Synthesis of *p*-Phenylene Sulfide Molecular Asterisks**

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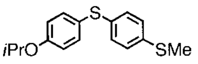
Research in supramolecular chemistry and nanotechnology has stimulated the synthesis of giant molecules with novel architectures, such as dendrimers[1] and various supramolecular systems.[2] We have developed an efficient synthesis of molecular asterisks; these lie at the interface between regular-sized molecules and macromolecules (see Scheme 1).[3] The preparations are simple and purification is relatively easy. Some molecular asterisks have a fluorescent core with interesting optical properties and are soluble in organic solvents such as $CHCl_3$, CH_2Cl_2, EtOAc, $PhCH_3$, and THF. These intriguing molecules—providing they can be appropriately functionalized—might find a variety of applications (multisite catalysis,[4] multivalent glycodendrimers,[5] fluorescent biosensors, new conductive materials,[6] etc.).

The strategy behind the synthesis of the molecular asterisks focused on three points:

1. A convergent approach was used to link the molecular wires to an aromatic core; this has facilitated the purification because the lack of one or more arms in the product led to considerable differences in the chemical properties.
2. The wires were attached to the core by a persulfuration of the arene unit, which is known as the MacNicol reaction.[7]
3. We needed wires of specific length. *p*-Phenylene sulfide oligomers were chosen because of their stability, solubility, and their conductivity after doping (important for the production of possible conductive asterisks).

Many methods are known for synthesizing poly(*p*-phenylene sulfide) polymers (PPS),[8] but PPS oligomers of definite length are rare.[9] Therefore, we developed practical syntheses of functionalized *p*-phenylene sulfide oligomers with chain lengths of two to six phenylene units, with a sulfanyl group at one end and another functional group at the other end.[10] We found that a combination of a methylsulfanyl and an isopropyloxy group was the best choice to enable the chemoselective nucleophilic deprotection of thiophenols in high yields.[10, 11]

Compound **1** was synthesized in 90% yield by the Pd-catalyzed coupling of 4-isopropyloxythiophenol to 4-bromothioanisole.[12] Demethylation of **1** with *i*PrSNa afforded the thiol **2** in 80% yield. The PPS chain with three phenylene units was synthesized in a sequence starting with the Cu_2O-promoted coupling[13] of thiophenol and 4-bromothioanisole to afford **3** (99% yield). Bromination of **3** to **4**, followed by Pd-catalyzed coupling with 4-isopropyloxythiophenol gave **5** in 75% yield (recrystallized). Demethylation with *i*PrSNa afforded **6** as a thiol (75% yield). The protected wire **7** with four phenylene groups was obtained from a Cu_2O coupling of the bromide **4** with the thiol **2** (63% yield). Demethylation of **7** with *t*BuSNa provided the thiol **8** (99% yield). Most of the PPS molecular wires are white solids. Their relative stability to oxidation and their good solubility in common solvents (CH_2Cl_2, $CHCl_3$, and toluene) make them promising building blocks in supramolecular chemistry.



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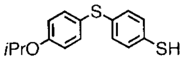

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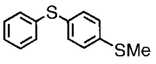

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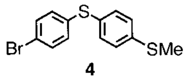

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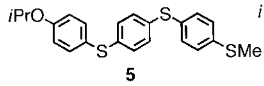

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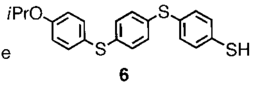

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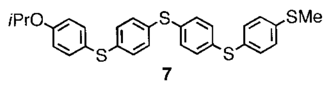

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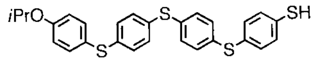

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The molecular asterisks were synthesized by applying the MacNicol reaction[7] of hexachlorobenzene (or dodecachlorocoronene[14]) and the *p*-phenylene sulfide chains **2**, **6**, and **8**; in this way we obtained functionalized molecular asterisks of second, third, and fourth generation[3] with a central aromatic core (Scheme 1a). Although the MacNicol reaction was usually carried out with a twofold excess of a thiol at 20°C, we found that the purification was not facilitated by such a large amount and the valued thiol was lost. We established that the reaction goes to completion by using a 1.5-fold excess of starting thiol relative to hexachlorobenzene at 50–60°C. The purification was greatly facilitated by simple triturations and solubility differences of the components in the crude mixture. The use of smaller amounts of thiol gave incomplete reactions. The molecular asterisks were obtained in yields of 72% (second generation), 92% (third generation), and 85% (fourth generation). They are bright yellow fluorescent solids that are highly soluble in organic solvents. ^1H (250 or 600 MHz) and ^{13}C NMR spectroscopy and elemental analyses (C, H; fourth generation) confirmed the structures and are indicative of a good purity. Mass spectrometry using secon-

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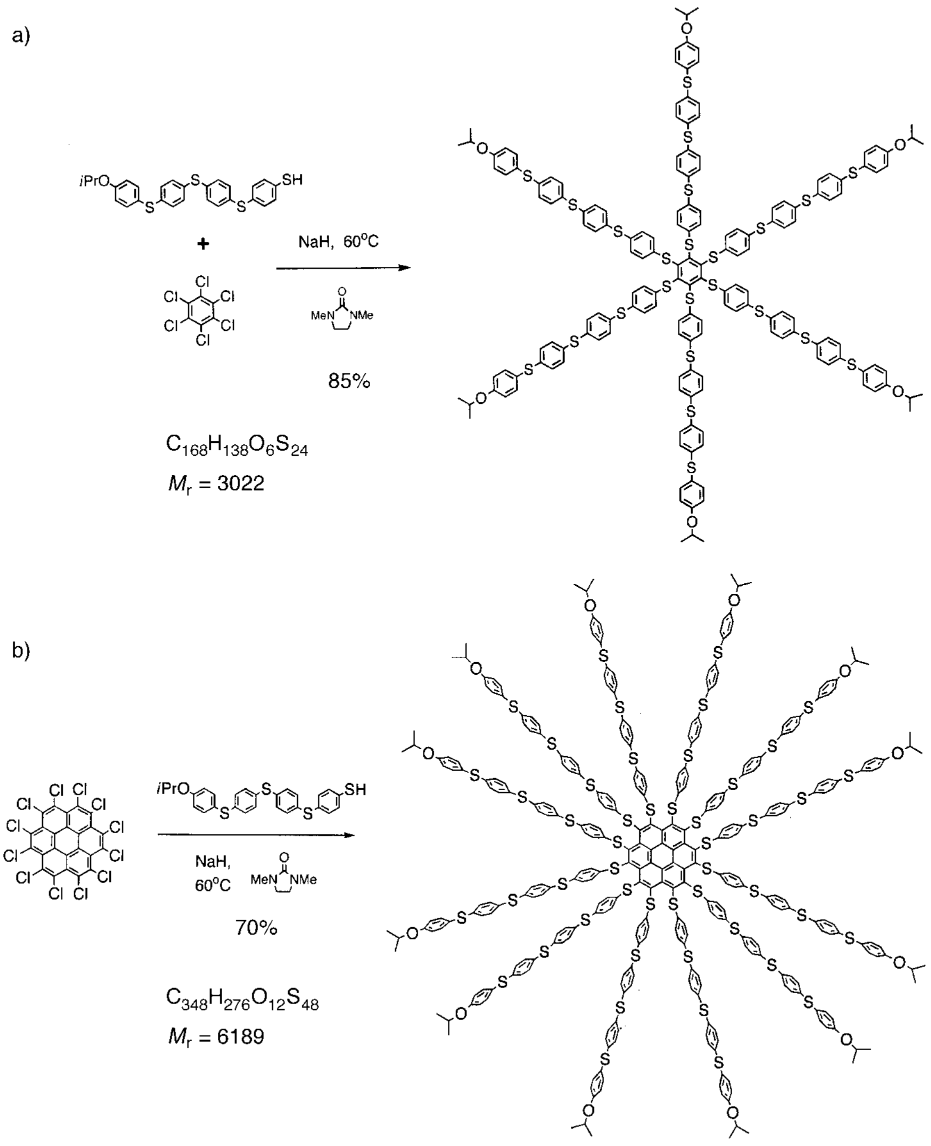

Scheme 1. a) Molecular asterisk with a benzene core; fourth generation (PPS-G4-[benzene]-O*i*Pr). b) Molecular asterisk with a coronene core—fourth generation (PPS-G4-[coronene]-O*i*Pr).

dary ion mass spectrometry (SIMS), desorption chemical ionization (DCI), and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) techniques established their molecular weight from the isotope average molecular ions found at *m*/*z* values of 1724.8 (second generation), 2371 (third generation), and 3019 (fourth generation). The stepwise loss of many side arms was observed in the MALDI-TOF spectra.

Dodecachlorocoronene reacted under optimized conditions with a slight excess of thiol (1.1-fold excess of thiol per chloro ligand) at 60 °C in 1,3-dimethyl-2-imidazolidinone (DMI) and in the presence of NaH to afford the molecular asterisks with 12 functionalized arms in yields of 95 % (second generation), 89 % (third generation), and 70 % (fourth generation) (Scheme 1 b). All of the coronene derivatives were found to be relatively air-stable deep red solids under usual conditions and were soluble in many solvents. The structures and their purity were analyzed by ^1H (250 or 600 MHz) and ^{13}C NMR spectroscopy, and elemental analyses (C, H; fourth generation). MALDI-TOF spectrometry provided the corresponding average isotope molecular ions for each coronene derivatives at *m*/*z* values of 3593 (second generation), 4893 (third generation), and 6192 (fourth generation). Again, the fragmentation of the molecular ion showed signals corresponding to a regular loss of side arms.

Physical and spectroscopic data of the molecular asterisks are given in Table 1. The UV spectra of the molecular asterisks having a benzene core displayed a weak absorption band at 334 nm (λ shoulder) corresponding to the central persulfurated core and a large maximum absorption (λ_{max}) assigned to the *p*-phenylene sulfide wires at about 280 nm. Both the difference in the relative intensities of the two absorption bands and the extinction coefficient at 280 nm increase with the number of *p*-phenylene sulfide units. Excitation at 334 nm produced a maximum fluorescence emission at about 560 nm (λ_{max}), which was negatively affected by oxygen. The quantum yields were measured relative to 9,10-diphenylanthracene ($\Phi = 1.0$)[15a] and tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate ($\Phi = 0.03$)[15b] under oxygen-free conditions.[15] Most molecular asterisks with a benzene core provided an approximate quantum yield (Φ) of 0.02. The UV spectra of the molecular asterisks with a coronene core displayed a maximum absorption band from the core at about 456 nm and an absorption band at 280 nm for the chains (λ_{max}). The extinction coefficients at 280 nm regularly increase with the generation number. No significant fluorescence was detected.

Table 1. Physical and spectroscopic data of the molecular asterisks.[a]

Core	Generation	M.p. [°C][b]	UV [λ_{max}][nm]	ε	Fluorescence [nm] [λ_{max}]	ϕ yield
benzene	2	145–146	286, 334	149000	560	–
benzene	3	119–120	278, 334	151000	517	0.02
benzene	4	90 (decomp)	280, 334	218000	525	0.02
coronene	2	151–152	288, 462	280000		
coronene	3	133–134	280, 450	285000		
coronene	4	85–86 (decomp)	278, 456	310000		

[a] All measurements were done in $CHCl_3$ at 22 °C, except for the ϕ measurements (in CH_2Cl_2). [b] Amorphous solids, not recrystallized. [c] λ(excitation) = 334 nm.

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In summary, we have created soluble PPS molecular asterisks containing a polysulfurated benzene or a coronene core. In contrast to many supramolecules, some molecular asterisks possess an active flurorescent core. Preliminary tests indicated that deprotection by BCl_3 could provide molecular asterisks with phenolic groups ready for further functionalization. Applications toward multisite catalysis,[4] dendritic conductors,[6] glycodendrimers,[5] and fluorescent biosensors are in progress. The easy electroreduction of the first-generation molecular asterisks[16a] and some wires[16b] also suggests that they could have interesting electrochemical properties and further work is also in progress in that direction.

Experimental Section

PPS-G4-[benzene]-O*i*Pr**:** Hexachlorobenzene (15.0 mg, 0.0527 mmol) and thiol **8** (234 mg, 0.475 mmol) under N_2 were placed in a dry two-necked flask. DMI (0.80 mL, over molecular sieves 3 Å) was injected by syringe. Powdered NaH 95 % (16 mg, 0.63 mmol) was weighed and placed in a lateral Gooch tube connected to the flask. Oxygen was removed by five freeze-thaw cycles with N_2. After the mixture had been cooled in an ice bath, NaH was added in small portions. The mixture turned bright yellow and stirring was continued for 30 min at 25 °C and then at 50 – 60 °C for two days. A solution of NaOH (3 M; 17 mL) was added while stirring vigorously for 10 min, followed by CH_2Cl_2 (28 mL). After separation of the organic phase, the latter was washed further with NaOH (1 M; 2 × 10 mL). After the organic phase had been dried over $MgSO_4$, filtration, followed by evaporation of the solvent gave a yellow oil. Thin-layer chromatography (EtOAc/*n*-hexane 1:4) indicated the expected yellow fluorescent product and a light impurity. Trituration in EtOH (2 × 15 mL) provided a yellow solid. This crude product was dissolved in a minimum amount of EtOAc (2 – 3 mL) and a white solid was removed by filtration. The yellow filtrate was evaporated to dryness. Repetitions of this procedure (4 or 5 times) with EtOAc ensured complete removal of the impurities. Afterwards, the yellow oil was triturared with EtOH (4 mL) to promote the precipitation of the compound PPS-G4-[benzene]-O*i*Pr as a yellow fluorescent solid (135 mg, 0.045 mmol; 85 % yield). M.p. 90 °C (decomp); TLC (SiO_2; EtOAc/*n*-hexane 1:4): $R_f = 0.32$; UV/Vis ($CHCl_3$): λ_{max} (ε) = 280 (218 000), 334 nm ; fluorescence emission (λ_{max} (CH_2Cl_2) = 525 nm); ^1H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.33$ (d, ^3J(H,H) = 6.0 Hz, 36 H; CH_3), 4.53 (sept, ^3J(H,H) = 6.0 Hz, 6 H; OCH), 6.79 (d, 12 H; J(H,H) = 8.4 Hz), 6.86 (d, 12 H, J(H,H) = 8.8 Hz), 7.03 (d, 12 H, J(H,H) = 8.4 Hz), 7.10 (d, 12 H, J(H,H) = 8.4 Hz), 7.13 (m, 24 H), 7.20 (d, 12 H, J(H,H) = 8.4 Hz), 7.37 (d, 12 H, J(H,H) = 6.4 Hz); ^{13}C NMR (62.8 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 22.0$ (CH_3), 70.1 (OCH), 116.8 (CH), 122.9 (C), 128.4 (CH), 129.1 (CH), 130.6 (CH), 131.3 (CH), 131.6 (CH), 132.6 (CH), 133.7 (C), 134.2 (C), 135.8 (CH), 136.0 (C), 136.2 (C), 139.3 (C), 147.7 (C), 158.6 (C); MALDI-TOF MS (dithranol matrix, resolution ≈3500): m/z: 3019 [M^+]; elemental analyses: calcd: C 66.76, H 4.60; found: C 66.96, H 4.61.

PPS-G4-[coronene]-O*i*Pr: The same procedure as above was followed with dodecachlorocoronene (20.7 mg, 0.0290 mmol), thiol **8** (189 mg, 0.384 mmol), and NaH (95 %; 13 mg; 0.51 mmol). After trituration with EtOH and purification, PPS-G4-[coronene]-O*i*Pr was obtained as a deep red solid (125 mg, 0.020 mmol; 70 % yield). M.p. 85 – 86 °C (decomp); TLC (SiO_2; EtOAc/*n*-hexane 3:7): $R_f = 0.4$; UV/Vis ($CHCl_3$): λ_{max} (ε) = 278 (310 000), 456 nm ; ^1H NMR (600 MHz, $CDCl_3$, 30 °C, TMS): $\delta = 1.31$ (d, ^3J(H,H) = 6.0 Hz, 72 H), 4.51 (sept, 12 H, ^3J(H,H) = 6.0 Hz), 6.3 (m, 24 H); 7.0 (d, 24 H, J(H,H) = 8.4 Hz), 6.7 – 7.2 (m, 120 H), 7.33 (m, 24 H); ^{13}C NMR (62.8 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 22.0$, 70.0, 116.8, 122.9, 127.2 – 127.7 (br.), 128.3, 130.4, 130.5 – 132.4 (br.), 132.5, 135.8, 136.1, 139.3, 158.6; MS MALDI-TOF (dithranol matrix, resolution ~3500): m/z: 6192 [M^+]; elemental analyses: calcd: C 67.54, H 4.49; found: C 67.48, H 4.30.

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