

SUPPORTING INFORMATION FOR

**Optical gap in herringbone and π -stacked crystals of
[1]benzothieno[3,2-b]benzothiophene and its brominated derivative**

Vijay S. Vyas,^a Rico Gutzler,^a Jürgen Nuss,^a Klaus Kern^{a,b} and Bettina V. Lotsch^{a,c,d}

^a Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

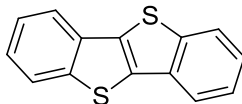
E-mail: b.lotsch@fkf.mpg.de; **Fax:** +49 711689-1612 ; **Tel:** +49 711689-1610

^b Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

^c Department of Chemistry, University of Munich (LMU), Butenandtstr. 5-13, 81377 Munich, Germany

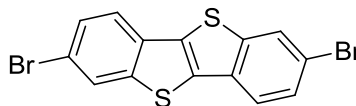
^d Nanosystems Initiative Munich (NIM) and Center for Nanoscience, Schellingstraße 4, 80799 Munich, Germany

Synthesis of [1]benzothieno[3,2-b]benzothiophene (**1**)



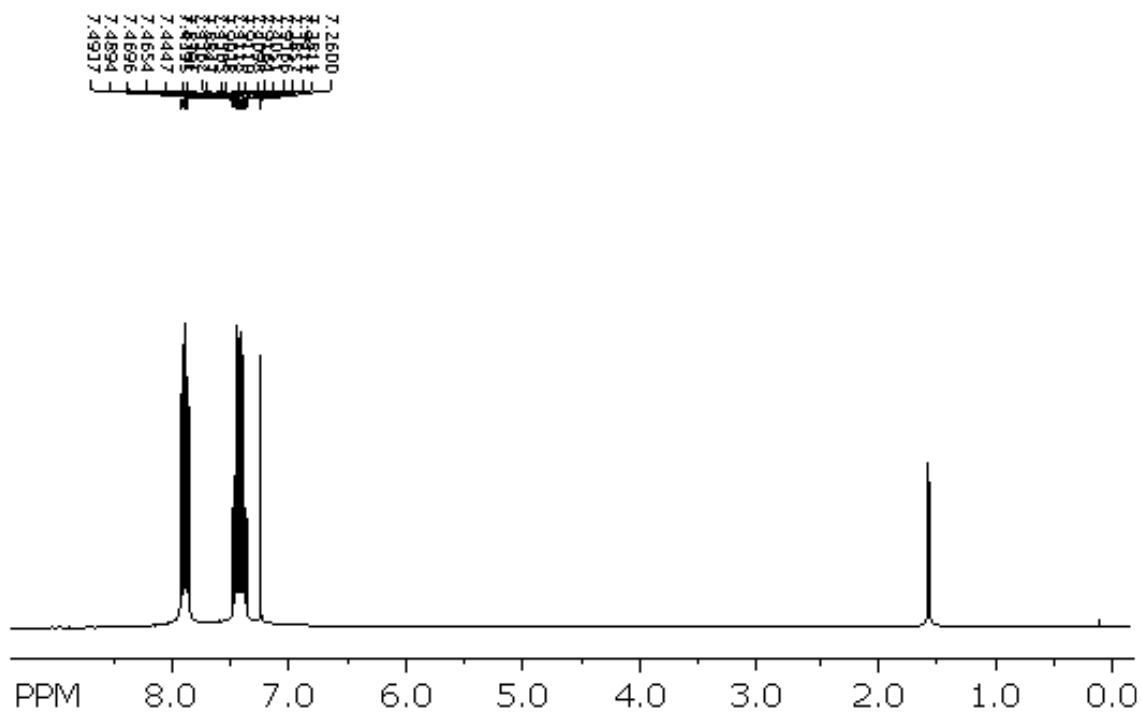
The title compound was prepared as per literature published procedure.^[S1] ¹H NMR 300 MHz (CDCl₃): δ 7.91 (4H, m), 7.44 (4H, m). ¹³C NMR 75 MHz (CDCl₃): δ 142.50, 133.67, 133.34, 125.22, 125.10, 124.26, 121.82.

Synthesis of 2,7-dibromo[1]benzothieno[3,2-b]benzothiophene (**2**)

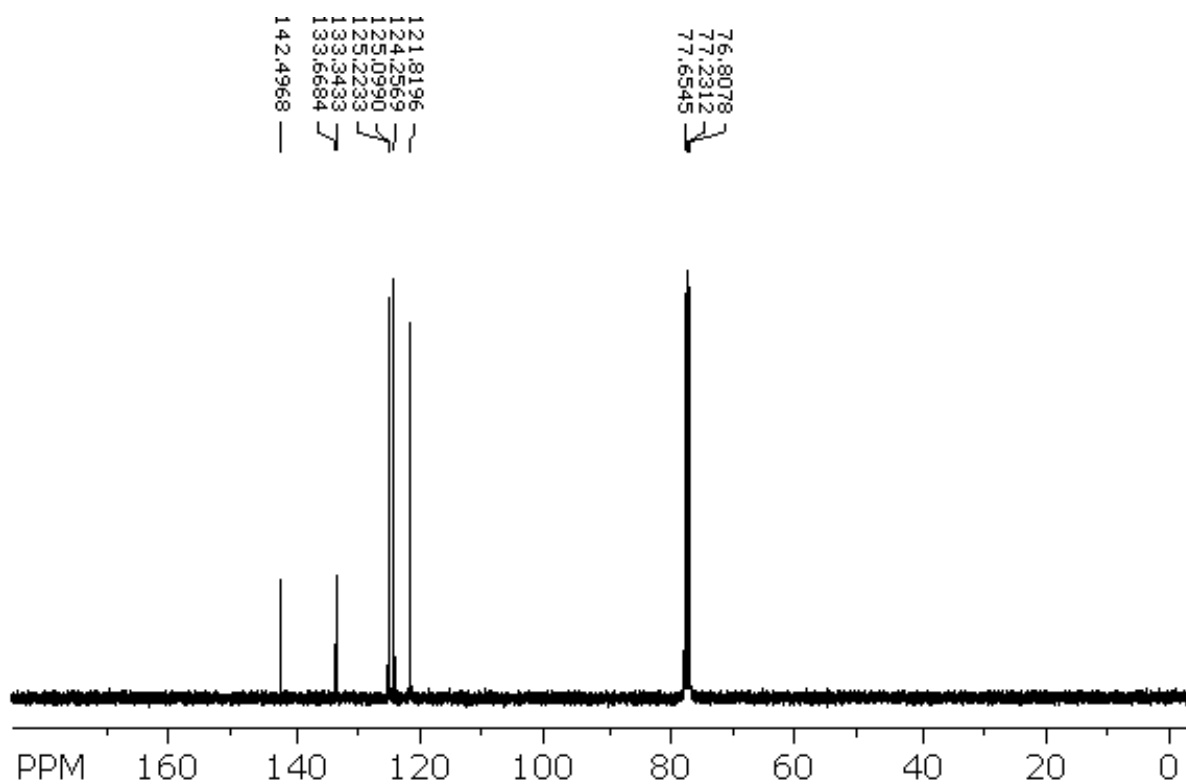


To an ice cold solution of [1]benzothieno[3,2-b]benzothiophene (0.1 g, 0.42 mmol) in dichloromethane (35 mL) with catalytic amount of iodine was added a solution of bromine (0.15 g, 0.9 mmol) in dichloromethane (15 mL) using a dropping funnel. The solution was stirred for 2 hour at 0 °C and then warmed to room temperature. The contents were stirred at room temperature for 8 hours. The reaction mixture was then precipitated by addition of methanol (50 mL). The precipitate was filtered and washed with 10 % hypo solution (20 mL x 3) followed by water (20 mL x 2), ethanol (20 mL x 2) and dichloromethane (20 mL x 2). The crude product was then chromatographed over silica gel using pentane as eluent to afford **2** (0.09 g, 57 %) shiny colorless solid. The final compound was further purified by crystallization using chloroform. ¹H NMR 300 MHz (CDCl₃): δ 8.03 (2H, dd, *J* = 1.75, 0.47 Hz), 7.70 (2H, dd, *J* = 8.48, 0.46 Hz), 7.55 (2H, dd, *J* = 8.48, 1.75 Hz). ¹³C NMR 75 MHz (C₂D₂Cl₄, 70 °C): δ 143.70, 133.29, 131.57, 128.46, 126.51, 122.45, 118.91. MS (MALDI): *m/z*: 398.5.

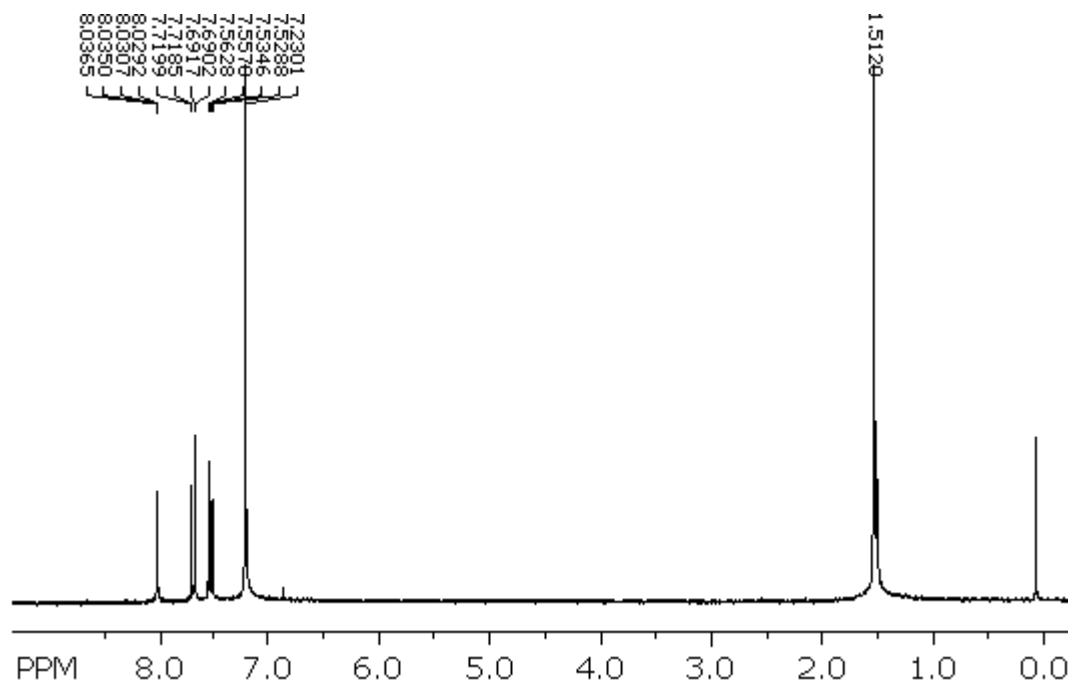
¹H NMR of [1]benzothieno[3,2-b]benzothiophene (**1**)



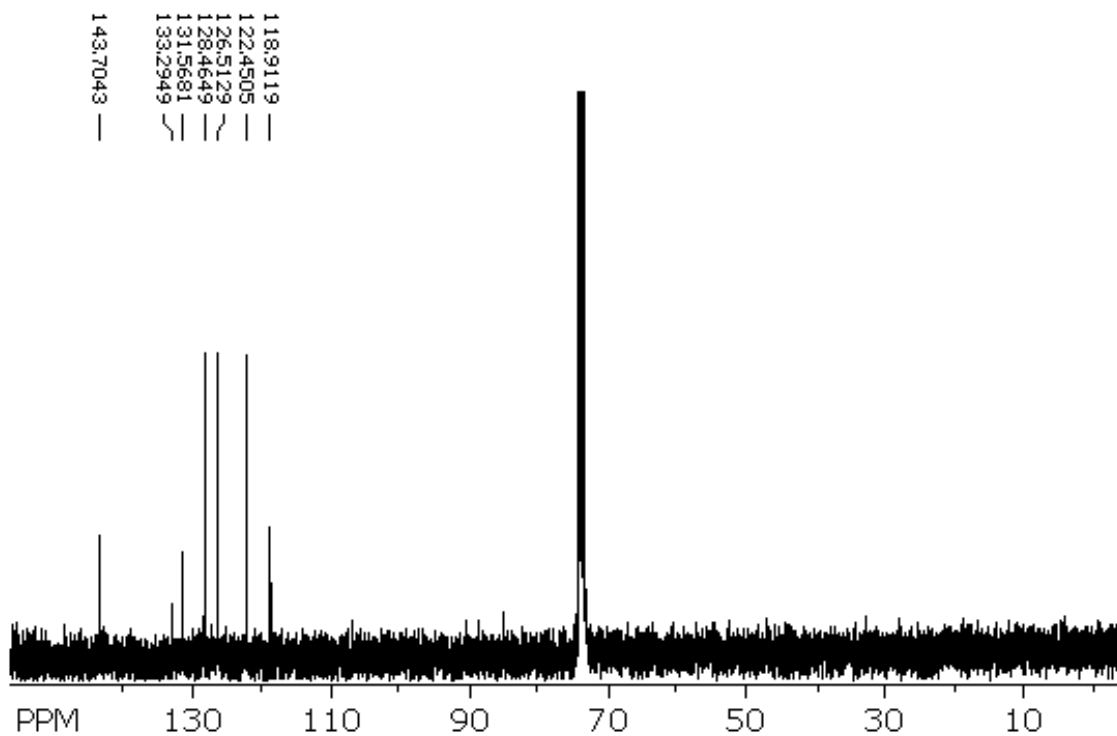
¹³C NMR of [1]benzothieno[3,2-b]benzothiophene (**1**)



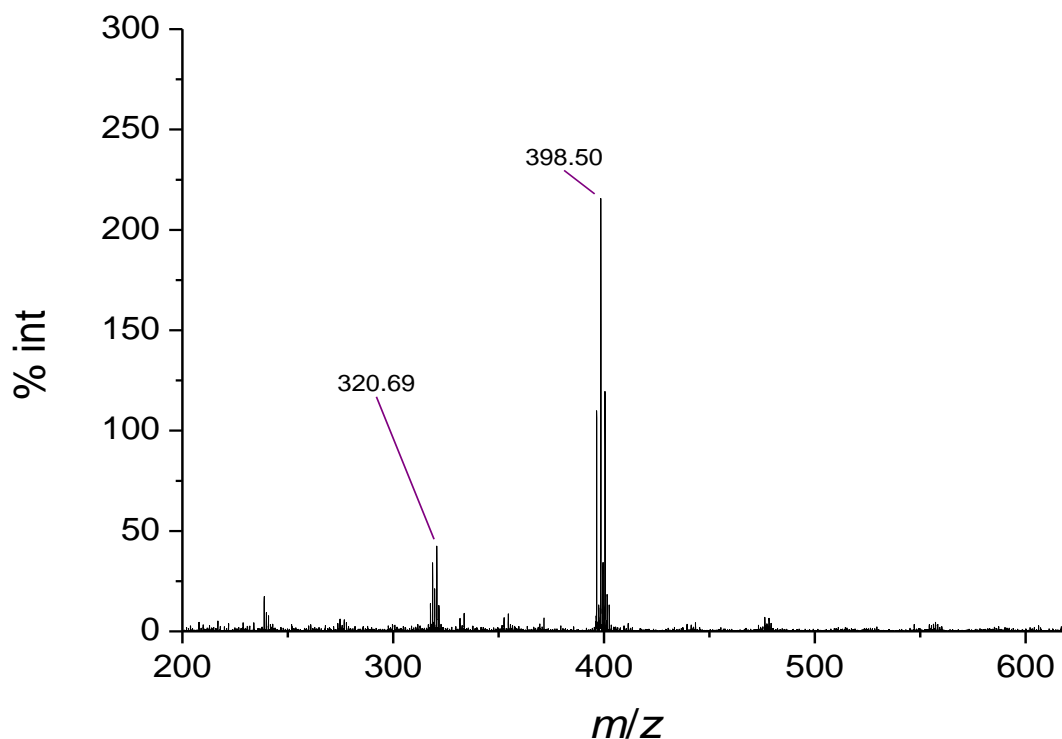
¹H NMR of 2,7-dibromo[1]benzothieno[3,2-b]benzothiophene (2)



¹³C NMR of 2,7-dibromo[1]benzothieno[3,2-b]benzothiophene (2)



MS (MALDI) of 2,7-dibromo[1]benzothieno[3,2-b]benzothiophene (**2**)



Optical and Electrochemical Studies.

UV-vis spectra were measured in dichloromethane solution (concentration: 10^{-6} M) at 22 °C on a Carey 5000 UV-vis-NIR spectrophotometer (Agilent). The emission spectra were recorded on a Horiba FluoroLog 3 Spectrofluorometer as dichloromethane solutions or in the crystalline state. Cyclic voltammograms (CVs) were recorded on a Princeton Applied Research VersaSTAT electrochemical workstation in dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆, 0.1 M) as supporting electrolyte at a scan rate of 50 mV/s. The electrode setup consisted of a glassy carbon working electrode, a platinum auxiliary electrode and Ag/AgCl as reference electrode. The potentials were calibrated with the standard ferrocene/ferrocenium redox couple ($E_{1/2} = 0.45$ V measured under identical conditions).

The electrochemical properties of **1** and **2** were investigated in dichloromethane with 0.1 M *n*-Bu₄NPF₆ at a scan rate of 50 mVps. The oxidative behavior of both the compounds is qualitatively rather similar (Figure 4). However, in accordance with the electron withdrawing influence of bromine in **2**, the oxidation half-wave potential ($E_{1/2} = 1.59$ V vs Ag/AgCl) shifted by about 110 mV when compared with **1** ($E_{1/2} = 1.48$ V). From the onset potential (1.38 eV for **1** and 1.49 eV for **2**), the HOMO values of the two compounds estimated using the equation $E_{\text{HOMO}} = -4.4 - E_{\text{onset}}^{\text{[S2]}}$ are -5.8 eV for **1** and -5.9 eV for **2**.

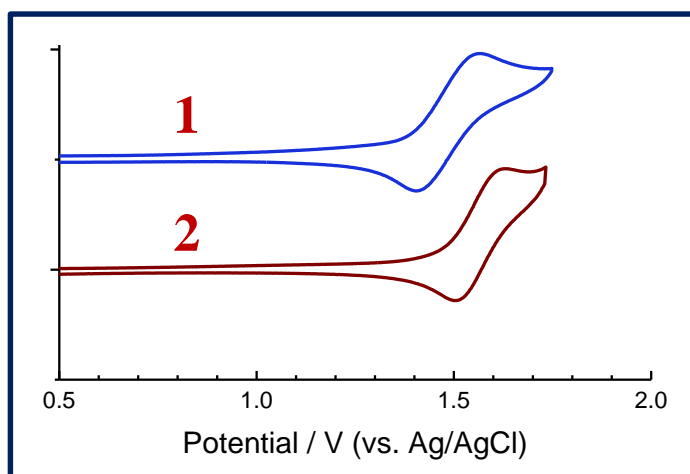


Figure 4. Cyclic Voltammograms of **1** and **2** recorded in dichloromethane.

Crystal Structure Determination

Colorless crystals suitable for single-crystal X-ray diffraction were cut out from plate like needles with several millimeters in length, and mounted with some grease onto nylon loops for X-ray diffraction. During crystal preparation it has turned out that especially the needles of C₁₂H₆S₂Br₂ (**2**) easily split up into sheaves that stick to each other. This behavior is the reason for the relatively poor crystal data of **2** in comparison to **1**.

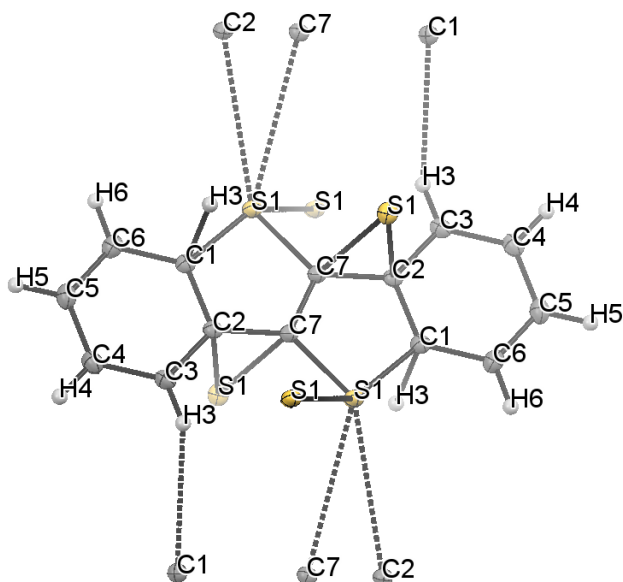
Diffraction data were collected on a three circle diffractometer (Bruker AXS, Karlsruhe, Germany) equipped with a SMART-CCD, using MoK_α radiation ($\lambda = 0.71073$ Å). The 100 K measurement

was performed using an N-Helix low temperature device (Oxford Cryosystems, Oxford, United Kingdom). The collection and reduction of data were carried out with the Bruker Suite software package.^[S3] The intensities were corrected for absorption effects by applying a multi-scan method with Sadabs^[S4]. Both structures were solved by Direct Methods and refined by full matrix least-squares fitting with the Shelxtl software package.^[S5] The positions of the hydrogen atoms in **1** were located from Fourier difference maps and refined together with the isotropic displacement parameters without any restraints. Because of the poor crystal quality of **2**, the positions of the hydrogen atoms were treated by applying a riding model for the *x*, *y* and *z* coordinates using AFIX.^[S6] The isotropic displacement parameters were restrained to 1.2 times of the attached carbon atoms. The crystallographic data are given in Table 1.

Table S1: Crystal data and structure refinement data of C₁₂H₈S₂ (**1**), and C₁₂H₆S₂Br₂ (**2**).

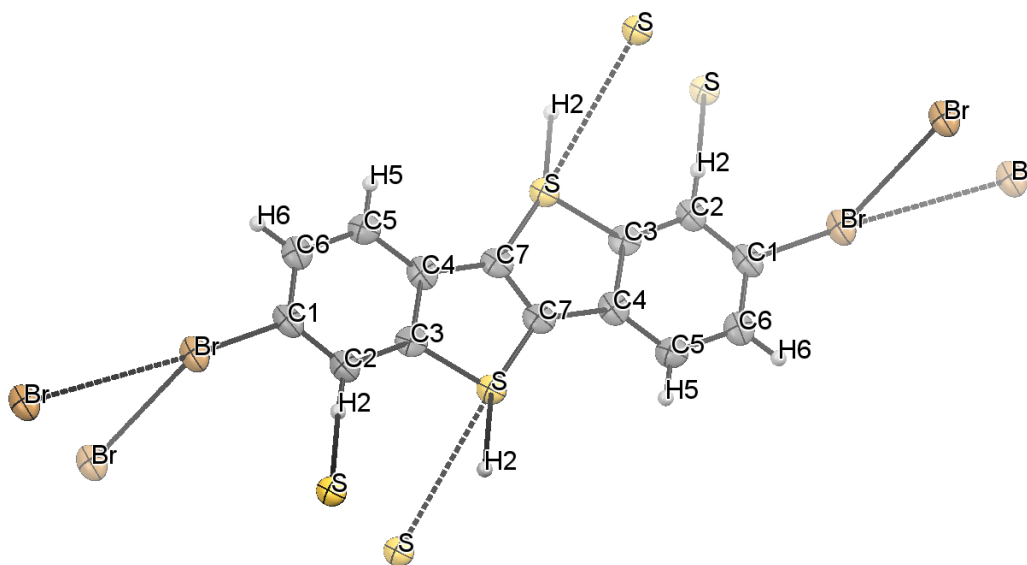
| | C ₁₂ H ₈ S ₂ (1) | C ₁₂ H ₆ S ₂ Br ₂ (2) |
|--|---|--|
| Temperature /K | 100.0(2) K | 298(2) K |
| Formula weight | 240.32 | 398.13 |
| Space group (no.), <i>Z</i> | <i>P</i> 2 ₁ / <i>c</i> (14), 2 | <i>P</i> 2 ₁ / <i>n</i> (14), 2 |
| Lattice constants /Å, /° | <i>a</i> = 11.801(2) <i>b</i> = 5.862(1) <i>c</i> = 7.933(1) <i>β</i> = 105.974(3) | 7.339(5) 3.915(3) 22.078(14) 99.08(1) |
| <i>V</i> /Å ³ , ρ _{xray} /g cm ⁻³ | 527.6(1), 1.513 | 626.4(7), 2.111 |
| Crystal size /mm ⁻³ | 0.35×0.25×0.05 | 0.30×0.10×0.02 |
| Diffractometer | SMART APEX II, Bruker AXS | SMART APEX I, Bruker AXS |
| X-ray radiation, λ/Å | | 0.71073 |
| Absorption correction | | SADABS ^[N2] |
| 2θ range /° | 3.6-72.8 | 3.7-52.9 |
| Index range | -19 ≤ <i>h</i> ≤ 19 -9 ≤ <i>k</i> ≤ 9 -13 ≤ <i>l</i> ≤ 13 | -7 ≤ <i>h</i> ≤ 9 -4 ≤ <i>k</i> ≤ 4 -26 ≤ <i>l</i> ≤ 21 |
| Reflection collected | 9359 | 2888 |
| Data, <i>R</i> _{int} | 2555, 0.018 | 1226, 0.050 |
| No. of parameters | 89 | 82 |
| Transmission: <i>t</i> _{max} , <i>t</i> _{min} | 0.977, 0.854 | 0.876, 0.236 |
| <i>R</i> ₁ [<i>F</i> ² > 2σ(<i>F</i> ²)] | 0.026 | 0.092 |
| <i>wR</i> (<i>F</i> ²) | 0.072 | 0.256 |
| Δρ _{max} , Δρ _{min} /e Å ⁻³ | 0.623, -0.413 | 2.730, -2.5385 |
| Deposition no. ^[N4] | CCDC-975935 | CCDC-975934 |

Table S2: List of intermolecular short contacts in the crystal structure of C₁₂H₈S₂ (**1**)



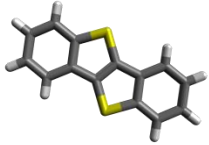

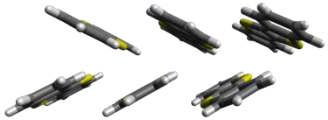

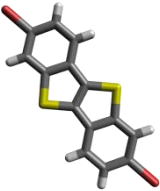
| Number | Atom1 | Atom2 | Distance betw. Atom 1 and Atom 2 | Deviation from the sum of VdW radii |
|--------|-------|-------|----------------------------------|-------------------------------------|
| 1 | S1 | S1 | 3.524 | -0.076 |
| 2 | S1 | S1 | 3.524 | -0.076 |
| 3 | C1 | H3 | 2.79 | -0.11 |
| 4 | C2 | S1 | 3.373 | -0.127 |
| 5 | C7 | S1 | 3.393 | -0.107 |
| 6 | H3 | C1 | 2.79 | -0.11 |
| 7 | S1 | C2 | 3.373 | -0.127 |
| 8 | S1 | C7 | 3.393 | -0.107 |
| 9 | S1 | C2 | 3.373 | -0.127 |
| 10 | S1 | C7 | 3.393 | -0.107 |
| 11 | H3 | C1 | 2.79 | -0.11 |
| 12 | C2 | S1 | 3.373 | -0.127 |
| 13 | C7 | S1 | 3.393 | -0.107 |
| 14 | C1 | H3 | 2.79 | -0.11 |

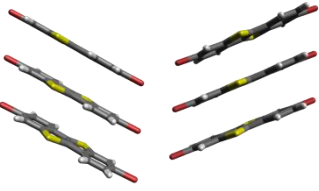
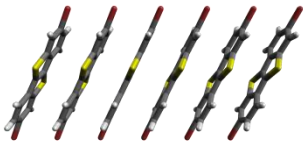
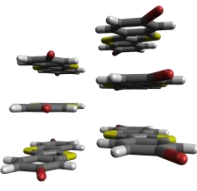
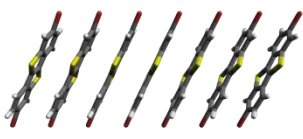
Table S3: List of intermolecular short contacts in the crystal structure of C₁₂H₆S₂Br₂ (**2**)



| Number | Atom1 | Atom2 | Distance betw. Atom 1 and Atom 2 | Deviation from the sum of VdW radii |
|--------|-------|-------|----------------------------------|-------------------------------------|
| 1 | S | H2 | 2.901 | -0.099 |
| 2 | H2 | S | 2.901 | -0.099 |
| 3 | S | S | 3.533 | -0.067 |
| 4 | S | S | 3.533 | -0.067 |
| 5 | S | H2 | 2.901 | -0.099 |
| 6 | H2 | S | 2.901 | -0.099 |
| 7 | Br | Br | 3.567 | -0.133 |
| 8 | Br | Br | 3.567 | -0.133 |
| 9 | Br | Br | 3.567 | -0.133 |
| 10 | Br | Br | 3.567 | -0.133 |

Table S4: Excitation wavelengths, energies and dipole transition moments

| Cluster | Wavelength (nm) | Excitation Energy (eV) | Oscillator Strength |
|---|-----------------|------------------------|---------------------|
| (a)  | 285.8 | 4.339 | 0.157799852 |
| | 269.0 | 4.609 | 0.401129875 |
| | 256.7 | 4.830 | 0.000000698 |
| | 251.3 | 4.934 | 0.000000114 |
| | 236.8 | 5.236 | 0.000004518 |
| | 229.4 | 5.404 | 0.556090435 |
| | 226.2 | 5.482 | 0.000113073 |
| | 215.1 | 5.764 | 0.000000011 |
| (b)  | 292.2 | 4.243 | 0.221954479 |
| | 291.7 | 4.250 | 0.007802587 |
| | 291.3 | 4.257 | 0.043475669 |
| | 290.4 | 4.270 | 0.104962705 |
| | 288.7 | 4.295 | 0.118861134 |
| | 288.3 | 4.301 | 0.201063722 |
| | 276.1 | 4.490 | 0.007754439 |
| | 275.3 | 4.504 | 0.002117757 |
| (c)  | 296.9 | 4.176 | 0.132486582 |
| | 295.7 | 4.193 | 0.193087190 |
| | 294.2 | 4.214 | 0.188695415 |
| | 293.1 | 4.230 | 0.160899494 |
| | 291.7 | 4.251 | 0.131175045 |
| | 290.5 | 4.268 | 0.127739091 |
| | 277.3 | 4.471 | 0.003366957 |
| | 276.9 | 4.478 | 0.000058254 |
| (d)  | 301.0 | 4.119 | 0.137298857 |
| | 295.3 | 4.198 | 0.000001432 |
| | 294.5 | 4.210 | 0.157611699 |
| | 293.7 | 4.222 | 0.191204193 |
| | 293.6 | 4.222 | 0.000261239 |
| | 293.2 | 4.228 | 0.451428326 |
| | 292.5 | 4.239 | 0.000003746 |
| | 279.5 | 4.436 | 0.019843874 |
| (e)  | 285.4 | 4.344 | 0.308840938 |
| | 271.5 | 4.567 | 0.504294352 |
| | 259.7 | 4.774 | 0.000014016 |
| | 254.6 | 4.870 | 0.000000011 |
| | 237.9 | 5.211 | 0.000104838 |
| | 234.5 | 5.287 | 0.813448074 |
| | 228.8 | 5.418 | 0.000249587 |
| | 225.3 | 5.502 | 0.000000029 |

| | | | |
|--|--|--|--|
| (f)  | 305.6 304.8 294.3 293.3 293.1 292.6 288.6 288.2 | 4.058 4.067 4.213 4.228 4.231 4.238 4.296 4.302 | 0.001608577 0.000163406 0.003556357 0.248604719 0.070201701 0.005454568 0.381581689 0.026912082 |
| (g)  | 309.7 305.7 300.1 295.5 293.4 293.2 291.7 291.2 | 4.004 4.055 4.131 4.195 4.225 4.228 4.250 4.257 | 0.000000002 0.000167038 0.000000055 0.046523379 0.000001192 0.161410756 0.000000193 0.044767617 |
| (h)  | 305.8 305.2 294.9 293.6 293.6 292.9 289.1 288.7 | 4.054 4.063 4.205 4.222 4.223 4.234 4.289 4.295 | 0.000000015 0.001535109 0.033673319 0.125459900 0.000089662 0.000000025 0.000003574 0.197118424 |
| π -stacked heptamer  | 310.1 307.2 302.8 297.8 295.2 293.4 293.3 292.0 | 3.998 4.036 4.095 4.163 4.200 4.226 4.227 4.246 | 0.000015882 0.000000007 0.000252301 0.000000093 0.087916493 0.000037159 0.137208286 0.000000228 |

- [S1] M. Saito, I. Osaka, E. Miyazaki, K. Takimiya, H. Kuwabara and M. Ikeda, *Tetrahedron Letters*, 2011, **52**, 285-288.
- [S2] S. Shinamura, I. Osaka, E. Miyazaki, A. Nakao, M. Yamagishi, J. Takeya and K. Takimiya, *J. Am. Chem. Soc.*, 2011, **133**, 5024-5035.
- [S3] *Bruker Suite*, Version 2008/3, Bruker AXS Inc., Madison USA **2008**.
- [S4] G. M. Sheldrick, SADABS — *Bruker AXS area detector scaling and absorption*, Version 2008/1, University of Göttingen, Germany **2008**.
- [S5] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.
- [S6] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-975935 and CCDC-975934. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].