

Supramolecular Organization Based on van der Waals Forces: Syntheses and Solid State Structures of Isomeric [6.6]Cyclophanes with 2,5-Diselena-hex-3-yne Bridges

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Dedicated to the memory of Prof. Mircea D. Banciu

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The *ortho*, *meta*, and *para* isomers **4–6** of [6.6]cyclophanes with 2,5-diselena-hex-3-yne bridges were synthesized by reacting the bis(selenocyanatomethyl)benzene derivatives **8a–8c** with the lithium salt of trimethylsilylethyne to yield **9a–9c**, deprotection of which afforded the bis(ethynylselenylmethyl)benzenes **10a–10c**. The condensation of the bis-lithium salts of **10a–10c** with **8a–8c** yielded the target compounds **4–6**. X-ray investigations on single crystals of **4–6** revealed intermolecular Se...Se interactions which contribute significantly to the solid-state structures of these species. In the case of the orthocyclophane **4**, we found short distances be-

tween one Se–C≡C–Se unit of each molecule leading to a linear chain of orthocyclophane rings. In the metacyclophane, **5**, the rings adopt a chair conformation and are piled on top of each other. The resulting molecular channels are connected with each other by intermolecular Se...Se interactions. For **6** also a chair conformation of the [6.6]paracyclophane unit was encountered. In the solid state the rings of **6** are connected by intermolecular Se...Se bridges.

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Introduction

Molecular entities assembling to cavities are of considerable interest in the field of host-guest chemistry.^[1,2] Examples for such assemblies are cyclic peptides,^[3] cyclodextrins^[4] or shape persistent cyclic hydrocarbons with phenolic groups,^[5] to name only a few. Recently, we found that cyclic tetrachalcogenaalkynes of the type **1** or **2** (Figure 1) adopt columnar structures in the solid state^[6,7] with cavities which allow the inclusion of organic solvents. The columnar structures are maintained by intermolecular forces between the chalcogen centers of neighboring columns. Varying the hydrocarbon chains between the rigid 1,2-dichalcogenaacetylene ($m = 1$) or 1,4-dichalcogenabutadiyne ($m = 2$) units shows that short chains up to five CH₂ groups are required to maintain a sizeable cavity within the ring. With longer (CH₂)_{*n*} chains the collapse of the cavity is observed.^[7c]

In this paper we report on systems in which part of each (CH₂)_{*n*} bridge in **2** is replaced by a benzene ring. This adds in terms of intermolecular interaction a new component: The chalcogen–chalcogen interactions now compete with π – π interactions.

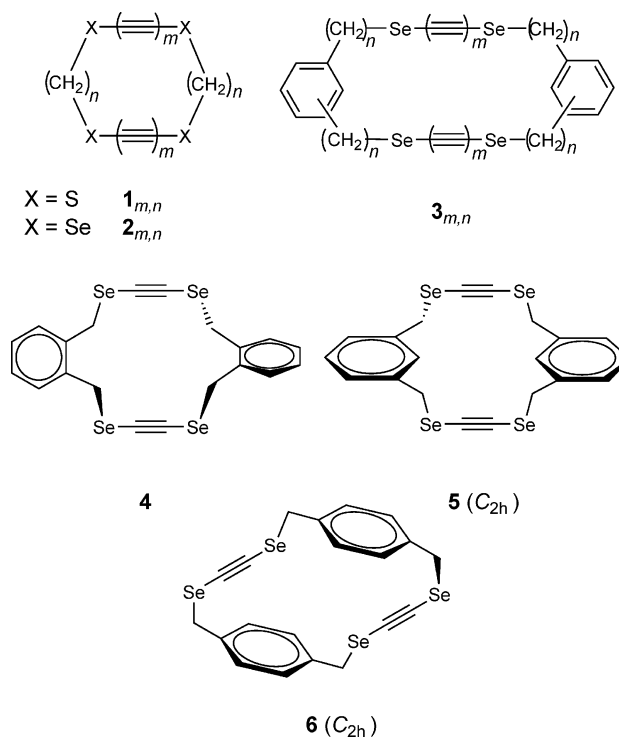


Figure 1. Tetrachalcogenaalkynes **1–3** and the [6.6]cyclophanes **4–6** with 2,5-diselena-hex-3-yne bridges.

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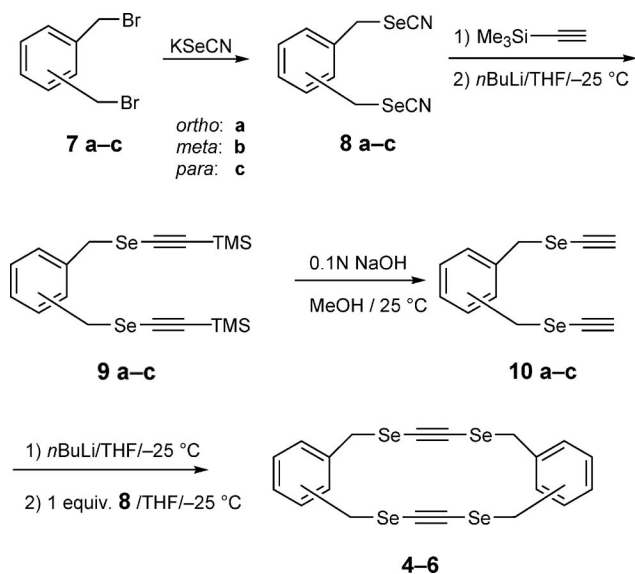
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As chalcogen centers we chose selenium (e.g. **3**) because its intermolecular interaction is expected to be considerably stronger than that of sulfur.^[8] Our endeavour was facilitated by recent progress in organoselenium chemistry^[9] and in the synthesis of chalcogeno-alkynes.^[6,7,10] As first representatives of **3** we report in this paper the synthesis and structural properties of the three isomeric [6.6]cyclophanes **4–6**.

Results and Discussion

Synthesis of [6.6]Cyclophanes **4–6**

Starting points of our synthesis were the three isomeric 1,*n*-bis(selenocyanatomethyl)-benzenes **8a–8c** (Scheme 1) which were generated from the corresponding 1,*n*-bis-(bromomethyl)benzenes **7a–7c**.



Scheme 1. General synthetic procedure for preparation of the [6.6]-cyclophanes **4–6**.

The reaction of **7a–7c** with KSeCN in acetone at room temperature^[11] afforded the bis(selenocyanatomethyl)benzenes **8a–8c** in good yields as colorless crystals. The reaction of **8a–8c** with lithiated trimethylsilylalkyne^[10] (TMSA) yielded the bisdiselenaalkadiynes **9a–9c** as yellow colored oils (**9a**, **9b**) or crystals (**9c**). The removal of the protecting group was achieved by treatment with 0.1 N NaOH solution affording the alkynes **10a–10c**. The alkynes were transformed into the bis-lithium salts and subsequently reacted with an equivalent of the selenocyanates **8**. The yields of the purified cyclophanes were low and varied between 7.4% (**5**) and 2% (**6**). The *anti*-conformation of the functional groups of 1,4-bis(ethynylselenylmethyl)benzene (**10c**) and 1,4-bis(selenocyanatomethyl)benzene (**8c**) found in the solid state might also contribute to the exceptional low yield of **6**. Due to this conformation the simultaneous coupling between both species should be rather low. Interestingly in the case of **8a** both functional groups show a *syn-cis* conformation. The molecular structures of **8c** and **10c** are depicted in Figure 2.

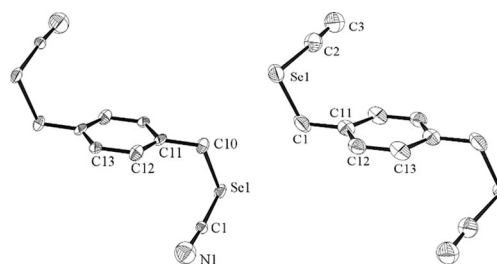


Figure 2. ORTEP representation (50% ellipsoid probability) of the molecular structures of 1,4-bis(seleno-cyanatomethyl)benzene (**8c** – left) and 1,4-bis(ethynylselenylmethyl)benzene (**10c** – right) in the solid state. Hydrogen atoms are not displayed for the sake of clarity.

Furthermore the overall low yields observed for **4–6** are also due to several side reactions which are specific for organoselenic compounds. When **10a–10c** are treated with *n*BuLi to generate the corresponding bis(lithium) salt the agent may abstract the proton at the alkyne unit or react with the Se center under substitution and elimination of LiC₂H.^[7a,10b]

Although all three cyclophanes are highly sensitive to air, light and humidity we were able to characterize them completely. The usual ionization methods for obtaining high-resolution mass spectra (EI, FAB or MALDI) proved not to be suitable for these species. Only by utilizing the FDI method we obtained the molecular peaks of the three isomers **4–6**. In the Supporting Information all three Liquid Injection Field Desorption Ionization (LIFDI) spectra are compared with the theoretical isotopic pattern.

Structural Investigations

We were able to grow single crystals of **4–6** which were suitable for X-ray diffraction studies. The molecular structure of **4** was already discussed in a preliminary report.^[12] The planes of the aromatic rings in **4** are twisted by 87° among each other. The torsion angles between the Se–CH₂ bonds along the Se(1)···Se(2) axis amount to 74.7° and along the Se(3)···Se(4) axis to 92.2°. This result is in line with other studies which show that for the CH₂–Se–C≡C–Se–CH₂ units in cyclic systems torsional angles between 60° and 90° are preferred due to the repulsion of the 4p lone pairs at the Se centers.^[7a]

In Figure 3 we show a section of the solid state of **4**. It is found that the rings are stacked on top of each other in the crystallographic *b*-direction. A remarkable feature of the structure of **4** is that only one Se–C≡C–Se unit of each molecule is involved in strong intermolecular interactions. This leads to a one dimensional thread of ···Se–C≡C–Se··· units in the crystallographic *c*-direction with the cyclophanes alternating on both sides. The Se···Se contacts along this thread (bold dashed lines) amount to only 3.48 Å and 3.52 Å, respectively. Parallel strings are connected by weaker Se···Se interactions (3.93 Å, light dashed lines) in the crystallographic *a*-direction. In both cases these distances are shorter than or close to the sum of the van der Waals radii for Se: 3.80 Å.^[13] It is remarkably that the

C(sp³)-Se-C(sp) angles amount to 102.1° and 102.6° for the selenium atoms involved into the short Se...Se contacts, whereas this angle at the selenium atoms with the weaker interaction is much smaller (99.1° and 98.1°). The first type of Se-C≡C-Se units leading to the threaded arrangement (see Figure 3), is more bent than the second one and shows a smaller torsion angle between the CH₂-Se bonds (74.7° as compared to 92.2° of the second one).

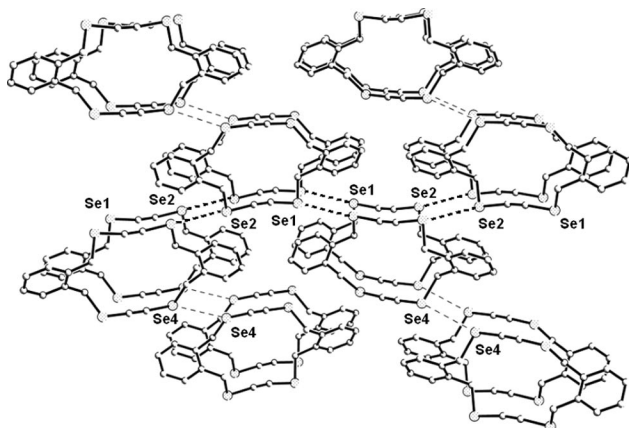


Figure 3. Threaded arrangement in the solid-state structure of **4** (50% ellipsoid probability). Thick dotted lines represent strong Se...Se interactions (Se1-Se1 3.476 Å, Se2-Se2 3.523 Å), thin dotted lines represent weak Se...Se interactions (Se4-Se4 3.934 Å). Hydrogen atoms are not displayed for the sake of clarity.

In the metacyclophane **5** the molecular structure shows a chair conformation with C_i symmetry. Both planes of the aromatic rings are parallel to each other and the torsion angle between the Se-CH₂ bonds along the Se(2)...Se(5) axis amounts to 58.2° (Figure 4).

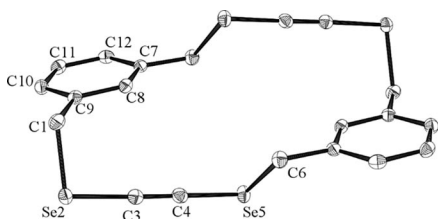


Figure 4. ORTEP representation of the molecular structure of **5** (50% ellipsoid probability) in the solid state. Hydrogen atoms are not displayed for the sake of clarity.

The bond angles C(sp³)-Se-C(sp) both amount to 98.0°. We notice in the crystal a stacking of the rings on top of each other in the crystallographic *b*-direction. The Se...Se distances are rather long in these stacks (>4.36 Å). So presumably weak Se...H and CH...π interactions are responsible for the stacking rather than Se...Se interactions. The various stacks of the metacyclophane rings are hold together with intermolecular Se...Se interactions, weak Se...H bonds^[14] and CH...π interactions.^[15] All types of interactions are indicated in Figure 5. The values found for the

Se...Se interactions (3.975 Å) are close to those reported for related systems^[7] and agree with the values computed for a van der Waals dimer consisting of two dimethylselenide units (*d* = 3.91 Å).^[8a]

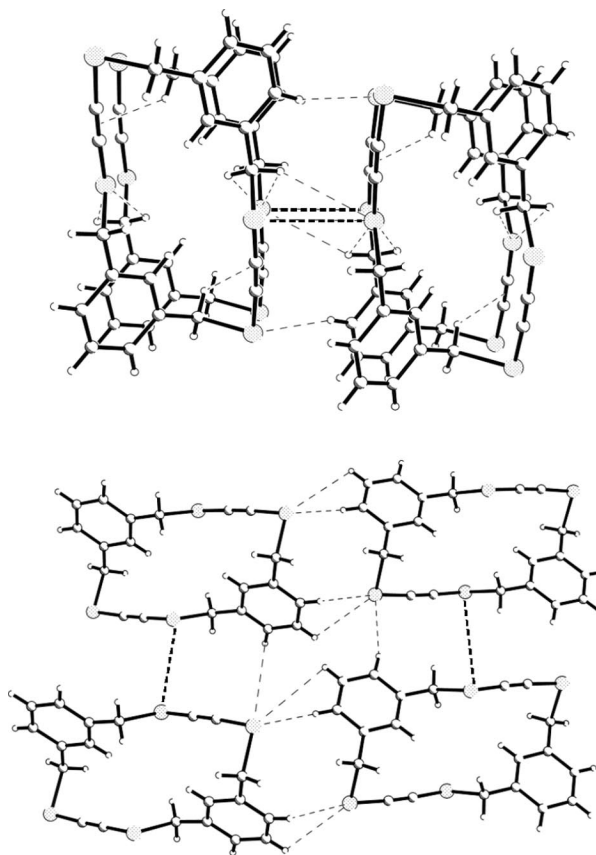


Figure 5. Plots of weak Se-H hydrogen bonds (light dashed lines), CH...π contacts (dotted lines) and Se...Se interactions (bold dashed lines) observed in the crystal lattice of **5**. Top: intermolecular weak interactions between different levels of the stacks. Bottom: intermolecular weak interactions connecting different stacks in the crystallographic *a-c* plane.

The Se...H bonds vary between 2.95 Å (intramolecular) and ca. 3.30 Å (intermolecular) and represent so called weak hydrogen bonds.^[14] CH...π interactions^[15] between the benzylic proton and the C(sp)-C(sp) unit from a molecule situated in the same stack with distances of 2.72 Å [H...C(sp)] are also involved in generating the stacks. Similar interactions have been observed in the case of orthocyclophane **4**, with distances even smaller, of ca. 2.69 Å [H...C(sp)].

The paracyclophane **6** also adopts a chair conformation (non-crystallographic C_{2h}) in the solid state. The planes of the two aromatic rings are symmetry imposed parallel. The torsion angle between the CH₂-Se bonds along the Se(1)...Se(2) axis amounts to 116.7°. This value is considerably larger than those values found for **4** and **5** indicating some strain energy due to the *para*-connection. The C(sp³)-Se-C(sp) angles in **6** were recorded to be 97.1° and 99.7°, respectively.

In the solid state each selenium atom of **6** (Figure 6) is involved into three short contacts (3.79 Å, 3.80 Å and 3.81 Å) to selenium atoms of three different neighboring molecules, giving rise to a structure with two-dimensional Se-regions showing multiply linked selenium networks.

The expected competition between selenium–selenium interactions and π – π interactions could be observed especially in the case of the cyclophanes **5** and **6**, which show a chair conformation in the solid-state structures, whereas for compound **4**, due to the twisting of the benzene rings, the π – π interactions were not favoured, leading to stronger Se...Se interactions. Compound **5**, having the weakest Se...Se interactions from all three isomers, shows in the solid-state structure a distance between two benzene planes that amounts to 3.51 Å. In the columnar structure, the benzene rings are in an offset arrangement, in which the benzylic CH₂ group is situated right under one benzene ring from the upper molecule in the stack. In the case of compound **6**, that has stronger Se...Se interactions than compound **5**, but weaker than the ones observed in compound **4**, the distance between two benzene ring planes amounts to 3.58 Å. These observations illustrate both the competitive relation between non-bonding interactions and also their complementary action that helps keep up a supramolecular structure.

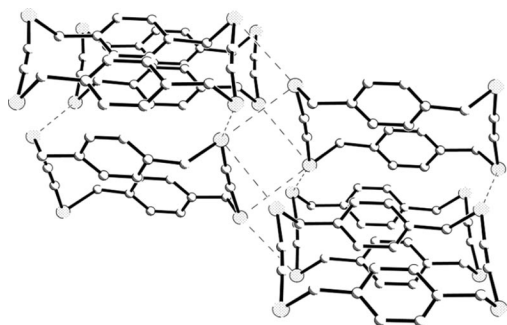


Figure 6. Plot of intermolecular Se...Se interactions in the solid-state structure of **6**. Dotted lines represent contacts smaller than sum of van der Waals radii (3.8 Å). Hydrogen atoms are not displayed for the sake of clarity.

It is interesting to compare the molecular structures of **4–6** with those of the related [6.6]cyclophanes **11–13** (Figure 7) with 1,4 dioxabut-2-yne bridges.^[16] In the latter cyclophanes the molecular structure is determined by the conjugation of the oxygen lone pairs with the benzene units giving rise for the most part to planar dimethoxybenzene units which lead to a rather planar ring (**11**) or rings with chair conformations (**12**, **13**). In contrast to **11–13**, the molecular structures of **4–6** are determined by the rigid CH₂–Se–C≡C–Se–CH₂ units which tend to adopt a torsional angle close to 90°. This leads in the case of **4** to a twisting of the benzene rings by 87° but to chair conformations for **5** and **6**.

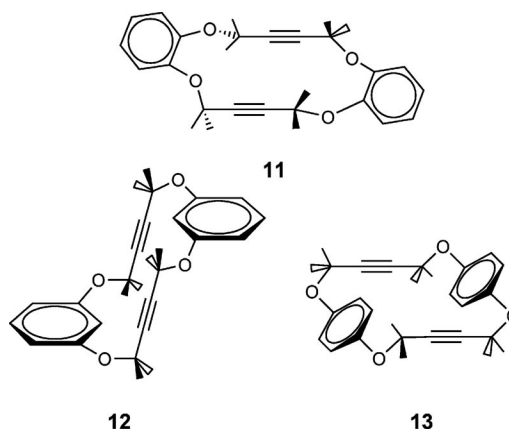


Figure 7. Isomeric [6.6]cyclophanes **11–13** with 1,6-dioxahex-3-yne bridges.

Conclusions

Utilizing a two-component condensation reaction between a 1,2-, 1,3- and 1,4-bis(selenocyanatomethyl)benzene (**8a–8c**) and the bis(lithium) salts of 1,2-, 1,3- and 1,4-bis(ethynylselanyl)benzene (**10a–10c**) yielded the corresponding [6.6]cyclophanes bridged with 2,5-diselenahex-3-yne units in the *ortho*-, *meta*- and *para*-positions. The yields of this condensation reaction varied between 2% and 7%. This low yield was also due to side reactions of seleno-substituted ethyne units with *n*-butyllithium. The solid-state structures of **4–6** revealed in all three cases columnar structures with short Se...Se contacts between the columns. Intramolecular and intermolecular short Se...H distances were also encountered.

Experimental Section

General Remarks: All melting points are uncorrected. The NMR spectra were measured, with a Bruker ARX500 spectrometer (¹H NMR at 500 MHz, ¹³C NMR at 125 MHz and ⁷⁷Se NMR at 95 MHz) and a Bruker ARX300 spectrometer (¹H NMR at 300 MHz and ¹³C NMR at 75 MHz) using the solvent for calibrating the ¹H NMR and the XSI scale for the heterogeneous nuclei. High-resolution mass spectra (HR-MS) were obtained with ZAB-3F (Vacuum Generators) and JEOL JMS 700 high resolution mass spectrometers. UV/Vis absorption spectra were recorded with a Hewlett–Packard HP 8452A Diode Array spectrometer. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer. All reactions were carried out in dry degassed solvents under argon atmosphere, unless otherwise stated.

X-ray Crystallographic Study: The data were collected on a Bruker APEX diffractometer at 100 K (for **4**, **5**) and a Bruker Smart diffractometer (for **6**, **8c** and **10c**) at 200 K using Mo-K α radiation (0.71073 Å). Relevant crystal and data collection parameters are given in Table 1 for **8c** and **10c**, respectively, for **4–6** in Table 2. In all cases, the collection strategies used 0.3 deg omega-scans covering a whole sphere in reciprocal space, intensities were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS^[17] based on the Laue symmetry of the reciprocal space, the structures were solved by direct methods and refined against *R*² using the SHELXTL-PLUS (5.10) software package.^[18]

Table 1. Crystal data and structural refinement for **8c** and **10c**.

	8c	10c
Empirical formula	C ₁₀ H ₈ N ₂ Se ₂	C ₁₂ H ₁₀ Se ₂
Formula weight	314.10	312.12
Crystal system	monoclinic	orthorhombic
Space group	<i>P2₁/c</i>	<i>Pbca</i>
Z	4	4
Unit cell dimensions		
<i>a</i> [Å]	22.2635(9)	5.9208(3)
<i>b</i> [Å]	5.9933(3)	8.5285(4)
<i>c</i> [Å]	8.3679(4)	22.4766(9)
β [°]	98.896(1)	90
<i>V</i> [Å ³]	1103.11(9)	1134.97(9)
<i>D</i> _{calcd.} [g/cm ³]	1.89	1.83
Absorption coeff. μ [mm ⁻¹]	6.66	6.47
Crystal shape	needle	polyhedron
Crystal size [mm ³]	2.00 × 0.04 × 0.02	0.20 × 0.18 × 0.06
Crystal colour	colorless	colorless
θ range for data collection	0.9 to 27.5°	1.8 to 27.5°
Index ranges	-28 ≤ <i>h</i> ≤ 28 -7 ≤ <i>k</i> ≤ 7 -10 ≤ <i>l</i> ≤ 10	-7 ≤ <i>h</i> ≤ 7 -11 ≤ <i>k</i> ≤ 11 -29 ≤ <i>l</i> ≤ 29
Reflections collected	9528	10337
Indep. reflections [<i>R</i> (int)]	2488 (0.0694)	1300 (0.3352)
Observed reflections	1835 [<i>I</i> > 2 σ (<i>I</i>)]	951 [<i>I</i> > 2 σ (<i>I</i>)]
Max./min. transmission	0.88/0.03	0.70/0.36
Data/restraints/parameters	2488/0/108	1300/0/64
Goodness-of-fit on <i>F</i> ²	1.30	1.14
<i>R</i> (<i>F</i>)	0.108	0.088
<i>R</i> _w (<i>F</i> ²)	0.257	0.190
($\Delta\rho$) _{max.} , ($\Delta\rho$) _{min.} [e Å ⁻³]	3.37 and -1.36	2.10 and -1.20

CCDC-662133 (for **4**), -718215 (for **5**), -718216 (for **6**), -718217 (for **8c**) and -718218 (for **10c**) contain the supplementary crystallographic data for the structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Preparation of the Bis(selenocyanato-methyl)benzenes **8a–c:** To a stirred solution of dibromoxylene in 200 mL of degassed dry acetone a solution of KSeCN in 200 mL of degassed acetone was added dropwise under argon atmosphere at room temperature over a period of 3 h. The reaction mixture was stirred for an additional hour and the resulting KBr was filtered off. The solvent was removed by rotary evaporation and the product was purified by column chromatography on deactivated silica, or used as raw product when the purity was higher than 98% as calculated from ¹H NMR spectroscopic data.

1,2-Bis(selenocyanatomethyl)benzene (8a**):** Starting materials: 10.6 g (40.0 mmol) of 1,2-bis-bromomethylbenzene (**7a**) and 14.4 g (100 mmol) potassium selenocyanate. The resulting residue from the solvent removal was purified by silica-gel chromatography using a mixture of *n*-hexane/diethyl ether (1:2), resulting in 11.2 g of **8a** as white solid (35.8 mmol, 89%), slightly light sensitive. m.p. 106 °C. MS (EI⁺; *m/z*; %): 314 [M]⁺ (0.9), 263.9 [C₈H₈Se₂]⁺ (7.8), 209.9 [M – SeCN]⁺ (52.8), 182.9 [C₈H₈Se]⁺ (28.4), 104 [C₈H₈]⁺ (BP, 100), 78 [C₆H₆]⁺ (18.2). ¹H NMR (500 MHz, CD₂Cl₂): δ_{H} = 4.42 (s, 4 H, CH₂), 7.38 (m, 2 H, H_{arom}), 7.41 (m, 2 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): δ_{C} = 30.9 (2 C, s-CH₂), 101.5 (2 C, q-C_{arom}), 130.0 (2 C, t-C_{arom}), 131.9 (2 C, t-C_{arom}), 134.5 (2 C, q-C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD₂Cl₂): δ_{Se} = 302.3 ppm. IR (KBr): $\tilde{\nu}$ = 3442 (vb), 3007 (w), 2148 (s), 2073 (m), 1630 (w), 1491 (m), 1451 (m) cm⁻¹.

Table 2. Crystal data and structural refinement for **4**, **5** and **6**.

	4	5	6
Empirical formula	C ₂₀ H ₁₆ Se ₄	C ₂₀ H ₁₆ Se ₄	C ₂₀ H ₁₆ Se ₄
Formula weight	572.17	572.17	572.17
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
Z	8	2	2
Unit cell dimensions			
<i>a</i> [Å]	24.293(2)	8.057(1)	10.7377(5)
<i>b</i> [Å]	5.2235(5)	4.7364(6)	9.2932(4)
<i>c</i> [Å]	30.239(3)	24.438(3)	10.0453(5)
β [°]	92.753(2)	98.151(2)	107.836(1)
<i>V</i> [Å ³]	3832.6(7)	923.2(2)	954.22(8)
<i>D</i> _{calcd.} [g/cm ³]	1.98	2.06	1.99
Absorption coefficient μ [mm ⁻¹]	7.66	7.95	7.69
Crystal shape	polyhedron	needles	polyhedron
Crystal size [mm ³]	0.20 × 0.08 × 0.05	0.32 × 0.06 × 0.03	0.20 × 0.11 × 0.01
Crystal colour	colorless	colorless	colorless
θ range for data collection [°]	1.7 to 28.3	1.7 to 28.3	3.0 to 24.1
Index ranges	-32 ≤ <i>h</i> ≤ 32 -6 ≤ <i>k</i> ≤ 6 -40 ≤ <i>l</i> ≤ 40	-10 ≤ <i>h</i> ≤ 10 -6 ≤ <i>k</i> ≤ 6 -32 ≤ <i>l</i> ≤ 32	-12 ≤ <i>h</i> ≤ 12 -10 ≤ <i>k</i> ≤ 10 -11 ≤ <i>l</i> ≤ 11
Reflections collected	19112	8715	6786
Independent reflections [<i>R</i> (int)]	4744 (0.0384)	2306 (0.0407)	1512 (0.0785)
Observed reflections	3821 [<i>I</i> > 2 σ (<i>I</i>)]	1963 [<i>I</i> > 2 σ (<i>I</i>)]	1105 [<i>I</i> > 2 σ (<i>I</i>)]
Max./min. transmission	0.70/0.31	0.80/0.19	0.96/0.31
Data/restraints/parameters	4744/0/217	2306/0/141	1512/0/109
Goodness-of-fit on <i>F</i> ²	1.01	1.05	1.10
<i>R</i> (<i>F</i>)	0.029	0.026	0.052
<i>R</i> _w (<i>F</i> ²)	0.058	0.056	0.093
($\Delta\rho$) _{max.} , ($\Delta\rho$) _{min.} [e Å ⁻³]	0.55 and -0.41	0.83 and -0.43	0.89 and -0.54

1,3-Bis(selenocyanatomethyl)benzene (8b): Starting materials: 5.3 g (20.0 mmol) of 1,3-bis-bromomethylbenzene (**7b**) and 8.8 g (60.8 mmol) potassium selenocyanate. The resulting residue from the solvent removal was purified by silica-gel chromatography using a mixture of *n*-hexane/diethyl ether (1:2), resulting in 4.2 g of **8b** as white solid (13.4 mmol, 67%). m.p. 108 °C. MS (EI⁺; *m/z*; %): 316 (0.9) [M]⁺; 210 (37.8) [M – SeCN]⁺; 116 (62.2) [M – 2SeCN]⁺; 104 (BP, 100) [M – C₈H₈]⁺; 78 (26.2) [C₆H₆]⁺; 51 (19.2) [M – C₄H₃]⁺.

¹H NMR (500 MHz, CD₂Cl₂): δ_H = 4.28 (s, 4 H, CH₂), 7.34–7.41 (m, 4 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): δ_C = 32.6 (2 C, s-CH₂), 101.8 (2 C, t-CN), 129.5 (2 C, t-C_{arom}), 129.8 (1 C, t-C_{arom}), 130.1 (1 C, t-C_{arom}), 137.4 (2 C, q-C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD₂Cl₂): δ_{Se} = 294.55 ppm. IR (KBr): ν̄ = 3444 (s), 2151 (s), 1630 (m), 1486 (w), 1444 (m) cm⁻¹.

1,4-Bis(selenocyanatomethyl)benzene (8c): Starting materials: 6.6 g (25.0 mmol) of 1,4-bis-bromomethylbenzene (**7c**) and 10.8 g (75 mmol) of potassium selenocyanate. The resulting residue from the solvent removal was purified by silica-gel column chromatography using a mixture of *n*-hexane/diethyl ether (1:2), resulting in 7.47 g of **8c** as a yellowish solid (23.78 mmol, 95.1%) slightly light sensitive. m.p.: 138 °C. MS (EI⁺; *m/z*; %): 316 [M]⁺ (8.3), 210 [M – SeCN]⁺ (74.8), 182 [C₈H₈Se]⁺ (4.2), 104 [C₈H₈]⁺ (BP, 100), 78 [C₆H₆]⁺ (7.2). ¹H NMR (500 MHz, CD₂Cl₂): δ_H = 4.28 (s, 4 H, CH₂), 7.39 (s, 4 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): δ_C = 32.5 (2 C, s-CH₂), 101.8 (2 C, q-SeC), 130.0 (4 C, t-C_{arom}), 136.9 (2 C, q-C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD₂Cl₂): δ_{Se} = 307.10 ppm. IR (KBr): ν̄ = 3428 (vb), 3048 (w), 3013 (w), 2955 (w), 2147 (s), 2073 (s), 1630 (m), 1509 (m), 1425 (m) cm⁻¹.

General Procedure for the Preparation of the Bis(trimethylsilyl)diselenaalkadiynes 9a–c: In a four-necked flask, trimethylsilylacetylene (TMSA) was dissolved in anhydrous THF at –35 °C. At this temperature *n*-butyllithium was added dropwise over a period of 20 min by using a syringe. Then the solution was stirred under the same conditions for two hours. The diselenocyanatoxylylene dissolved in anhydrous THF was added dropwise over a period of 45 min at –35 °C. After stirring for one hour at this temperature the mixture was warmed up to room temperature. 50 mL of saturated NH₄Cl solution and 100 mL *n*-hexane were added. The aqueous layer was separated and extracted four times with *n*-hexane. After combining the organic layers the mixture was dried with MgSO₄ overnight. The mixture was filtered, the solvent evaporated and the resulting product was purified by silica-gel column chromatography.

1,2-Bis(trimethylsilyl)ethynylselenylmethylbenzene (9a): Starting materials: 6.3 g (20 mmol) of **8a** dissolved in 350 mL of THF, 25 mL (40 mmol) of *n*BuLi (1.6 M in *n*-hexane) and 4 g (40 mmol) of TMSA dissolved in 350 mL of THF. Chromatography using a mixture of light petroleum and diethyl ether (20:1) afforded 5.8 g of **9a** (63.1%) as yellow-brown oil. MS (EI⁺; *m/z*; %): 458 [M]⁺ (<1), 427 [M – 2·CH₃]⁺ (1.2), 264 [C₈H₈Se₂]⁺ (2.3), 183 [C₈H₈Se]⁺ (13.6), 143 [C₁₁H₁₁]⁺ (40.9), 128 [C₁₀H₈]⁺ (29.0), 104 [C₈H₈]⁺ (31.2), 97 (28.5) [C₅H₅Si]⁺; 73 [Si(CH₃)₃]⁺ (BP, 100). ¹H NMR (500 MHz, CDCl₃) δ_H = 0.15 [s, 18 H, Si(CH₃)₃], 4.21 (s, 4 H, CH₂), 7.22 (m, 2 H, H_{arom}), 7.27 (m, 2 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CDCl₃) δ_C = –0.1 [6 C, Si(p-CH₃)₃], 30.0 (2 C, s-CH₂), 86.1 (2 C, q-SeC≡CSi), 109.7 (2 C, q-SeC≡CSi), 128.0 (2 C, t-C_{arom}), 131.1 (2 C, t-C_{arom}), 135.5 (2 C, q-C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CDCl₃) δ_{Se} = 250.17 ppm. IR (film): ν̄ = 2958 (s) 2897 (m) 2350 (w) 2087 (s) 1491 (w) 1262 (m) 1172 (m) 945 (w) 859 (vs)

843 (vs) 760 (s) 700 (m). HRMS (positive EI): calcd. for ¹²C₁₈¹H₂₆²⁶Si₂⁸⁰Se₂ [M⁺], 457.9903; found, 457.9886 (–1.8 mmu).

1,3-Bis(trimethylsilyl)ethynylselenylmethylbenzene (9b): Starting materials: 1.1 g (3.4 mmol) of **8b** dissolved in 100 mL of THF; 5.23 mL (8.4 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) and 0.82 g (8.35 mmol) of TMSA dissolved in 100 mL of THF. Chromatography using a mixture of *n*-hexane and diethyl ether (12:1) afforded 1.0 g (66.2%) of **9b** as yellow oil. MS (EI⁺; *m/z*; %): 458 [M]⁺ (1.1), 143 [C₁₁H₁₁]⁺ (40.9), 128 [C₁₀H₈]⁺ (29.0), 104 [C₈H₈]⁺ (31.2), 73 [Si(CH₃)₃]⁺ (BP, 100.0). ¹H NMR (500 MHz, CD₂Cl₂) δ_H = 0.15 [s, 18 H, Si(CH₃)₃], 4.00 (s, 4 H, CH₂), 7.22–7.27 (m, 4 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂) δ_C = 0.0 (6 C, *p*-CH₃), 33.0 (2 C, s-CH₂), 86.6 (2 C, q-SeC), 109.8 (2 C, q-SiC), 128.5 (2 C, t-C_{arom}), 129.0 (1 C, t-C_{arom}), 129.5 (1 C, t-C_{arom}), 138.7 (2 C, q-C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD₂Cl₂) δ_{Se} = 267.64 ppm. IR (KBr): ν̄ = 2958 (s), 2897 (w), 2087 (s), 1605 (w), 1487 (w), 1443 (w). HRMS (positive EI): calcd. for ¹²C₁₈¹H₂₆²⁶Si₂⁸⁰Se₂ [M⁺], 457.9903; found 457.9913 (+1.0 mmu).

1,4-Bis(trimethylsilyl)ethynylselenylmethylbenzene (9c): Starting materials: 5.0 g (16.0 mmol) of **8c** dissolved in 300 mL of THF; 20.0 mL (32.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) and 3.1 g (32 mmol) TMSA dissolved in 350 mL of THF. Chromatography using a mixture of *n*-hexane and diethyl ether (20:1) afforded 3.3 g (45.4%) of **9c** as pale yellow crystals. m.p. 52–54 °C. MS (EI⁺; *m/z*; %): 458 [M]⁺ (1.1), 442 [M – CH₃]⁺ (0.7), 354 [C₁₃H₁₁Se₂Si]⁺ (6.7), 281 [C₁₃H₁₇SeSi]⁺ (12.3), 162 [C₄H₆SeSi]⁺ (4.3), 143 [C₁₁H₁₁]⁺ (10.9), 128 [C₁₀H₈]⁺ (12.0), 104 [C₈H₈]⁺ (BP, 100), 73 [Si(CH₃)₃]⁺ (65.0). ¹H NMR (500 MHz, CD₂Cl₂): δ_H = 0.15 [s, 18 H, Si(CH₃)₃], 4.01 (s, 4 H, CH₂), 7.28 (s, 4 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): δ_C = 0.0 (6 C, *p*-CH₃), 32.8 (2 C, s-CH₂), 86.7 (2 C, q-SeC), 109.8 (2 C, q-SiC), 129.4 (4 C, t-C_{arom}), 137.6 (2 C, q-C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD₂Cl₂): δ_{Se} = 269.1 ppm. IR (KBr): ν̄ = (≈ 3100–3600, s), 3022 (w), 2957 (m), 2899 (w), 2082 (s), 1636 (w), 1511 (m), 1419 (m), 1253 (s), 1247 (s), 1169 (s) cm⁻¹. HRMS (positive EI): calcd. for ¹²C₁₈¹H₂₆²⁶Si₂⁸⁰Se₂ [M⁺], 457.9903; found 457.9929 (+2.5 mmu).

General Procedure for the Preparation of the Diselenaalkadiynes 10a–c: To a solution of bis(trimethylsilyl)diselenaalkadiynes in 100 mL of anhydrous MeOH and 5 mL of anhydrous THF, in a 500 mL three-necked flask, the 0.1 N NaOH solution was added dropwise during a period of 15 min at room temperature. Then the mixture was stirred for two hours. The reaction was stopped by adding 150 mL of ice-water mixture and 150 mL of diethyl ether. After separation of the organic layer the aqueous layer was extracted four times with 80 mL of diethyl ether. The combined organic layers were washed three times with saturated NH₄Cl solution and three times with brine. After drying over MgSO₄, the solvent was evaporated and the product purified by silica-gel chromatography.

1,2-Bis(ethynylselenylmethyl)benzene (10a): Starting materials: 4.9 g (10.8 mmol) of 1,2-bis(trimethylsilyl)ethynylselenylmethylbenzene (**9a**) and 11 mL (1.1 mmol) 0.1 N NaOH solution. Chromatography on silica gel using a mixture of *n*-hexane/diethyl ether (6:1) afforded 3.03 g (9.7 mmol, 90%) of **10a** as yellow-brownish oil. MS (EI⁺; *m/z*; %): 313 [M – H]⁺ (<1), 233 [C₁₂H₉Se]⁺ (11.3), 152 [C₁₂H₈]⁺ (17.9), 128 [C₁₀H₈]⁺ (100.0), 104 [C₈H₈]⁺ (63.3), 78 [C₆H₆]⁺ (32.5). ¹H NMR (500 MHz, CDCl₃): δ_H = 2.90 (s, 2 H, C≡CH), 4.23 (s, ²J_{Se,H} = 13.1 Hz, 4 H, CH₂), 7.25 (m, 2 H, H_{arom}), 7.31 (m, 2 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CDCl₃): δ_C = 29.6 (2 C, s-CH₂), 65.7 (2 C, t-CH), 90.1 (2 C, q-SeC), 128.2 (2 C, t-C_{arom}), 131.1 (2 C, t-C_{arom}), 135.3 (2 C, q-C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CDCl₃): δ_{Se} = 229.14 ppm. IR (KBr): ν̄ = 3277 (s), 3061

(w), 3020 (w), 2954 (w), 2028 (w), 1491 (m), 1452 (m), 1420 (w), 1376 (w), 1300 (w) cm^{-1} . HRMS (positive EI): calcd. for $^{12}\text{C}_{12}^{1}\text{H}_9^{80}\text{Se}_2 [\text{M} - \text{H}]^+$ 312.9035; found 312.9065 (+3.0 mmu).

1,3-Bis(ethynylselenylmethyl)benzene (10b): Starting materials: 1.0 g (2.1 mmol) of 1,3-bis[[trimethylsilyl]ethynylselenyl]methyl]benzene (**9b**) and 1.8 mL (0.2 mmol) 0.1 N NaOH solution. Chromatography on silica gel using a mixture of *n*-hexane and diethyl ether (6:1) afforded 0.63 g (2.0 mmol, 95%) of **10b** as yellowish oil. MS (EI⁺; *m/z*; %): 313 [$\text{M} - \text{H}$]⁺ (0.4), 233 [$\text{C}_{12}\text{H}_9\text{Se}$]⁺ (15.1), 153 [C_{12}H_9]⁺ (11.8), 129 [C_{10}H_9]⁺ (49.5), 128 [C_{10}H_8]⁺ (BP, 100.0), 104 [C_8H_8]⁺ (43.0), 78 [C_6H_6]⁺ (28.0). ¹H NMR (500 MHz, CD_2Cl_2): $\delta_{\text{H}} = 2.94$ (s, 2 H, C \equiv CH), 4.04 (s, $^2J_{\text{Se,H}} = 14.9$ Hz, 4 H, CH_2), 7.24–7.30 (m, 4 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CD_2Cl_2) $\delta_{\text{C}} = 32.4$ (2 C, s- CH_2), 65.9 (2 C, t-CH), 90.3 (2 C, q-SeC), 128.5 (2 C, t- C_{arom}), 129.2 (1 C, t- C_{arom}), 129.7 (1 C, t- C_{arom}), 138.5 (2 C, q- C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD_2Cl_2): $\delta_{\text{Se}} = 246.5$ ppm. IR (KBr): $\tilde{\nu} = 3277$ (s), 3025 (w), 2939 (w), 2028 (m), 1604 (m), 1486 (m), 1443 (m) cm^{-1} . HRMS (positive EI): calcd. for $^{12}\text{C}_{12}^{1}\text{H}_{10}^{80}\text{Se}_2 [\text{M}]^+$ 313.9113; found 313.9139 (+2.6 mmu).

1,4-Bis(ethynylselenylmethyl)benzene (10c): Starting materials: 3.0 g (6.5 mmol) of compound **9c**, 6.5 mL (0.7 mmol) of 0.1 N NaOH solution, 300 mL of MeOH (solvent) and 15 mL of THF (cosolvent). The product was purified by silica-gel chromatography using a mixture of *n*-hexane and diethyl ether (6:1), to give 1.95 g of pure **10c** (6.2 mmol, 95.8%) as pale yellow crystals. m.p. 77–79 °C. MS (EI⁺; *m/z*; %): 314 [M]⁺ (0.1), 289 [$\text{C}_{10}\text{H}_9\text{Se}_2$]⁺ (1.3), 209 [$\text{C}_{10}\text{H}_9\text{Se}$]⁺ (12.1), 184 [$\text{C}_8\text{H}_8\text{Se}$]⁺ (1.4), 153 [C_{12}H_9]⁺ (6.8), 128 [C_{10}H_8]⁺ (16.4), 104 [C_8H_8]⁺ (BP, 100), 78 [C_6H_6]⁺ (21.0). ¹H NMR (300 MHz, CDCl_3): $\delta_{\text{H}} = 2.89$ (s, 2 H, C \equiv CH), 4.05 (s, $^2J_{\text{Se,H}} = 14.2$ Hz, 4 H, CH_2), 7.30 (s, 4 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CDCl_3): $\delta_{\text{C}} = 32.0$ (2 C, s- CH_2), 65.7 (2 C, t-CH), 89.9 (2 C, q-SeC), 129.2 (4 C, t- C_{arom}), 136.8 (2 C, q- C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CDCl_3) $\delta_{\text{Se}} = 247.8$ ppm. IR (KBr): $\tilde{\nu} = \text{ca. } 3100\text{--}3600$ (s), 3262 (s), 3247 (m), 3052 (w), 2084 (w), 1636 (w), 1510 (w), 1419 (w) cm^{-1} . HRMS (positive EI): calcd. for $^{12}\text{C}_{12}^{1}\text{H}_{10}^{80}\text{Se}_2 [\text{M}]^+$ 313.9113; found 313.9141 (+2.8 mmu).

General Procedure for the Preparation of the Tetraselenacyclodiyenes

4–6: To a solution of diselenaalkadiyne in anhydrous THF in a three-necked flask, *n*-butyllithium (1.6 M solution in *n*-hexane) was added dropwise during 15 min, while maintaining the temperature below –25 °C. The mixture was stirred for one hour at this temperature. To ca. 500 mL of anhydrous THF in a 2l three-necked flask, cooled to –50 °C, the solutions of diselenaalkadiynes and dilithiated diselenaalkadiynes in anhydrous THF were added simultaneously via separate dropping funnels over a time period of 6–7 h. After complete addition the reaction mixture was warmed up to room temperature overnight. The solvent was evaporated to give the raw product which was cleaned by fast silica-gel chromatography with toluene to remove salts and polymers. Further purification was done using silica-gel chromatography with appropriate solvent mixtures.

Note: Melting points could not be determined for compounds **4–6** because all samples decomposed upon heating in the 60–80 °C range.

Gas-chromatography of the compounds was unsuccessful, as they decomposed on the chromatographic column as well as in the transfer line. Mass spectra could only be recorded using the LIFDI (FD⁺) method and all compounds confirmed the calculated isotopic pattern.

2,5,14,17-Tetraselena[6,6]orthocyclophane-3,15-diyne (4): Starting materials: 2.8 g (9 mmol) of **10a** dissolved in 250 mL of anhydrous

THF; 11 mL of *n*BuLi (1.6 M in *n*-hexane, 18 mmols); 2.8 g (9 mmol) of **8a** dissolved in 250 mL of anhydrous THF. The raw product was purified using silica-gel chromatography. First, a mixture of *n*-hexane and toluene (3:1) was used as eluent and an enriched fraction was further purified by chromatography using a mixture of *n*-hexane and diethyl ether (10:1). Thin yellow needles were recrystallized from CH_2Cl_2 /*n*-hexane to give the final product **4** (0.182 g, 0.32 mmol, 3.6% yield). ¹H NMR (500 MHz, CDCl_3): $\delta_{\text{H}} = 4.47$ (s, $^2J_{\text{Se,H}} = 7.9$ Hz, 8 H, CH_2), 7.22 (br. s, 8 H, H_{arom}) ppm. ¹³C NMR (125 MHz, CDCl_3): $\delta_{\text{C}} = 33.0$ (4 C, s- CH_2), 85.9 (4 C, q-SeC \equiv CSe), 128.4 (4 C, t- C_{arom}), 130.9 (4 C, t- C_{arom}), 135.5 (4 C, q- C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CDCl_3): $\delta_{\text{Se}} = 235.04$ ppm. IR (KBr): $\tilde{\nu} = 3100\text{--}3600$ (s), 1772 (w), 1636 (m), 1559 (w), 1507 (w), 1490 (w), 1452 (w), 1419 (w), 1384 (w), 1249 (w) cm^{-1} . MS (LIFDI, ion mode FD⁺) calcd. for $^{12}\text{C}_{20}^{1}\text{H}_{16}^{80}\text{Se}_4 [\text{M}]^+$ 573.79; found 573.60.

2,5,14,17-Tetraselena[6,6]metacyclophane-3,15-diyne (5): Starting materials: 0.57 g (1.8 mmol) of **10b**, dissolved in 300 mL of anhydrous THF, 2.25 mL (3.6 mmol) *n*-butyllithium (1.6 M in *n*-hexane), 0.57 g (1.8 mmol) of **8b** dissolved in 300 mL of anhydrous THF. Addition time was 7 hours. After warming up to room temp., the solvents were evaporated and the residue was filtered through silica-gel with toluene to remove salts and polymers. The raw product was further purified using silica-gel chromatography with a mixture of *n*-hexane/toluene (4:1), and then an enriched fraction was further purified by chromatography with a mixture of *n*-hexane/toluene (1:2). Finally, product **5** was separated by chromatography on silica-gel with a mixture of *n*-hexane/diethyl ether (5:1), obtaining 0.076 g of **5** (0.133 mmol, 7.4%) as thin colourless needles. ¹H NMR (500 MHz, CD_2Cl_2): $\delta_{\text{H}} = 3.93$ (s, $^2J_{\text{Se,H}} = 17.4$ Hz, 8 H, CH_2), 7.10–7.33 (m, 8 H, CH_{arom}) ppm. ¹³C NMR (125 MHz, CD_2Cl_2) $\delta_{\text{C}} = 33.9$ (4 C, s- CH_2), 85.7 (4 C, q-SeC), 128.3 (2 C, t- C_{arom}), 128.9 (1 C, t- C_{arom}), 130.7 (1 C, t- C_{arom}), 138.4 (2 C, q- C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD_2Cl_2) $\delta_{\text{Se}} = 288.52$ ppm. IR (CD_2Cl_2): $\tilde{\nu} = 3679$ (bs), 3600 (m), 2930 (s), 2853 (m), 2371 (w), 2335 (m), 1605 (s), 1487 (w), 1464 (w), 1442 (w), 1187 (m) cm^{-1} . MS (LIFDI, ion mode FD⁺) calcd. for $^{12}\text{C}_{20}^{1}\text{H}_{16}^{80}\text{Se}_4 [\text{M}]^+$ 573.79; found 573.62.

2,5,14,17-Tetraselena[6,6]paracyclophane-3,15-diyne (6): Starting materials: 0.78 g (2.5 mmol) of compound **10c** in 250 mL of anhydrous THF, 3.1 mL (5.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) and 0.78 g (2.5 mmol) of compound **8c** in 250 mL of anhydrous THF. Addition time was 5 hours. After warming up to room temp. the solvents were evaporated and the residue was filtered through silica-gel with toluene to remove salts and polymers. An enriched fraction of the first column was used to purify the product, through chromatography on deactivated silica-gel with *n*-hexane/diethyl ether (5:1). After rotary evaporation of the solvents the product was recrystallized from a mixture of dichloromethane and *n*-hexane, resulting in 0.04 g of **6** (0.08 mmol, 1.8%) as thin colourless crystals. ¹H NMR (500 MHz, CD_2Cl_2): $\delta_{\text{H}} = 3.89$ (s, $^2J_{\text{Se,H}} = 20.3$ Hz, 8 H, CH_2), 7.15 (s, 8 H, H_{arom}) ppm. ¹³C NMR (75 MHz, CD_2Cl_2): $\delta_{\text{C}} = 33.4$ (4 C, s- CH_2), 84.4 (4 C, q-SeC), 129.3 (8 C, t- C_{arom}), 138.4 (4 C, q- C_{arom}) ppm. ⁷⁷Se NMR (95 MHz, CD_2Cl_2): $\delta_{\text{Se}} = 299.81$ ppm. IR (CDCl_3): $\tilde{\nu} = 3581$ (w), 2957 (s), 2927 (s), 2856 (m), 2241 (w), 1712 (w), 1650 (w), 1604 (w), 1557 (w), 1457 (m), 1366 (w), 1182 (m), 1017 (m) cm^{-1} . MS (LIFDI, ion mode FD⁺): calcd. for $^{12}\text{C}_{20}^{1}\text{H}_{16}^{80}\text{Se}_4 [\text{M}]^+$ 573.79; found 573.67.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of synthesized compounds (S1–S12) and MS spectra of compounds **4–6** (S13–S14).

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