Supporting Information for:

Cyclopenta[b]thiopyran and Cyclopenta[b]selenopyran Based Heteroarenes: Electronic Communication Between S- and/or Se-Fused Aromatics

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S1
EXPERIMENTAL SECTION

Materials and reagents.

All chemicals and reagents were purchased from commercial sources and used as received unless otherwise specified. Anhydrous tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. Dichloromethane (DCM) and chloroform were distilled from CaH$_2$. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.

Characterizations.

$^1$H NMR (400 MHz) and $^{13}$C$\{^1$H$\}$ NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra were recorded on PerkinElmer Lambda 750 spectrophotometer. Cyclic and differential pulse voltammetry measurements were performed on a CHI660E electrochemical workstation in a three-electrode electrochemical cell. A carbon glass coated electrode was used as the working electrode and an Ag/Ag$^+$ electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in dichloromethane was the electrolyte. Continuous wave X-band electron spin resonance spectra were obtained with a JEOL (FA200) spectrometer. Time-dependent density functional theory (TD-DFT) calculations were conducted with the Gaussian 03 program using B3LYP method and 6-31G(d) basis set.$^{S1}$ The geometries were optimized on basis of their single crystal structures using the default convergence criteria without any constraints.

Synthesis.

Synthesis of 1,5-di(1-decynyl)-2,6-di(2-thienyl)naphthalene (2).
Scheme S1. Synthetic routes for SS, SSe, SeSe, RS, and RSe.

To a degassed solution of 1 (1.01 g, 1.8 mmol) in DMF (10 mL) was added Pd(PPh₃)₂Cl₂ (0.126 g, 0.18 mmol) and 2-(tri-n-butylstannyl)thiophene (2.02 g, 5.4 mmol). Then the mixture was stirred at 90 °C overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE) to give a brownish-yellow solid (0.82 g, yield: 81%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.39 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 3.3 Hz, 2H), 7.41 (d, J = 4.9 Hz, 2H), 7.15 (t, J = 3.8 Hz, 2H), 2.62 (t, J = 6.9 Hz, 4H), 1.71 (m, 4H), 1.51 (m, 4H), 1.29 (m, 16H), 0.88 (t, J = 6.6 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ (ppm): 142.9, 134.3, 133.4, 127.9, 127.4, 127.2, 127.1, 126.3, 118.1, 102.3, 78.4, 32.1, 29.5, 29.4, 29.4, 28.6, 22.9, 20.4, 14.3. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₃₈H₄₅S₂, 565.2963; found. 565.2935.
Synthesis of 1,5-di(1-decynyl)-2,6-di(2-selenophenyl)naphthalene (3).

To a degassed solution of 1 (1.01 g, 1.8 mmol) in DMF (10 mL) was added Pd(PPh₃)₂Cl₂ (0.126 g, 0.18 mmol) and 2-(tri-n-butylstannyln)elenephene (1.68 g, 4.5 mmol). Then the mixture was stirred at 90 °C overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE/DCM = 10/1) to give a brownish-yellow solid (1.00 g, yield: 85%). ¹H NMR (400 MHz, CD₂Cl₂) δ (ppm): 8.43 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 5.6 Hz, 2H), 7.94 (d, J = 3.6 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.45 (t, J = 4.0 Hz, 2H), 2.71 (t, J = 7.2 Hz, 4H), 1.81 (m, 4H), 1.61 (m, 4H), 1.40 (m, 16H), 0.94 (t, J = 5.2 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂) δ (ppm): 148.1, 136.3, 133.7, 133.1, 132.5, 130.8, 129.7, 129.6, 129.5, 127.3, 127.0, 117.7, 103.8, 78.4, 32.1, 29.5, 29.4, 28.6, 22.9, 20.5, 14.1. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₃₈H₄₅Se₂, 661.1852; found 661.1822.

Synthesis of 6-bromo-1,5-di(1-decynyl)-2-(2-selenophenyl)naphthalene (4).

To a degassed solution of 1 (0.40 g, 0.716 mmol) in DMF (5 mL) was added Pd(PPh₃)₂Cl₂ (0.051 g, 0.072 mmol) and 2-(tri-n-butylstannyl)selenophene (0.302 g, 0.716 mmol). Then the mixture was stirred at 90 °C overnight under nitrogen atmosphere. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE/DCM = 20/1) to give a brownish-yellow solid (0.25 g, yield: 57%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.26 (t, J = 8.8 Hz, 2H), 8.14 (d, J = 5.6 Hz, 1H), 7.86 (d, J = 4.0 Hz, 1H), 7.83 (d, J = 9.2 Hz, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.41 (t, J = 5.6 Hz, 1H), 2.65 (m, 4H), 1.79 (m, 4H), 1.62 (m, 2H), 1.54 (m, 2H), 1.43 (m, 16H), 0.90 (m, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ (ppm): 148.1, 136.6, 133.7, 133.1, 132.5, 130.8, 129.7, 129.6, 128.0, 127.8, 126.5, 124.9, 123.4, 118.1, 103.9, 101.7, 78.4, 77.8, 32.1, 29.5, 29.4, 29.3, 29.0, 28.6,
23.0, 20.6, 20.2, 14.4. HRMS (ESI-TOF) m/z: [M + H]^+ calcd for C_{34}H_{42}BrSe, 609.1635; found. 609.1623.

Synthesis of 1,5-di(1-decynyl)-2-(2-selenophenyl)-6-(2-thienyl)naphthalene (5).
To a degassed solution of 4 (0.49 g, 0.806 mmol) in DMF (10 mL) was added Pd(PPh_3)_2Cl_2 (0.057 g, 0.0806 mmol) and 2-(tri-n-butylstannyl)thiophene (0.603 g, 1.611 mmol). Then the mixture was stirred at 90 °C overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE/DCM = 10/1) to give a brownish-yellow solid (0.45 g, yield: 92%). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.40 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 5.2 Hz, 1H), 7.87 (t, J = 8.8 Hz, 2H), 7.79 (t, J = 8.8 Hz, 2H), 7.42 (m, 2H), 7.16 (d, J = 3.2 Hz, 1H), 2.66 (m, 4H), 1.77 (m, 4H), 1.51 (s, 4H), 1.30 (s, 16H), 0.89 (s, 6H). ^13C{^1H} NMR (100 MHz, CDCl_3) δ (ppm): 148.4, 145.4, 142.9, 136.3, 134.3, 133.4, 132.3, 129.6, 129.5, 128.0, 127.5, 127.3, 127.2, 127.1, 126.4, 118.1, 117.8, 103.5, 102.3, 78.7, 78.4, 32.1, 29.5, 29.4, 29.4, 28.7, 28.6, 23.0, 20.7, 20.5, 14.4. HRMS (ESI-TOF) m/z: [M + H]^+ calcd for C_{38}H_{45}SSe, 613.2407; found 613.2403.

Synthesis of 1-(1-decynyl)-2-(2-thienyl)naphthalene (7).
To a degassed solution of 6^{S3} (0.13 g, 0.38 mmol) in DMF (2 mL) was added Pd(PPh_3)_2Cl_2 (0.027 g, 0.038 mmol) and 2-(tri-n-butylstannyl)thiophene (0.21 g, 0.57 mmol). Then the mixture was stirred at 90 °C overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE) to give a brownish-yellow oil (0.11 g, yield: 82%) ^1H NMR (400 MHz, THF-d_8) δ (ppm): 8.45 (d, J = 8.5 Hz, 1H), 7.85-7.78 (m, 2H), 7.75 (m, 2H), 7.55 (m, 1H), 7.51-7.44 (m, 2H), 7.12 (m, 1H), 2.64 (t, J = 7.1 Hz, 2H), 1.73 (m, 2H), 1.54 (m, 2H), 1.37 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H). ^13C{^1H} NMR (100 MHz, THF-d_8) δ (ppm): 142.9, 134.5, 134.2, 132.5, 128.0, 127.9, 127.3,
Synthesis of 1-(1-decynyl)-2-(2-selenophenyl)naphthalene (8).

To a degassed solution of 2-bromo-1-(1-decynyl)naphthalene (0.13 g, 0.38 mmol) in DMF (2 mL) was added Pd(PPh$_3$)$_2$Cl$_2$ (0.027 g, 0.038 mmol) and 2-(tri-$n$-butylstannyl)selenophene (0.24 g, 0.57 mmol). Then the mixture was stirred at 90 °C overnight. After removing the solvents in vacuo, the mixture was separated and purified by column chromatography (eluted with PE) to give a brownish-yellow oil (0.13 g, yield: 84\%). H NMR (400 MHz, THF-d$_8$) $\delta$ (ppm): 8.45 (d, $J = 8.4$ Hz, 1H), 8.16 (d, $J = 5.6$ Hz, 1H), 7.90 (d, $J = 4.8$ Hz, 1H), 7.83 (m, 3H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 6.8$ Hz, 1H), 7.36 (m, 1H), 2.68 (t, $J = 7.2$ Hz, 2H), 1.77 (m, 2H), 1.58 (m, 2H), 1.39 (m, 8H), 0.91 (t, $J = 6.8$ Hz, 3H). C{$^1$H} NMR (100 MHz, THF-d$_8$) $\delta$ (ppm): 148.3, 136.2, 134.5, 132.4, 132.1, 129.3, 129.0, 128.0, 127.9, 127.0, 127.0, 126.2, 126.0, 117.4, 102.9, 78.8, 32.1, 29.5, 29.4, 29.3, 28.6, 22.8, 20.1, 13.7. HRMS (ESI-TOF) $m/z$: [M + H]$^+$ calcd for C$_{24}$H$_{27}$Se 395.1278; found 395.1270.


To a degassed solution of 2 (0.31 g, 0.55 mmol) in dry toluene (15 mL) was added PtCl$_2$ (0.03 g, 0.11 mmol). The mixture was heated overnight under 110 °C and then cooled to room temperature. After removing toluene in vacuum, the product was separated and purified through column chromatography (eluted with PE/DCM = 30/1) to give SS as dark green crystals (0.16 g, yield: 51\%). H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.51 (d, $J = 8.6$ Hz, 2H), 8.31 (d, $J = 8.6$ Hz, 2H), 8.03 (d, $J = 7.1$ Hz, 2H), 7.57 (d, $J = 9.1$ Hz, 2H), 7.15 (t, $J = 9.1$, 2H), 3.38-3.33 (m, 4H), 1.92 (m, 4H), 1.41 (m, 4H), 1.27 (m, 16H), 0.88 (t, $J = 6.7$ Hz, 6H). C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 137.4, 130.6, 128.4, 127.3, 126.4, 126.3, 123.3,
122.8, 118.3, 118.1, 117.2, 32.1, 30.1, 29.9, 29.8, 29.6, 29.0, 22.9, 14.3. HRMS (ESI-TOF) m/z: \([M + H]^+\) calcd for C$_{38}$H$_{45}$S$_2$ 565.2963; found 565.2965.

**Synthesis of 7,14-dioctynaphtho[2,1-f;6,5'-f']bis(cyclopenta[b]selenopyran) (SeSe).**

To a degassed solution of 3 (0.30 g, 0.55 mmol) in dry toluene (30 mL) was added PtCl$_2$ (0.03 g, 0.11 mmol). The mixture was heated overnight under 110 °C and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE/DCM = 30/1) to give SeSe as dark green crystals (0.12 g, yield: 40%). $^1$H NMR (400 MHz, THF-$d_8$) δ (ppm): 8.44 (d, $J = 8.4$ Hz, 2H), 8.27 (d, $J = 8.4$ Hz, 2H), 8.13 (d, $J = 9.2$ Hz, 2H), 7.95 (d, $J = 7.2$ Hz, 2H), 7.40 (t, $J = 9.2$ Hz, 2H), 3.28 (t, $J = 7.6$ Hz, 4H), 2.08-1.90 (m, 4H), 1.62 (m, 4H), 1.44-1.30 (m, 16H), 0.90 (t, $J = 3.6$ Hz, 6H). $^{13}$C($^1$H) NMR (100 MHz, THF-$d_8$) δ (ppm): 137.1, 130.9, 130.5, 129.0, 128.3, 127.7, 122.8, 122.6, 120.45, 120.4, 118.11, 118.07, 32.1, 31.2, 30.1, 29.9, 29.6, 28.6, 22.8, 13.7. HRMS (ESI-TOF) m/z: \([M + H]^+\) calcd for C$_{38}$H$_{45}$Se$_2$, 661.1852; found 661.1850.

**Synthesis of 7,14-dioctyl-thiopyran[5'',6''-1',2']indeno[5',4':4,5]indeno[2,1-b]selenopyran (SSe).**

To a degassed solution of 5 (0.30 g, 0.49 mmol) in dry toluene (30 mL) was added PtCl$_2$ (0.03 g, 0.098 mmol). The mixture was heated overnight under 110 °C and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE/DCM = 30/1) to give SSe as dark green crystals (0.12 g, yield: 40%). $^1$H NMR (400 MHz, THF-$d_8$) δ (ppm): 8.51 (d, $J = 8.4$ Hz, 1H), 8.45 (d, $J = 8.8$ Hz, 1H), 8.33 (d, $J = 8.4$ Hz, 1H), 8.30 (d, $J = 8.8$ Hz, 1H), 8.14 (t, $J = 6.4$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 9.2$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.23 (t, $J = 7.2$ Hz, 1H), 3.39 (t, $J = 7.2$ Hz, 2H), 3.29 (t, $J = 7.2$ Hz, 2H), 2.08-1.90 (m, 4H), 1.63 (m, 4H).
4H), 1.46-1.30 (m, 16H), 0.91 (t, J = 5.6 Hz, 6H). $^{13}$C{$_{1}$H} NMR (100 MHz, THF-$_{d}$$_{8}$) δ (ppm): 137.3, 137.1, 131.0, 130.6, 130.5, 129.2, 128.6, 128.2, 127.6, 127.3, 127.3, 126.4, 125.5, 123.3, 123.0, 122.7, 122.6, 120.4, 118.3, 118.0, 117.7, 117.2, 54.1, 35.4, 32.1, 31.2, 30.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.0, 28.6, 27.2, 22.8, 13.7. HRMS (ESI-TOF) m/z: [M + H]$^{+}$ calcd for C$_{38}$H$_{45}$S$_{2}$Se, 613.2407; found 613.2410.


To a degassed solution of 7 (0.35 g, 1.01 mmol) in dry toluene (30 mL) was added PtCl$_{2}$ (0.05 g, 0.20 mmol). The mixture was heated overnight under 110 °C and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE) to give RS as blue oil (0.25 g, yield: 71%).

$^{1}$H NMR (400 MHz, THF-$_{d}$$_{8}$) δ (ppm): 8.60 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.2 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 6.8 Hz, 1H), 7.51 (t, J = 6.8 Hz, 1H), 7.22 (m, 1H), 3.33 (t, J = 7.6 Hz, 2H), 1.93 (m, 2H), 1.59 (m, 2H), 1.40-1.30 (m, 8H), 0.90 (t, J = 6.4 Hz, 3H). $^{13}$C{$_{1}$H} NMR (100 MHz, THF-$_{d}$$_{8}$) δ (ppm): 136.5, 134.9, 130.3, 128.8, 127.8, 127.7, 126.7, 125.2, 125.1, 125.0, 124.7, 123.7, 123.2, 121.3, 119.0, 117.1, 32.1, 30.0, 29.8, 29.5, 29.1, 29.0, 22.8, 13.7. HRMS (ESI-TOF) m/z: [M + H]$^{+}$ calcd for C$_{24}$H$_{27}$S 347.1833; found 347.1845.


To a degassed solution of 8 (0.30 g, 0.76 mmol) in dry toluene (30 mL) was added PtCl$_{2}$ (0.04 g, 0.15 mmol). The mixture was heated overnight under 110 °C and then cooled to room temperature. After removing toluene in vacuo, the product was separated and purified through column chromatography (eluted with PE) to give RSe as blue oil (0.21 g, yield: 70%).

$^{1}$H NMR (400 MHz, THF-$_{d}$$_{8}$) δ (ppm): 8.53 (d, J = 8.4 Hz, 1H), 8.18 (t, J = 8.4 Hz, 2H), 7.96
(m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 6.8 Hz, 1H), 7.48 (t, J = 6.8 Hz, 1H), 7.39 (m, 1H), 3.22 (t, J = 7.6 Hz, 2H), 1.92 (m, 2H), 1.60 (m, 2H), 1.42-1.29 (m, 8H), 0.90 (t, J = 6.4 Hz, 3H). \(^{13}\text{C}^{1}\text{H}\) NMR (100 MHz, THF-\(d_8\)) \(\delta\) (ppm): 136.3, 135.0, 130.4, 130.2, 129.5, 128.9, 128.2, 127.5, 125.2, 124.9, 124.6, 123.5, 122.5, 121.6, 120.3, 118.9, 32.1, 30.7, 30.0, 29.8, 29.5, 28.6, 22.8, 13.7. HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) calcld for C\(_{24}\)H\(_{27}\)Se 395.1278; found 395.1265.
Table S1 S-C and Se-C bond lengths for heteroarenes SS, SSe, and SeSe.

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<th>S-C bond length (Å)</th>
<th>Se-C bond length (Å)</th>
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<td><strong>SS</strong></td>
<td>1.7158(18) / 1.7376(17)</td>
<td>----</td>
</tr>
<tr>
<td><strong>SSe</strong></td>
<td>1.695(17) / 1.870(16)</td>
<td>1.791(17) / 1.920(15)</td>
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<tr>
<td><strong>SeSe</strong></td>
<td>----</td>
<td>1.879(4) / 1.876(4)</td>
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Table S2 Crystal data and structure refinement details for isomers SS, SSe, and SeSe.

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<th></th>
<th>SS</th>
<th>SSe</th>
<th>SeSe</th>
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<tr>
<td>formula</td>
<td>C_{38}H_{44}S_2</td>
<td>C_{38}H_{44}SSe</td>
<td>C_{38}H_{44}Se_2</td>
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<tr>
<td>formula wt.</td>
<td>564.85</td>
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<td>658.65</td>
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<td>T (K)</td>
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<td>173</td>
<td>300</td>
</tr>
<tr>
<td>wavelength (Å)</td>
<td>1.54178</td>
<td>1.54178</td>
<td>1.54178</td>
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<tr>
<td>crystal size</td>
<td>0.16 x 0.15 x 0.12</td>
<td>0.05 x 0.04 x 0.03</td>
<td>0.24 x 0.22 x 0.18</td>
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<td>crystal syst.</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
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<td>space group</td>
<td>Pǐ</td>
<td>P1</td>
<td>Pǐ</td>
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<tr>
<td>a (Å)</td>
<td>4.9037(8)</td>
<td>4.9067(2)</td>
<td>5.0411(3)</td>
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<tr>
<td>b (Å)</td>
<td>9.209(3)</td>
<td>9.2799(3)</td>
<td>9.2861(5)</td>
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<td>c (Å)</td>
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<td>17.3392(6)</td>
<td>17.3658(10)</td>
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<td>a (deg.)</td>
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<td>78.036(10)</td>
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<td>β (deg.)</td>
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<td>87.305(10)</td>
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<td>γ (deg.)</td>
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<td>80.354(10)</td>
<td>80.527(2)</td>
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<td>V (Å³)</td>
<td>753.8(3)</td>
<td>761.39(5)</td>
<td>785.30(8)</td>
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<tr>
<td>Z / D_{calcd.} (mg/m³)</td>
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<td>1 / 1.334</td>
<td>1 / 1.393</td>
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<td>μ (mm⁻¹)</td>
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<td>0.753/0.604</td>
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<tr>
<td>final R indices</td>
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<td>R₁ = 0.1062</td>
<td>R₁ = 0.0404</td>
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<tr>
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<td>wR₂ = 0.3024</td>
<td>wR₂ = 0.1127</td>
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<td>R indices (all data)</td>
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<td>R = 0.0434</td>
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<tr>
<td></td>
<td>wR₂ = 0.0824</td>
<td>wR₂ = 0.3353</td>
<td>wR₂ = 0.1144</td>
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Table S3 Selected bond lengths for SS.

<table>
<thead>
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<td>1.7376(17)</td>
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<tr>
<td>C1-C2</td>
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<tr>
<td>C2-C3</td>
<td>1.4280(20)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.3510(20)</td>
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<tr>
<td>C4-C8</td>
<td>1.4400(20)</td>
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<td>C4-C5</td>
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<tr>
<td>C5-C6</td>
<td>1.3600(20)</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.4720(20)</td>
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<tr>
<td>C6-C12</td>
<td>1.5040(20)</td>
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<tr>
<td>C7-C8</td>
<td>1.4050(20)</td>
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<tr>
<td>C7-C11</td>
<td>1.4280(20)</td>
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<tr>
<td>C9-C10</td>
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<td>C18-C19</td>
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**Table S4** Selected bond lengths for SSe.

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<th>Bond</th>
<th>Length/Å</th>
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<td>1.41(2)</td>
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<td>1.695(17)</td>
<td>C17-C18</td>
<td>1.45(2)</td>
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<td>S1-C5</td>
<td>1.870(16)</td>
<td>C17-C23</td>
<td>1.46(2)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.39(2)</td>
<td>C18-C19</td>
<td>1.48(2)</td>
</tr>
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<td>C2-C3</td>
<td>1.44(2)</td>
<td>C19-C20</td>
<td>1.34(2)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.39(2)</td>
<td>C20-C21</td>
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<td>C21-C22</td>
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<td>C23-C24</td>
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<td>C24-C25</td>
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<td>C7-C12</td>
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<td>C27-C28</td>
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<td>C29-C30</td>
<td>1.55(2)</td>
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<td>C9-C8</td>
<td>1.44(2)</td>
<td>C31-C32</td>
<td>1.48(2)</td>
</tr>
<tr>
<td>C10-C11</td>
<td>1.45(2)</td>
<td>C32-C33</td>
<td>1.56(2)</td>
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<td>C11-C12</td>
<td>1.457(15)</td>
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<td>C11-C16</td>
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<td>C34-C35</td>
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<td>C13-C14</td>
<td>1.37(2)</td>
<td>C35-C36</td>
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<td>C13-C12</td>
<td>1.38(2)</td>
<td>C36-C37</td>
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<td>C14-C15</td>
<td>1.36(2)</td>
<td>C37-C38</td>
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<td>C15-C16</td>
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Table S5 Selected bond lengths for SeSe.

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<th>Length/Å</th>
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<td>1.355(5)</td>
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<td>C4-C8</td>
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<td>1.356(5)</td>
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<td>C6-C7</td>
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<td>C6-C12</td>
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<tr>
<td>C7-C8</td>
<td>1.399(5)</td>
</tr>
<tr>
<td>C7-C11</td>
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<td>1.504(6)</td>
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<td>C14-C15</td>
<td>1.522(6)</td>
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<td>C15-C16</td>
<td>1.520(6)</td>
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<tr>
<td>C16-C17</td>
<td>1.510(6)</td>
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<td>C18-C19</td>
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**Table S6** Calculated energies, oscillator strength and compositions of major electronic transitions for SS.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Osc. Strength (f)</th>
<th>Major Contributions</th>
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</thead>
<tbody>
<tr>
<td>657.14</td>
<td>0.0780</td>
<td>H→L (97%)</td>
</tr>
<tr>
<td>425.74</td>
<td>0.5051</td>
<td>H-2→L (89%)</td>
</tr>
<tr>
<td>409.36</td>
<td>0.1037</td>
<td>H-1→L+1 (92%)</td>
</tr>
<tr>
<td>353.10</td>
<td>1.2313</td>
<td>H→L+2 (88%)</td>
</tr>
<tr>
<td>319.85</td>
<td>0.1013</td>
<td>H-3→L (83%), H-2→L+2 (10%)</td>
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</table>
Table S7 Calculated energies, oscillator strength and compositions of major electronic transitions for SeSe.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Osc. Strength (f)</th>
<th>Major Contributions</th>
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</thead>
<tbody>
<tr>
<td>652.99</td>
<td>0.1006</td>
<td>H→L (98%)</td>
</tr>
<tr>
<td>428.52</td>
<td>0.4641</td>
<td>H-2→L (89%)</td>
</tr>
<tr>
<td>414.27</td>
<td>0.1284</td>
<td>H-1→L+1 (92%)</td>
</tr>
<tr>
<td>354.59</td>
<td>1.0959</td>
<td>H→L+2 (88%)</td>
</tr>
<tr>
<td>321.67</td>
<td>0.1287</td>
<td>H-3→L (83%)</td>
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</tbody>
</table>
Table S8 Calculated energies, oscillator strength and compositions of major electronic transitions for $\text{SSe}$.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Osc. Strength (f)</th>
<th>Major Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>649.26</td>
<td>0.0926</td>
<td>$\text{H} \rightarrow \text{L}$ (97%)</td>
</tr>
<tr>
<td>425.29</td>
<td>0.456</td>
<td>$\text{H}-2 \rightarrow \text{L}$ (88%)</td>
</tr>
<tr>
<td>410.30</td>
<td>0.1195</td>
<td>$\text{H}-1 \rightarrow \text{L}+1$ (91%)</td>
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<tr>
<td>364.74</td>
<td>0.0038</td>
<td>$\text{H}-2 \rightarrow \text{L}+1$ (92%)</td>
</tr>
<tr>
<td>353.70</td>
<td>1.1532</td>
<td>$\text{H} \rightarrow \text{L}+2$ (87%)</td>
</tr>
<tr>
<td>319.46</td>
<td>0.1018</td>
<td>$\text{H}-3 \rightarrow \text{L}$ (82%)</td>
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</tbody>
</table>
**Table S9** Calculated energies, oscillator strength and compositions of major electronic transitions for RS.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Osc. Strength (f)</th>
<th>Major Contributions</th>
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<tbody>
<tr>
<td>561.11</td>
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<td>H→L (98%)</td>
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<td>373.31</td>
<td>0.2074</td>
<td>H-1→L (87%)</td>
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<td>335.67</td>
<td>0.3279</td>
<td>H-2→L (18%), H→L+1 (72%)</td>
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<tr>
<td>317.82</td>
<td>0.1877</td>
<td>H-2→L (71%)</td>
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<tr>
<td>287.97</td>
<td>0.2533</td>
<td>H-1→L+1 (32%), H→L+2 (51%)</td>
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<tr>
<td>272.99</td>
<td>0.106</td>
<td>H-1→L+1 (52%)</td>
</tr>
<tr>
<td>259.68</td>
<td>0.062</td>
<td>H-3→L (60%), H→L+3 (30%)</td>
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<tr>
<td>257.43</td>
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<tr>
<td>251.33</td>
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<td>H→L+4 (95%)</td>
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Table S10 Calculated energies, oscillator strength and compositions of major electronic transitions for RSe.

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<th>Wavelength (nm)</th>
<th>Osc. Strength (f)</th>
<th>Major Contributions</th>
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<tbody>
<tr>
<td>567.77</td>
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<tr>
<td>379.24</td>
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<td>H-1→L (90%)</td>
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<td>0.256</td>
<td>H-2→L (22%), H→L+1 (72%)</td>
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<td>320.89</td>
<td>0.2076</td>
<td>H-2→L (69%)</td>
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<td>289.61</td>
<td>0.2493</td>
<td>H→L+2 (57%)</td>
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<tr>
<td>275.07</td>
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</tr>
<tr>
<td>273.77</td>
<td>0.0665</td>
<td>H-1→L+1 (42%), H→L+2 (28%)</td>
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<tr>
<td>262.3</td>
<td>0.0045</td>
<td>H-3→L (90%)</td>
</tr>
<tr>
<td>258.80</td>
<td>0.2121</td>
<td>H→L+3 (82%)</td>
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</table>
Fig. S1 ORTEP diagram with an ellipsoid contour probability level of 50% and crystal packing (hydrogen atoms are omitted for ease of viewing) of SS.
Fig. S2 ORTEP diagram with an ellipsoid contour probability level of 50% and crystal packing (hydrogen atoms are omitted for ease of viewing) of SSe.
Fig. S3 ORTEP diagram with an ellipsoid contour probability level of 50% and crystal packing (hydrogen atoms are omitted for ease of viewing) of SeSe.
Fig. S4 Calculated frontier orbitals of the S- and Se-fused heteroarenes.
**Fig. S5** Differential pulse voltammograms of heteroarenes SS, SSe, SeSe, RS, and RSe in DCM solutions (0.1 mM).
Fig. S6 UV-vis-NIR absorption spectra of heteroarenes (a) SS, (b) SSe, (c) SeSe, and (d) RS and RSe in DCM solutions upon titration of SbCl$_5$. 
Fig. S7 ESR spectra of $\text{SS}^\cdot$, $\text{SSe}^\cdot$, $\text{SeSe}^\cdot$, $\text{RS}^\cdot$, and $\text{RSe}^\cdot$ recorded in DCM at room temperature.
Fig. S8 $^1$H NMR spectrum of 2 in CDCl$_3$.

Fig. S9 $^{13}$C($^1$H) NMR spectrum of 2 in CDCl$_3$. 
Fig. S10 $^1$H NMR spectrum of 3 in CD$_2$Cl$_2$.

Fig. S11 $^{13}$C{$^1$H} NMR spectrum of 3 in CD$_2$Cl$_2$. 
**Fig. S12** $^1$H NMR spectrum of 4 in CDCl$_3$.

**Fig. S13** $^{13}$C{$^1$H} NMR spectrum of 4 in CDCl$_3$. 
Fig. S14 $^1$H NMR spectrum of 5 in CDCl$_3$.

Fig. S15 $^{13}$C{$^1$H} NMR spectrum of 5 in CDCl$_3$
**Fig. S16** $^1$H NMR spectrum of 7 in THF-$d_8$.

**Fig. S17** $^{13}$C{$_1^1$H} NMR spectrum of 7 in THF-$d_8$. 
Fig. S18 $^1$H NMR spectrum of 8 in THF-$d_8$.

Fig. S19 $^{13}$C{$^1$H} NMR spectrum of 8 in THF-$d_8$. 
Fig. S20 $^1$H NMR spectrum of SS in CDCl$_3$.

Fig. S21 $^{13}$C{$^1$H} NMR spectrum of SS in CDCl$_3$.
**Fig. S22** $^1$H NMR spectrum of SeSe in THF-$d_8$.

**Fig. S23** $^{13}$C-$^1$H NMR spectrum of SeSe in THF-$d_8$. 
Fig. S24 $^1\text{H}$ NMR spectrum of SSe in THF-$d_8$.

Fig. S25 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of SSe in THF-$d_8$. 
Fig. S26 $^1$H NMR spectrum of RS in THF-$d_8$.

Fig. S27 $^{13}$C{$^1$H} NMR spectrum of RS in THF-$d_8$. 
Fig. S28 $^1$H NMR spectrum of RSe in THF-$d_8$.

Fig. S29 $^{13}$C-$^1$H NMR spectrum of RSe in THF-$d_8$. 
References.

