

# Polysulfurated Pyrene-Cored Dendrimers: Luminescent and Electrochromic Properties

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**Abstract:** We have synthesized a novel class of dendrimers, consisting of a polysulfurated pyrene core with appended poly(thiophenylene) dendrons (**PyG0**, **PyG1**, and **PyG2**, see Scheme 1), which exhibit remarkable photophysical and redox properties. In dichloromethane or cyclohexane solution they show a strong, dendron-localized absorption band with a maximum at around 260 nm and a band in the visible region with a maximum at 435 nm, which can be assigned to the pyrene core strongly perturbed by the four sulfur substituents. The dendrimers exhibit a strong

( $\Phi=0.6$ ), short-lived ( $\tau=2.5$  ns) core-localized fluorescence band with maximum at approximately 460 nm in cyclohexane solution at 293 K. A strong fluorescence is also observed in dichloromethane solution at 293 K, in dichloromethane/chloroform rigid matrix at 77 K, and in the solid state (powder) at room temperature. The dendrimers undergo reversible chemical and elec-

trochemical one-electron oxidation with formation of a strongly colored deep blue radical cation. A second, reversible one-electron oxidation is observed at more positive potential values. The photophysical and redox properties of the three dendrimers are finely tuned by the length of their branches. The strong blue fluorescence and the yellow to deep blue color change upon reversible one-electron oxidation can be exploited for optoelectronic devices.

**Keywords:** dendrimers • electrochemistry • electrochromism • luminescence • pyrene

## Introduction

Dendrimers<sup>[1]</sup> are complex, repeatedly branched treelike compounds that can be synthesized with well-defined composition and a high degree of order. They usually consist of a core upon which radially branched layers are covalently attached. Because of their treelike multi-branched structure, dendrimers can form internal dynamic niches in which small molecules or ions can be hosted.<sup>[2,3]</sup> By using suitable syn-

thetic strategies it is possible to prepare dendrimers that contain selected functional units in predetermined sites of their structure. Such compounds can often exhibit remarkable chemical, physical, and biological properties, with a wide range of potential applications in different fields such as medicine, biology, chemistry, physics, and engineering.<sup>[4]</sup>

In the last few years, several families of dendrimers containing units capable of interacting with photons and/or electrons have been synthesized, and their properties have been the object of detailed investigations. Dendrimers containing photoactive components,<sup>[5,6]</sup> in the core and/or in the branches, are particularly interesting since: 1) luminescence signals offer a handle to better understand the dendritic structures and superstructures; 2) cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting; 3) changes in the photophysical properties can be exploited for sensing purposes with signal amplification; and 4) photochemical reactions can change the structure and other properties of dendrimers and could lead to a controlled release of molecules.<sup>[2a]</sup> Dendrimers containing several equivalent electroactive units in the branches may display multi-electron transfer properties and play the role of nanobatteries.<sup>[7]</sup>

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200801198>.

When the electroactive component is the dendrimer core, its electron transfer processes can be slowed down or completely prevented by the dendrimer branches.<sup>[8]</sup>

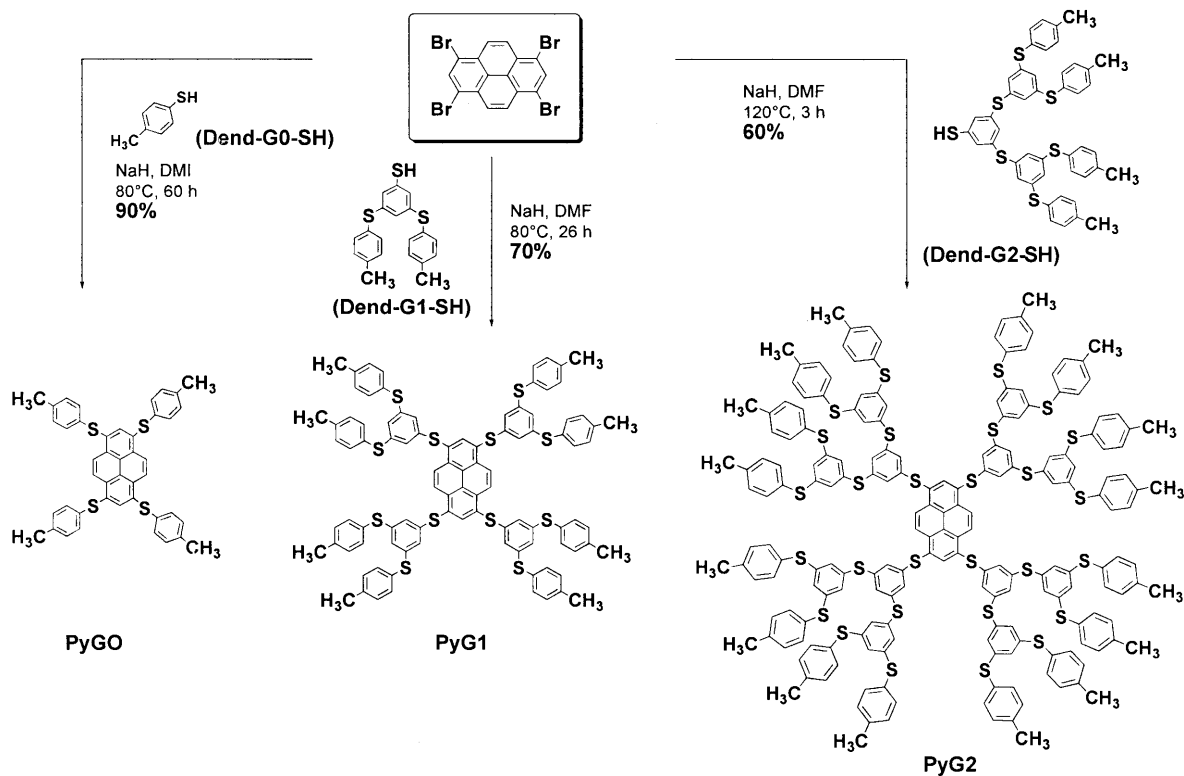
Herein we report on the synthesis, characterization, photophysical behavior (absorption spectra, emission spectra and lifetime, fluorescence anisotropy), and redox properties (chemical and electrochemical oxidation, and electrochromism) of a novel class of dendrimers (**PyG0**, **PyG1**, and **PyG2**, Scheme 1) consisting of a polysulfurated pyrene core, namely a 1,3,6,8-tetra(arylthio)pyrene moiety, with appended thiophenylene units. Pyrene and its derivatives have interesting photophysical and electrochemical properties, and, for this reason, they have been widely used in the fields of organic light-emitting devices,<sup>[9]</sup> field-effect transistors,<sup>[10]</sup> liquid crystals,<sup>[11]</sup> biological markers,<sup>[12]</sup> ion sensors,<sup>[13]</sup> and conformational probes.<sup>[14]</sup> On the other hand, polysulfurated pyrene derivatives are unusual, in spite of the fact that sulfur substituents directly bound to an aromatic core are known to stabilize charged species, giving rise to complexes with thiophilic metal ions and charge-transfer complexes with organic molecules.<sup>[15]</sup> In particular, 1,3,6,8-tetramethylthiopyrene is a good organic p-conductor when doped.<sup>[16,17]</sup>

The novelty of the present work is due both to the incorporation<sup>[18]</sup> of an uncommon tetrathiopyrene core into a dendritic structure and to the presence of polysulfurated dendrons containing thioether functions. These new features lead to unprecedented photophysical, redox, and electrochromic properties useful for optoelectronic applications.

## Results and Discussion

**Synthesis and characterization:** Most pyrene derivatives are monosubstituted, but a practical precursor to tetrafunctional derivatives is 1,3,6,8-tetrabromopyrene, which has been produced easily on the gram scale since 1937, by the bromination of pyrene at elevated temperatures in nitrobenzene.<sup>[19]</sup> Bromine substitutions are often achieved by  $S_NAr$  or by metal-catalyzed C–C bond coupling procedures. These methods have opened up new routes to a family of C-functionalized pyrene compounds.

We succeeded in the polysulfuration of 1,3,6,8-tetrabromopyrene<sup>[19]</sup> by using simple nucleophilic aromatic substitutions with thiolate anions in polar solvents.<sup>[16,17]</sup> As shown in Scheme 1, we prepared **PyG0** (90% yield) from 4-methylbenzenethiol after heating in DMF at 80 °C in the presence of a strong base (NaH). This reference compound established the basis of our studies on the whole dendrimer family. The next generation pyrene dendrimers were similarly prepared (**PyG1**: 70% yield; **PyG2**: 60% yield). They were well characterized by elemental analysis and by various NMR and mass spectrometry techniques (ESI, ESI-MS with  $Ag^+$ , MALDI-TOF, and HRMS). In all cases, the molecular ions (or the  $Ag^+$  complex) were obtained as the main signals. No significant lack of thiophenylene arms were observed, confirming full substitution. This was further substantiated by the symmetry observed in the  $^1H$  and  $^{13}C$  NMR spectra and the virtual absence of incomplete substitution products. Dendrons **Dend-G1-SH** or **Dend-G2-SH**



Scheme 1. Synthesis of polysulfurated pyrene dendrimers.

have already been described in the literature by one of our group.<sup>[20]</sup> They were prepared in good overall yields on a gram scale. 4-Methylbenzenethiol is commercially available.

**Photophysical properties: Absorption spectra:** The absorption spectra of compounds **PyG0**, **PyG1**, and **PyG2** in dichloromethane solutions are shown in Figure 1, in which the

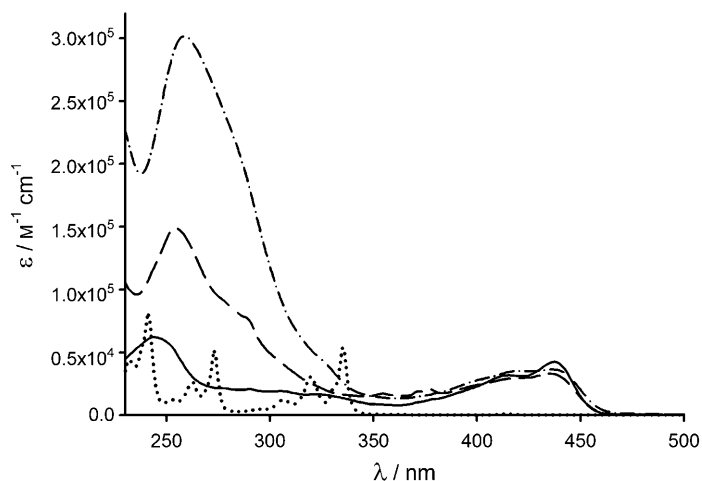


Figure 1. Absorption spectra of **PyG0** (solid line), **PyG1** (dashed line), and **PyG2** (dashed-dotted line) in dichloromethane solution at 293 K. For comparison purposes the spectrum of pyrene (dotted line) is also shown.

spectrum of pyrene is also shown for comparison purposes. The spectra of the dendrimers are quite different from that of pyrene. The broad absorption band in the visible region with a maximum at 435 nm, which is essentially the same for the three dendrimers, can be straightforwardly assigned to the pyrene core strongly perturbed by the four sulfur substituents. The band with a maximum around 260 nm, which increases in intensity with the dendrimer generation, can be assigned to the dendrimer branches. The displacement to lower energy on increasing dendrimer generation and the lack of simple correlation with the number of thiophenylene units contained in the branches show that such chromophoric groups do not behave independently from one another.

**Emission spectra and lifetime:** In cyclohexane solution at 293 K, the three dendrimers exhibit an intense fluorescence band (Figure 2a), strongly red-shifted compared to that of

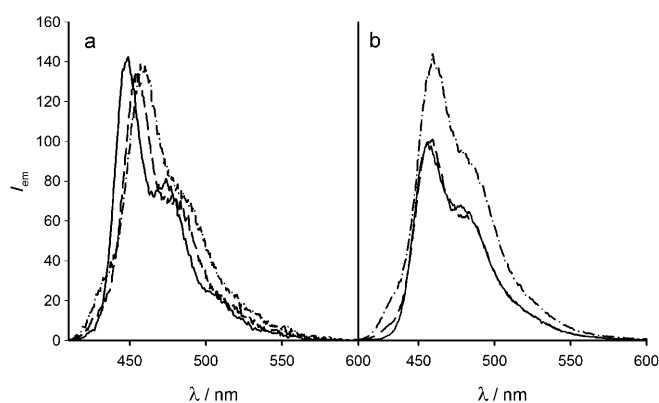


Figure 2. Emission spectra in cyclohexane (a) and in dichloromethane (b) solution at 293 K of **PyG0** (solid line), **PyG1** (dashed line), and **PyG2** (dashed-dotted line).  $\lambda_{\text{ex}} = 390$  nm.

pyrene (Table 1). The energy separation between the two vibrational features ( $1400 \text{ cm}^{-1}$ ) corresponds to a C=C aromatic vibration. The emission bands occur at slightly different energies for the three dendrimers (Figure 2a), but they exhibit the same quantum yield and the same lifetime (Table 1). A remarkable difference compared to pyrene<sup>[21]</sup> is that the excited state lifetime is so short that it is unaffected by the presence of oxygen. A strong fluorescence is also observed in a dichloromethane solution at 293 K (Figure 2b), but in this solvent the fluorescence quantum yields and lifetimes of **PyG0** and **PyG1** are somewhat lower than those of **PyG2** (Table 1). This result suggests the presence of a deactivation path involving the solvent, which is prevented in **PyG2** by the shielding effect of the dendrons. In the rigid dichloromethane/chloroform 1:1 matrix at 77 K, the fluorescence band is blue-shifted by 15 nm compared to the solution spectrum, as expected for an excited state with some charge-transfer character. There is no evidence of phosphorescence.

The strong fluorescence is present also in the solid state (powder) as a broader band at lower energy (green emission) with the same lifetime. This result contrasts with the behavior of pyrene, in which excimer formation strongly diminishes its emission quantum yield.

**Fluorescence anisotropy:** Fluorescent dendrimers often exhibit fluorescence anisotropy.<sup>[22]</sup> In the case of dendrimers with a fluorescent core, the only available depolarization

Table 1. Photophysical and electrochemical properties of the investigated compounds in deaerated solutions.

Solvent Compounds	Absorption dichloromethane		cyclohexane		Emission dichloromethane			$E_{1/2}$ [V] (vs. SCE) dichloromethane		
	$\lambda_{\text{max}}$ [nm] <sup>[a]</sup>	$\epsilon$ [ $\text{M}^{-1} \text{cm}^{-1}$ ]	$\lambda_{\text{max}}$ [nm]	$\tau$ [ns]	$\Phi_{\text{em}}$	$\lambda_{\text{max}}$ [nm]	$\tau$ [ns]	$\Phi_{\text{em}}$	I	II
pyrene	335	54000	370	650	0.65	375	277	0.61	1.30	–
<b>PyG0</b>	435	39000	448	2.5	0.60	457	1.4	0.33	0.85	1.19
<b>PyG1</b>	435	34000	452	2.5	0.60	457	1.6	0.35	1.10	1.28
<b>PyG2</b>	435	36000	457	2.6	0.60	460	2.4	0.55	1.09	1.35

[a] Lowest energy band.

path is the rotation of the molecules during the excited state lifetime.<sup>[23]</sup> In cyclohexane solution at 293 K, the anisotropy value increases with dendrimer generation (0.04, 0.07, and 0.10 for **PyG0**, **PyG1**, and **PyG2**, respectively), as expected because of the increase in dimension of the rotating species.

**Redox behavior:** We investigated the chemical and electrochemical oxidation of the three dendrimers in dichloromethane solution.

**Chemical oxidation:** Titration of **PyG0** with  $\text{AuCl}_4^-$  in dichloromethane solution causes strong changes in the absorption spectrum (Figure 3), namely the disappearance of the

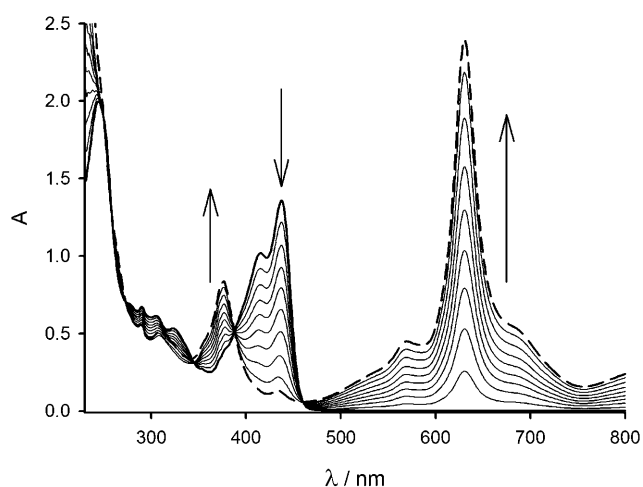


Figure 3. Changes in the absorption spectra upon titration of a  $3.3 \times 10^{-5}$  M dichloromethane solution of **PyG0** with a  $3.18 \times 10^{-3}$  M acetonitrile solution of  $\text{HAuCl}_4$ . Solid curve: original solution of **PyG0**; dashed curve: end of the titration (one-electron oxidation product).

band at 435 nm and the formation of a deep blue species that exhibits a strong, structured, and narrow absorption band with a maximum at 630 nm ( $\epsilon = 72000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and a weaker and broader band with its maximum at 915 nm ( $\epsilon = 29000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The changes in the absorption spectrum are accompanied by the quenching of the dendrimer fluorescence. The oxidation reaction is quantitative for **PyG0**, as shown by the complete fluorescence quenching (Figure 4). The product obtained is the one-electron oxidation species of the dendrimer, as shown by the electrochemical and spectroelectrochemical experiments described below. The observed spectral changes show clearly that the oxidation process involves the perturbed pyrene core.

Titration of **PyG1** and **PyG2** with  $\text{AuCl}_4^-$  causes changes in the absorption spectra and fluorescence intensity as in the case of **PyG0**, but the oxidation reaction is not quantitative, as shown by the fluorescence quenching plots in Figure 4. Such different behavior of the two larger dendrimers can be attributed to a competition for the added  $\text{Au}^{\text{III}}$  species between the redox reaction with the pyrene core and the coordi-

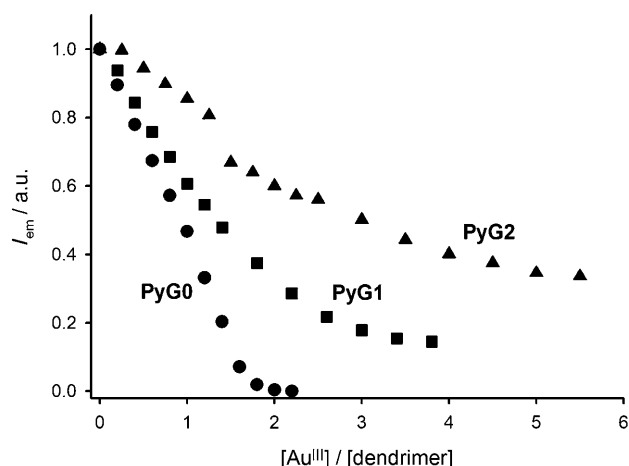


Figure 4. Normalized emission intensity changes at 457 nm for **PyG0** (circles), **PyG1** (squares), and **PyG2** (triangles) in dichloromethane solutions upon titration with  $\text{HAuCl}_4$ .  $\lambda_{\text{ex}} = 390 \text{ nm}$ .

dination reaction with the sulfur units of the dendrimer branches.

**Electrochemical experiments:** Cyclovoltammetric measurements in dichloromethane solution with tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as supporting electrolyte indicated that each dendrimer undergoes two consecutive, reversible, one-electron oxidation processes followed by another ill-defined irreversible process (Figure 5, Table 1). Both the first and the second oxidation waves move to more positive potentials on increasing dendrimer generation.<sup>[24]</sup> They can be assigned to the perturbed pyrene core, suggesting a stronger electron-donating character due to the sulfur substituents.<sup>[16b]</sup> No evidence of decreasing heterogeneous electron-transfer rate with increasing dendron size has been found.

**Spectroelectrochemical experiments:** The first one-electron oxidation process leads to spectral changes (Figure 6) coincident with those observed on chemical oxidation with  $\text{AuCl}_4^-$  (Figure 3), that is, the disappearance of the core absorption band with its maximum at 435 nm and the formation of a very strong band at 630 nm and a weaker band at 915 nm. The one-electron electrochemical oxidation is quantitative for each one of the three dendrimers, contrary to what happens for the oxidation by  $\text{AuCl}_4^-$  (vide supra). The formation of the deep blue radical cation is fully reversible. Further oxidation causes a decrease in the intensity of the 630 and 915 nm bands and the formation of a new, broader, and lower intensity band with a maximum at 660 nm (Figure 6). These spectral changes, which can be reversed by electrochemical reduction, can be assigned to a two-electron oxidation product from the neutral, original dendrimer.

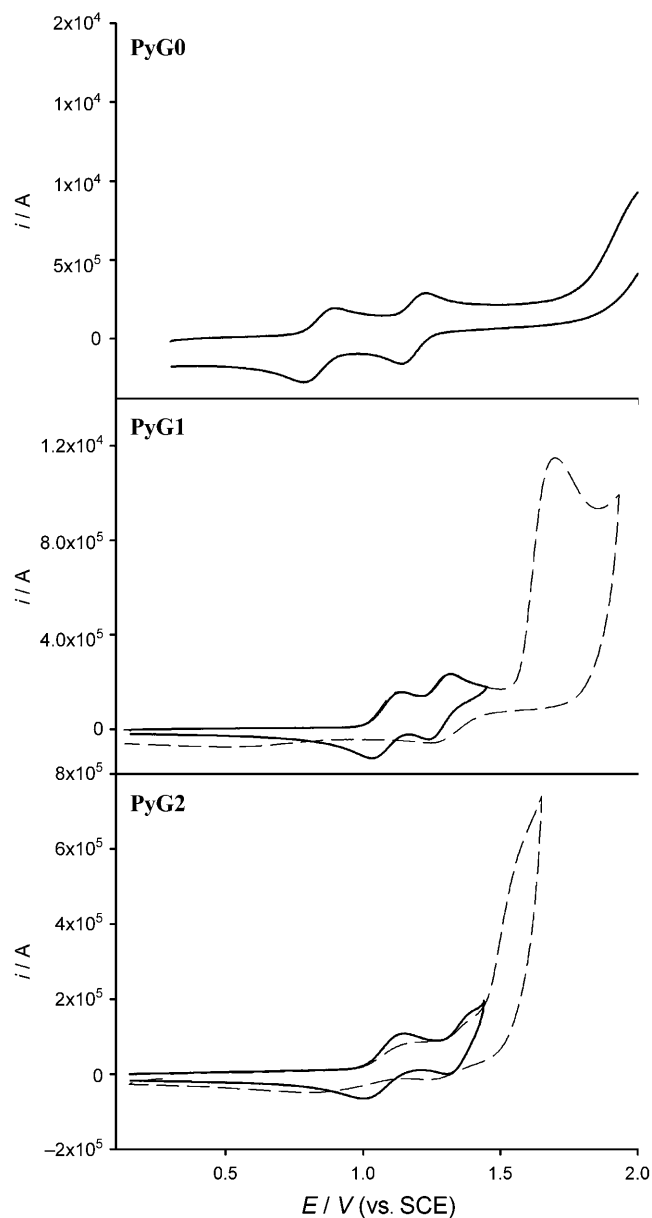


Figure 5. Cyclic voltammograms for **PyG0** (a), **PyG1** (b), and **PyG2** (c) in dichloromethane/TBAPF<sub>6</sub> solution at 293 K. Scan rate = 0.1 V s<sup>-1</sup>.

## Conclusion

We have synthesized a new series of polysulfurated pyrene-cored dendrimers **PyG0**, **PyG1**, and **PyG2** (Scheme 1). They exhibit remarkable photophysical and redox properties. In cyclohexane solution they show a strong branch-localized absorption band in the UV region, a core-localized absorption band in the visible region, and a strong core-localized fluorescence band ( $\lambda_{\text{max}} = 460$  nm,  $\Phi = 0.6$ ,  $\tau = 2.5$  ns), even in the presence of oxygen. Strong fluorescence is also exhibited in dichloromethane solution at 293 K, in the rigid matrix (CH<sub>2</sub>Cl<sub>2</sub>:CHCl<sub>3</sub>) at 77 K, and in the solid state at room temperature. All the dendrimers undergo two successive one-electron reversible electrochemical oxidation pro-

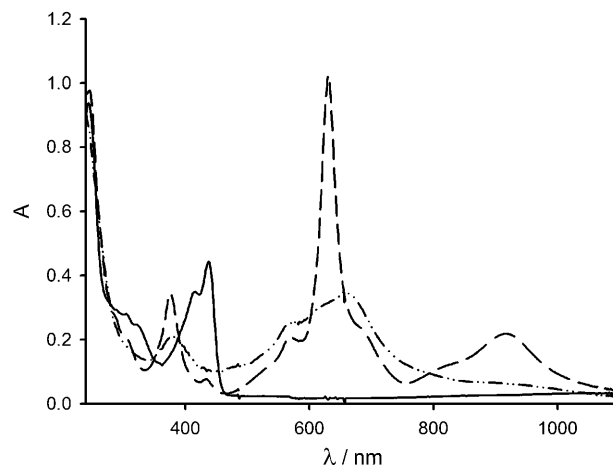


Figure 6. Absorption spectra in dichloromethane solution of **PyG0** (solid curve) and its one-electron (dashed curve) and two-electron (dashed-dotted curve) oxidation product.

cesses in dichloromethane solution. The first one-electron oxidation process, which can also be performed using AuCl<sub>4</sub><sup>-</sup> as an oxidant, leads to the formation of a deep blue radical cation. The photophysical and redox properties of the three dendrimers are fine-tuned by the length of their branches: 1) the dendron localized absorption band at  $\approx 260$  nm increases strongly in intensity and moves slightly to the red on increasing dendrimer generation; 2) in dichloromethane solution, the quantum yield and lifetime of the fluorescence band and the values of the half-wave potentials increase with dendrimer generation; 3) the dendrimer branches partially protect the core from oxidation by AuCl<sub>4</sub><sup>-</sup>. The strong blue fluorescence and the yellow to deep blue color change upon reversible one-electron oxidation might be exploited for optoelectronic and electrochromic applications.

## Experimental Section

**Synthesis: General:** <sup>1</sup>H NMR (200.13 or 500.13 MHz) and <sup>13</sup>C NMR (50.32 or 125.77 MHz) spectra were recorded on Bruker instruments AC200 or Avance500 respectively, in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> (293 K, dried over activated 4 Å molecular sieves, chemical shifts ( $\delta$ ) in ppm and coupling constants (*J*) in Hz). Me<sub>4</sub>Si (0.00 ppm) served as an internal standard, or residual signals for CHCl<sub>3</sub> (<sup>1</sup>H NMR,  $\delta = 7.26$  ppm; <sup>13</sup>C NMR,  $\delta = 77.36$  ppm) or DMSO (<sup>1</sup>H NMR,  $\delta = 2.54$  ppm; <sup>13</sup>C NMR,  $\delta = 40,45$  ppm). Mass spectra were recorded on an Ion-Trap ThermoFinnigan LCQ (Thermo Electron) spectrometer using ESI mode (API: atmospheric pressure ionization source, positive mode, ion-spray voltage 4.5–5.0 kV; capillary temperature: 200–250 °C) or EI mode (direct introduction, Automass probe (IPC), temperature range 60–350 °C with 100 °C min<sup>-1</sup>, max. 3 min). MALDI-TOF spectra were recorded on a Bruker Reflex II and dithranol was used as a matrix (molar ratio of dithranol/sample was about 250:1). HRMS spectra were recorded on a QStar Elite (Applied Biosystems SCIEX-API: atmospheric pressure ionization source, positive mode, ion-spray voltage 5.5 kV). Melting points (uncorrected) were determined in an open capillary with an Electrothermal 9100 apparatus (0.2 °C min<sup>-1</sup>). Microanalyses were performed at the Spectropole de Marseille, France.

**Chemicals:** Aluminium TLC precoated silica gel plates from SDS 60F<sub>254</sub> (15–60 µm) were used. Visualization: UV (254, 315, 365 nm), iodine-SiO<sub>2</sub> and/or a Ce/Mo developer (100 mL H<sub>2</sub>SO<sub>4</sub>, 900 mL H<sub>2</sub>O, 25 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>H<sub>2</sub>O, 10 g Ce(SO<sub>4</sub>)<sub>2</sub> - followed by heating). Column chromatography purifications were achieved over silica gel 60 from SDS (40–63 µm). Most reagents were purchased from Sigma-Aldrich or Acros Organics and used as received. DMF was dried over CaH<sub>2</sub> overnight, distilled under reduced pressure and kept over freshly activated 3 Å molecular sieves (250 °C for 3 h). Similarly, DMI was also kept over 3 Å molecular sieves. Powdered NaH (95 %) was used as received. The synthesis of some compounds has been reported previously: 1,3,6,8-tetrabromopyrene,<sup>[19]</sup> **Dend-G1-SMe**,<sup>[20,25]</sup> **Dend-G1-SH**,<sup>[20,24]</sup> **Dend-G2-SMe**,<sup>[20]</sup> **Dend-G2-SH**.<sup>[20]</sup>

**General procedure for pyrene dendrimers synthesis (PyG0, PyG1, PyG2):** The thiol (*p*-methylbenzenethiol, **Dend-G1-SH** or **Dend-G2-SH** (4.58 equiv) and 1,3,6,8-tetrabromopyrene<sup>[12]</sup> (1.00 equiv) were weighed in an oven-dried two-neck flask capped with septa. Under a flow of nitrogen, dry DMF or dry DMI (1,3-dimethyl-2-imidazolidinone) was added using a syringe. NaH was weighed in a closed Gooch tube (U-shape) and the latter was installed on the main flask after removing the septa. After cooling in an ice-bath for a few minutes while stirring vigorously, NaH was added carefully in small portions over a period of 5–10 mins, to control an effervescent and exothermic reaction. After release of the gas, the mixture was stirred at 80 °C (oil bath temperature) for 24–60 h (120 °C for 30 h for **PyG2**). A color change was observed and a yellow precipitate appeared over time (see separate procedure for **PyG2**, after this point). The solid was collected and washed several times with ethanol, while stirring vigorously each time for a few minutes. The final yellow solid was collected and dried in vacuo for several hours.

**PyG0:** 4-Methylbenzenethiol (1.10 g, 8.87 mmol), 1,3,6,8-tetrabromopyrene (1.00 g, 1.94 mmol), NaH (95 %) (0.224 g, 9.33 mmol), DMI (16.0 mL), temperature 80 °C for 60 h; **PyG0** was obtained as a yellow solid (1.205 g, 90 %); m.p. 285–288 °C; <sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub>): δ = 8.60 (s, 4H, Pyr), 7.87 (s, 2H, Pyr), 7.14 (d<sub>app</sub>, <sup>3</sup>J(H,H) = 8.1 Hz, 8H, S-Ph-S), 7.03 (d<sub>app</sub>, <sup>3</sup>J(H,H) = 8.1 Hz, 8H; S-Ph-S), 2.32 ppm (s, 12H; CH<sub>3</sub>); <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>): δ = 137.5, 134.2, 132.4, 132.0, 131.5, 130.6, 130.4, 126.1, 125.4, 21.5 ppm (CH<sub>3</sub>); MS (EI): *m/z* (%): 567.5 (9) [*M*-CH<sub>2</sub>PhS], 690.3 (100) [*M*]<sup>+</sup>, 691.3 (50) [*M*+1]<sup>+</sup>, 692.3 (30) [*M*+2]<sup>+</sup>, 693.3 (10) [*M*+3]<sup>+</sup>; HRMS (ESI, chem. ionization with AgOTf) calcd for [C<sub>44</sub>H<sub>34</sub>S<sub>4</sub> + Ag]<sup>+</sup>: 799.0587 [*M*+Ag]<sup>+</sup>; found: 799.0565 [*M*+Ag]<sup>+</sup>; elemental analysis calcd (%) for C<sub>44</sub>H<sub>34</sub>S<sub>4</sub>: C 76.48, H 4.96, S 18.56; found: C 74.78, H 4.88, S 18.34.

**PyG1: Dend-G1-SH** (3.15 g, 8.89 mmol), 1,3,6,8-tetrabromopyrene (1.01 g, 1.95 mmol), solid NaH (purity 95 %) (0.224 g, 9.33 mmol), DMF (15.0 mL), bath temperature 80 °C for 26 h; the color changed from orange to yellow; **PyG1** was obtained as a yellow solid (2.20 g, 70 %); *R*<sub>f</sub> = 0.71 (petroleum ether in toluene, 70/30 v/v); m.p. 168–171 °C; <sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub>): δ = 8.54 (s, 4H; Pyr), 8.12 (s, 2H; Pyr), 7.11 (d<sub>app</sub>, <sup>3</sup>J(H,H) = 8.0 Hz, 16H; S-Ph-S), 6.86 (d<sub>app</sub>, <sup>3</sup>J(H,H) = 8.0 Hz, 16H; S-Ph-S), 6.77 (s, 4H), 6.67 (s, 8H), 2.78 ppm (s, 24H; CH<sub>3</sub>); <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>): δ = 141.0, 138.8, 138.6, 133.8, 130.4, 129.8, 128.9, 126.7, 125.7, 125.5, 21.5 ppm (CH<sub>3</sub>); MS (ESI, chem. ionization with AgOTf): *m/z* (%): 1611.3 (12) [*M*]<sup>+</sup>, 1719.2 (100) [*M*+Ag]<sup>+</sup>; MS (MALDI-TOF, dithranol, THF): 1613.3 [*M*+H]<sup>+</sup>; HRMS (ESI, chem. ionization with AgOTf) calcd for [C<sub>96</sub>H<sub>74</sub>S<sub>12</sub> + Ag]<sup>+</sup>: 1719.1469 [*M*+Ag]<sup>+</sup>; found: 1719.1494 [*M*+Ag]<sup>+</sup>; elemental analysis calcd (%) for C<sub>96</sub>H<sub>74</sub>S<sub>12</sub>: C 71.51, H 4.63, S 23.86; found: C 69.55, H 4.51, S 23.57.

**PyG2: Dend-G2-SH** (622 mg, 0.763 mmol), 1,3,6,8-tetrabromopyrene (77.3 mg, 0.149 mmol), NaH (95 %) (17.2 mg, 0.717 mmol), DMF (1.5 mL), bath temperature 120 °C for 3 h. After the mixture had been allowed to cool, the orange solution was taken up in dichloromethane (30 mL) and aqueous NaOH (30 mL, 1.0 M). The aqueous solution was discarded and the DCM phase was further washed with aqueous NaOH (3 × 10 mL, 1.0 M). After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtration, and evaporation of solvent, a yellow oil was obtained. Column chromatography (SiO<sub>2</sub>, petroleum ether/toluene: 60/40 v/v), evaporation of solvents and drying in vacuo afforded **PyG2** (310 mg, 60 %, yellow solid); *R*<sub>f</sub> = 0.23 (toluene in petroleum ether, 40 % v/v); <sup>1</sup>H NMR (500.13 MHz,

CDCl<sub>3</sub>): δ = 8.65 (s, 4H; Pyr), 8.11 (s, 2H; Pyr), 7.16 (d<sub>app</sub>, <sup>3</sup>J(H,H) = 8.0 Hz, 32H; S-Ph-S), 7.03 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 32H; S-Ph-S), 6.82 (s, 12H), 6.71 (m, 24H), 2.28 ppm (s, 48H; CH<sub>3</sub>); <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>): δ = 140.7, 139.2, 138.8, 138.5, 138.0, 133.8, 133.06, 130.6, 130.4, 129.9, 129.3, 129.2, 127.9, 126.8, 126.1, 21.6 ppm (CH<sub>3</sub>); MS (MALDI-TOF, dithranol, THF): 3455 [*M*+H]<sup>+</sup> (isotopic envelope); elemental analysis calcd (%) for C<sub>200</sub>H<sub>154</sub>S<sub>28</sub>: C 69.52, H 4.49, S 25.98; found: C 69.56, H 4.53, S 26.21.

**Photophysical experiments:** The experiments were carried out in air-equilibrated cyclohexane and dichloromethane solution at 298 K. Luminescence measurements at 77 K were performed in dichloromethane/chloroform (1:1 v/v). UV/Vis absorption spectra were recorded with a Perkin Elmer 240 spectrophotometer, using quartz cells with pathlength of 1.0 cm. Fluorescence spectra were obtained with a Perkin Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube. The estimated experimental errors are: 2 nm on the band maximum, 5 % on the molar absorption coefficient.

**Redox experiments:** Cyclic voltammetric (CV) experiments were carried out in argon-purged dichloromethane (Romil Hi-Dry™) solutions with tetrabutylammonium hexafluorophosphate as supporting electrolyte at room temperature with an Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm<sup>2</sup>, Amel); its surface was routinely polished with 0.3 mm alumina-water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and an Ag wire was used as a quasi-reference electrode. Ferrocene (*E*<sub>1/2</sub> = +0.395 V vs. SCE) was present as an internal standard.

Spectroelectrochemistry was performed in an optically transparent thin-layer electrochemical (OTTLE) cell equipped with quartz windows, two Pt minigrids as working and counter electrodes, and a silver wire as a quasi-reference electrode. Prior to electrolysis, a thin-layer cyclic voltammogram at a scan rate of 5 mV s<sup>-1</sup> was recorded in order to choose the proper electrolysis potential. Absorption spectra were recorded by an Agilent Technologies 8543 diode array spectrophotometer.

## Acknowledgements

We thank the Univ. de la Méditerranée (Marseille), the instrument center Spectropole of Marseille, CNRS France. We acknowledge Dr. L. Massi (mass spectrometry), Dr. H.-J. Raeder and Dr. A. Rouhanipour (MALDI-TOF, Max Planck Institute for Polymer Research, Mainz, Germany); Prof. A. Samat (Univ. de la Méditerranée), Dr. Y. M. Chabre (UQAM, Montréal), and Prof. R. Giasson (Univ. de Montréal). This work was funded by the France-Canada Funds (2000–2002) and by MIUR (PRIN 2006034123\_003) in Italy.

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Received: June 18, 2008  
Published online: October 8, 2008