

## Electron Transport Mechanism

Electric Current through a Molecular Rod—  
Relevance of the Position of the Anchor Groups\*\*

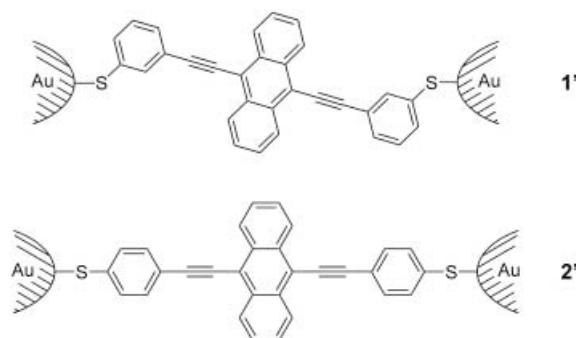
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The understanding of electronic transport through a single molecule is an interesting scientific challenge, which became experimentally addressable only very recently. This interest is further enhanced by the possibility of building electronic devices with molecules, a vision often referred to as “molecular electronics”.<sup>[1]</sup> Tunnel currents through molecular films have been studied on surfaces with STM<sup>[2]</sup> or with electrode pairs provided by crossed wire junctions<sup>[3]</sup> and mercury droplets against metallic surfaces.<sup>[4]</sup> Contacts between single molecules were either made by STM techniques on diluted molecular films<sup>[5]</sup> or by the mechanically controlled break-junction (MCB) technique.<sup>[6–9]</sup> The latter has turned out to be particularly powerful to contact single molecules that are covalently linked to both electrodes, as has been demonstrated by the comparison of the electronic characteristics of molecules differing in spatial symmetry.<sup>[8]</sup> The observed current–voltage ( $I/U$ ) characteristics depend not only on the molecular properties but also on the configuration of the microscopic contacts. The rather strong covalent bonding to the atomically disordered metallic electrode causes sample-to-sample fluctuations, which are undesired for both controlled scientific investigation and engineering of electronic

properties. Herein we present a strategy to decouple electronically molecular properties from disordered electrodes by varying the relative position (*meta* versus *para*) of the thiol anchor group on the molecular rod. The lack of conjugation in the *meta* position and therefore the reduced electronic communication compared to the *para* position in rodlike  $\pi$ -systems is known and has been shown, for example, in electrochemical investigations<sup>[10]</sup> and in theoretical studies.<sup>[11]</sup> Herein we demonstrate the validity of this concept for the anchor groups of single immobilized molecular rods between two electrodes.

A complementary attempt, in which the current was suppressed by internally interrupting the molecular  $\pi$  system with a *trans*-configured Pt<sup>II</sup> ion increased the junction resistance considerably.<sup>[9]</sup>

We present the synthesis and characterization of the molecular rods **1** and **2**, both consist of a bis-9,10-phenylethynylantracene core and acetyl protected thiol anchor groups in *meta* and *para* positions respectively (Scheme 1). Analogously with our previous experiments,<sup>[8]</sup> deprotection of the acetylsulfanyl groups at the gold surfaces of the electrodes of an MCB yields the immobilized molecular rods (**1'** and **2'**) as single-molecule junctions. By using this set-up the electron transport properties of **1'** and **2'** have been investigated.

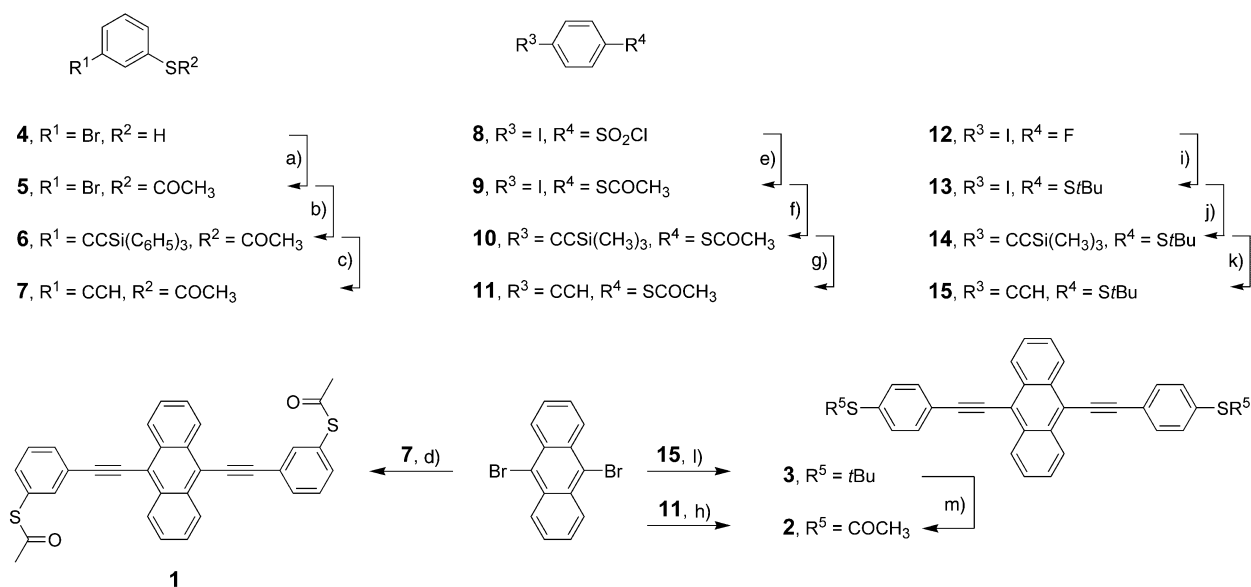


The synthesis of the molecular rods **1** and **2** is shown in Scheme 1. Protection of 3-bromothiophenol **4** with acetic anhydride in acetonitrile with  $\text{CoCl}_2$  as catalyst gave the acetyl-protected 3-bromothiophenol **5**. The bromine ion of **5** was substituted with triphenylsilyl (TPS) ethynyl by using Sonogashira coupling conditions to yield the TPS-protected **6**. Deprotection of the TPS group of **6** with tetrabutylammonium fluoride (TBAF) in THF and subsequent reprotection of the thiol group with acetic anhydride in acetic acid gave the ethynylbenzene **7**. In a Sonogashira coupling reaction the acetylene **7** substituted both bromine atoms of 9,10-dibromoanthracene with  $[\text{Pd}(\text{PPh}_3)_4]$  and  $\text{CuI}$  as catalysts. The strongly fluorescent target compound **1** was isolated as an orange solid after column chromatography with a yield of 3%. Compound **1** is soluble in aprotic organic solvents such as THF, toluene,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$ .

The molecular rod **2** with its sulfur anchor groups in the *para* position was synthesized by two different synthetic routes. In analogy to the synthesis of **1**, the corresponding acetylsulfanyl-4-ethynylbenzene (**11**) was synthesized starting

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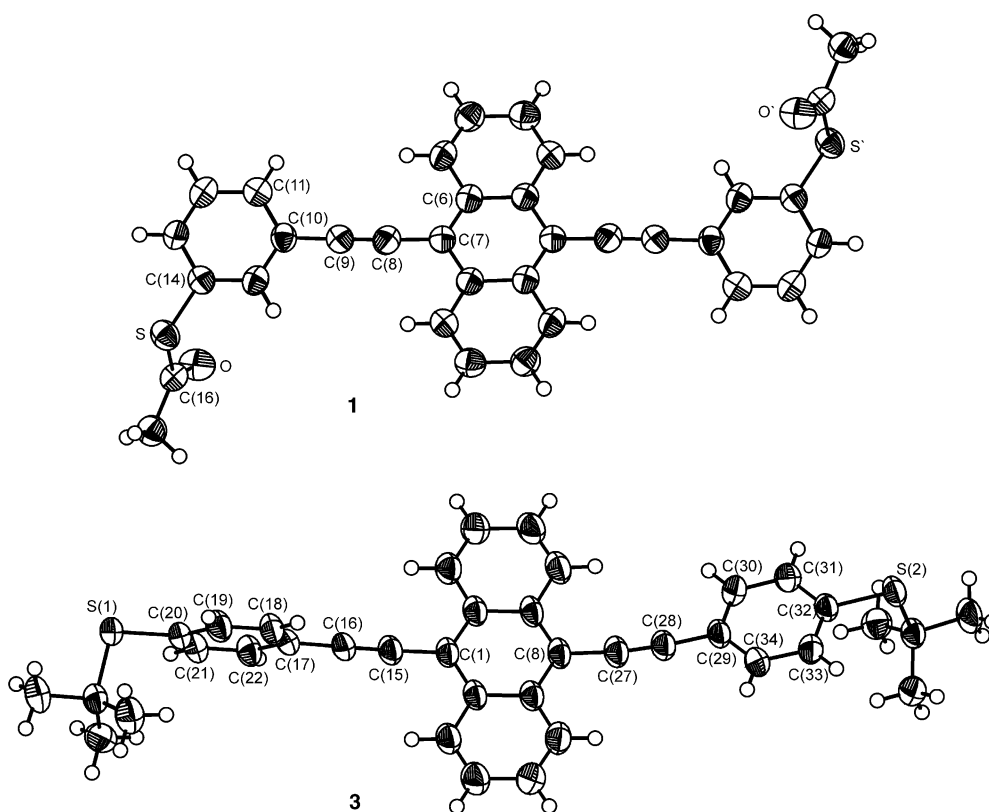
**Scheme 1.** Synthesis of the acetyl protected molecular rods **1** and **2**. a) Ac<sub>2</sub>O, CoCl<sub>2</sub>, CH<sub>3</sub>CN, RT, 93 %; b) HCCSi(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>, CuI, *i*Pr<sub>2</sub>NH, reflux, 38 %; c) TBAF, THF, AcOH, Ac<sub>2</sub>O, 0 °C, 68 %; d) [Pd(PPh<sub>3</sub>)<sub>4</sub>], CuI, Et<sub>3</sub>N, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 90 °C, 3 %; e) 1) Zn, Me<sub>2</sub>SiCl<sub>2</sub>, DMA, (CH<sub>2</sub>Cl)<sub>2</sub>, 75 °C; 2) AcCl, 50 °C, 98 %; f) HCCSi(CH<sub>3</sub>)<sub>3</sub>, [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], CuI, *i*Pr<sub>2</sub>EtN, 40 °C, 98 %; g) TBAF, THF, AcOH, Ac<sub>2</sub>O, 0 °C, 69 %; h) [Pd(PPh<sub>3</sub>)<sub>4</sub>], CuI, Et<sub>3</sub>N, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 90 °C, 5 %; i) Na*t*Bu, DMF, 70 °C, 44 %; j) HCCSi(CH<sub>3</sub>)<sub>3</sub>, [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], CuI, *i*Pr<sub>2</sub>EtN, RT, 93 %; k) TBAF, THF, 0 °C, 100 %; l) [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], CuI, Et<sub>2</sub>NH, r.f., 71 %; m) BBr<sub>3</sub>, AcCl, CH<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, RT, 49 %.

with 4-iodobenzenesulphonyl chloride (**8**), which was transformed into the acetyl protected 4-iodothiophenol **9** in 98 % yield by using reported reaction conditions.<sup>[12]</sup> As iodide is a better leaving group than bromide, milder conditions could be used for the Sonogashira coupling reaction of **9** than those of **5**. Thus, the introduction of the trimethylsilyl(TMS)-protected acetylene gave the ethynylbenzene **10**. By using similar reaction conditions as those described above for **6**, compound **10** was deprotected to give **11**. Similar conditions to those used for the Sonogashira coupling reactions to obtain **7** were applied to substitute both bromine groups of 9,10-dibromoanthracene with acetylene **11** to yield the molecular rod **2** in 5 % yield after column chromatography. Compound **2** is strongly fluorescent with comparable solubility properties to those of **1**. The limited availability of **2**, due to the poor yield of the final synthetic step and the fact that all attempts to crystallize **2** failed, tempted us to investigate an alternative route to **2** with the intermediate **3** as a model compound for X-ray analysis. Substitution of the fluoride of **12** by using sodium *tert*-butylthiolate gave the 1-*tert*-butylsulfanyl-4-iodobenzene (**13**). As with **9**, the TMS-protected acetylene was introduced and deprotected to yield the ethynylbenzene **15**. Both bromides of 9,10-dibromoanthracene were substituted with **15** to yield the *tert*-butyl-protected rod **3**. Finally, the conversion of the *tert*-butylsulfanyl groups into acetylsulfanyl groups with BBr<sub>3</sub> in the presence of acetyl chloride,<sup>[13]</sup> gave the rod **2** in 49 % yield.

All compounds were characterized by mass spectroscopy, <sup>1</sup>H- and <sup>13</sup>C NMR spectroscopy, and elemental analysis. In addition, the solid-state structures of rods **1** and **3** were analyzed by X-ray analysis (Figure 1).<sup>[14]</sup> Slow evaporation of a solution of **1** in chloroform and a solution of **3** in diethyl

ether gave single crystals suitable for X-ray analysis. The inversion symmetric compound **1** crystallizes in the triclinic space group *P* $\bar{1}$  and shows an almost coplanar orientation of the phenyl rings and the anthracene motif (torsion angle C(6)–C(7)–C(10)–C(11): 9.1(1)°). The intramolecular sulfur-to-sulfur distance in **1** is 1.78(2) nm. Compound **3** crystallizes in the monoclinic (space group *C2/c*).<sup>[14]</sup> Surprisingly, the molecular structure has no inversion centre and reveals two different *t*BuS-phenyl groups. While the phenyl ring C(17)–C(22) is 78.2(1)° twisted relative to the anthracene fragment, the phenyl ring C(29)–C(34) departs only by 8.1(1)° from the anthracene plain. These different orientations of the substituents probably result from packing forces, as NMR investigations in solution show no evidence of distinguishable phenyl or *tert*-butyl groups. As both sulfur atoms are on the molecules axis, the intramolecular sulfur-to-sulfur distance (1.99(2) nm) is only slightly affected by these packing forces and slightly shorter than the calculated distance (2.18 nm).<sup>[15]</sup>

The electronic transport properties have been investigated by using the MCB technique to immobilize in different experiments single molecules **1'** and **2'** between Au-electrodes. Both acetyl-protected rods **1** and **2** have been immobilized from 5 × 10<sup>−4</sup> M solutions in THF. Details of the immobilizing protocol and the *I*/*U* characteristics of **2'** have been described elsewhere.<sup>[8,9]</sup> The rod fixed in the *para* position, **2'**, displayed *I*/*U* curves at room temperature, which are reproducible for a stable junction but are subject to considerable sample-to-sample fluctuations when the experiment is repeated. These fluctuations arise from the single-molecule nature of the experiment. A typical example is shown in Figure 2a. Often, broad steplike increases of the currents were observed, the current ranges from 0.2 μA to



**Figure 1.** Molecular structures of **1** and **3** (ORTEP, thermal ellipsoids set at the 50% probability level). Selected bond lengths [pm] and bond angles [°]: **1**: S-(14) 176.6(3), S-C(16) 177.6(4), C(16)-O 119.8(4), C(7)-C(8) 141.3(5), C(8)-C(9) 119.7(5), C(9)-C(10) 142.8(5); C(14)-S-C(16) 101.2(2), C(7)-C(8)-C(9) 178.0(4), C(8)-C(9)-C(10) 179.5(4); **3**: C(1)-C(15) 144.4(4), C(15)-C(16) 119.8(4), C(16)-C(17) 144.6(4), C(8)-C(27) 143.9(4), C(17)-C(28) 120.1(4), C(28)-C(29) 144.1(4); C(1)-C(15)-C(16) 175.1(3), C(15)-C(16)-C(17) 177.0(3), C(8)-C(27)-C(28) 173.6(3), C(27)-C(28)-C(29) 175.1(3).

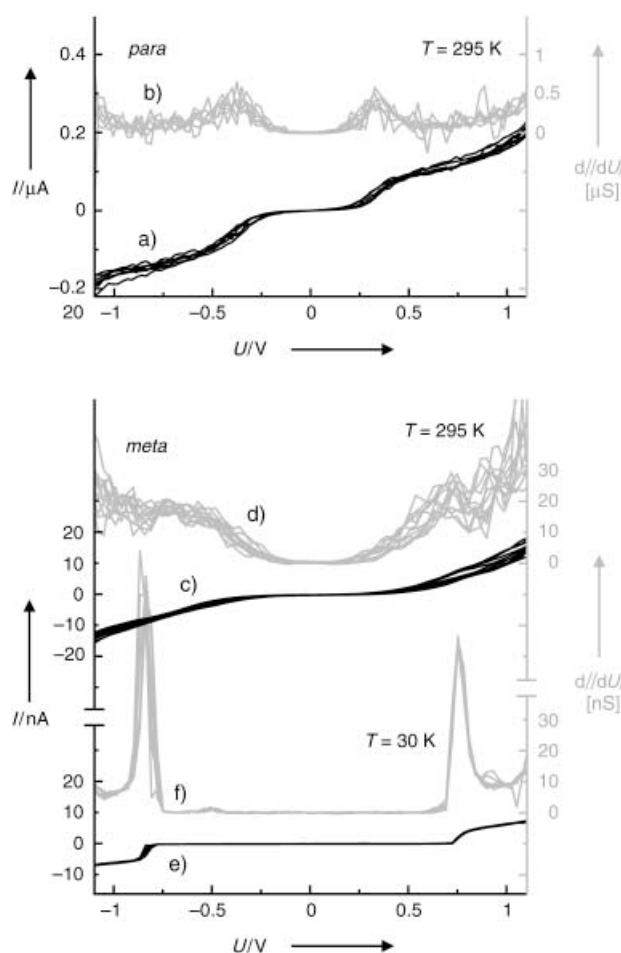
1  $\mu\text{A}$  at  $U = 1$  V for different junctions. The immobilization of **1** between the Au electrodes of a bridge contact resulted in a stable configuration **1'** that also allowed us to record reproducible  $I/U$  curves at room temperature (Figure 2c). The recorded currents for **1'** were about 10 nA at  $U = 1$  V almost two orders of magnitude smaller than the values recorded for **2'** under similar conditions. The  $I/U$  curves of **1'** have a barely visible less-resolved steplike feature at  $U \approx 0.75$  V, which can better be visualized in the broad maximum of the first derivative (Figure 2d). This can presumably be attributed to resonant tunneling through the HOMO, as has already been calculated theoretically for molecule **2'**.<sup>[16]</sup> Our recent progress with the MCB technique<sup>[17]</sup> allowed to record **1'** at low temperatures of  $\approx 30$  K (Figure 2e) as well. The low-temperature  $I/U$  curves of **1'** display a beautifully resolved steplike feature at  $U \approx 0.75$  V. This clear difference indicates that the molecule junction is fluctuating considerably at room temperature and the measurement averages over various microscopic configurations. The observed conductance values are not exponentially suppressed compared to room temperature data, which indicates that not thermally activated hopping, but mainly tunneling governs the electron propagation.<sup>[18]</sup>

The comparison between the molecules **1'** and **2'** allows the following conclusions to be drawn: a) The conductance

does depend on the structure of the molecule and can thus be intentionally altered on a molecular level by varying the position of the anchor group in the synthesis of the molecules. b) The obtained reduction of the current level observed for **1'** with respect to **2'** with anchor groups in the *meta* positions is particularly useful for designing stable molecular junctions as the reduction in the current allows for higher stability. However, the room temperature data are still quite noisy. c) The dominating current path seems to be through the Au-S-C bonds (and not direct injection from the metal to the  $\pi$  system of the rod). d) According to our limited data set, the reproducibility of the  $I/U$  curves seems to be improved because the molecule is electronically less coupled to the disordered electrodes.

The data further corroborate that the low-temperature technique<sup>[17]</sup> gives the expected result: the appearance of highly symmetric  $I/U$  curves indicate that both contacts are equivalent.

The results indicate that electronic properties can be tuned by carefully designing molecular structures. Here we have addressed exclusively the aspect of the anchor group position. Many particular electronic functions may be composed by the design of the molecules. To this end, we are currently working on rectifying and switching systems based on molecular structures.



**Figure 2.**  $I/U$  characteristics reproducibly recorded for a stable junction in a MCB and their numerical derivative  $dI/dU$ . a)  $I/U$  and b)  $dI/dU$  for Au-2'-Au at room temperature. c)  $I/U$  and d)  $dI/dU$  for Au-1'-Au at room temperature and e)  $I/U$  and f)  $dI/dU$  at  $T \approx 30$  K.

### Experimental Section

9,10-Bis[[3-(acetylsulfanyl)phenyl]ethynyl]anthracene **1**: 9,10-Dibromoanthracene (0.200 g; 0.595 mmol) was dissolved in argon-saturated triethylamine (1 mL) and toluene (15 mL). Tetrakis(triphenylphosphane)palladium(0) (0.0688 g, 0.0595 mmol), copper iodide (0.017 g, 0.0893 mmol) and (3-ethynyl)phenyl thioacetate (0.262 g, 1.488 mmol) were added subsequently. The reaction mixture was heated to 90°C under an argon atmosphere for 25 h and, cooled, then poured on 2N hydrochloric acid/ice. The aqueous phase was extracted with toluene, the toluene layers dried over  $MgSO_4$  and evaporated to dryness. The crude product was purified by column chromatographies (silica gel, cyclohexane,  $CH_2Cl_2$ ) to afford **1** (0.010 g, 0.019 mmol; 3%) as an orange solid. M.p.: 203–205°C (decomp);  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 8.65–8.69 (m, 4H), 7.80–7.83 (m, 4H), 7.64–7.68 (m, 4H), 7.46–7.52 (m, 4H), 2.49 ppm (s, 6H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  = 193.61 (CO), 137.34, 134.77, 132.65, 132.15, 129.42, 128.55, 127.23, 127.05, 124.64, 118.36 (Ar), 101.31, 87.53 (C≡C), 30.34 ppm ( $CH_3$ ); MALDI-TOF-MS: 525.81 [ $M^+$ ], 514.75, 505.75, 451.70 [ $M^+$ -SAcetyl], 409.70; elemental analysis calcd (%) for  $C_{34}H_{22}O_2S_2$ : C 77.54, H 4.21; found: C 77.17, H 4.35.

9,10-Bis[[4-(acetylsulfanyl)phenyl]ethynyl]anthracene **2**: 9,10-Bis[[4-(*tert*-butylsulfanyl)phenyl]ethynyl]anthracene **3** (0.0234 g, 0.042 mmol) was dissolved in a mixture of dry argon-saturated  $CH_2Cl_2$  (1.5 mL) and dry argon-saturated toluene (1.5 mL). The

mixture was cooled to 0°C, acetyl chloride (0.1256 g, ca. 0.12 mL, 1.6 mmol) was added, then boron tribromide (1.0M solution in  $CH_2Cl_2$ ; 0.09 mL; 0.09 mmol) was added dropwise. After removal of the ice bath, the reaction was stirred at room temperature for 3 h and poured into ice-water (about 100 mL). The aqueous phase was extracted with diethyl ether, the ethereal layers washed with water until neutral, dried over  $MgSO_4$  and evaporated to dryness. Column chromatography (silica gel,  $CH_2Cl_2$ /hexane 2:1) and subsequent washing with diethyl ether afforded **2** (0.0108 g, 0.021 mmol; 49%) as a yellow-red solid. m.p. 248–249°C;  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 8.65–8.69 (m, 4H), 7.81 (d,  $J$  = 8 Hz, 4H), 7.65–7.68 (m, 4H), 7.51 (d,  $J$  = 8 Hz, 4H), 2.48 ppm (s, 6H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  = 193.43 (CO), 134.47, 132.26, 132.17, 128.63, 127.21, 127.06, 124.57, 118.41 (Ar), 101.74, 88.14 (C≡C), 30.38 ppm ( $CH_3$ ); MALDI-TOF-MS: 525.91 [ $M^+$ ], 452.80 [ $M^+$ -SAc]; elemental analysis calcd (%) for  $C_{34}H_{22}O_2S_2$ : C 77.54, H 4.21; found: C 77.38, H 4.32.

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**Keywords:** anchor-group position · electron transport · molecular electronics · single-molecule studies · structure–activity relationships

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- [14] **1**:  $a = 629.7(1)$ ,  $b = 909.0(2)$ ,  $c = 1108.5(2)$  pm,  $\alpha = 85.83(3)$ ,  $\beta = 89.55(3)$ ,  $\gamma = 79.36(3)^\circ$ ,  $V = 621.9(2) \times 10^6$  pm<sup>3</sup>; triclinic  $P\bar{1}$ ,  $Z = 1$ ,  $\rho_{\text{calc}} = 1.406$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 0.247$  mm<sup>-1</sup>, STOE IPDS2, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 200$  K,  $2\theta_{\text{max}} = 45^\circ$ ; 2929 reflections measured, 1542 independent reflections ( $R_{\text{int}} = 0.0733$ ), 1321 independent reflections with  $F_o > 4\sigma(F_o)$ . The structure was solved by direct methods and refined, by full-matrix least-square techniques against  $F^2$ , 172 parameters (S, O, C refined anisotropically, H atoms were calculated at ideal positions);  $R1 = 0.0602$ ;  $wR2 = 0.1806$  (all data); Gof: 1.057; maximum peak  $0.305$  e Å<sup>-3</sup>. **3**:  $a = 2691.8(5)$ ,  $b = 594.7(1)$ ,  $c = 3779.9(8)$  pm,  $\beta = 96.88(3)^\circ$ ,  $V = 6007(2) \times 10^6$  pm<sup>3</sup>; monoclinic  $C2/c$ ,  $Z = 8$ ,  $\rho_{\text{calc}} = 1.227$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 0.203$  mm<sup>-1</sup>, STOE IPDS2, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 200$  K,  $2\theta_{\text{max}} = 48^\circ$ ; 9082 reflections measured, 4476 independent reflections ( $R_{\text{int}} = 0.0661$ ), 3156 independent reflections with  $F_o > 4\sigma(F_o)$ . The structure was solved by direct methods and refined, by full-matrix least-square techniques against  $F^2$ , 361 parameters (S, C refined anisotropically, H atoms were calculated at ideal positions);  $R1 = 0.0540$ ;  $wR2 = 0.1438$  (all data); Gof: 0.928; maximum peak  $0.262$  e Å<sup>-3</sup>. CCDC-210255 (**1**) and CCDC-210256 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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- [18] Data were also recorded at four intermediate temperatures between room temperature and 30 K which are not shown. The improvement of the data quality towards lower T develops continuously.

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