Synthesis of "V-Shaped" *syn*-Bidentate Ligands Based on Mesitylene-Derived [1.1.1.1]Metacyclophane Blocked in a 1,3-Alternate Conformation

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A series of five new *syn*-bidentate ligands **14**–**18** based on the [1.1.1.1]metacyclophane backbone blocked in a 1,3-alternate conformation was achieved. The common building block for the preparation of ligands bearing two interaction sites located in a *syn* fashion (CN, SMe, *p*-pyridyl, *p*-methoxyphenyl and *p*-methylthiophenyl) is the dibromo derivative **12**. All reported ligands were fully characterised by classical analytical methods and their 1,3-alternate conformation demonstrated.

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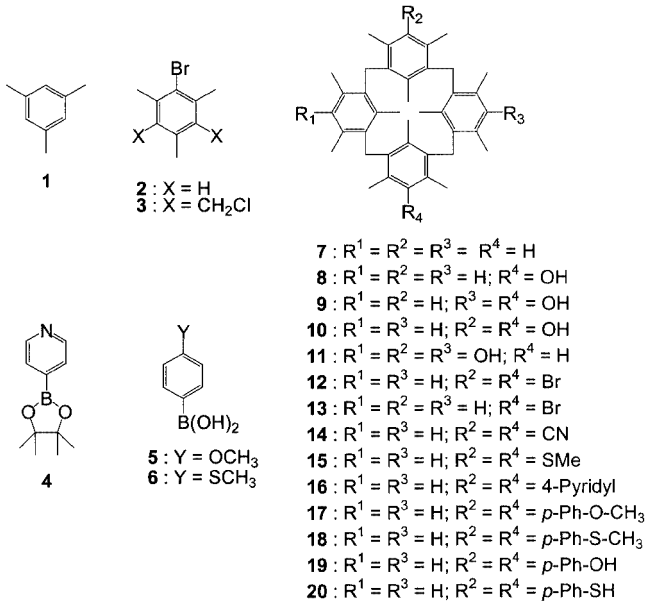
Introduction

Molecular tectonics[1,2] is an area of chemical research dealing with the formation of molecular networks based on the self-assembly of molecular tectons[3,4] (active molecular building blocks). The formation of molecular networks with predicted connectivity and topology, i.e. periodic infinite molecular assemblies based on the translation of recognition patterns, relies on the design of molecular tectons bearing within their structure the information (recognition and iteration) guiding the self-assembly processes. Over the last decade, we have been concerned with the design of tectons and their use in the formation of a variety of molecular networks based on inclusion phenomena[5] and hydrogen-[6−8] or coordination bonding.[9−11]

In a continuation of our approach to the design of molecular networks, we report here the design and synthesis of a series of five new tectons **14**−**18** (Scheme 1) based on the [1.1.1.1]metacyclophane **A** (Scheme 2).

For the design of tectons **14**−**18** (Scheme 1), we though that we could take advantage of the thermally stable 1,3-alternate conformation adopted by the cyclophane **A** (Scheme 2). Indeed, this compound is an interesting backbone since it allows the positioning of up to four interaction sites in an alternate fashion above and below the main plane of the cyclophane (see Scheme 1). Since in order to allow iteration of the assembling processes a tecton, by definition, must possess at least two interaction sites oriented



Scheme 1

in a divergent fashion, the mono-functionalised cyclophane **B** is of no interest in the context of the generation of molecular networks. The other derivatives **C**−**F**, however, are of interest in this context. We have previously reported the synthesis of the tetrasubstituted cyclophane derivatives **F** bearing a variety of interaction sites occupying the apices of a pseudo tetrahedron.[12] Furthermore, we have demonstrated the ability of some of the reported tectons to generate well-defined and predicted 1-,[13] 2-[14] and 3-D[15] molecular networks in the solid state in the presence of appropriate metal ions.

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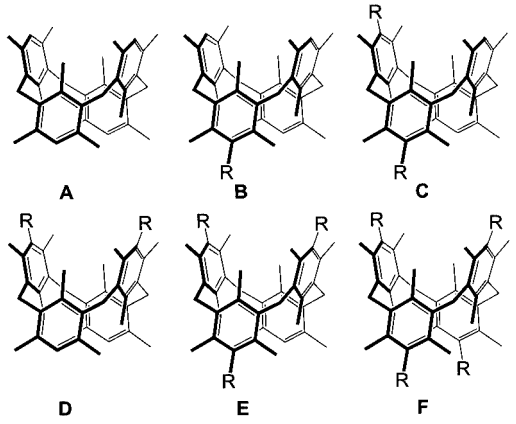

Scheme 2

The disubstitution of the backbone **A** can, in principle, generate the two positional isomers **C** and **D**. Whereas for the **C** isomer the functionalisation of the two adjacent aromatic moieties leads to the positioning of the two interaction sites in a divergent manner, i.e. one located above and the other below the main plane of the cyclophane backbone, for the other isomer **D**, obtained upon substitution of the two distal aromatic rings, the two interaction sites are convergently oriented on the same face of the backbone. The trisubstituted derivative **E** bears three interaction sites located one on one face and two on the other face of the cyclophane. Both isomers **C** and **D**, as well as the trisubstituted derivative **E**, are of interest for the formation of either discrete species of the metallamacrocycle type or of infinite coordination networks in the presence of metal centers.

Results and Discussion

The synthesis of compounds **14**−**18** was based on the use of the dibromo derivative **12** as the common starting material. The synthesis of compound **12** was attempted following the strategy reported for the preparation of disubstituted compound **10** bearing two distal hydroxy groups.[16] The $SnCl_4$-catalysed reaction of equimolar amounts of the commercially available mesitylene (**1**) and 3,5-bis(chloromethyl)-2,4,6-trimethylbromobenzene (**3**), prepared from bromomesitylene (**2**),[12] in nitroethane at room temperature and under argon, produced, within 12 h, a copious precipitate. This observation is in agreement with the previously reported procedure dealing with the synthesis of the dihydroxy derivative **10**.[16] Indeed, it has been observed that the precipitate obtained in that case contains a mixture of compounds **7**−**11**, bearing from zero to three hydroxy groups. The presence of compounds other than **10** can be explained by the reversible nature of the Friedel−Crafts reaction leading to the formation of the C−C bonds. Interestingly, for the reaction of **3** with mesitylene, the precipitate contains only a 5:1 mixture (determined by ^{1}H NMR spectroscopy) of the monobromo derivative **13** and the dibromo compound **12** of the **D** type. No trace of the disubstituted derivative of the **C** type was observed. Unfortunately, the purification of the mixture appeared to be very tedious since no separation between **12** and **13** could be achieved using thin layer chromatography. Fortunately, since compound **12** is less soluble in THF than the monosubstituted compound **13**, it was found that upon stirring the mixture in a small volume of boiling THF followed by filtration of the insoluble material (operation repeated several times on the solid residue), the mixture can be enriched in the desired compound **12**. However, this procedure affords only small quantities of the pure compound **12** and does not allow the isolation of a pure sample of compound **13** for complete characterisation. Despite this difficulty, we nevertheless used the 5:1 mixture in subsequent reactions hoping that the mono- and disubstituted compounds could be separated by column chromatography. For the following transformations, the yields reported were calculated assuming that the starting mixture was mainly composed of **12**.

The ability of the compound **12** to undergo aromatic nucleophilic substitution was investigated. In a classical Rosenmund−von-Braun-type reaction,[17] the compound **14**, bearing two distal nitrile groups, was obtained in 78% yield upon treatment of **12** with CuCN in refluxing DMF. Furthermore, a bromine/lithium exchange[18] reaction was achieved upon treatment of compound **12** in THF at −78 °C with 4.4 equivalents of *t*BuLi. The quenching of the dilithio derivative with CH_3SSCH_3 afforded the disubstituted compound **15**, bearing two thiomethyl groups, in 64% yield.

The synthesis of diaryl derivatives **16**−**18** by a palladium-catalysed cross-coupling reaction was also investigated. The first targeted ligand was the compound **16** bearing two distal pyridyl groups connected at the 4-position with respect to the nitrogen atom of the pyridine ring. Compound **16** was obtained in 65% yield by a Suzuki cross-coupling reaction[19] between compound **12** and *p*-pyridylboronic ester **4**.[20] The reaction, catalysed by $Pd(PPh_3)_4$, was carried out in the presence of anhydrous Cs_2CO_3 at 130 °C in an anhydrous toluene/DMF mixture. For the synthesis of compounds **17** (65% yield) and **18** (60% yield), bearing two distal *p*-methoxyphenyl and *p*-methylthiophenyl groups, the same Suzuki palladium-catalysed cross-coupling reaction was performed in aqueous media[21] between compound **12** and the arylboronic acid derivatives **5**[22] and **6** in the presence of $Pd(PPh_3)_4$ and Na_2CO_3. In terms of the coordination ability of compounds **17** and **18**, it would have been of interest to obtain the unprotected compounds **19** and **20**. Unfortunately, all reactions reported in the literature dealing with the removal of methyl groups from methoxyphenyl[23] or methylthiophenyl[24] failed. In the case of the compound **17**, the classical deprotection reaction with BBr_3 or PPh_2Li was found to lead to the rupture of the macrocyclic backbone.

The 1,3-alternate conformation of all disubstituted compounds **12** and **14**−**18** was confirmed by ^{1}H NMR spectroscopy. Indeed, based on the symmetry of the backbone, one would expect five singlets corresponding to the *para*- and *ortho*-CH_3 groups, as well as to the H atoms belonging to the unsubstituted aromatic rings, and an AB system corresponding to the bridging methylene groups. In all cases, this

pattern was observed. However, depending on the nature of the substituent, slight differences in chemical shift were observed (see Exp. Sect.).

The 1,3-alternate conformation adopted by compound **18**, bearing two *p*-methylthiophenyl groups, was further confirmed in the solid state by X-ray diffraction of a single crystal obtained by slow diffusion of EtOH into a $CHCl_3$ solution of **18** (Figure 1). The crystal is composed solely of **18**; no solvent molecules are present in the lattice. Compound **18** indeed adopts the 1,3-alternate conformation in which the *p*-methylthiophenyl and hydrogen substituents are located in an alternate fashion above and below the main CH_2 plane of the cyclophane. The two PhSMe substituents are not perpendicular to the main plane of the cyclophane backbone but tilted towards the exterior, thus affording a "V-shaped" topology (angle of ca. 45°) for the bis-monodentate ligand. The tilting of two opposite aromatic rings of the cyclophane skeleton is not identical. Whereas the two aromatic units bearing the PhSMe substituent are tilted by ca. 115° and 112°, the other two are tilted by ca. 107° and 109° with respect to the main CH_2 plane of the cyclophane backbone. The distance between the two S atoms located on the same face of the molecule is 13.89 Å (average d_{C-S} of 1.78 Å with an average C−S−C angle of 102.9°). Owing to the steric hindrance induced by the *ortho*-methyl groups of the cyclophane skeleton, the free rotation of the *p*-methylthiophenyl moiety around the C−C bond is hindered and an average dihedral angle between the two aromatic rings of ca. 90° is observed. This blocked rotation was also observed in solution by ^1H and ^{13}C NMR spectroscopy, which revealed a non-equivalence between the protons and carbon atoms pointing towards the interior and the exterior of the cyclophane backbone.

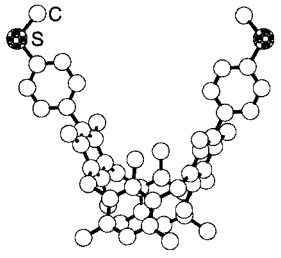

Figure 1. Crystal structure of compound **18** possessing two *p*-methylthiophenyl groups located in a distal fashion showing the 1,3-alternate conformation adopted by the cyclophane backbone; H atoms are omitted for clarity; for selected bond lengths and angles see text

Conclusion

In conclusion, a strategy leading to the synthesis of five new "V-shaped" bis-monodentate ligands based on the [1.1.1.1]metacyclophane backbone blocked in a 1,3-alternate conformation was developed. Due to the rigidity and thermal stability of the blocked 1,3-alternate conformation adopted by the cyclophane backbone, the "V-shaped" ligands reported present interesting structural features with respect to the formation of either discrete metallamacrocycles or infinite coordination networks. Work along these lines is currently being pursued.

Experimental Section

General: All commercially available reagents were used without further purification. Reaction solvents were distilled by standard methods prior to use. Compounds were purified by column chromatography on Kieselgel 60 (Merck; 43−60 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 300 MHz and at 50 MHz, respectively. Microanalyses were performed by the "Service de Microanalyses de la Fédération de Recherche Chimie", Université Louis Pasteur.

Crystal Structure Characterisation: X-ray diffraction data collection was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K_α radiation. Diffraction data were corrected for absorption and analysed using OpenMolen package.[25] All non-H atoms were refined anisotropically. CCDC-192878 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

X-ray Data for 18: Red crystals, 173 K, $C_{54}H_{60}S_2$, M = 773.21, monoclinic, a = 18.5211(3), b = 12.2319(2), c = 20.0816(3) Å, β = 108.889(5)°, U = 4304.5(1) Å^3, space group $P2_1/n$, Z = 4, D_c = 1.19 g·cm^{-3}; μ = 0.160 mm^{-1}, 5406 data with $I > 3\sigma(I)$, R = 0.067, Rw = 0.083.

Synthetic Procedures

11,25-Dibromo-4,18-dihydro-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl-[1.1.1.1]metacyclophane (12): Anhydrous $SnCl_4$ (0.5 mL) was added at room temperature to a stirred anhydrous $EtNO_2$ solution (75 mL) of **1** (2.04 g, 17 mmol) and **3** (5 g, 17 mmol),. After a few seconds a copious precipitate appeared. The resulting mixture was stirred under argon at room temperature overnight. The precipitate was then filtered and washed three times with a small cold portion of $EtNO_2$ (15 mL) and then triturated three times with MeOH (50 mL). The resulting white powder was then refluxed for 30 min in THF (50 mL) and filtered. The insoluble material was collected and the same procedure was repeated 3−4 times to afford almost pure sample of compound **12** (3.5 g, 60%) as a fine white powder. Mp > 300 °C. $C_{40}H_{46}Br_2$ (686.6): calcd. C 69.97, H 6.75; found C 69.51, H 6.93. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.13 (s, 6 H, *para*-CH_3), 1.18 (s, 6 H, *para*-CH_3), 2.33 (s, 12 H, *ortho*-CH_3), 2.61 (s, 12 H, *ortho*-CH_3), 3.91 and 4.06 (AB, J = 18 Hz, 8 H, Ar-CH_2-Ar), 6.81 (s, 2 H, *H*-Ar) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.0, 18.4, 21.3, 22.5, 33.6, 130.4, 130.5, 133.3, 133.4, 134.9, 135.5, 137.3, 138.9 ppm.

4,18-Dihydro-11,25-dicyano-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl-[1.1.1.1]metacyclophane (14): A stirred suspension of **12** (1.12 g, 1.63 mmol) and CuCN (350 mg, 3.91 mmol) in dry DMF (50 mL) was refluxed under argon for 5 h. The brownish solution was cooled to 100 °C, before a solution of $FeCl_3$ (1.65 g, 10 mmol) in 10% aqueous HCl (30 mL) was slowly added. The resulting mixture was further stirred at 100 °C for 1 h. The mixture was allowed to cool to room temperature and filtered. The brown

and sticky solid thus obtained was washed with 10% aqueous HCl (30 mL), water (30 mL) and Et_2O (3 × 50 mL) to give pure compound **14** in 78% yield (736 mg) as a white solid after chromatography (SiO_2, CH_2Cl_2). Mp > 300 °C. $C_{42}H_{46}N_2 \cdot 1.75H_2O$ (610.3): calcd. C 82.65, H 8.17, N 4.59; found C 82.77, H 7.78, N 4.46. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.07 (s, 6 H, *para*-CH_3), 1.24 (s, 6 H, *para*-CH_3), 2.34 (s, 12 H, *ortho*-CH_3), 2.63 (s, 12 H, *ortho*-CH_3), 3.85 and 3.99 (AB, *J* = 25.5 Hz, 8 H, Ar-CH_2-Ar), 6.83 (s, 2 H, *H*-Ar) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 18.3, 18.5, 19.9, 21.3, 32.1, 113.0, 130.8, 133.7, 135.1, 136.6, 137.1, 138.6, 141.3 ppm.

4,18-Dihydro-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl-11,25-dithiomethyl-[1.1.1.1]metacyclophane (15): *t*BuLi (1.7 M in pentane, 1.13 mL, 1.92 mmol) was added dropwise at −78 °C and under argon to a stirred solution of **12** (300 mg, 0.44 mmol) in dry THF (40 mL). The resulting yellow solution was stirred at −78 °C for 30 min, before neat CH_3SSCH_3 (0.2 mL, 2.18 mmol) was added and the mixture was slowly allowed to warm to room temperature (2 h.). Excess CH_3SSCH_3 was quenched with $NaBH_4$ (206 mg, 5.45 mmol) and stirring at room temperature was continued for a further 30 min. The mixture was then poured into an aqueous NaOH solution (1 M, 100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The organic layer was washed with aqueous NaOH (1 M, 100 mL), dried over $MgSO_4$ and the solvents evaporated to dryness. The resulting solid was purified by chromatography (SiO_2, CH_2Cl_2/hexane, 2:8) to afford pure **15** (174 mg) as a white solid in 64% yield. Mp > 300 °C. $C_{42}H_{52}S_2$ (621.0): calcd. C 81.23, H 8.44, S 10.33; found C 81.09, H 8.65, S 9.44. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.12 (s, 6 H, *para*-CH_3), 1.20 (s, 6 H, *para*-CH_3), 2.15 (s, 6 H, −SCH_3) 2.33 (s, 12 H, *ortho*-CH_3), 2.76 (s, 12 H, *ortho*-CH_3), 3.90 and 4.04 (AB, *J* = 17 Hz, 8 H, Ar-CH_2-Ar), 6.80 (s, 2 H, *H*-Ar) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 17.6, 18.4, 19.6, 20.1, 21.4, 33.3, 130.5, 133.1, 134.3, 135.6, 136.5, 137.6, 137.9, 138.4 ppm.

4,18-Dihydro-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl-11,25-bis(4-pyridyl)-[1.1.1.1]metacyclophane (16): The arylboronic ester **4** (990 mg, 4.8 mmol) was added in one portion to a stirred solution of **12** (1.32 g, 1.93 mmol), $Pd(PPh_3)_4$ (140 mg, 0.12 mmol) and Cs_2CO_3 (1.9 g, 5.8 mmol) in a mixture of dry toluene and DMF (1:1, v/v, 100 mL) and the mixture was degassed by argon bubbling while heating at 100 °C. The mixture was then further heated to 130 °C under argon for 48 h. The resulting mixture was cooled to room temperature and concentrated to dryness. The solid residue was dissolved in CH_2Cl_2 (150 mL) and filtered. The organic layer was washed with 5% aqueous NaOH (2 × 100 mL), dried over $MgSO_4$ and the solvents evaporated to dryness. Pure compound **16** (850 mg, 65%) was obtained as a white solid after chromatography (Al_2O_3, solid deposit, CH_2Cl_2/MeOH, 99:1). Mp > 300 °C. $C_{50}H_{54}N_2 \cdot 0.75H_2O$ (696.5): calcd. C 86.22, H 8.03, N 4.02; found C 85.82, H 7.80, N 4.24. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.24 (s, 6 H, *para*-CH_3), 1.29 (s, 6 H, *para*-CH_3), 2.04 (s, 12 H, *ortho*-CH_3), 2.36 (s, 12 H, *ortho*-CH_3), 3.93 and 4.02 (AB, *J* = 17 Hz, 8 H, Ar-CH_2-Ar), 6.83 (s, 2 H, *H*-Ar), 7.07 (d, *J* = 5 Hz, 2 H, *H*-Py), 7.09 (d, *J* = 5 Hz, 2 H, *H*-Py), 8.68 (d, *J* = 5 Hz, 2 H, *H*-Py),. 8.70 (d, *J* = 5 Hz, 2 H, *H*-Py) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 17.5, 18.4, 19.1, 21.4, 32.3, 124.9, 125.3, 130.5, 130.6, 133.3, 135.4, 135.9, 137.5, 137.9, 149.9, 150.0, 152.2 ppm.

4,18-Dihydro-11,25-bis(4-methoxyphenyl)-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl-[1.1.1.1]metacyclophane (17): The arylboronic acid **5** (2.85 g, 18.8 mmol) was added in one portion to a stirred solution of **12** (4.3 g, 6.26 mmol), $Pd(PPh_3)_4$ (434 mg, 0.37 mmol) and Na_2CO_3 (4 g, 37.7 mmol) in a mixture of toluene/EtOH/H_2O (10:3:2, v/v/v, 150 mL), degassed with argon. The mixture was then refluxed under argon for 72 h. The resulting mixture was cooled to room temperature and concentrated to dryness. The residue was dissolved in $CHCl_3$ (150 mL), the organic phase was washed with aqueous NaOH (5%, 2 × 100 mL), water (2 × 100 mL), dried with $MgSO_4$ and concentrated to dryness. Pure compound **17** (3 g, 65%) was obtained as a white solid after chromatography (SiO_2, solid deposit, CH_2Cl_2/hexane, 2:8). Mp > 300 °C. $C_{54}H_{60}O_2 \cdot 0.75CH_2Cl_2$ (804.8): calcd. C 81.71, H 7.70; found C 81.34, H 7.78. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.27 (s, 6 H, *para*-CH_3), 1.29 (s, 6 H, *para*-CH_3), 2.07 (s, 12 H, *ortho*-CH_3), 2.36 (s, 12 H, *ortho*-CH_3), 3.88 (s, 6 H, -OCH_3), 3.94 and 4.02 (AB, 2d, *J* = 17.1 Hz, 8 H, Ar-CH_2-Ar), 6.82 (s, 2 H, *H*-Ar), 6.95−7.06 (m, 8 H, *H*-Ar) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 17.5, 18.3, 19.2, 21.4, 32.5, 55.2, 113.5, 113.8, 127.7, 130.4, 130.7, 131.9, 133.1, 134.8, 135.8, 136.2, 137.4, 140.3, 157.9 ppm.

4,18-Dihydro-11,25-bis(4-methylthiophenyl)-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl-[1.1.1.1]metacyclophane (18): The arylboronic acid **6** (1.83 g, 10.9 mmol) was added in one portion to a stirred solution of **12** (2.5 g, 3.64 mmol), $Pd(PPh_3)_4$ (250 mg, 0.22 mmol) and Na_2CO_3 (2.31 g, 21.8 mmol) in a mixture of toluene/EtOH/H_2O (10:4:1, v/v/v, 150 mL), degassed with argon. The mixture was then refluxed under argon for 72 h. The resulting mixture was cooled to room temperature and concentrated to dryness. The residue was dissolved in $CHCl_3$ (150 mL), the organic phase was washed with aqueous NaOH (5%, 2 × 100 mL), water (2 × 100 mL), dried with $MgSO_4$ and concentrated to dryness. Pure compound **18** (1.7 g, 60%) was obtained as a white solid after chromatography (SiO_2, solid deposit, CH_2Cl_2/hexane, 2:8). Mp > 300 °C. $C_{54}H_{60}S_2 \cdot 0.25H_2O$ (777.7): calcd. C 83.40, H 7.84, S 8.24; found C 83.39, H 8.05, S 7.99. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.26 (s, 6 H, *para*-CH_3), 1.29 (s, 6 H, *para*-CH_3), 2.07 (s, 12 H, *ortho*-CH_3), 2.36 (s, 12 H, *ortho*-CH_3), 2.56 (s, 6 H, -SCH_3), 3.94 and 4.02 (AB, *J* = 17.1 Hz, 8 H, Ar-CH_2-Ar), 6.82 (s, 2 H, *H*−Ar), 6.98−7.07 (m, 4 H, *H*-Ar), 7.29−7.37 (m, 4 H, *H*−Ar) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 15.9, 17.5, 18.4, 19.2, 21.4, 32.4, 126.6, 129.9, 130.3, 130.4, 131.6, 133.1, 135.0, 135.7, 136.0, 137.5, 137.7, 140.0, 140.7 ppm.

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