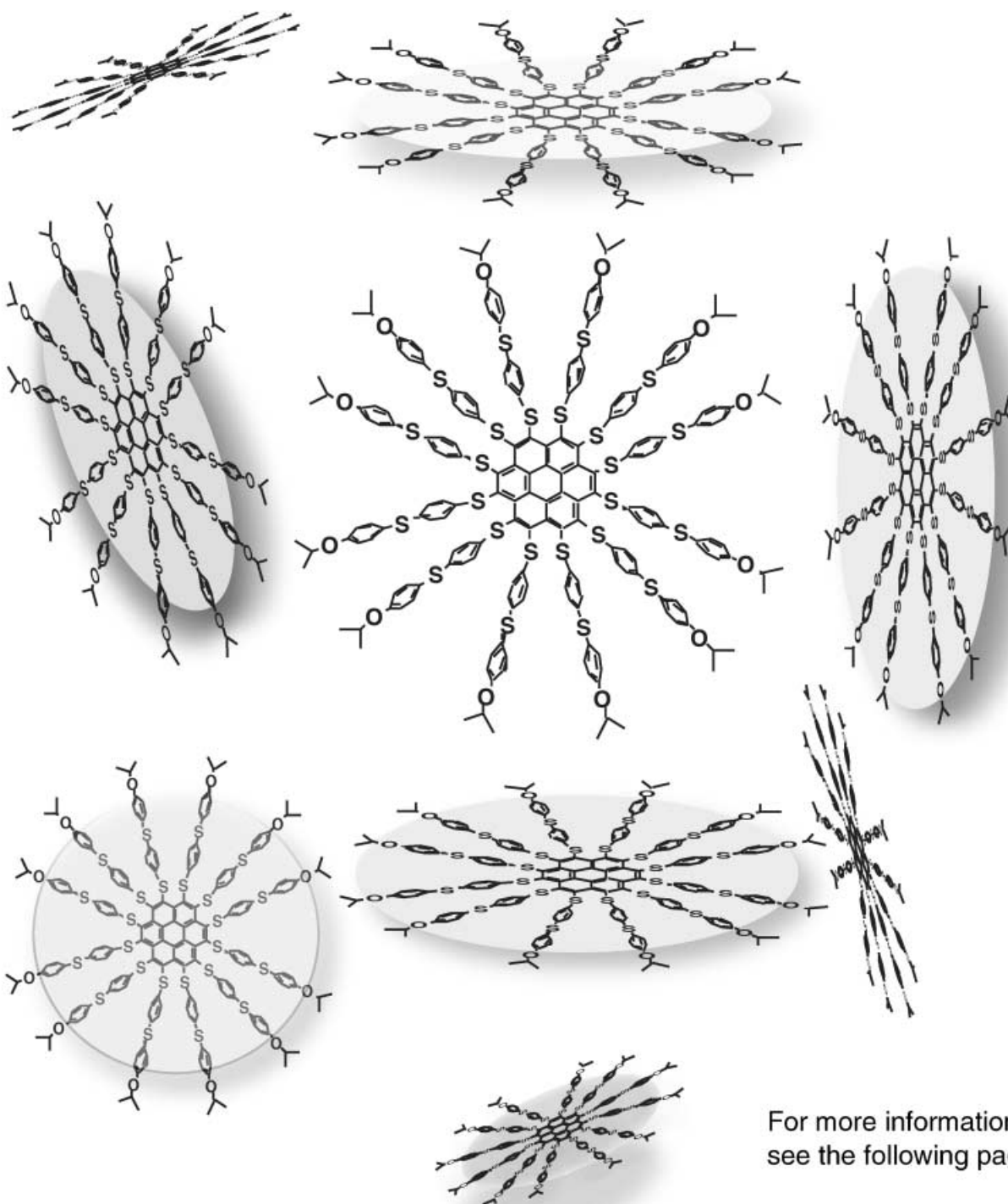


# MOLECULAR ASTERISKS



# Star-Shaped Nanomolecules Based on *p*-Phenylene Sulfide Asterisks with a Persulfurated Coronene Core

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**Abstract:** Persulfurated *p*-phenylene sulfide (PPS) molecular asterisks (6–9) from “generations” 1 to 4 were efficiently prepared. They represent a new class of electron-accepting PPS star-shaped nanomolecules. Spectroelectrochemistry, cyclic voltammetry and UV-visible studies were performed for the asterisks and for functionalized *p*-phenylene sulfide oligomers (1–4). These

data confirmed for the first time that an electronic delocalization through the whole asterisk molecule exists in the radical anionic or dianionic forms, in spite of divalent sulfur bridges be-

tween phenyl groups. They could be seen as globular spheres with a three-dimensional electronic network and delocalization. Electrochemical studies indicated that sulfur substituents strongly stabilize the reduced form of the asterisk relative to coronene itself, and the ease of reduction depends on the PPS chain length.

**Keywords:** aromatic substitution • dendrimers • electrochemistry • nanostructures • sulfur

## Introduction

At the interface of small organic compounds (<1000 Da) and polymers (>20000 Da), the chemistry of mid-size molecules (1000–20000 Da) represents a growing field in material

science, in nanoscience, and in biological chemistry. This development was facilitated by routine analyses from modern mass spectrometry techniques.<sup>[1]</sup> Giant monomolecular structures, such as dendrimers<sup>[2]</sup> or various supramolecular systems,<sup>[3]</sup> have been common and popular over the last years. Multiple functionalization at the periphery of those entities has been a major goal for the quest of new or improved properties, especially in dendrimer chemistry. However, the design of molecular templates with multiple functional sites as highly branched molecules is also increasingly attractive due to their simplicity, for example, radialenes,<sup>[4]</sup> functionalized porphyrins,<sup>[5]</sup> hexasubstituted benzene derivatives<sup>[6]</sup> or other multidirectional molecules.<sup>[7]</sup>

Following this trend, we have created a class of nanomolecules, called molecular asterisks,<sup>[8]</sup> from an expeditious connection of poly(*p*-phenylene sulfide) oligomers<sup>[9]</sup> onto a coronene core. Several objectives were pursued: 1) to create highly branched asterisks as multifunctional and electron-accepting nanomolecules based on persulfurated aromatics, 2) to study their fundamental physical–organic properties by UV-visible and spectroelectrochemistry, and 3) to explore the electronic properties (UV and delocalization) of those nanomolecules by modulating their shape (star-shaped versus linear PPS oligomers). The layout of this paper is given in the following paragraphs.

Firstly, the importance of poly(*p*-phenylene sulfide) polymers (PPS) as classic conducting and thermoplastic materials is shown from their commercial exploitation by Phillips Petroleum since 1967.<sup>[10]</sup> They were the first malleable conducting polymers (after doping) that did not contain a purely carbon backbone.<sup>[11]</sup> Our interest in this field is relat-

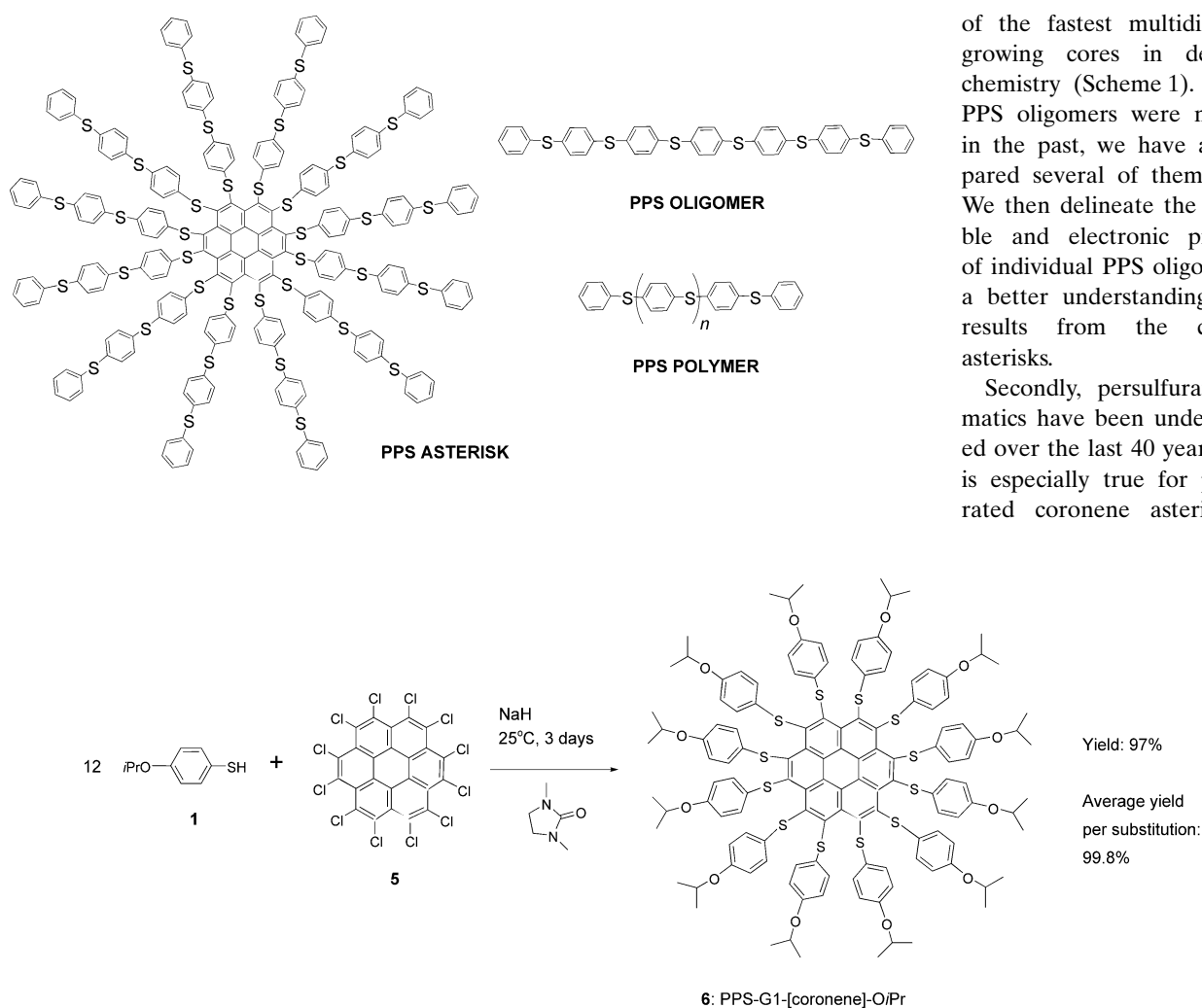
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Scheme 1. Efficiency in the persulfuration of coronene with 12 bonds broken and 12 bonds formed at 25 °C.

ed to the concept of branching PPS oligomers at a central electro-communicating template for modifying the shape and the physical–organic properties of the macromolecules. A persubstituted coronene unit with 12 arms represents one

**Abstract in French:** Des astérisques moléculaires (**6–9**) de sulfure de p-phénylène (PPS) ont été préparés de façon efficace. Ils représentent une classe nouvelle de nanomolécules PPS de forme étoilée pouvant accepter des électrons. Des études de spectroélectrochimie, de voltamétrie cyclique et d'UV-Vis ont été complétées sur les astérisques et sur des oligomères de PPS (**1–4**). Ces données confirment pour la première fois une délocalisation électronique à travers tout L'astérisque moléculaire, soit sous la forme d'un radical-anion ou celle d'un dianion, en dépit de ponts soufrés divalents entre les groupes phényle. Les astérisques sont représentés par un réseau globulaire tridimensionnel avec délocalisation électronique. Les études électrochimiques ont indiqué que les substituants soufrés stabilisent fortement la forme réduite de l'astérisque, par comparaison avec le coronène lui-même, et la facilité de réduction dépend de la longueur des chaînes PPS.

of the fastest multidirectional growing cores in dendrimer chemistry (Scheme 1). Because PPS oligomers were neglected in the past, we have also prepared several of them (**1–4**).<sup>[9]</sup> We then delineate the UV-visible and electronic properties of individual PPS oligomers for a better understanding of our results from the coronene asterisks.

Secondly, persulfurated aromatics have been underexploited over the last 40 years;<sup>[12]</sup> this is especially true for persulfurated coronene asterisks, for

which there is still a lack of fundamental physical–organic studies. With a persulfurated benzene core, a few applications were found as liquid crystals,<sup>[13]</sup> as  $\pi$ -donors or precursors for organic conductors,<sup>[14]</sup> and as bioinorganic mimics of ferredoxins;<sup>[15]</sup> also many X-ray structure determinations of “host–guest” partners in inclusion chemistry have been reported.<sup>[16]</sup> In 1997, one of us and other collaborators reported the first electrochemical study<sup>[17]</sup> and the molecular asterisks were developed in 1998.<sup>[8]</sup> In 2002, a new class of membrane for ion-selective electrodes appeared.<sup>[18]</sup> Our work encouraged studies toward micellar systems<sup>[19]</sup> and oligothiophene liquid crystals.<sup>[20]</sup> An intriguing fact is the mild and efficient coupling of sulfanylated PPS chains to perchlorocoronene **5**. As a specific example, the average yield per substitution could be as high as 99.8% in the coronene case for twelve substitutions in a row, involving the breakage of twelve C–Cl bonds and the formation of twelve new C–S bonds at room temperature (Scheme 1).<sup>[21]</sup> Perchlorocoronene **5** was prepared in one step from coronene in a near quantitative yield.<sup>[21]</sup>

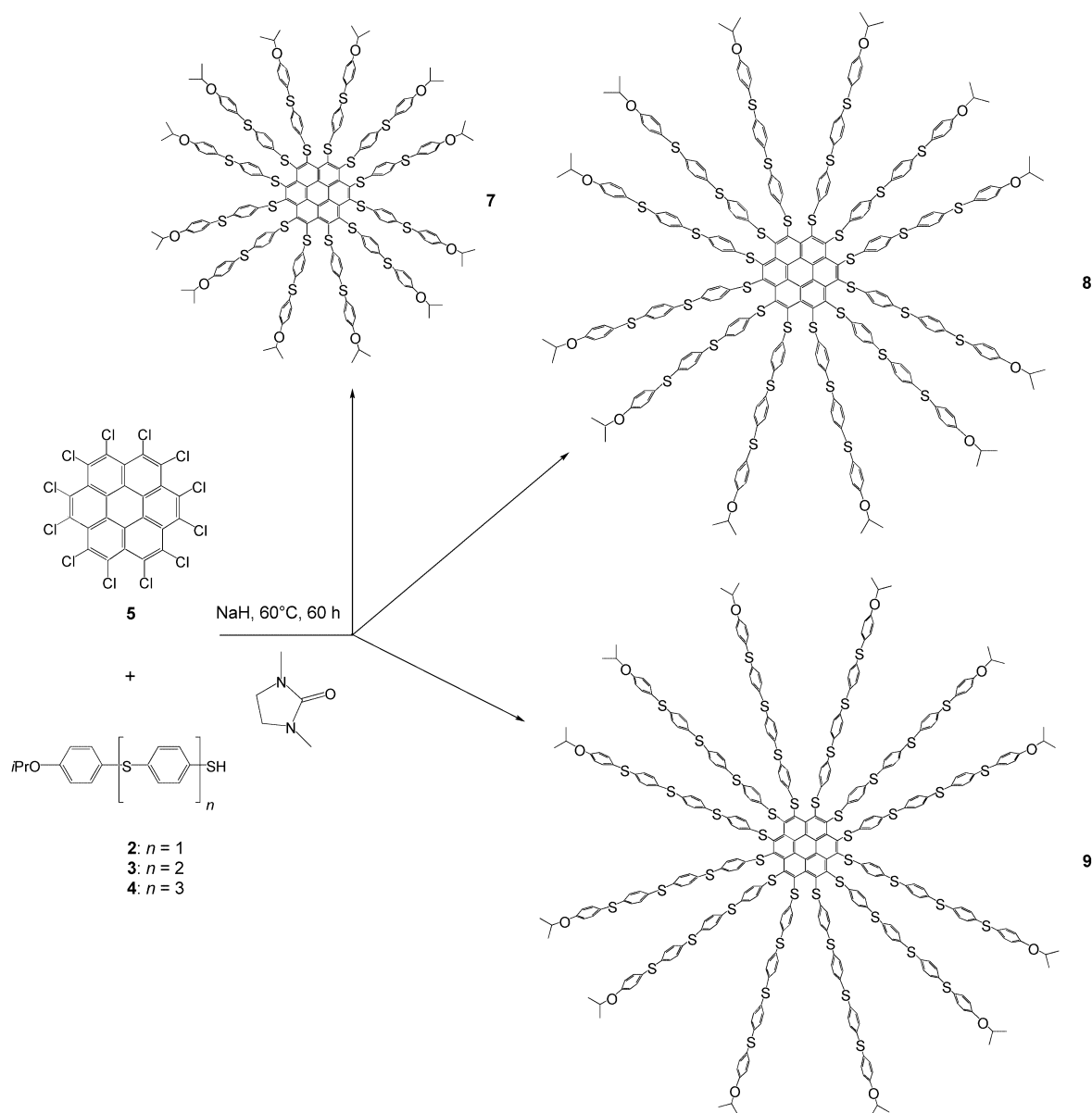
Thirdly, we collected and analyzed physical–organic data from a growing set of coronene asterisks from “generations” 1 to 4. UV-visible and electrochemical properties provide a

better understanding of the electronic delocalization within PPS macromolecules. Spectroelectrochemistry indicates that relatively stable radical anions and dianions are formed.

## Results and Discussion

**Synthesis:** The preparation of the asterisks was achieved in a convergent manner, because it facilitated the purification (Scheme 2). If some arms were missing, it could provide a major difference in the chemical properties of the product and the impurities. Our procedures did not usually require chromatographic separations, but simple triturations in ethanolic solvents. The asterisk size could be tailored by a control of the PPS chain length. The remaining task was to explore the syntheses of functionalized PPS oligomers and to optimize their couplings, as will be shown in the next sections.

**PPS oligomers:** Many methods are known for synthesizing poly(*p*-phenylene sulfide) polymers (PPS),<sup>[22]</sup> but the oligomers were often separated as minor components after a PPS polymerization.<sup>[23]</sup> Therefore, we achieved simple syntheses of *p*-phenylene sulfide oligomers with the chain lengths varying from two to four phenyl rings and with a sulfanyl group at one end and a protected phenolic function at the other (Scheme 2).<sup>[9]</sup> Deprotection of terminal phenols gives an asterisk with a hydrophilic periphery for possible uses in aqueous media. The selection of protective groups came after a long survey and various assays. Many of them did not survive under highly nucleophilic conditions at 100–150 °C with thiophilic metal salts (such as Pd or Cu salts) during usual Ar–S coupling procedures. We finally found that thiomethyl and isopropoxy groups were the best partners as orthogonal protective groups for a chemoselective deprotection of thiophenols. In our hands, the nucle-



Scheme 2. General syntheses of PPS-*Gn*-[coronene]-OiPr asterisks 7–9.

ophilic deprotection of arylthiomethyl groups with MeSNa in DMF at 160 °C, or in NMP at 200 °C, most often provided an inseparable mixture of thiol and starting material.<sup>[24]</sup> Classic reducing conditions with Na/NH<sub>3</sub><sup>[25]</sup> or Na/pyridine at 100 °C<sup>[26]</sup> led to uncontrolled cleavage of C–S bonds in the chains. For these reasons, we improved the methodology by using the reagents *i*PrSNa or *t*BuSNa; the latter provided almost quantitative yields of thiols, while the isopropoxy group came under slight attack by less-hindered thiolates.<sup>[27]</sup> Other synthetic strategies based on the introduction of a sulfhydryl or a thiomethyl group from brominated or iodated *p*-phenylene sulfides were not efficient at a later stage of the synthesis. Oligomers **1–4** were prepared following the above considerations on a multiple gram scale, with the avoidance of chromatographic separation. We next turned our attention to the assembly of coronene asterisks.

**PPS coronene asterisks:** Reactions of PPS oligomers **1–4** with dodecachlorocoronene **5** provided the asterisks **6–9** by means of the MacNicol reaction.<sup>[21]</sup> In this way, we built up one set of growing asterisks functionalized at the periphery by isopropoxy groups (Scheme 2: PSS-*Gn*-[coronene]-OiPr; *n* = 1, 2, 3, 4). The MacNicol reaction is sensitive to the solvent used, and a polar aprotic solvent such as DMI (1,3-dimethyl-2-imidazolidinone) was the most proficient. We also needed to optimize the yields and the purification. At first, dodecachlorocoronene **5** reacted with a twofold excess of thiolate at 20 °C, but only modest yield of 65% was obtained along with some difficulty in getting rid of the excess starting material. Traditionally, most reactions of perchlorocoronene used an unnecessary twofold excess of sodium thiolate. After optimizing the conditions at 60 °C in DMI, a 1.1-fold excess of sodium thiolate afforded the asterisks (Scheme 2: *n* = 1, 2, 3, 4) in yields of 97 (G1), 95 (G2), 93 (G3), and 70% (G4). All of them were relatively air-stable and could be stored at –10 to –20 °C for years without significant decomposition. They are crystalline dark red solids often soluble in many solvents.

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and elemental analyses confirmed the structures and are indicative of a good purity (see Experimental Section). At 80–100 °C in C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>, we could distinguish every set of AA',BB' apparent hydrogen doublets by <sup>1</sup>H NMR spectroscopy; this proves the symmetrical nature of the molecules. If any substituents were missing or if any impurities were present, we could differentiate those signals by <sup>1</sup>H NMR spectroscopy by comparison with the pure product. Most relative errors in the percentage of H, C and S were satisfactory. Specific analysis for chlorine indicated 0.00%; it indisputably demonstrates that twelve substitutions occurred. We further ascertained the structures by using several mass spectrometry techniques (FAB, DCI, SIMS, and MALDI-TOF), which provided the corresponding average isotopic molecular ions for each functionalized coronene generation at *m/z* = 2293.8 (G1: SIMS; 2294 calcd), 3593.1 (G2: MALDI-TOF; 3593 calcd) or 3593.9 (G2: FAB), 4892.8 (G3: MALDI-TOF; 4890 calcd) and 6192 (G4: MALDI-TOF; 6188 calcd). The fragmentation patterns show signals corresponding to a regular loss of some arms in MALDI-TOF for larger asterisks, leading to a

delocalized cation made up of the core and the rest of the molecule.

**Spectroscopic properties:** This study was performed with the samples at a concentration of 1.00 × 10<sup>–5</sup> M in dioxane at 25 °C, at which the concentration and the absorption fits the Beer–Lambert law, in order to avoid intermolecular interactions. We focused our attention on a comparison of the generations and the role played by the PPS chain in the UV absorption of the asterisks. We were interested in knowing more about the electronic delocalization through the sulfur linkages, the communication between the core and the chains, and the extent of perturbation associated with the chain length.

**PPS oligomers:** In order to distinguish the role and the contribution of the PPS chains in the absorption spectra and the electronic distribution, we recorded the UV-visible spectroscopic properties of short PPS oligomers from one to four phenyl groups, with and without an isopropoxy group. Only the results of the oligomers functionalized by an isopropoxy group are shown in Figure 1. For compound **1 a**

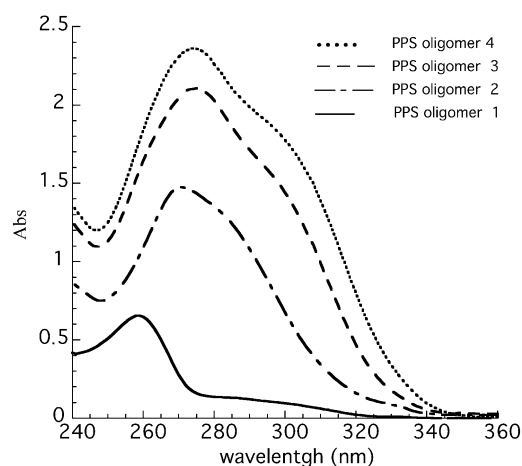


Figure 1. UV-visible absorption spectra of PPS oligomers **1–4** in dioxane at 5.00 × 10<sup>–5</sup> M.

band at 259 nm ( $\epsilon = 13050 \text{ M}^{-1} \text{ cm}^{-1}$ ) was observed. This corresponds to a disubstituted benzene nucleus, and is attributed to the benzene ring possessing an isopropoxy group and a sulfur atom in the *para* positions. The second-generation (G2) functionalized PPS chain showed a band at 271 nm and a shoulder at 290 nm, corresponding to an absorption found in the second-generation asterisk PPS-G2-[coronene]-OiPr (**7**). The last transition at 290 nm was assigned to a phenyl ring substituted by two sulfur atoms in *para* positions. The intensity of this band increased with the generation number and the number of S-Ph-S units. A slight red shift is observed as the chain increases its length from the second (G2) to the third generation (G3). Similar reports were made by Heitz in 1983.<sup>[23c]</sup> It was attributed to an electronic delocalization between the S-Ph-S units or to the extension of a conjugation in solution.

**PPS-Gn-(Coronene)-OiPr:** All of the coronene asterisks displayed a maximum absorption from the persulfurated core in the visible region at about 460 nm and a large absorption band varying between 250–280 nm, depending on the PPS chain (Figure 2). The molar extinction coefficients near 280 nm quickly expands with the generation number from G1 to G4 (compounds **6–9**). This is expected from the augmentation of the S-Ph-S units.

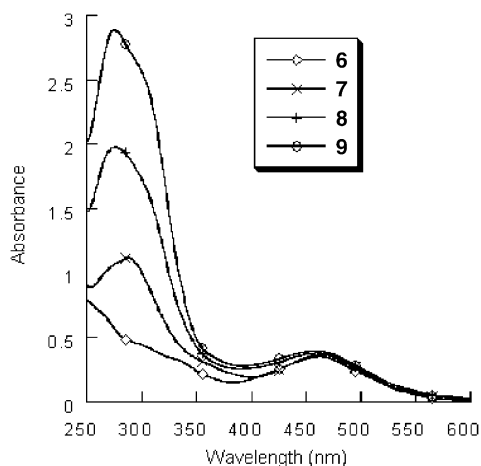


Figure 2. UV-visible absorption spectra of PPS-Gn-[coronene]-OiPr asterisks **6–9** in dioxane at  $5.00 \times 10^{-6}$  M.

For the asterisk with a coronene core (G1), we noticed a band at 255 nm ( $\epsilon = 154800 \text{ M}^{-1} \text{ cm}^{-1}$ ) for compound **6** that corresponds to the absorption of the *i*PrO-Ph-S units. The high value of  $\epsilon$  reflects a large number of *i*PrO-Ph-S units (twelve units). From G1 to G2, a new band appeared at 280 nm ( $\epsilon = 222400 \text{ M}^{-1} \text{ cm}^{-1}$ ). It was attributed to the unit S-Ph-S. The intensity of this last band increases with the generation number, thus confirming this assignment. The second-generation asterisk **7** still conserved its band at 250 nm, assigned to the *i*PrO-Ph-S unit. However, it slightly overlapped with the absorption of the stronger S-Ph-S band. The absorption spectra of **8** (G3) and **9** (G4) did not significantly change, except for their intensities and a broadening of the band near 280 nm, due to the S-Ph-S units.

The persulfurated coronene cores almost showed a constant absorption at a maximum of 460 nm from **6–9** (G1–G4), in spite of a light increase of the molar coefficients of extinction. Compared to the absorption spectra of coronene itself, which has a major maximum absorption near 419 nm, we found that persulfuration caused a red shift of about 41 nm (to 460 nm). Again, the  $\pi \rightarrow \pi^*$  transition energy is lowered by sulfur substituents. The absorption band at 460 nm was almost insensitive to the length of the PPS chain. However, coronene has several transitions and it complicates the interpretation of the results. The absorption at 460 nm, in the blue-green region, is consistent with the observed transmitted red color.

In summary, the UV-visible properties of the coronene asterisks in the ground state (neutral species) apparently did not clearly indicate an electronic delocalization within the PPS chains and between the chains and the core. However,

the electrochemical data from the next section will be conclusive for a delocalization of electrons through the entire coronene asterisk and through the PPS chains.

**Electrochemical properties:** Electroreduction of organosulfur compounds has been less studied than their oxidation. In the work of Lehn, Gingras, and co-workers,<sup>[17]</sup> it was found that hexakis(phenylthio)benzene derivatives, with substituents at the *para* positions of the terminal benzene rings, followed a linear Hammett relationship with the  $\sigma$  parameters of the substituents during their reduction by cyclic voltammetry. In other words, an electron-withdrawing substituent facilitated the electroreduction. A second point showed the dependence on the aromatic cores in the reduction potentials and in the number of electrons transferred. The number of sulfurated substituents connected to the benzene core was also important. For instance, pentakis(phenylthio)benzene was less easily reduced ( $-1.95$  V vs SCE) than hexakis(phenylthio)benzene ( $-1.56$  V vs SCE). Finally, molecular wires incorporating four or five sulfur substituents and a bridging  $\pi$  system on a benzene core were less easily reduced than the coronene asterisks.<sup>[28]</sup> A cation sensor with electrochemical signaling made from a derivative of hexakis(phenylthio)benzene and a macrobicyclic ligand was also reported.<sup>[28c]</sup> In spite of these nice studies, not much is known with polysulfurated coronene.

Molecular asterisks from the first to the fourth generation functionalized at the outer periphery by isopropoxy groups were measured by cyclic voltammetry; some of the experimental conditions are given in Table 1 and Figure 3. It

Table 1. Reduction potentials of asterisks PPS-Gn-[coronene]-OiPr (**6–9**;  $n = 1–4$ ) at half-wave ( $E_{1/2}$  vs SCE) in DMF at 1 mM with 0.1 M TBDHP as electrolyte.

Asterisk	$E_{1/2}$ [V]	
<b>6</b>	−1.06	−1.50
<b>7</b>	−0.92	−1.30
<b>8</b>	−0.86	−1.23
<b>9</b>	−0.83	−1.23

is known that a persulfurated coronene core reversibly accepts two electrons between  $-1.6$  and  $-1.0$  V (vs SCE)<sup>[17]</sup> for two consecutive one-electron transfers. The cyclic voltammogram for coronene asterisk **6** (Figure 3) also indicated two single-electron transfer waves at  $-1.06$  and  $-1.50$  V (vs SCE). The count for the electron transfer was verified by coulometry and electrolysis. Coronene itself has two reductive waves at  $-2.04$  and  $-2.57$  V (vs SCE).<sup>[29]</sup> Again, a large stabilization from the sulfur substituents facilitates the reduction to a radical anion and then to a dianion. The stabilizing effects are close to 1.1 V in both reductions.

The increase of the PPS chain length is favorable to both sets of electron transfer. In the case of the radical anion formation, a difference of the reduction potentials of 0.14, 0.06, and 0.03 V is observed in going from the first to the fourth generation. However, there is virtually no change in the

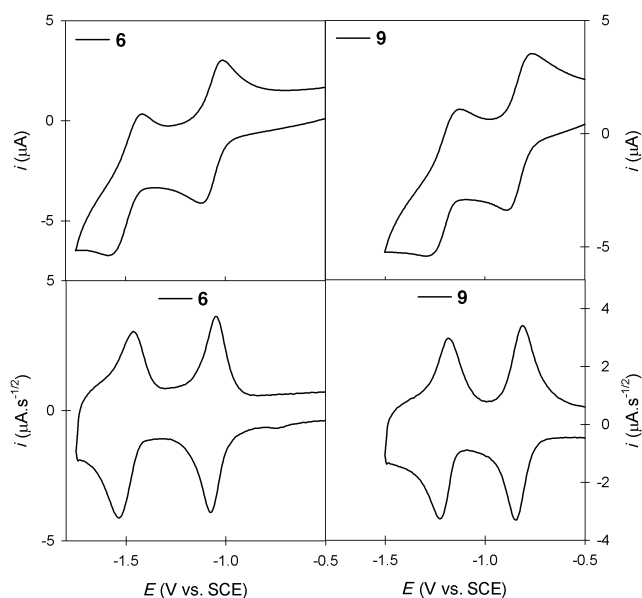


Figure 3. Cyclic voltammograms (top) and deconvoluted cyclic voltammograms (bottom: calculated with CONDECON™) of PPS-G1[coronene]-OiPr (**6**, 1 mM) and PPS-G4[coronene]-OiPr (**9**, 1 mM) in 0.2 M TBAHP/DMF.

properties on going from **8** (G3) to **9** (G4). In the case of the dianion formation, a difference of reduction potentials of 0.20, 0.07, and 0.00 V is observed in going from the first to the fourth generation. A constancy of the electrochemical properties is obtained for **9** (G4). The analysis of those results again suggests a stabilization of the properties in going from the third to the fourth generation. The following conclusions are found: an electronic delocalization is felt through the whole of the PPS chains and through the entire molecule, up to the fourth-generation coronene asterisk. An electronic communication exists between the core, the sulfide linkages, and the phenylene sulfide arms. The electrochemical data indicate relatively stable charged species from the quasi-reversible reductive patterns. Sulfur substituents are excellent charge stabilizer in persulfurated aromatics. A decrease of the current intensities is observed on going from the first to the fourth generation. It is thought that the mobility of those macromolecules is hampered because of their size. As expected, the diffusion coefficients and the electron transfers are attenuated with increasing the asterisk size.

In the positive direction, several oxidation waves were observed in CH<sub>2</sub>Cl<sub>2</sub> (Figure 4). The electro-oxidation behavior is independent of the asterisk size. The first oxidation wave is an irreversible one-electron process. The increasing scan rate (up to 100 V s<sup>-1</sup>) did not allow us to detect a possible reversibility. On the other hand, it is worth noting that the second oxidation wave is a reversible multielectronic process: is it the oxidation of the asterisk core? At this stage,

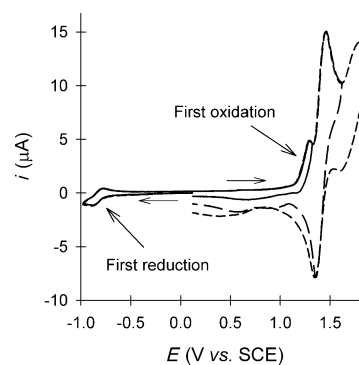


Figure 4. Cyclic voltammograms of PPS-G4[coronene]-OiPr (**9**, 1 mM) in 0.2 M TBAHP/CH<sub>2</sub>Cl<sub>2</sub> obtained in the positive direction

the number of electron transfer has not been estimated and further work will be performed in order to determine the electrochemical behavior of PPS-G $n$ -[coronene]-OiPr in the positive direction.

**Spectroelectrochemical properties:** In order to obtain additional information for the successive generations of asterisks, electroreductions of PPS-G $n$ -[coronene]-OiPr (**6–9**; Table 2) were analyzed by time-resolved and near-IR spectroelectrochemistry under thin-layer conditions. In such conditions, the stability of compounds is absolutely necessary

Table 2. Spectroelectrochemistry and UV-visible absorption for neutral, radical anion, or dianion PPS-G $n$ -[coronene]-OiPr asterisks (**6–9**) under dry oxygen-free argon.

	$\lambda_{\max}$ [nm] ( $\epsilon$ ) neutral <sup>[a]</sup>	$\lambda_{\max}$ [nm] ( $\epsilon$ ) neutral <sup>[a]</sup>	$\lambda_{\max}$ [nm] radical anion <sup>[b]</sup>	$\lambda_{\max}$ [nm] dianion <sup>[b]</sup>	M.p. [°C]
<b>6</b>	255 (154 800)	460 (69 000)	963	798	164.0–165.01
<b>7</b>	280 (222 400)	460 (73 200)	969	805	151.0–152.0
<b>8</b>	275 (394 200)	460 (75 200)	985	812	133.0–134.0
<b>9</b>	277 (575 400)	460 (79 000)	992	820	90 (decomp)

[a] 0.001 M dioxane. [b] 0.2 M TBAHP/DMF.

and use of a glove box, containing dry, oxygen-free (<1 vpm) argon, avoid the oxidation of the asterisks in DMF.

In a negative doped state, it is possible to observe the optical characteristics of the radical anion and the dianion. Figure 5 shows the electronic spectra of asterisk **9** in DMF at the first and second reduced state. The first reduction leads to the development of two new bands with maxima at 640 and 992 nm, characteristic of the radical anion. Beyond the second reduction, the spectrum shows only a single broad absorption band with a maximum at 820 nm, which can be unequivocally assigned to the dianion. The same results were observed with decreasing the asterisk size. Moreover, and in agreement with CV data, a red shift (~30 nm between asterisks **6** and **9**) was also observed with increasing size. These results show that it is possible to generate radical anions and dianions from these asterisks in harsh thin-layer conditions. Without oxygen and water, these reduced forms are stable for several hours.

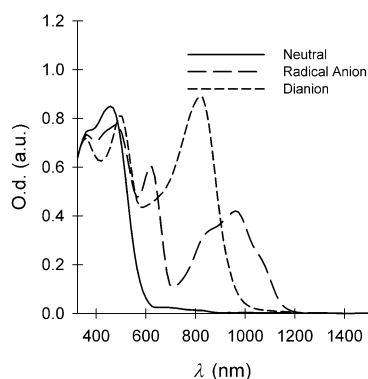


Figure 5. Spectroelectrochemistry of PPS-G4-[coronene]-O/Pr (**9**, 1 mM) asterisk in 0.2 M TBAHP/DMF obtained in the negative doped state.

## Conclusion

In this work, we report the efficient synthesis of PPS oligomers and highly branched PPS asterisks (**6–9**), as multifunctional and electron-accepting nanomolecules with a persulfurated coronene core. The asterisks were assembled by a convergent approach by connecting sulfanylated *p*-phenylene sulfide chains (**1–4**) onto dodecachlorocoronene **5**. Characterization of the asterisks was achieved by a combination of mass spectrometry techniques (DCI, FAB, SIMS, MALDI-TOF),  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and elemental analyses. The data were indicative of a fully persulfurated coronene core.

Physical–organic properties of those nanomolecules were evaluated by UV-visible spectroscopy, electrochemistry, and spectroelectrochemistry. Prior to the analysis of these results, we collected UV-visible data of PPS oligomers. We then assigned several UV absorption bands in order to evaluate the electrochemical and spectroelectrochemical properties. More importantly, it was found that an electronic delocalization occurred through the entire asterisk (**6–9**) and it could be seen as a somewhat globular sphere with a three-dimensional electronic network. This delocalization was also observed in the reduced form (radical anion or dianion) from a red shift of the UV bands. On reaching asterisk **9** (fourth generation), many properties remained almost constant, showing the limit of the delocalization. Electrochemical studies indicated that sulfur substituents strongly stabilize the reduced form relative to coronene itself. The easy electroreduction and oxidation of the asterisks suggests interesting properties in material sciences, dendrimer, or supramolecular chemistry. Due to the affinity of sulfur for soft transition metals, as already shown in our studies for making membranes of use in ion-selective electrodes, supported metallic nanoclusters could be an example of some future utilizations. We are now investigating the solid-state properties of those molecules toward nanomaterials.

## Experimental Section

**Instruments:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{CDCl}_2\text{CDCl}_2$  (TMS int. standard) with Bruker instruments AC200

(200 MHz), AC250 (250 MHz), AC400 (400 MHz) and Varian Unity 600 (600 MHz). Abbreviations s, d, t, sept., app, and m stand for singlet, doublet, triplet, septuplet, apparent, and multiplet, respectively. FT-IR spectra were recorded with a Perkin–Elmer 883 or Perkin–Elmer Spectrum 1000 instruments with dry KBr disks (about 1% w/w of sample). MALDI-TOF MS spectra were recorded at the Institute for Biological Sciences (IBS) of the National Research Council of Canada, Ottawa (Canada); from a mixture of 0.5  $\mu\text{g}$  of asterisk with 1  $\mu\text{L}$  of a dithranol matrix (10  $\mu\text{g}$  dithranol per 1  $\mu\text{L}$  of  $\text{CHCl}_3$ ) with a PerSeptive Biosystems Elite-STR mass spectrometer in linear mode. An external calibration was achieved with an error of  $\pm 0.3$  Da for  $M < 4000$  Da; resolution 3500. SIMS, EI, and CI mass spectra (70 eV) were recorded with a VG Micro-mass 7070F at the Université Libre de Bruxelles (Belgium). DCI MS ( $\text{CH}_4/\text{N}_2\text{O}$ ) were obtained at the Université Catholique de Louvain (Belgium). UV-visible spectra were recorded from a quartz cell (optical path: 1.0 cm) on a Cary 300 and Cary 5E in dioxane at the mentioned concentration. Melting points (uncorrected) were determined in an open capillary with an Electrothermal SMP3 ( $0.2^\circ\text{Cmin}^{-1}$ ) apparatus. Microanalyses were done at the Université Louis-Pasteur, Strasbourg and Université Paris-Sud, Orsay (France).

**Chemicals:** Aluminium or plastic TLC precoated silica gel plates SIL G/UV<sub>254</sub> Macherey-Nagel or Merck were used. Visualization: UV or ceric ammonium sulfate/ $\text{H}_2\text{SO}_4$  aq/ammonium molybdate solution. Column chromatography was achieved with silica gel Kieselgel 60 Merck (230–400 mesh). Most reagents were purchased from Sigma–Aldrich or Acros and used as received. DMF was dried over  $\text{CaH}_2$  overnight and distilled under reduced pressure. DMF and DMI were kept and dried over activated ( $250^\circ\text{C}/3$  h) 3 Å molecular sieves. Powdered NaH 95% was used as received. The preparation and characterization of compounds **1–4** are given in reference [9], and for **5** in reference [21b].

**Asterisk PPS-G1-[coronene]-O/Pr (6):** Perchlorocoronene (20.0 mg, 0.031 mmol) was placed in a dry 10 mL, two-necked flask under  $\text{N}_2$ . Thiol **1** (97.0 mL, 114 mg, 0.67 mmol) and DMI (0.80 mL) were injected by means of a syringe. Powdered 95% NaH (20.0 mg, 0.81 mmol) was weighed and placed in a lateral Gooch tube connected to the flask. Oxygen was removed by three freeze-thaw cycles with  $\text{N}_2$ . After cooling in an ice bath, NaH was added in small portions. A foam was formed and the mixture turned deep red. Stirring was continued at  $25^\circ\text{C}$  for 3 days (less time might be needed). A solution of 1 M NaOH (20 mL) was added while stirring vigorously, followed by toluene (5.0 mL). After separation of the organic phase, it was washed further with 1 M NaOH ( $2 \times 10$  mL). After drying over  $\text{MgSO}_4$ , filtration, and evaporation of the solvent, a red oil was obtained (119 mg). The crude product was purified on a chromatography column ( $\text{SiO}_2$ , ethyl acetate/hexane 3:7 v/v). A solid was obtained (63.0 mg, 97%). M.p.  $164.0\text{--}165.0^\circ\text{C}$  (dark red microcrystalline solid);  $R_f = 0.60$ ; UV/Vis (dioxane,  $1 \times 10^{-5}$  M):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 255 (154 800), 460 nm (69000);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.22$  ( $d_{\text{app}}$ ,  $J = 5.8$  Hz, 36H;  $\text{CH}_3$ ), 4.31 (sept,  $J = 5.8$  Hz, 6H; OCH), 6.50 ppm ( $s_{\text{app}}$ , 48H; arom);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 22.80$  ( $\text{CH}_3$ ); 70.64 (CH), 116.84 (C), 129.72 (C), 131.40 (C), 156.78 ppm (C); DCI ( $\text{CH}_4/\text{N}_2\text{O}$ ) MS for  $\text{C}_{132}\text{H}_{132}\text{O}_{12}\text{S}_{12}$ :  $m/z$ : 2295.2 [ $M^+$ ]; SIMS:  $m/z$ : 2293.8 [ $M^+$ ]; elemental analysis calcd (%) for  $\text{C}_{132}\text{H}_{132}\text{O}_{12}\text{S}_{12}$ : C 69.09, H 5.76, S 16.75, Cl 0.00; found: C 68.98, H 5.74, S 15.70, Cl 0.00.

**Asterisk PPS-G2-[coronene]-O/Pr (7):** Perchlorocoronene (200 mg, 0.28 mmol) and thiol **2** (1.02 g, 3.70 mmol) were placed in a dry 50 mL, two-necked flask under  $\text{N}_2$ . Anhydrous DMI (10 mL) was injected by means of a syringe. Powdered 95% NaH (101 mg, 4.44 mmol) was weighed and placed in a lateral Gooch tube connected to the flask. Oxygen was removed by three freeze-thaw cycles with  $\text{N}_2$ . After cooling in an ice bath, NaH was added in small portions for 15 min, while stirring vigorously. A foam was formed and the mixture turned deep red. Stirring was continued for at  $25^\circ\text{C}$  for 1 h and then at  $60^\circ\text{C}$  for 60 h. After cooling, a solution of 1 M NaOH (5 mL) was added while stirring vigorously, followed by  $\text{CH}_2\text{Cl}_2$  (10 mL). The mixture was poured into a solution of 1 M NaOH (100 mL) and the organic phase was separated. The aqueous layer was further extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  (50 mL). After drying over  $\text{MgSO}_4$ , filtration, and evaporation of the solvent, a red oil was obtained. The crude product was triturated in absolute EtOH (50 mL) and a red solid was formed. Triturations were repeated with absolute EtOH ( $3 \times 50$  mL) and with hexane (50 mL). After drying under vacuum, a red solid was recov-



ered (0.957 g, 95%). M.p. 151.0–152.0°C (microcrystalline dark red solid);  $R_f=0.27$  (SiO<sub>2</sub>, ethyl acetate/hexane 1:4); UV/Vis (dioxane,  $1 \times 10^{-5}$  M):  $\lambda_{\max}(\epsilon)=280$  (222400), 462 nm (73200); <sup>1</sup>H NMR (600 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80°C):  $\delta=7.34$  (d<sub>app</sub>,  $J=7.8$  Hz, 24H), 6.89 (s<sub>app</sub>, 24H), 6.82 (d<sub>app</sub>,  $J=7.8$  Hz, 24H), 6.46 (d<sub>app</sub>,  $J=7.8$  Hz, 24H), 4.40 (s<sub>app</sub>, 12H), 1.24 ppm (s, 72H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, 20°C):  $\delta=158.30$ , 135 (brm), 130–123 (brm), 116.80, 70.0 (CH), 21.9 ppm (CH<sub>3</sub>). DCI-MS (CH<sub>4</sub>) for C<sub>204</sub>H<sub>180</sub>O<sub>12</sub>S<sub>24</sub>:  $m/z$ : 3585 [ $M^+$ ]; FAB-MS (NBA):  $m/z$ : 3593.9 [ $M^+$ ]; MALDI-TOF MS (dithranol):  $m/z$ : 3593.1 [ $M^+$ ]; elemental analysis calcd (%) for C<sub>204</sub>H<sub>180</sub>O<sub>12</sub>S<sub>24</sub>: C 68.21, H 5.06, S 21.42, Cl 0.00; found: C 68.05, H 4.82, S 21.36, Cl 0.00.

**Asterisk PPS-G3-[coronene]-O*i*Pr (8):** The same general procedure as for **7** was followed. The amount of reagents was varied as follows: dodecachlorocoronene (200 mg, 0.280 mmol), NaH (106 mg, 4.44 mmol), thiol **3** (1.42 g, 3.69 mmol), and DMI (10 mL). After heating in an oil bath at 60°C for 60 h and cooling, a solution of 1 M NaOH (5 mL) was added, while stirring vigorously, followed by CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was poured into a solution of 1 M NaOH (100 mL) and the organic phase was separated. The aqueous layer was further extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic layers were washed with H<sub>2</sub>O (50 mL). After drying over Na<sub>2</sub>SO<sub>4</sub>, filtration and evaporation of the solvent, a red oil was recovered. The crude product was triturated in absolute EtOH (50 mL) and a red solid was formed. Triturations were repeated with absolute EtOH (3 × 50 mL) and with hexane (50 mL). After drying under vacuum, a red solid was recovered (1.27 g, 93%). M.p. 133.0–134.0°C (microcrystalline dark red solid);  $R_f=0.27$  (SiO<sub>2</sub>, EtOAc/hexane 1:4); UV/Vis (dioxane,  $1 \times 10^{-5}$  M):  $\lambda_{\max}(\epsilon)=275$  (394200), 460 nm (75200); <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80°C, TMS):  $\delta=1.35$  (d,  $J=6.0$  Hz, 72H), 4.49 (sept,  $J=6.0$  Hz, 12H), 6.51 (d<sub>app</sub>,  $J=8.3$  Hz, 24H; arom), 6.83 (d<sub>app</sub>,  $J=8.6$  Hz, 24H; *ortho* of O*i*Pr), 6.94 (d<sub>app</sub>,  $J=8.25$  Hz, 24H; arom), 7.08 (d<sub>app</sub>,  $J=8.3$  Hz, 24H; arom), 7.16 (d<sub>app</sub>,  $J=8.3$  Hz, 24H; arom), 7.33 ppm (d<sub>app</sub>,  $J=8.6$  Hz, 24H; *meta* of O*i*Pr); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta=22.71$  (CH<sub>3</sub>), 70.51 (CH), 117.42 (CH), 124.13 (C), 128.91 (CH), 129.94 (CH), 132.02 (CH), 132.82 (C), 133.01 (CH), 134.11 (C), 136.44 (C), 138.62 (CH), 139.01 (C), 159.04 ppm (C); MALDI-TOF MS (dithranol, resolution ~3500) for C<sub>276</sub>H<sub>228</sub>O<sub>12</sub>S<sub>36</sub>:  $m/z$ : 4893 [ $M^+$ ]; elemental analysis calcd (%) for C<sub>276</sub>H<sub>228</sub>O<sub>12</sub>S<sub>36</sub>: C 67.78, H 4.70, S 23.53, Cl 0.00; found: C 67.77, H 4.63, S 23.65, Cl 0.00.

**Asterisk PPS-G4-[coronene]-O*i*Pr (9):** The same procedure as for **7** was followed. The amount of reagents was varied as follows: dodecachlorocoronene (20.7 mg, 0.0290 mmol), thiol **4** (189 mg, 0.384 mmol), and 95% NaH (13 mg, 0.51 mmol). After trituration with EtOH and hexane, **9** was obtained as a red solid (125 mg, 70%). M.p. 85–86°C (decomp, amorphous dark red solid);  $R_f=0.40$  (SiO<sub>2</sub>, EtOAc/hexane 3:7); UV/Vis (dioxane,  $1 \times 10^{-5}$  M):  $\lambda_{\max}(\epsilon)=277$  (575400), 460 nm (79000); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 30°C, TMS):  $\delta=1.31$  (d,  $J=6.0$  Hz, 72H), 4.51 (sept,  $J=6.0$  Hz, 12H), 6.3 (m, 24H), 7.0 (d<sub>app</sub>,  $J=8.4$  Hz, 24H), 6.7–7.2 (m, 120H), 7.33 ppm (m, 24H); <sup>13</sup>C NMR (62.8 MHz, CDCl<sub>3</sub>, 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, resolution ~3500) for C<sub>348</sub>H<sub>276</sub>O<sub>12</sub>S<sub>48</sub>:  $m/z$ : 6192 [ $M^+$ ]; elemental analysis calcd (%) for C<sub>348</sub>H<sub>276</sub>O<sub>12</sub>S<sub>48</sub>: C 67.54, H 4.49; found: C 67.48, H 4.30.

**Electrochemical section:** Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum millielectrode of 0.126 cm<sup>2</sup> and a platinum wire counter electrode. A silver wire served as a quasi-reference electrode and its potential was checked against the ferrocene/ferrocinium couple (Fc<sup>+</sup>/Fc) before and after each experiment. The electrolytic media involved DMF and 0.2 M of tetrabutylammoniumhexafluorophosphate (TBAHP). All experiments were performed in a glove box containing dry, oxygen-free (<1 vpm) argon, at room temperature. Electrochemical experiments were carried out with an EGG PAR 273A potentiostat with positive feedback compensation. Based on repetitive measurements, absolute errors on potentials were found to be around ±5 mV. The setup for spectroelectrochemical experiments has been described previously.<sup>[50]</sup>

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