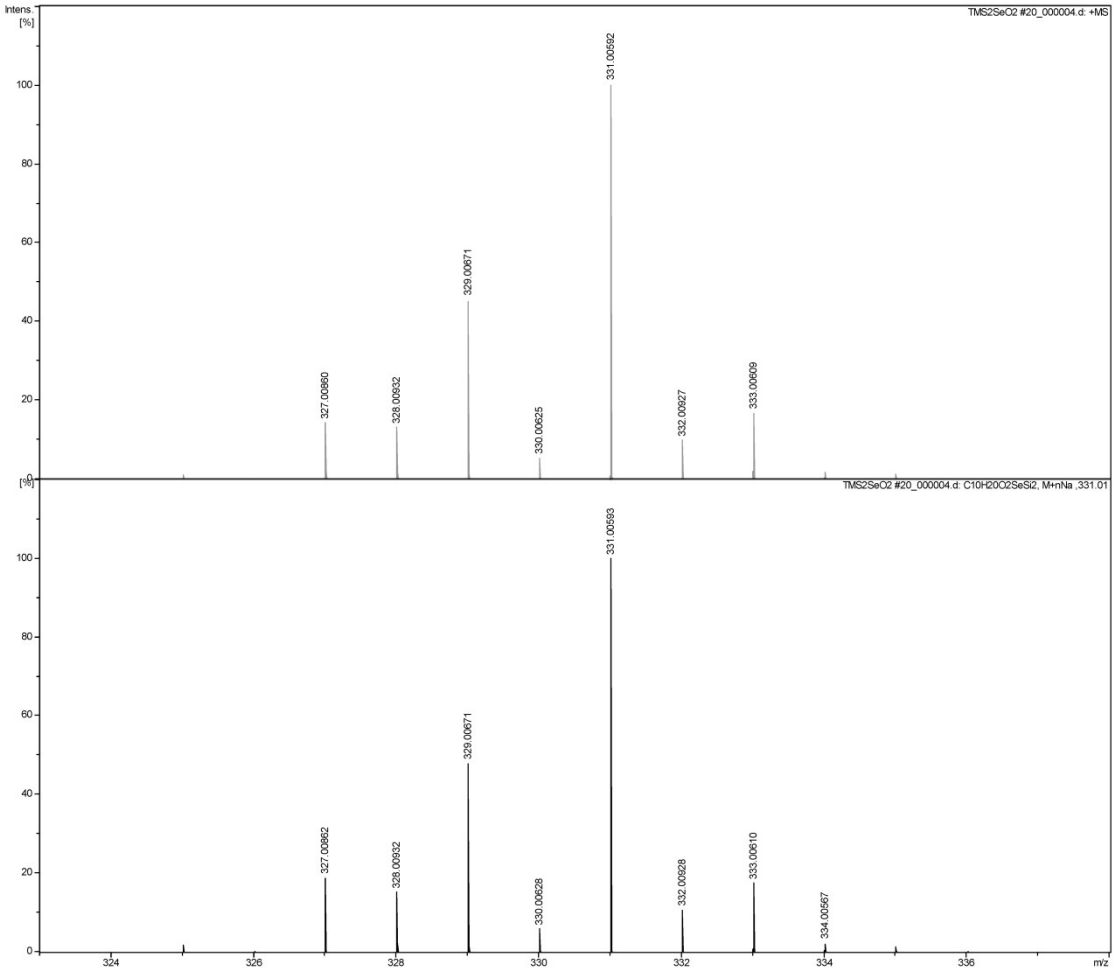


Fig. S3. HRMS(ESI, positive) spectrum of 2,5-Bis(trimethylsilyl)selenophene-1,1-dioxide (**5**): top; obsd., bottom; calcd.

b. 2,5-Bis(trimethylsilyl)selenophene (6)

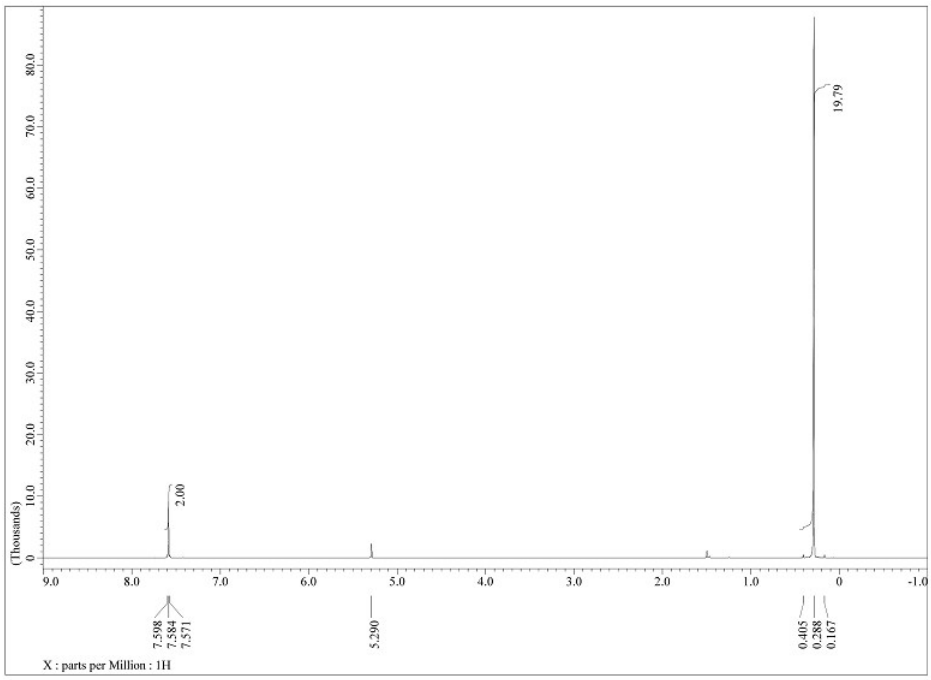


Fig. S4. ^{1}H NMR spectrum of 2,5-Bis(trimethylsilyl)selenophene (**6**) in CD_2Cl_2.

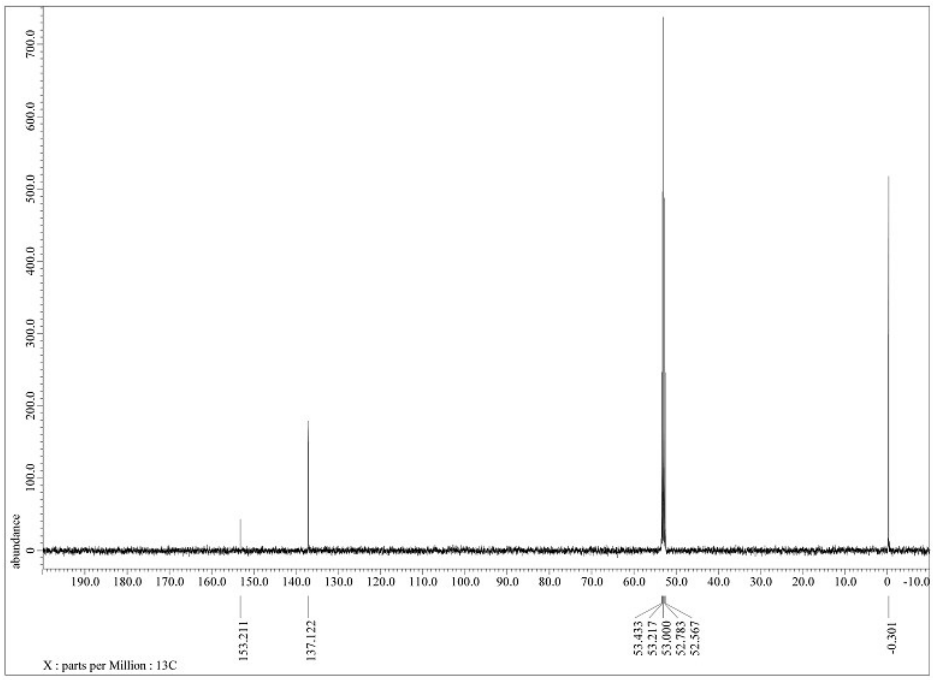


Fig. S5. ^{13}C NMR spectrum of 2,5-Bis(trimethylsilyl)selenophene (**6**) in CD_2Cl_2.

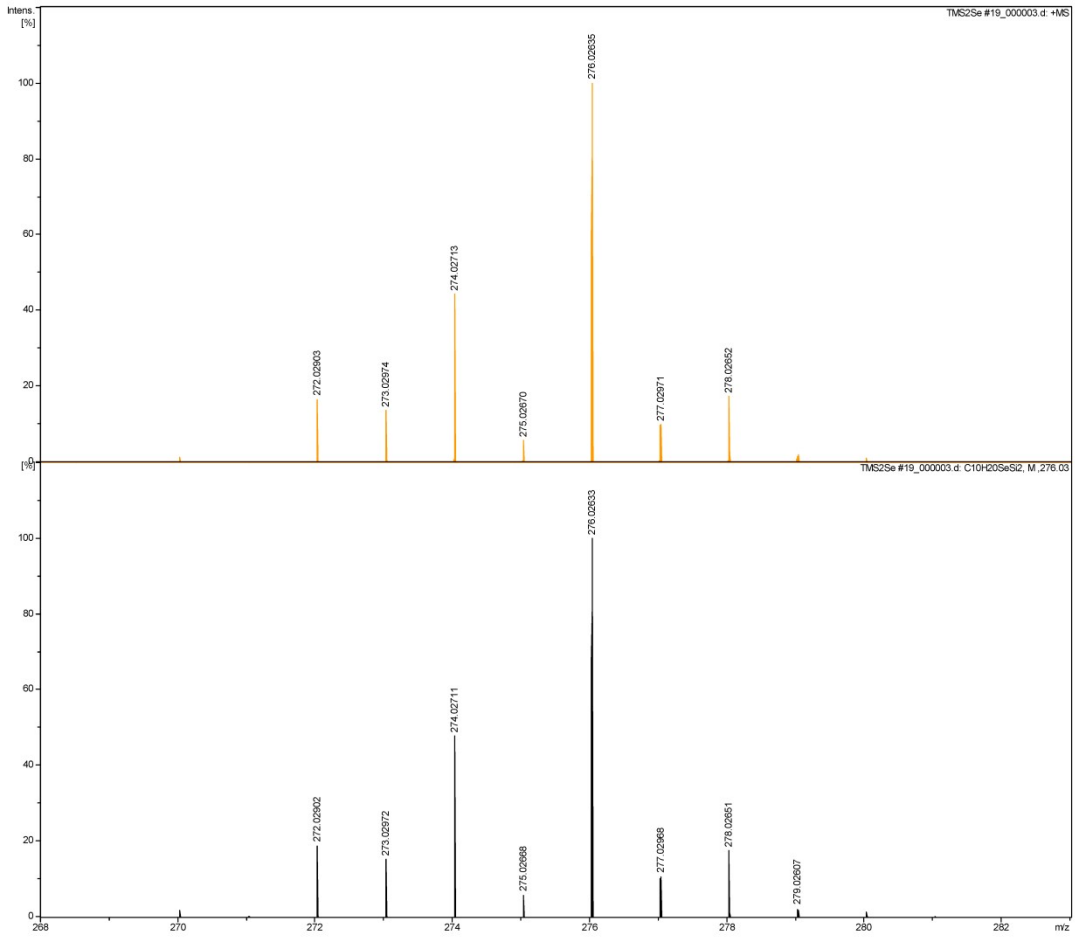


Fig. S6. HRMS(APCI, positive) spectrum of 2,5-Bis(trimethylsilyl)selenophene (**6**).: top; obsd., bottom; calcd.

c. 2,5-Bis(dimethylsilyl)selenophene (7)

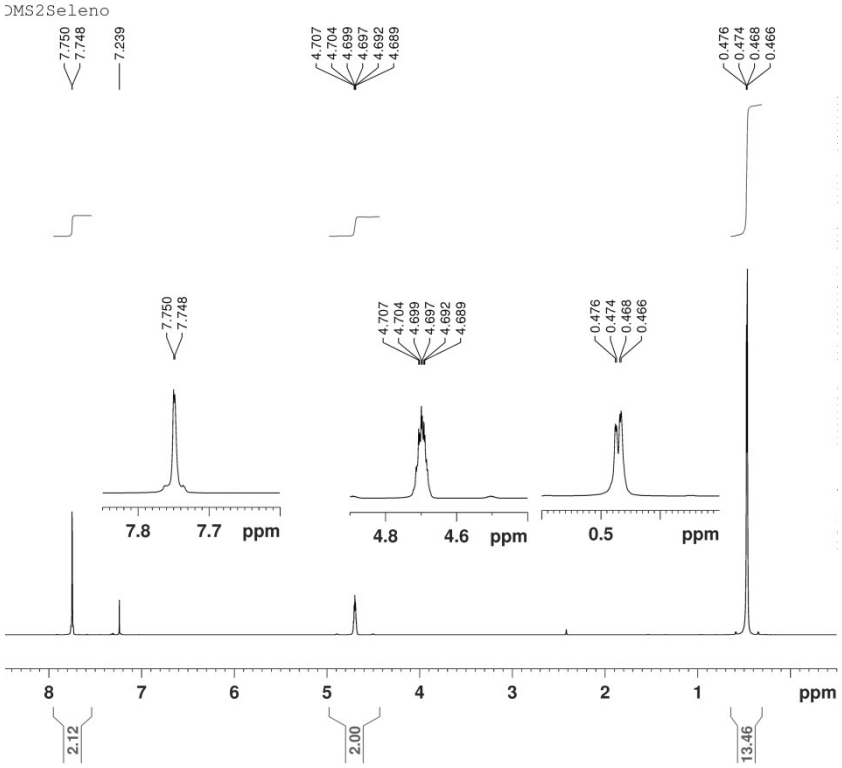


Fig. S7. ^{1}H NMR spectrum of 2,5-Bis(dimethylsilyl)selenophene (**7**) in $CDCl_3$.

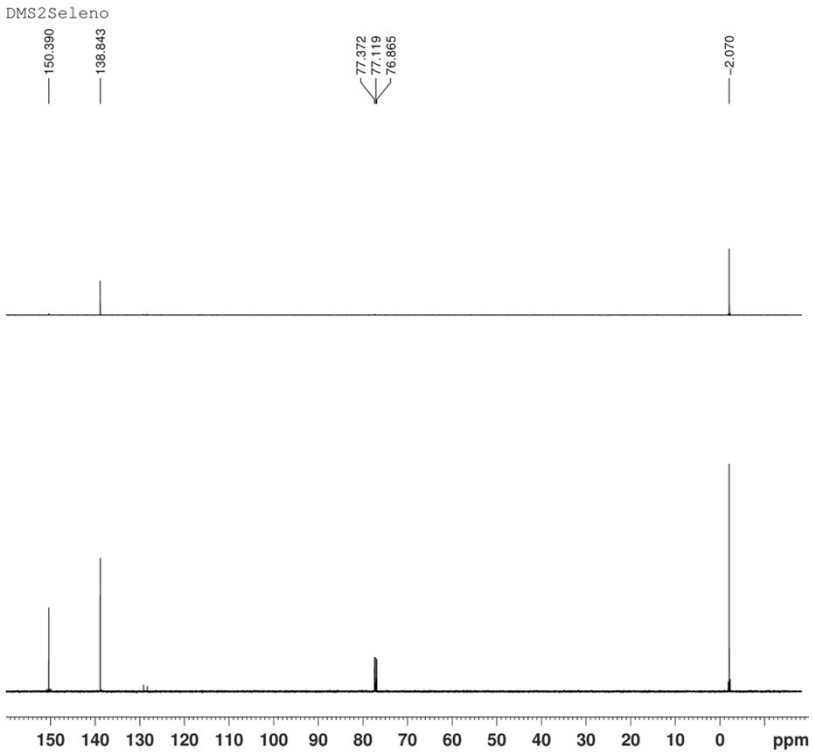
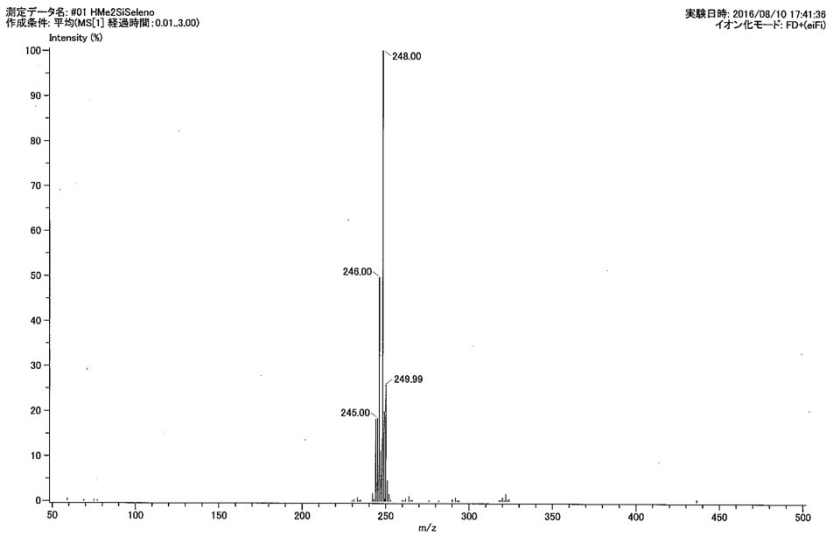
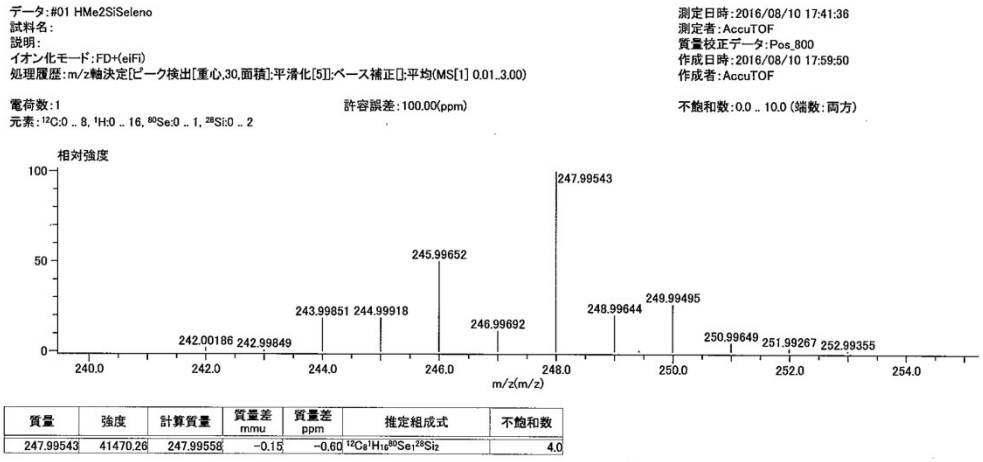


Fig. S8. ^{13}C NMR spectrum of 2,5-Bis(dimethylsilyl)selenophene (**7**) in $CDCl_3$.





質量	強度	計算質量	質量差 mmu	質量差 ppm	推定組成式	不飽和数
247.99543	41470.26	247.99558	−0.15	−0.60	$^{12}C_8{}^1H_{16}{}^{80}Se_1{}^{28}Si_2$	4.0

Fig. S9. HRMS(FD/FI, positive) spectrum of 2,5-Bis(dimethylsilyl)selenophene (**7**).: top; a whole spectrum., bottom; an enlarged spectra.

d. 2,5-Bis(phenylimethylsilyl)selenophene (9)

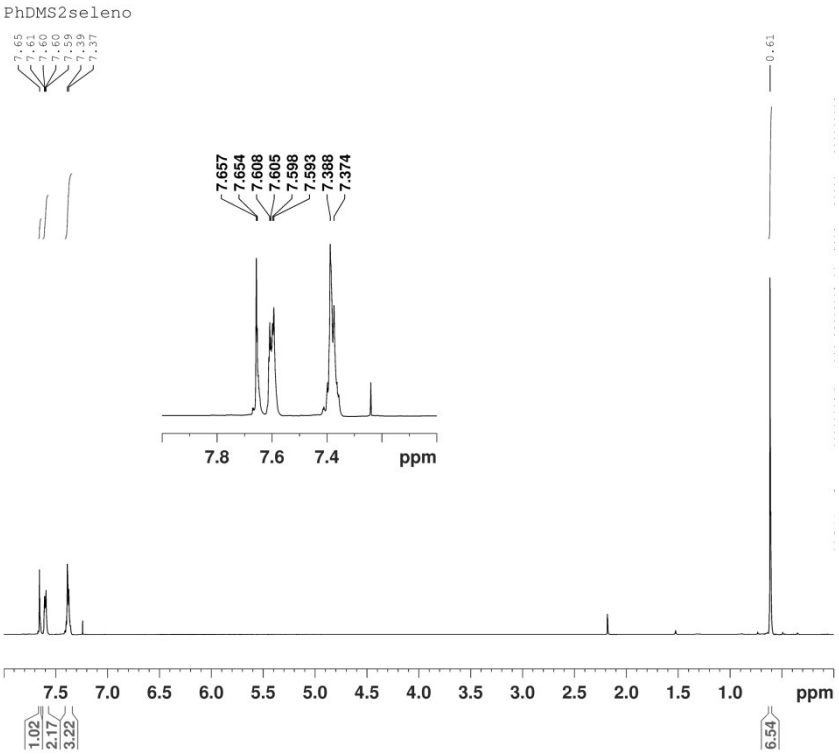


Fig. S10. ^{1}H NMR spectrum of 2,5-Bis(phenyldimethylsilyl)selenophene (**9**) in $CDCl_3$.

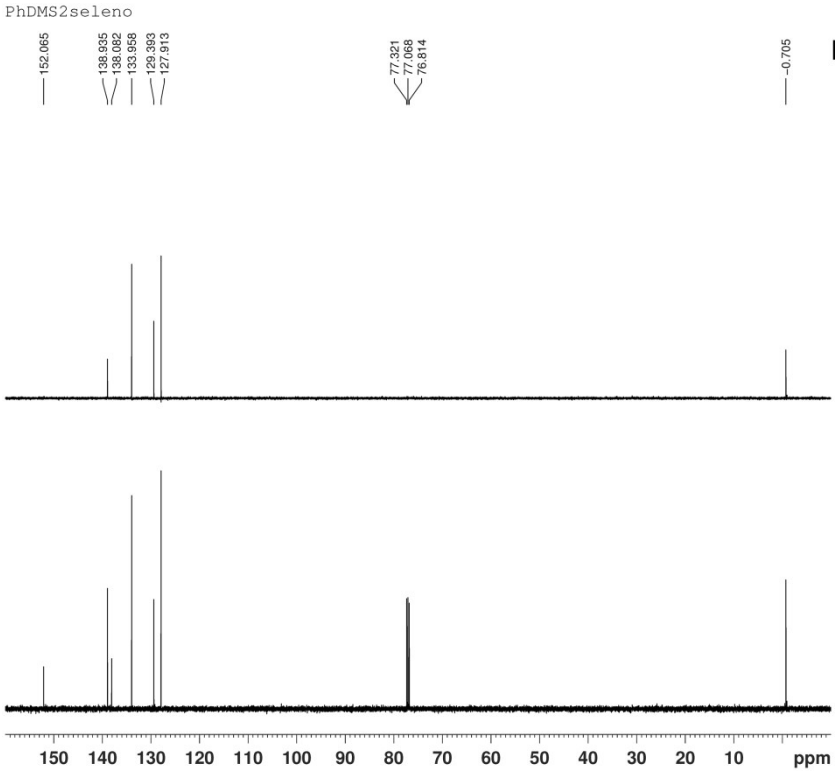


Fig. S11. ^{13}C NMR spectrum of 2,5-Bis(phenyldimethylsilyl)selenophene (**9**) in $CDCl_3$.

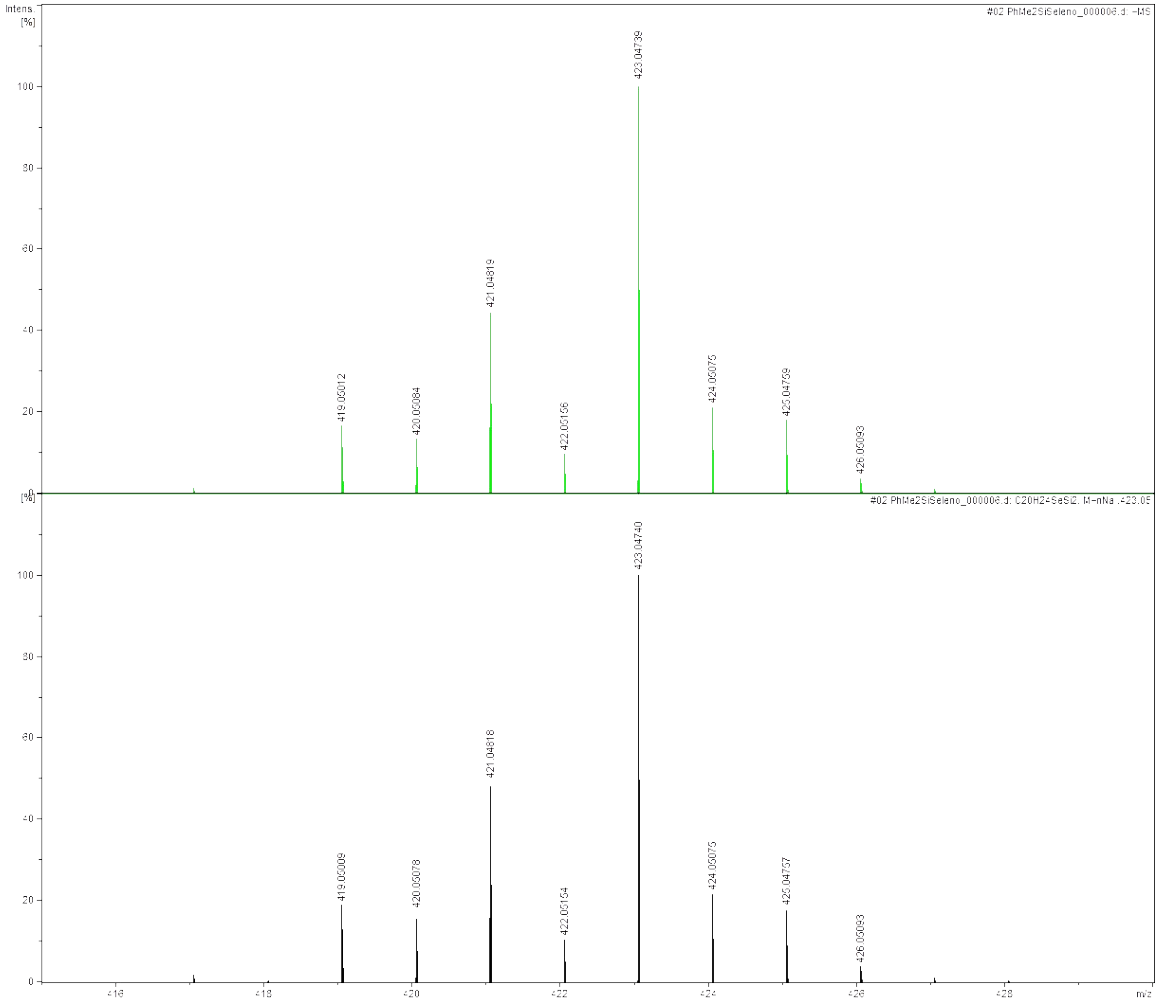


Fig. S12. HRMS(ESI, positive) spectrum of 2,5-Bis(phenyldimethylsilyl)selenophene (**9**).: top; obsd., bottom; calcd.

e. 2,5-Bis(phenyldimethylsilyl)selenophene-1,1-dioxide (10)

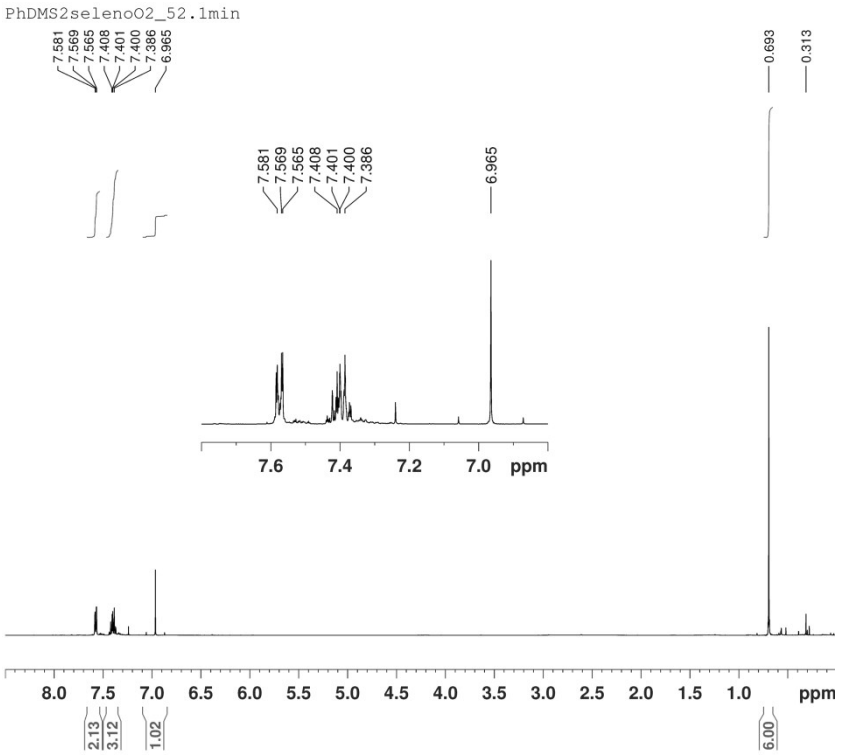


Fig. S13. ^{1}H NMR spectrum of 2,5-Bis(phenyldimethylsilyl)selenophene-1,1-dioxide (**10**) in in $CDCl_3$.

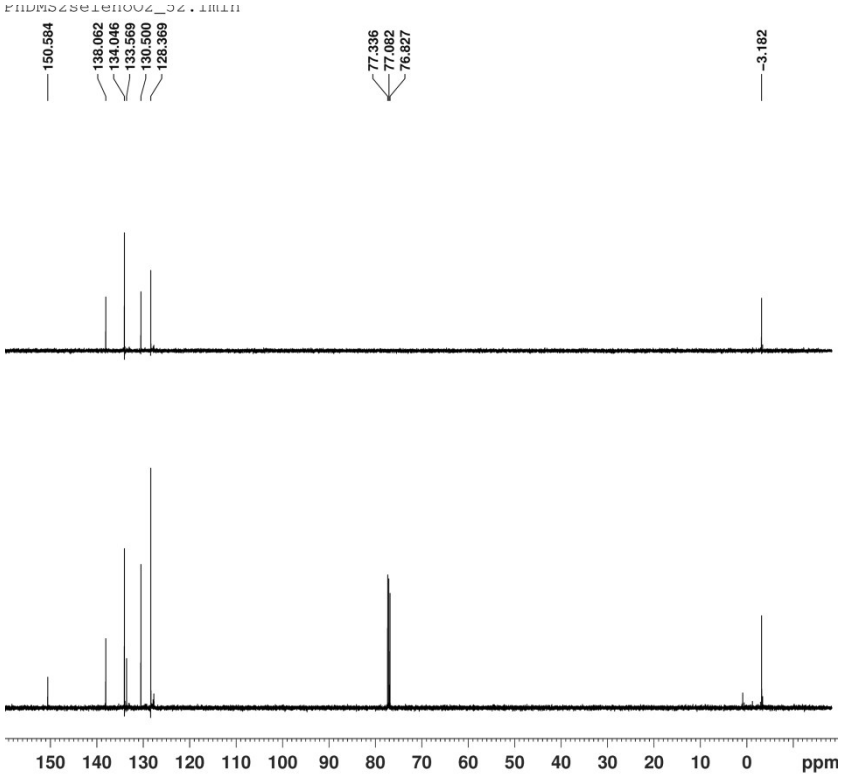


Fig. S14. ^{13}C NMR spectrum of 2,5-Bis(phenyldimethylsilyl)selenophene-1,1-dioxide (**10**) in in $CDCl_3$.

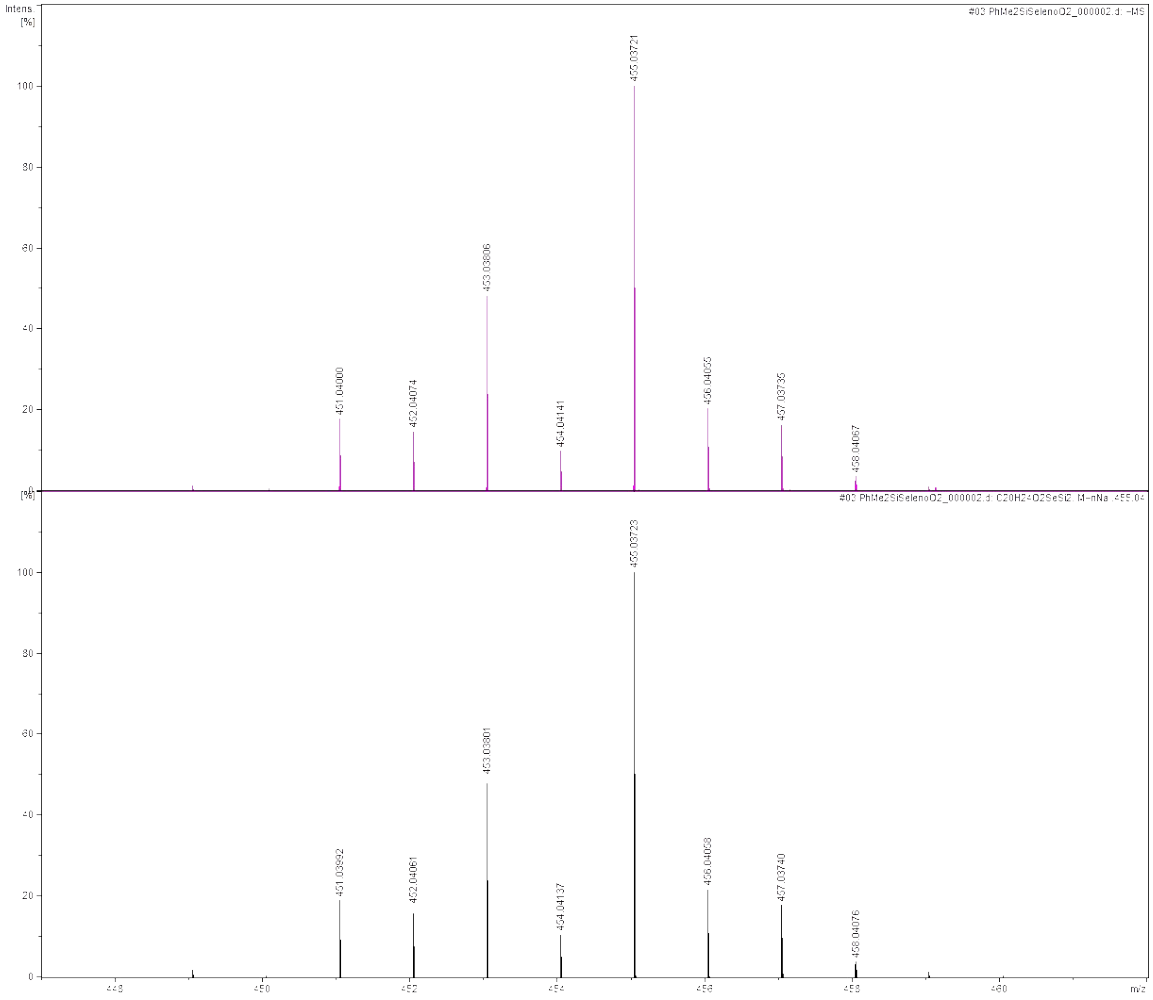


Fig. S15. HRMS(ESI, positive) spectrum of 2,5-Bis(phenyldimethylsilyl)selenophene-1,1-dioxide (**10**): top; obsd., bottom; calcd.

2. Details of Kinetic Study for the Oxidation

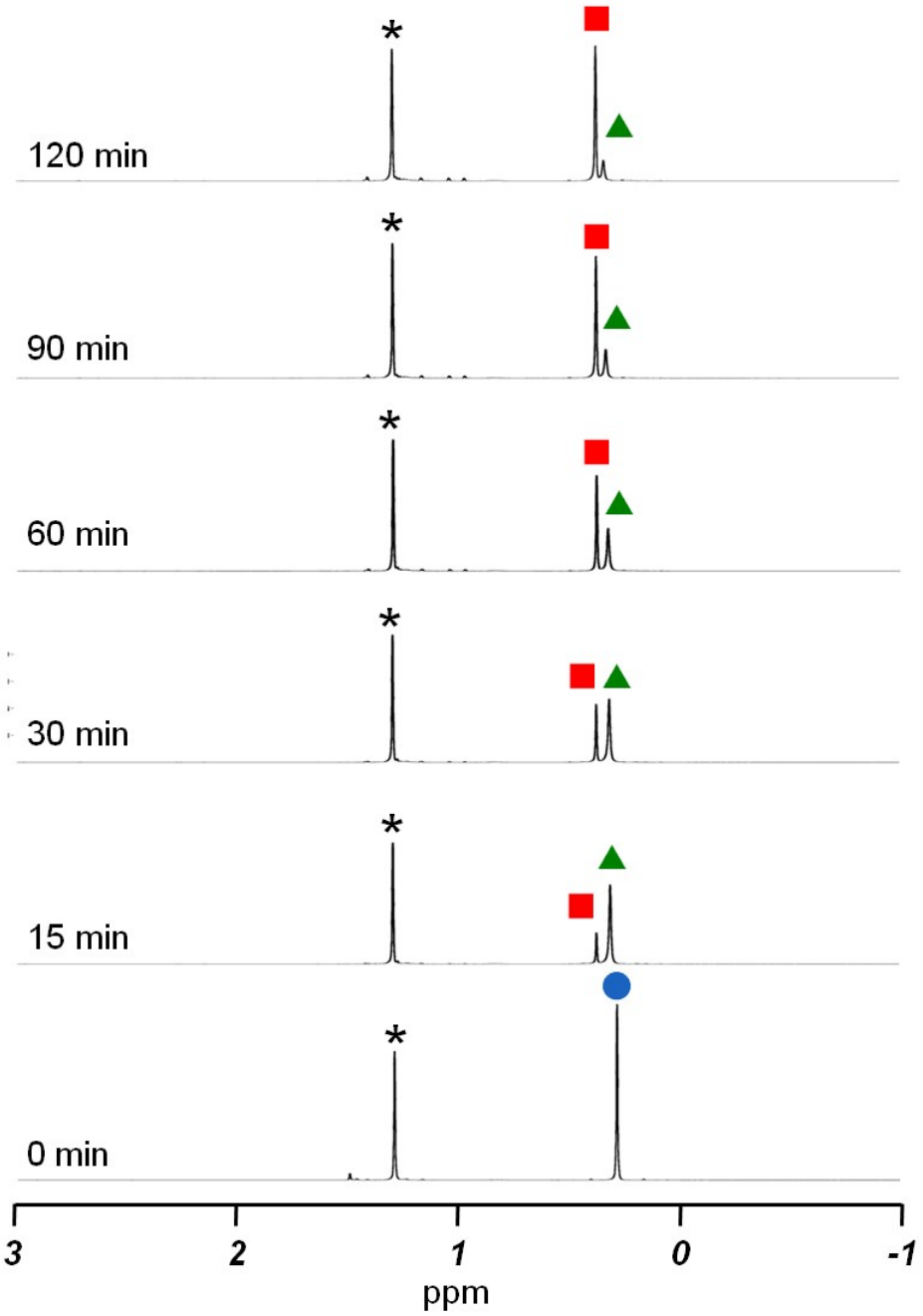


Fig. S16. Oxidation reaction of selenophene (**6**) traced by ^{1}H NMR spectra: at 298 K: [*A*] (selenophene, blue cycle); [*B*] (monooxide, green triangle); and [*C*] (dioxide, red square) (Asterisks (*) indicate signals of 1,3,5-tri-*tert*-butylbenzene as internal standard.).

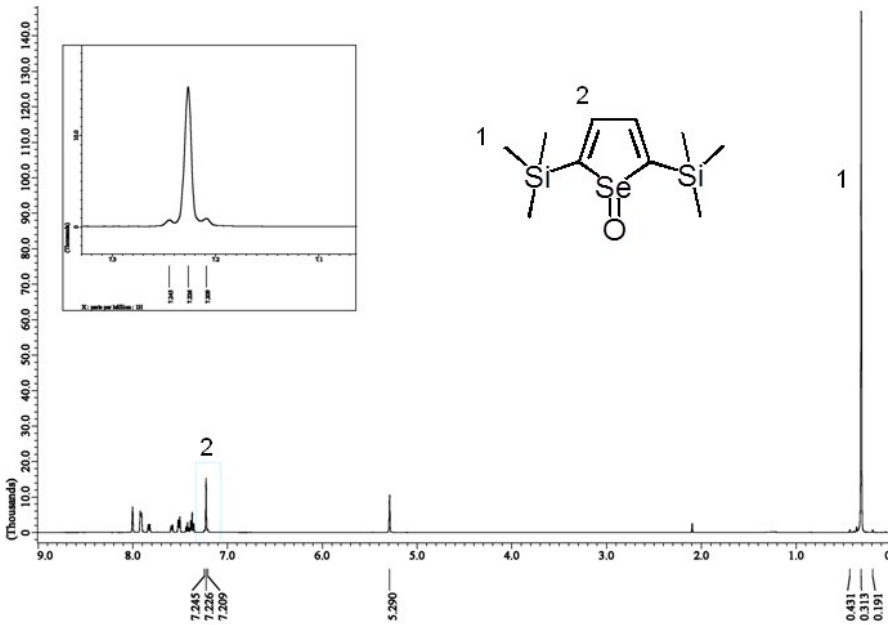


Fig. S17. ^{1}H NMR spectrum of temporary observed selenophene monooxide.

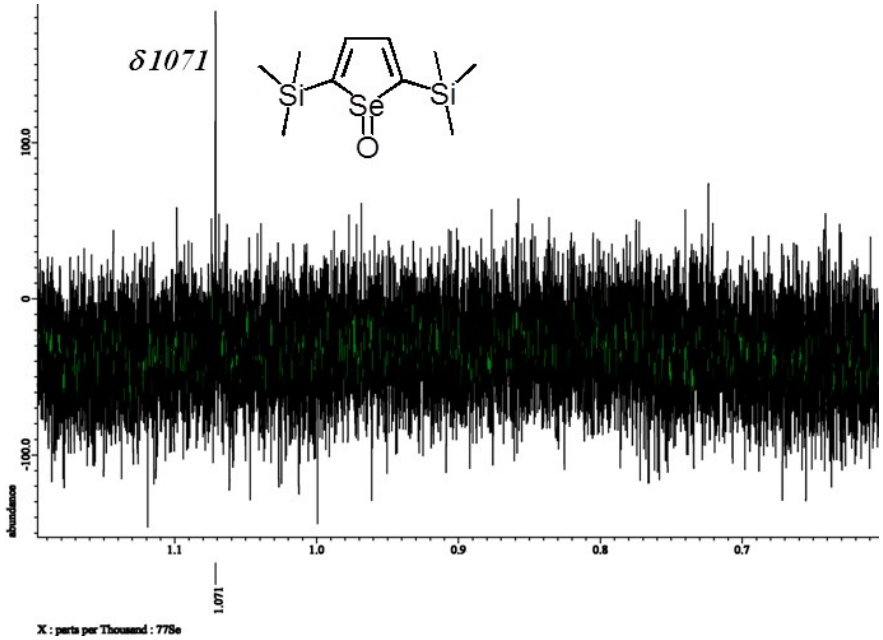


Fig. S18. ^{77}Se NMR spectrum of temporary observed selenophene monooxide.

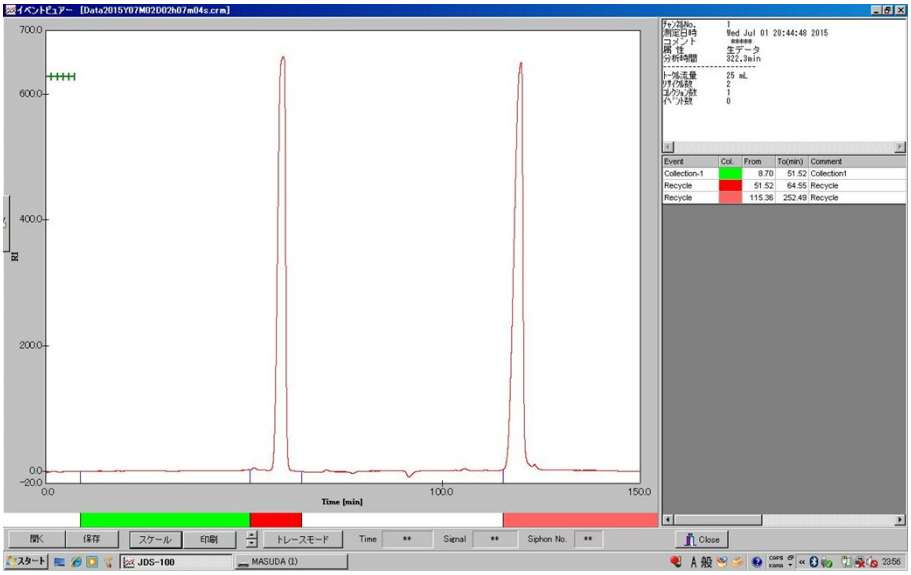


Fig. S19. A recycling GPC chart (RI detector, 2 cycles) for the analysis of the crude product(s) after hydrolysis in the oxidation of 2,5-bis(dimethylsilyl)selenophene (**7**) with *m*CPBA. The single peak indicates a fraction of **7**.

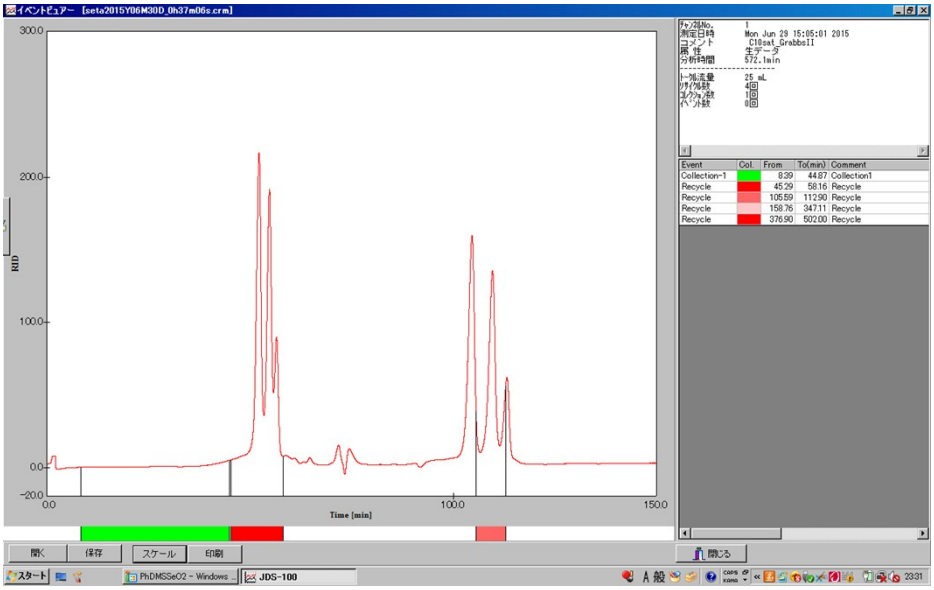


Fig. S20. A recycling GPC chart (RI detector, 2 cycles) for the analysis of the crude product(s) after hydrolysis in the oxidation of 2,5-bis(phenyldimethylsilyl)selenophene (9) with *m*CPBA. The signals at 52.1, 52.4, and 56.6 min were ascribed to the fractions of 2,5-bis(phenyldimethylsilyl)selenophene- 1,1-dioxide (**10**), **9**, and $PhMe_2Si$-O-$SiMe_2Ph$, respectively.

3. Details of DSC Analysis

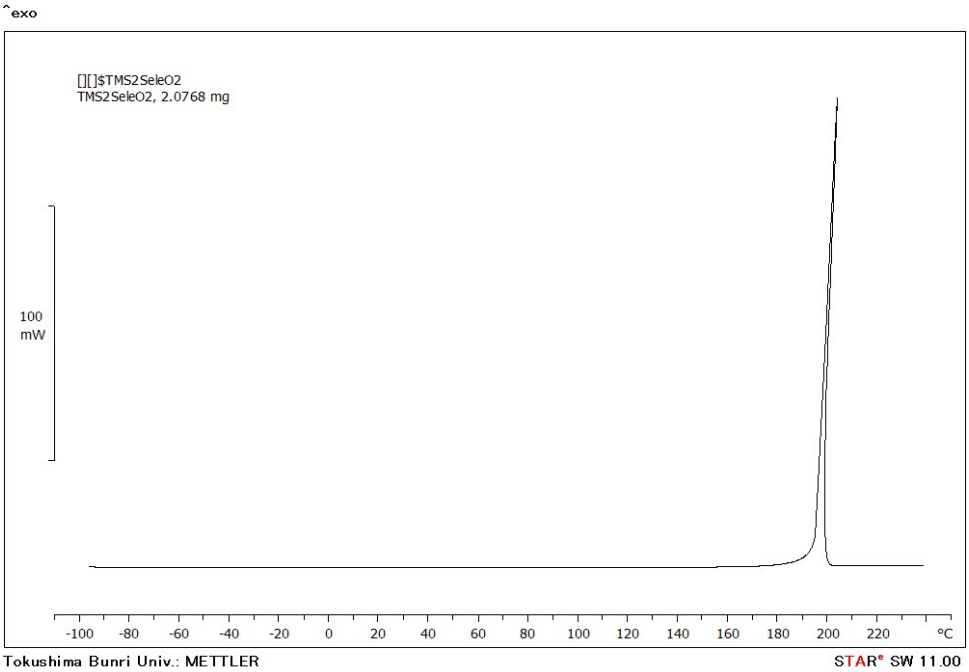


Fig. S21. DSC chart of powder of 2,5-Bis(trimethylsilyl)selenophene-1,1-dioxide (**5**).

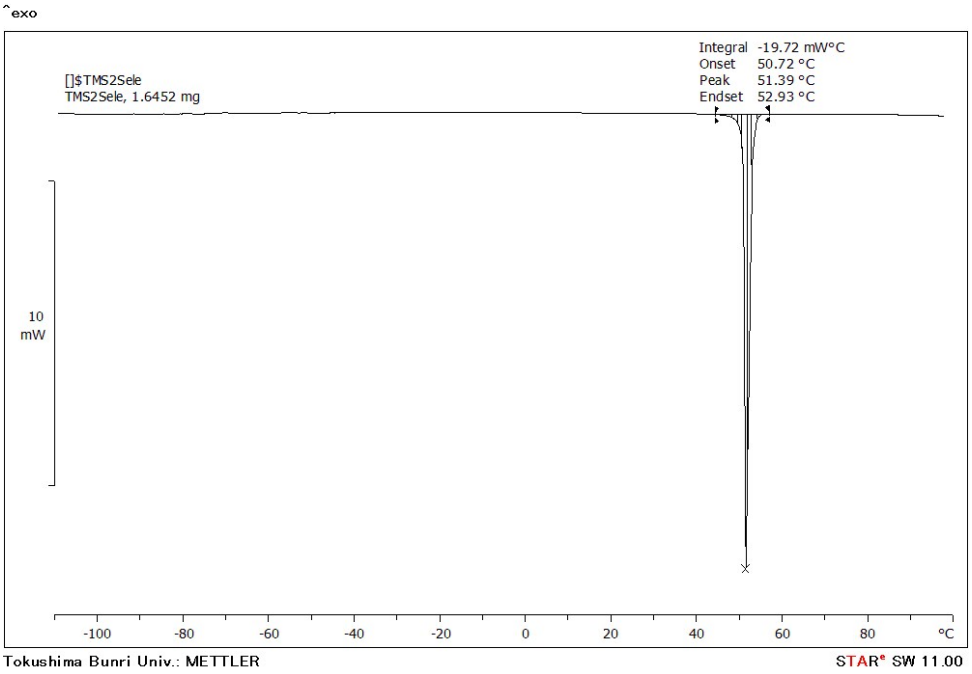


Fig. S22. DSC chart of powder of 2,5-Bis(trimethylsilyl)selenophene (**6**).

4. Details of X-ray Crystallography

Table S1. Crystal Data of **5** and **6**

		5	**6**
CCDC #		1472766	1472767
Compound Name		Selenophene-1,1-dioxide	Selenophene
Empirical formula		C10H20O2SeSi2	C10H20SeSi2
Cryst shape		prism	prism
Cryst color		colorless	colorless
Cryst size		0.30 x 0.20 x 0.20 mm3	0.40 x 0.40 x 0.10 mm3
Formula weight / g mol-1		370.40	275.40
Crystal system		Tetragonal	Monoclinic
Space group		P-4	Pmmn
Z		2	4
Temperature / K		100	100
Cell parameter	a	11.0742(16) Å	14.666(4) Å
	b	11.0742(16) Å	14.776(4) Å
	c	6.4127(9) Å	6.4741(16) Å
	α	90°	90°
	β	90°	90°
	γ	90°	90°
	V	786.4(3) Å3	1403.0(6) Å3
Calculated density		1.298 Mg/m3	1.304 Mg/m3
F(000)		316	568
Absorption coefficient		2.523 mm-1	2.810 mm-1
θ range for collecn (deg)		3.177 to 28.493°	1.96 to 26.89°
Index ranges		-11<=h<=14, -14<=k<=13, -6<=l<=8	-18<=h<=15, -17<=k<=18, -8<=l<=4
Reflections collected		4426	6412
Independent reflections		1826 [R(int) = 0.0261]	1550 [R(int) = 0.0359]
Completeness		99.6 %	99.9 %
Goodness-of-fit on F2		0.945	1.033
Final R indices [I>2sigma(I)]		R1 = 0.0238, wR2 = 0.0709	R1 = 0.0238, wR2 = 0.0587
R indices (all data)		R1 = 0.0240, wR2 = 0.0709	R1 = 0.0270, wR2 = 0.0600
Largest diff. peak and hole		1.027 and -0.533 e.Å-3	0.470 and -0.475 e.Å-3

5. Details of DFT Calculations

a. Optimized Structure and Total Energy at B3LYP/6-31G(d) Level

I. Theoretical calculations of 2,5-Bis(trimethylsilyl)selenophene-1,1-dioxide (5)

total energy: = -3521.8754088 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	0.000000	0.000000	0.644749
2	8	0	1.405512	0.000000	1.491849
3	8	0	-1.405512	0.000000	1.491849
4	6	0	0.000000	1.403555	-0.739710
5	6	0	0.000000	-1.403555	-0.739710
6	6	0	-0.000043	0.742898	-1.908629
7	6	0	0.000043	-0.742898	-1.908629
8	1	0	-0.000034	1.263832	-2.864105
9	1	0	0.000034	-1.263832	-2.864105
10	14	0	0.000456	3.217631	-0.223511
11	14	0	-0.000456	-3.217631	-0.223511
12	6	0	0.002690	4.291370	-1.778178
13	6	0	-1.552568	3.494330	0.812538
14	6	0	1.551321	3.492394	0.816211
15	6	0	-0.002690	-4.291370	-1.778178
16	6	0	1.552568	-3.494330	0.812538
17	6	0	-1.551321	-3.492394	0.816211
18	1	0	0.002257	5.351664	-1.496633
19	1	0	0.891361	4.116755	-2.395793
20	1	0	-0.883890	4.116664	-2.398751
21	1	0	-1.513481	4.460874	1.328930
22	1	0	-2.454114	3.479102	0.189320
23	1	0	-1.662410	2.703719	1.562986
24	1	0	1.511748	4.458293	1.333767
25	1	0	2.454155	3.477512	0.194847
26	1	0	1.659298	2.700594	1.565676
27	1	0	-0.002257	-5.351664	-1.496633
28	1	0	-0.891361	-4.116755	-2.395793
29	1	0	0.883890	-4.116664	-2.398751
30	1	0	1.513481	-4.460874	1.328930
31	1	0	2.454114	-3.479102	0.189320
32	1	0	1.662410	-2.703719	1.562986
33	1	0	-1.511748	-4.458293	1.333767
34	1	0	-2.454155	-3.477512	0.194847
35	1	0	-1.659298	-2.700594	1.565676

II. Theoretical calculations of 2,5-Bis(trimethylsilyl)selenophene (6)

total energy: =-3371.5616089 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	0.000000	0.000000	0.855300
2	6	0	0.005920	1.327722	-0.480559
3	6	0	-0.005920	-1.327722	-0.480559
4	6	0	0.003502	0.714404	-1.710531
5	6	0	-0.003502	-0.714404	-1.710531
6	1	0	0.006550	1.283953	-2.636760
7	1	0	-0.006550	-1.283953	-2.636760
8	14	0	0.000000	3.156367	-0.068834
9	14	0	0.000000	-3.156367	-0.068834
10	6	0	0.204948	4.141457	-1.671142
11	6	0	-1.632608	3.618125	0.770627
12	6	0	1.427213	3.536155	1.114905
13	6	0	-0.204948	-4.141457	-1.671142
14	6	0	1.632608	-3.618125	0.770627
15	6	0	-1.427213	-3.536155	1.114905
16	1	0	0.220260	5.217060	-1.456591
17	1	0	1.142232	3.892584	-2.181954
18	1	0	-0.618601	3.957396	-2.370873
19	1	0	-1.649669	4.682594	1.035918
20	1	0	-2.487522	3.422436	0.113118
21	1	0	-1.786067	3.042807	1.691174
22	1	0	1.420871	4.592842	1.409776
23	1	0	2.396669	3.323777	0.649655
24	1	0	1.362415	2.935971	2.030315
25	1	0	-0.220260	-5.217060	-1.456591
26	1	0	-1.142232	-3.892584	-2.181954
27	1	0	0.618601	-3.957396	-2.370873
28	1	0	1.649669	-4.682594	1.035918
29	1	0	2.487522	-3.422436	0.113118
30	1	0	1.786067	-3.042807	1.691174
31	1	0	-1.420871	-4.592842	1.409776
32	1	0	-2.396669	-3.323777	0.649655
33	1	0	-1.362415	-2.935971	2.030315

b. Calculated Electronic Transitions at TD-B3LYP/6-3111++G(d,p)//B3LYP/6-31G(d) Level

Table S2. Calculated Electronic Transitions in 2,5-Bis(trimethylsilyl)selenophene-dioxide (**5**) at TD-B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) Level

Transition	**Energy / nm**	**Oscillator strength**	**symmetry**	**Assignment** (CI expansion coef.)
a	340.33	0.0000	Singlet-A	HOMO-1→LUMO (0.70376)
b	324.62	0.0779	Singlet-B	HOMO→LUMO (0.68540) + HOMO-4→LUMO (-0.12175)
c	292.89	0.0114	Singlet-A	HOMO-2→LUMO (0.70022)
d	271.51	0.0006	Singlet-B	HOMO-3→LUMO (0.69228)
e	265.93	0.0840	Singlet-B	HOMO-4→LUMO (0.69224) + HOMO→LUMO (0.11411)
f	242.97	0.0198	Singlet-A	HOMO-5→LUMO (0.70277)
g	240.49	0.0104	Singlet-B	HOMO-6→LUMO (0.70302)
h	236.30	0.0000	Singlet-A	HOMO-7→LUMO (0.70368)
i	230.99	0.0183	Singlet-B	HOMO-8→LUMO (0.67430) + HOMO-1→LUMO+1 (-0.17608)

Table S3. Calculated Electronic Transitions in 2,5-Bis(trimethylsilyl)selenophene (**6**) at TD-B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) Level

Transition	**Energy / nm**	**Oscillator strength**	**symmetry**	**Assignment** (CI expansion coef.)
a	253.33	0.0510	Singlet-A	HOMO-1→LUMO (0.67966) + HOMO→LUMO+11 (-0.11473)
b	252.66	0.2812	Singlet-B	HOMO→LUMO (0.68540)
c	234.69	0.0000	Singlet-A	HOMO-1→LUMO+2 (0.52486) + HOMO-1→LUMO+3 (-0.43661) + HOMO-1→LUMO+8 (0.17132)
d	234.15	0.0050	Singlet-B	HOMO→LUMO+2 (0.56710) + HOMO→LUMO+3 (-0.38732) + HOMO→LUMO+8 (0.15462)
e	230.08	0.0000	Singlet-A	HOMO→LUMO+1 (0.69724)

6. Details of Solid-State Fluorescence Study

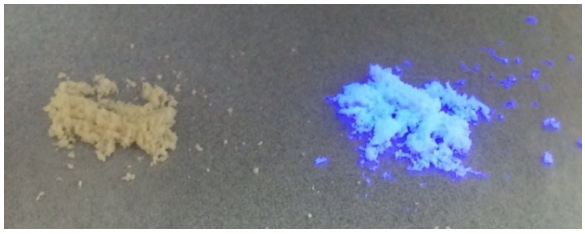


Fig. S23. Photograph of powder of selenophene-1,1-dioxode **5** (left) and thiophene-1,1-dioxode **3** (right) upon irradiation of 254 nm light. Due to instability of the compound of **5** the powder was slightly colored.

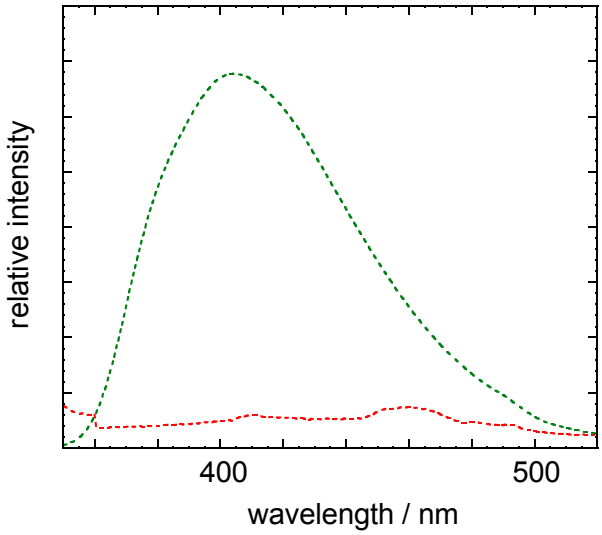


Fig. S24. Fluorescence spectra of powder of 2,5-bis(trimethylsilyl)selenophene-1,1-dioxide (5, red line) and 2,5-bis(trimethylsilyl)thiophene-1,1-dioxide (3, green line) (conditions: 296 K, ex. 308 nm).