Highly Crowded Twisted Thienylene-Phenylene Structures: Evidence for Through-Space Orbital Coupling in a [4]Catenated Topology

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Supporting Information

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Highly crowded twisted thienylene-phenylene structures: Evidence for through-space orbital coupling in a [4]catenated topology

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$^1$H-NMR spectra and high resolution mass spectra (HRMS)

**Figure S1** High resolution MALDI FTICR mass spectrum of 9.

**Figure S2** $^1$H-NMR spectrum of 9 measured in tetrachloroethane-d$_2$. The colour code is given at the formula (right).

**Figure S3** HRMS (MALDI-FTICR) of mono-reacted Diels-Alder adduct 12; m/z calculated C$_{56}$H$_{30}$S$_{10}$: m/z = 1021.95350 [M+] δm/m = 1.4 ppm; m/z = 407.97635 [M+] corresponds to 11.
Figure S4  High resolution MALDI FTICR mass spectrum of the raw product of cyclooligomerization of diyne 7.

Figure S5  High resolution MALDI FTICR mass spectrum of cyclopentamers 13 (left) and isotopic pattern of the molecular peak (top: experiment, bottom: calculated). The peak at m/z = 1320.1043 corresponds to the molecule plus matrix DCTB.

Figure S6  $^1$H-NMR spectra of HPLC separated fractions of cyclopentamers 13 measured in CD$_2$Cl$_2$. Blue circles denote protons in 3-position of thiophenes, green circles in 4-position, and red circles in 5-position.
Figure S7  HRMS (MALDI-FTICR) of thienylene-phenylene 14; m/z calculated C_{48}H_{34}S_{8}: 855.96382; found: 855.96114 [M]^+ (δm/m = 3.1 ppm), 1106.10659 [M+DCTB]^+.  

Figure S8  ^1^H-NMR spectrum of thienylene-phenylene 14 measured in CD_{2}Cl_{2}. Blue circles denote protons in 3-position of thiophenes, green circles in 4-position, and red circles in 5-position. The black circles correspond to the signals of the benzo[b]thiophene unit.  

Figure S9  H,H-COSY spectrum of thienylene-phenylene 14 measured in CD_{2}Cl_{2}. The black, purple, and yellow circles correspond to the signals of the benzo[b]thiophene unit. Crucial interaction of thiophene protons of benzo[b]thiophene unit is highlighted in red.
**SCHEME S1** Proposed mechanism for the cobalt-mediated formation of cyclopentamers 11 from butadiyne 7.

**SCHEME S2** Proposed mechanism for the rhodium-mediated formation of benzo[b]thiophene derivative 12 by from thienylene-phenylene 8.
Single crystal X-ray structure analysis of thienylene-phenylenes 8, 9, and 14

Table S1a Crystallographic data of precursor 8 (CCDC number: 1884748)

| Bond precision: C-C = 0.0030 A | Wavelength= 0.71073 |
|-------------------------------|----------------------|
| Cell:                         |                      |
| a=50.14(2)                   | b=7.352(3)           |
| alpha=90                     | beta=100.86(2)       |
| c=16.854(8)                  | gamma=90             |
| Temperature:                 |                      |
| 293 K                        |                      |
| Volume                        |                      |
| Calculated                   | Reported             |
| 6102(5)                      | 6102(5)              |
| Space group                  |                      |
| C 2/c                         | C 2/c                |
| Hall group                   | -C 2yc               |
| Moiety formula               | C36 H18 S6           |
| Sum formula                  | C36 H18 S6           |
| Mr                            | 642.86               |
| Dx,g cm⁻³                    | 1.400                |
| Z                             | 8                    |
| Mu (mm⁻¹)                    | 0.474                |
| F000                          | 2640.0               |
| F000'                         | 2646.69              |
| h,k,lmax                     | 58,8,19              |
| Nref                          | 5204                 |
| Tmin,Tmax                    | 0.930,0.986          |
| Tmin’                         | 0.917                |

Correction method= # Reported T Limits: Tmin=0.700 Tmax=0.745
AbsCorr = NONE

Data completeness= 0.999
R(reflections)= 0.0345( 4640)
S = 1.079
Theta(max)= 24.687
wR2(reflections)= 0.0886( 5200)
Npar= 501

Figure S10a Labelled molecular structure from crystal structure analysis of precursor 8. For clarity, only one of the two disordered molecules (cis-trans isomerization at certain thiophene rings) is illustrated. Ellipsoids for non-hydrogen atoms are shown at 50% probability.
Table S1b  Selected bond distances of precursor 8.

| Atom 1 | Atom 2 | Length (Å) | Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|--------|--------|------------|
| C20    | C25    | 1.411(3)   | C20    | C22    | 1.433(3)   |
| C25    | C19    | 1.414(3)   | C22    | C15    | 1.201(3)   |
| C19    | C18    | 1.418(2)   | C15    | C14    | 1.420(3)   |
| C18    | C26    | 1.417(3)   | C14    | C23    | 1.35(1)    |
| C26    | C24    | 1.410(3)   | C23    | C27    | 1.41(1)    |
| C24    | C20    | 1.410(3)   | C27    | C28    | 1.362(5)   |
| C25    | C7     | 1.483(3)   | C28    | S002   | 1.727(4)   |
| C7     | C34    | 1.36(1)    | S002   | C14    | 1.722(2)   |
| C34    | C29    | 1.52(1)    | C19    | C8     | 1.434(3)   |
| C29    | C6     | 1.335(3)   | C8     | C2     | 1.201(3)   |
| C6     | S006   | 1.615(4)   | C2     | C16    | 1.423(3)   |
| S006   | C7     | 1.693(4)   | C16    | C1     | 1.38(1)    |
| C18    | C3     | 1.479(3)   | C1     | C10    | 1.44(1)    |
| C3     | C21    | 1.392(3)   | C10    | C31    | 1.331(4)   |
| C21    | C9     | 1.419(3)   | C31    | S004   | 1.668(3)   |
| C9     | C11    | 1.354(3)   | S004   | C16    | 1.707(3)   |
| C11    | S001   | 1.714(2)   | C26    | C4     | 1.437(3)   |
| S001   | C3     | 1.736(2)   | C4     | C17    | 1.204(3)   |
| C24    | C12    | 1.486(3)   | C17    | C13    | 1.421(3)   |
| C12    | C38    | 1.25(1)    | C13    | C35    | 1.36(1)    |
| C38    | C30    | 1.53(1)    | C35    | C32    | 1.42(1)    |
| C30    | C5     | 1.333(4)   | C32    | C33    | 1.36(1)    |
| C5     | S005   | 1.667(3)   | C33    | S003   | 1.724(5)   |
| S005   | C12    | 1.715(3)   | S003   | C13    | 1.714(3)   |

Table S1c  Selected angles of precursor 8.

| Atom 1 | Atom 2 | Atom 3   | Angle (deg.) |
|--------|--------|----------|--------------|
| C24    | C26    | C4       | 116.5(2)     |
| C26    | C4     | C17      | 170.9(2)     |
| C4     | C17    | C13      | 175.5(2)     |
| C17    | C13    | C35      | 126.0(6)     |
| C24    | C20    | C22      | 118.9(2)     |
| C20    | C22    | C15      | 177.2(2)     |
| C22    | C15    | C14      | 178.4(2)     |
| C15    | C14    | C23      | 127.3(5)     |
| C18    | C19    | C8       | 120.7(2)     |
| C19    | C8     | C2       | 177.9(2)     |
| C8     | C2     | C16      | 179.5(2)     |
| C2     | C16    | C1       | 129.5(5)     |
Table S1d  Selected torsion angles of precursor 8.

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Torsion (deg.) |
|--------|--------|--------|--------|----------------|
| C19    | C18    | C3     | S001   | -48.0(2)       |
| C19    | C25    | C7     | S006   | -63.0(3)       |
| C26    | C24    | C12    | S005   | -81.3(2)       |
| C25    | C19    | C16    | S004   | 18.4(2)        |
| C25    | C20    | C14    | S002   | 27.1(2)        |
| C18    | C26    | C13    | S003   | -18.9(2)       |

Figure S10b  Packing mode of 8 perpendicular (a) and parallel (b) to the [-5 2 7] plane. Intermolecular interactions have been analysed (see also table S1e): S-S and C-H atomic contacts at distances below van der Waals radii are labelled with cyan and green dotted lines, respectively. Distances between the planes in b) are 4.045 Å.

Table S1e  Intermolecular short contacts, below van der Waals radii, of 8.

| Atom Mol. 1 | Atom Mol. 2 | Length (Å) | Mol. 1   | Mol. 2   |
|-------------|-------------|------------|----------|----------|
| S003        | S005        | 3.543      | x,y,z    | x,-1+y,z |
| H21         | C22         | 2.807      | x,y,z    | x,-1+y,z |
| S004        | S006        | 3.288      | x,y,z    | 1-x,y,1/2-z |
| S006        | S001        | 3.554      | x,y,z    | x,1-y,-1/2+z |
| H27         | C17         | 2.830      | x,y,z    | x,2-y,-1/2+z |
Intramolecular short contacts in hexasubstituted benzene derivative 8 (see also table S1f): Short atomic (C-C and C-S) contacts below van der Waals radii are labelled in cyan. The interactions between ipso-C atoms are highlighted with magenta lines (a). The toroidal short-contact topology is sketched in (b).

Table S1f  Intramolecular short contacts, below van der Waals radii, of 8.

| Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|
| C8     | C3     | 2.923      |
| C3     | C4     | 2.933      |
| C4     | C12    | 2.814      |
| C12    | C22    | 2.827      |
| C22    | C7     | 2.871      |
| C7     | C8     | 2.864      |
| S001   | C2     | 3.455      |
| S001   | C8     | 3.111      |
| S006   | C8     | 3.234      |
| C4     | C21    | 3.034      |
| C12    | C17    | 3.382      |
| C22    | C34    | 3.196      |
| C22    | C38    | 3.338      |
**Table S2a** Crystallographic data of 9 (CCDC number: 1884754)

| Bond precision: | C-C = 0.0042 Å | Wavelength=1.54184 |
|----------------|----------------|-------------------|
| **Cell:**      |                |                   |
| a             | 13.0074(6)     | b=18.8041(7)      |
| alpha         | 104.484(4)     | beta=97.403(4)    |
| c             | 20.8851(9)     | gamma=92.008(4)   |
| Temperature:  | 150 K          |                   |
| Volume        | Calculated     | Reported          |
|               | 4892.7(4)      | 4892.7(4)         |
| Space group   | P 1            | P 1               |
| Hall group    | -P 1           | -P 1              |
| Moiety formula| C119.97 H77.97 S6 [+solvent] | C119.97 H77.97 S5.99 |
| Sum formula   | C119.97 H77.97 S6 [+solvent] | C119.97 H77.97 S5.99 |
| Mr            | 1711.55        | 1711.47           |
| D,μ (cm⁻³)    | 1.162          | 1.162             |
| Z             | 2              | 2                 |
| Mu (mm⁻³)     | 1.660          | 1.660             |
| F000          | 1787.3         | 1787.0            |
| F000'         | 1795.49        |                   |
| h,k,lmax      | 16,23,26       | 16,23,26          |
| Nref          | 19951          | 19155             |
| Tmin,Tmax     | 0.773,0.847    | 0.621,1.000       |
| Tmin'         | 0.694          |                   |

Correction method= # Reported | T Limits: Tmin=0.621 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.960 | Theta(max)= 74.256
R(reflections)= 0.0808( 13890) | wR2(reflections)= 0.2644( 19155)
S = 1.106 | Npar= 1960

**Figure S11** Molecular structure of dendrimer 9 with ellipsoids at 50% probability for heavy atoms (a): each penta(hetero)arylphenyl unit has been distinctly coloured. Labelled molecular structure of 9 depicted in two images for clarity: central phenyl ring with two 2-thienyl groups and one penta(hetero)arylphenyl unit (b) and central phenyl ring with the remaining two penta(hetero)arylphenyl units and 2-thienyl group (c). For clarity also, only one of the two disordered molecules (cis-trans isomerization at certain thiophene rings) is illustrated and hydrogen atoms and ellipsoids have been avoided.
Table S2b Selected bond distances of 9.

| Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|
| C12    | C37    | 1.486(4)   |
| C29    | C33    | 1.490(4)   |
| C18    | C38    | 1.507(5)   |
| C17    | C4     | 1.506(5)   |
| C45    | C35    | 1.515(4)   |
| C15    | C14    | 1.501(4)   |
| C53    | C35    | 1.472      |
| C86    | C53    | 1.332      |
| C42    | C86    | 1.452      |
| C43    | C42    | 1.312      |
| C44    | C43    | 1.511      |
| C35    | C44    | 1.351      |
| C21    | C4     | 1.394(4)   |
| C19    | C21    | 1.472      |
| C16    | C19    | 1.353      |
| C13    | C16    | 1.473      |
| C41    | C13    | 1.324      |
| C4     | C41    | 1.472      |
| C27    | C14    | 1.472      |
| C36    | C27    | 1.312      |

| Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|
| C24    | C36    | 1.472      |
| C52    | C24    | 1.352      |
| C32    | C52    | 1.502      |
| C14    | C32    | 1.342      |
| C17    | C12    | 1.415(4)   |
| C29    | C17    | 1.417(4)   |
| C45    | C29    | 1.420(5)   |
| C18    | C45    | 1.410(4)   |
| C15    | C18    | 1.412(4)   |
| C12    | C15    | 1.416(5)   |
| C33    | C3     | 1.321      |
| C3     | C67    | 1.542      |
| C67    | C73    | 1.343      |
| C73    | S4     | 1.502      |
| C4     | S4     | 1.342(5)   |
| C3     | C33    | 1.742(5)   |
| C3     | C3     | 1.312      |
| C1     | C48    | 1.483      |
| C4     | C48    | 1.343      |
| C4     | C74    | 1.343      |
| C74    | S6CA   | 1.722      |
| S6CA   | C38    | 1.788(5)   |

Table S2c Selected torsion angles of 9.

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Torsion (deg.) |
|--------|--------|--------|--------|----------------|
| C15    | C12    | C37    | S0AA   | -40.5(4)       |
| C45    | C29    | C33    | S4     | -45.0(4)       |
| C45    | C18    | C38    | S6CA   | -43.1(4)       |
| C29    | C17    | C4     | C21    | -71.9(4)       |
| C4     | C41    | C28    | S1     | -80.2          |
| C41    | C13    | C20    | C91    | -70.2          |
| C13    | C16    | C5     | C26    | -57.3          |
| C16    | C19    | C11    | C6     | -59.2          |
| C19    | C21    | C25    | C120   | -66.5(8)       |
| C29    | C45    | C35    | C44    | -66.5(8)       |
| C35    | C44    | C58    | S9     | -63.2          |
| C44    | C43    | C57    | C68    | -68.1(1)       |
| C43    | C42    | C51    | C100   | -63.2          |
| C42    | C86    | C61    | C70    | -65.2          |
| C86    | C53    | C54    | C49    | -62.3          |
| C12    | C15    | C14    | C27    | -76.7(9)       |
| C14    | C27    | C62    | S0BA   | -81.1(1)       |
| C27    | C36    | C39    | C46    | -51.3(3)       |
| C36    | C24    | C142   | C63    | -66.2          |
| C24    | C52    | C102   | C104   | -67.2          |
| C52    | C32    | C40    | C30    | -65.3          |
Table S2d  Intermolecular short contacts, below van der Waals radii, of 9.

| Atom Mol. 1 | Atom Mol. 2 | Length  | Mol. 1   | Mol. 2   |
|-------------|-------------|---------|----------|----------|
| C97         | H96         | 2.736   | x,y,z    | -1+x,y,z |
| H118        | C83         | 2.776   | x,y,z    | -1+x,y,z |
| H98         | C75         | 2.887   | x,y,z    | -x,1+y,z |
| C22         | H95         | 2.796   | x,y,z    | -x,-y,1-z|
| H30         | H117        | 2.387   | x,y,z    | -x,1-y,1-z|
| H68         | H107        | 2.309   | x,y,z    | -x,1-y,1-z|
| C117        | H117        | 2.880   | x,y,z    | -x,1-y,1-z|
| H117        | H117        | 2.261   | x,y,z    | -x,1-y,1-z|
| H8          | C93         | 2.854   | x,y,z    | 1-x,-y,2-z|
| C48         | C82         | 3.395   | x,y,z    | 1-x,1-y,1-z|
| H48         | C82         | 2.523   | x,y,z    | 1-x,1-y,1-z|
| H63         | C82         | 2.857   | x,y,z    | 1-x,-y,1-z|
| C74         | H114        | 2.347   | x,y,z    | 1-x,1-y,1-z|

Table S2e  Intramolecular short contacts, below van der Waals radii, between ipso-C atoms of 9.

| Atom1  | Atom2  | Length (Å) |
|--------|--------|------------|
| C62    | C39    | 2.93(2)    |
| C39    | C142   | 2.74(3)    |
| C142   | C102   | 3.09(3)    |
| C102   | C40    | 2.84(2)    |
| C40    | C15    | 2.95(2)    |
| C15    | C62    | 2.939(6)   |
| C14    | C37    | 2.908(5)   |
| C37    | C4     | 2.900(4)   |
| C4     | C33    | 2.907(4)   |
| C33    | C35    | 2.919(5)   |
| C35    | C38    | 2.942(4)   |
| C38    | C14    | 2.921(4)   |
| C45    | C54    | 3.04(3)    |
| C54    | C61    | 2.87(3)    |
| C61    | C51    | 2.81(1)    |
| C51    | C57    | 3.00(1)    |
| C57    | C58    | 2.81(2)    |
| C58    | C45    | 2.93(2)    |
| C17    | C28    | 3.00(3)    |
| C28    | C20    | 2.72(4)    |
| C20    | C5     | 3.02(3)    |
| C5     | C11    | 2.92(4)    |
| C11    | C25    | 2.839(8)   |
| C17    | C25    | 2.985(4)   |
Table S2f  Intramolecular short contacts, below van der Waals radii, of 9 excluding contacts between \textit{ipso}-C atoms.

| Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|
| C1     | C14    | 2.976      |
| C1     | C32    | 3.258      |
| C1     | C49    | 3.162      |
| C2     | C4     | 2.926      |
| C2     | C21    | 3.391      |
| C2     | C41    | 3.270      |
| C3     | C4     | 2.942      |
| C3     | C21    | 3.158      |
| C3     | C120   | 3.366      |
| C5     | C6     | 3.142      |
| C5     | C94    | 3.175      |
| C6     | C22    | 3.336      |
| C10    | C25    | 3.116      |
| C11    | C22    | 3.032      |
| C11    | C120   | 3.009      |
| C12    | C28    | 3.302      |
| C12    | C62    | 3.306      |
| C15    | C84    | 3.262      |
| C17    | C34    | 3.284      |
| C18    | C40    | 3.257      |
| C18    | C54    | 3.298      |
| C20    | C26    | 3.136      |
| C20    | C89    | 3.054      |
| C21    | C33    | 3.241      |
| C23    | C45    | 3.390      |
| C25    | C29    | 3.333      |
| C25    | C33    | 3.248      |
| C27    | C37    | 3.383      |
| C28    | C37    | 3.244      |
| C28    | C91    | 3.059      |
| C29    | C58    | 3.277      |
| C30    | C38    | 3.175      |
| C30    | C102   | 3.226      |
| C32    | C38    | 3.276      |
| C33    | C44    | 3.171      |
| C33    | C58    | 3.298      |
| C33    | C120   | 3.275      |
| C37    | C41    | 3.305      |
| C37    | C62    | 3.340      |
| C37    | C89    | 3.344      |
| C38    | C40    | 3.182      |
| C38    | C49    | 3.239      |
| C38    | C53    | 3.291      |

| Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|
| C38    | C54    | 3.209      |
| C39    | C63    | 2.956      |
| C39    | C109   | 3.216      |
| C40    | C103   | 3.272      |
| C46    | C62    | 3.118      |
| C47    | C57    | 3.020      |
| C47    | C68    | 3.350      |
| C49    | C61    | 3.033      |
| C50    | C61    | 3.298      |
| C51    | C66    | 3.199      |
| C51    | C70    | 3.127      |
| C54    | C80    | 3.191      |
| C55    | C63    | 3.361      |
| C55    | C142   | 2.941      |
| C57    | C100   | 3.205      |
| C58    | C68    | 3.093      |
| C73    | C120   | 3.364      |
| C84    | C103   | 3.318      |
| C89    | C94    | 3.328      |
| C99    | C102   | 3.032      |
| C99    | C104   | 3.231      |
| C108   | C113   | 3.243      |
| S0AA   | C14    | 2.962      |
| S0AA   | C27    | 3.438      |
| S0AA   | C32    | 3.176      |
| S0AA   | C89    | 3.241      |
| S4     | C35    | 2.980      |
| S4     | C44    | 3.271      |
| S4     | C53    | 3.329      |
| S4     | C120   | 3.258      |
| S9     | C45    | 3.415      |
| S9     | C108   | 3.351      |
| S9     | C118   | 3.413      |
| C15    | S0BA   | 3.420      |
| C30    | S6CA   | 3.144      |
| C35    | S6CA   | 2.955      |
| C44    | S6CA   | 3.298      |
| C53    | S6CA   | 3.346      |
| C79    | S1     | 3.282      |
| C91    | S1     | 3.469      |
| S1     | C112   | 3.378      |
| S0BA   | C115   | 3.326      |
| S0BA   | C116   | 3.235      |
**Table S3a**  Crystallographic data of 14 (CCDC number: 1884744)

| Bond precision: | C-C = 0.0030 Å | Wavelength=1.54184 |
|-----------------|----------------|--------------------|
| Cell:           |                |                    |
| a=9.5703(4)     | b=11.4821(4)   | c=19.3739(5)       |
| alpha=102.118(3)| beta=96.605(3)| gamma=98.016(3)   |
| Temperature:    |                |                    |
| 150 K           |                |                    |
| Volume          |                |                    |
| Calculated      | 2038.14(13)    | Reported           |
| Reported        | 2038.14(12)    |                    |
| Space group     | P -1           | P -1               |
| Hall group      | -P 1           | -P 1               |
| Moiety formula  | C48 H24 S8     | C48 H24 S8         |
| Sum formula     | C48 H24 S8     | C48 H24 S8         |
| Mr              | 857.15         | 857.15             |
| Dx, g cm⁻³      | 1.397          | 1.397              |
| Z               | 2              | 2                  |
| Mu (mm⁻¹)       | 4.327          | 4.327              |
| F000            | 880.0          | 880.0              |
| F000’           | 887.04         |                    |
| h,k,lmax        | 11,14,24       | 11,14,23           |
| Nref            | 8291           | 8009               |
| Tmin, Tmax      | 0.390,0.510    | 0.487,0.653        |
| Tmin’           | 0.295          |                    |

Correction method= # Reported T Limits: Tmin=0.487 Tmax=0.653
AbsCorr = GAUSSIAN

Data completeness= 0.966
R(reflections)= 0.0457( 7227)
S = 1.026

Theta(max)= 74.214
wR2(reflections)= 0.1303( 8009)
Npar= 727

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**Figure S12a**  Labelled molecular structure from the crystal structure analysis of compound 14 depicted in two images for clarity: central phenyl ring with three 2-thienyl and two 2-thienylethynyl groups (a) and the 7-benzothiophene unit (b). For clarity also, only one of the two disordered molecules (cis-trans isomerization at certain thiophene rings) is illustrated. Ellipsoids for non-hydrogen atoms are shown at 50% probability.
Table S3b  Selected bond distances of 14.

| Atom 1 | Atom 2 | Length (Å) | Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|--------|--------|------------|
| C2BA   | C27    | 1.407(3)   | C23    | C25    | 1.196(3)   |
| C27    | C28    | 1.414(3)   | C25    | C36    | 1.408(3)   |
| C28    | C29    | 1.400(2)   | C36    | C1AA   | 1.56(2)    |
| C29    | C22    | 1.401(3)   | C1AA   | C6     | 1.47(1)    |
| C22    | C6AA   | 1.414(3)   | C6     | C5     | 1.34(1)    |
| C6AA   | C2BA   | 1.412(3)   | C5     | S6BA   | 1.702(8)   |
| C2BA   | C30    | 1.480(3)   | S6BA   | C36    | 1.626(4)   |
| C30    | C9AA   | 1.345(6)   | C29    | C5AA   | 1.494(3)   |
| C9AA   | C47    | 1.41(1)    | C5AA   | C21    | 1.424(3)   |
| C47    | C42    | 1.36(1)    | C21    | C24    | 1.386(3)   |
| C42    | S3BA   | 1.712(5)   | C24    | C38    | 1.388(3)   |
| S3BA   | C30    | 1.736(3)   | C38    | C3AA   | 1.412(3)   |
| C28    | C39    | 1.478(3)   | C3AA   | C3AA   | 1.426(3)   |
| C39    | C2AA   | 1.47(2)    | C3AA   | C8AA   | 1.397(3)   |
| C2AA   | C3     | 1.46(2)    | C3AA   | C5AA   | 1.424(3)   |
| C3     | C2     | 1.335(9)   | C3AA   | C0BA   | 1.433(3)   |
| C2     | S4BA   | 1.710(6)   | C3AA   | C0BA   | 1.351(3)   |
| S4BA   | C39    | 1.661(3)   | C0BA   | C35    | 1.722(2)   |
| C22    | C32    | 1.483(3)   | C35    | S1BA   | 1.720(2)   |
| C32    | C26    | 1.452(8)   | S1BA   | C38    | 1.730(2)   |
| C26    | C7     | 1.44(1)    | C8AA   | C41    | 1.481(3)   |
| C7     | C49    | 1.34(2)    | C41    | C33    | 1.365(3)   |
| C49    | S7BA   | 1.69(1)    | C33    | C45    | 1.419(3)   |
| S7BA   | C32    | 1.670(4)   | C45    | C44    | 1.350(4)   |
| C6AA   | C7AA   | 1.430(3)   | C44    | S0AA   | 1.715(2)   |
| C7AA   | C31    | 1.196(3)   | S0AA   | C41    | 1.736(2)   |
| C31    | C37    | 1.413(3)   | C21    | C34    | 1.429(3)   |
| C37    | C4AA   | 1.357(8)   | C34    | C43    | 1.198(3)   |
| C4AA   | C40    | 1.41(1)    | C43    | C46    | 1.417(3)   |
| C40    | C51    | 1.35(1)    | C46    | C9BA   | 1.38(1)    |
| C51    | S5BA   | 1.715(9)   | C9BA   | C1     | 1.40(3)    |
| S5BA   | C37    | 1.715(3)   | C1     | C48    | 1.36(3)    |
| C27    | C23    | 1.429(3)   | C48    | S8BA   | 1.71(2)    |
|        |        |            |        |        | S8BA      | 1.683(4)   |
Table S3c  Selected bond angles of 14.

| Atom 1 | Atom 2 | Atom 3 | Angle (deg.) |
|--------|--------|--------|--------------|
| C2BA   | C6AA   | C7AA   | 119.7(2)     |
| C6AA   | C7AA   | C31    | 178.6(2)     |
| C7AA   | C31    | C37    | 177.0(2)     |
| C28    | C27    | C23    | 118.1(2)     |
| C27    | C23    | C25    | 173.7(2)     |
| C23    | C25    | C36    | 178.0(2)     |
| C5AA   | C21    | C34    | 118.1(2)     |
| C21    | C34    | C43    | 174.3(2)     |
| C34    | C43    | C46    | 173.8(2)     |

Table S3d  Selected torsion angles of 14.

| Atom 1 | Atom 2 | Atom 3 | Atom 4  | Torsion (deg.) |
|--------|--------|--------|---------|----------------|
| C29    | C28    | C39    | S4BA    | 83.3(3)        |
| C6AA   | C2BA   | C30    | S3BA    | 55.5(3)        |
| C6AA   | C22    | C32    | S7BA    | 76.1(3)        |
| C2BA   | C6AA   | C37    | S5BA    | -25.4(2)       |
| C2BA   | C27    | C36    | S6BA    | -17.1(3)       |
| C22    | C29    | C5AA   | C21     | -85.3(2)       |
| C5AA   | CBA    | C41    | S0AA    | -49.3(3)       |
| C5AA   | C21    | C46    | S8BA    | 7.0(2)         |

Figure S12b  Packing mode of 14: perpendicular (a) and parallel (b) to the [9 -4 4] plane. Intermolecular contacts observed between atoms at distances below van der Waals radii are labelled by dotted cyan lines (see also table S3e). The out-of-plane pending 7-benzo[b]thiophene units have been foggy up for clarity. Ellipsoids for non-hydrogen atoms are shown at 50% probability in a) and are omitted in b) for clarity.
### Table S3e  Intermolecular short contacts, below van der Waals radii, of 14.

| Atom 1 | Atom 2 | Length (Å) | Mol. 1 | Mol. 2 |
|--------|--------|------------|--------|--------|
| H1     | C31    | 2.786      | x,y,z  | -1+x,y,z |
| H35    | C23    | 2.753      | x,y,z  | x,-1+y,z |
| H35    | C25    | 2.886      | x,y,z  | x,-1+y,z |
| H7     | C31    | 2.753      | x,y,z  | -x,-y,-1-z |
| S1BA   | C1AA   | 3.491      | x,y,z  | x,-y,-z  |
| S1BA   | H1AA   | 2.891      | x,y,z  | x,-y,-z  |
| H2AA   | C6     | 2.858      | x,y,z  | -x,1-y,-z |
| S7BA   | C40    | 3.457      | x,y,z  | 1-x,-y,-1-z |
| S7BA   | H40    | 2.962      | x,y,z  | 1-x,-y,-1-z |
| S4BA   | H45    | 2.984      | x,y,z  | 1-x,-y,-z  |
| S0AA   | H5     | 2.935      | x,y,z  | 1-x,1-y,-z |
| H5     | C44    | 2.847      | x,y,z  | 1-x,1-y,-z |

### Table S3f  Intramolecular short contacts, below van der Waals radii, of 14.

| Atom 1 | Atom 2 | Length (Å) |
|--------|--------|------------|
| C30    | C23    | 2.894      |
| C23    | C39    | 2.802      |
| C39    | C5AA   | 2.888      |
| C5AA   | C32    | 2.962      |
| C32    | C7AA   | 2.815      |
| C7AA   | C30    | 2.893      |
| S0AA   | S7BA   | 3.402      |
| S0AA   | C22    | 3.409      |
| S0AA   | C29    | 3.215      |
| S3BA   | C7AA   | 3.176      |
| S3BA   | S8BA   | 3.523      |
| C26    | C7AA   | 3.399      |
| C0BA   | C33    | 3.174      |
| C2AA   | C23    | 3.250      |
| C7AA   | S7BA   | 3.419      |
| C9AA   | C23    | 3.065      |
| C22    | C34    | 3.290      |
| C28    | C34    | 3.340      |
| C29    | C43    | 3.368      |
Figure S12c  Intramolecular short contacts in 14 (see also table S3f): Short atomic (C-C and C-S) contacts below van der Waals radii are labelled in cyan. The interactions between ipso-C atoms are highlighted with magenta lines.

Electrochemistry of thienylene-phenylenes 8 and 9

Figure S13  Cyclic voltammograms of precursor 8 (black curve) and dendrimer 9 (blue curve) measured in DCM at r.t., tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M), scan speed 100 mV/s, c= 5⋅10⁻⁴ mol/L, potentials vs ferrocene/ferricenium (Fc/Fc⁺).