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Synthesis of phosphorus dendrimers bearing chromophoric end groups: toward organic blue light-emitting diodes

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Abstract—Several series of phosphorus dendrimers decorated by potential fluorescent end groups (naphthalene, anthracene, and pyrene) have been synthesized. Unexpectedly, we found that it is absolutely necessary to link the fluorophore to the dendrimer through an alkyl link, and not directly through heteroelements such as oxygen or nitrogen, in order to preserve the fluorescence. One series of dendrimers from generation 1 (6 pyrene end groups) to generation 4 (48 pyrene end groups) has been tested for the elaboration of organic light-emitting diodes (OLEDs). The threshold voltage for the emission of light is high (over 20 V), however, electroluminescence is observed in all cases.

1. Introduction

Dendrimers[1–3] constitute a very special type of polymers, whose hyperbranched and perfectly defined structure arouse the interest of thousands of researchers since about 20 years. Their stepwise synthesis allows the grafting where the desired (core, branches, and surface) functional groups were chosen to impart properties in particular in materials science, catalysis, or biology. Among these functional groups, fluorescent entities occupy a special place; they have been grafted to several types of dendrimers and for a lot of purposes,[4,5] including analytical uses such as the detection of dendritic defects[6] or the measurement of hydrodynamic radius,[7] and also for several applications such as labeling of biological entities[8] or elaboration of electroluminescent materials usable as light-emitting diodes. Indeed, organic light-emitting diodes (OLEDs) have key advantages for full-color flat-panel displays, such as high luminescence efficiency, color purity, wide viewing angle, low weight, and lower drive voltages.[9–11] Several types of fluorescent and electroactive dendrimers have already been used for researches in this field, based in particular on fully conjugated dendrimers such as poly(distyrylbenzene),[12] poly(*p*-phenylene),[13] or poly(phenylenevinylene)[14] dendrimer, and also on non-fully conjugated dendrimers (generally of type poly (benzyl ether)) possessing one fluorescent unit at the core.[15,16] However, none of these examples concerns phosphorus-containing dendrimers, despite the known influence of the type of skeleton on the properties (stability, solubility, polarity, density, etc.). We have already reported the grafting of fluorescent entities at the core,[17–19] in the interior,[20] or as end groups of phosphorus dendrimers,[21,22] as well as the synthesis of electroactive phosphorus dendrimers, possessing in most cases ferrocene,[23–25] thiophene,[26] or TTF[27,28] unit. We report here the grafting of several potential fluorescent entities (naphthalene, anthracene, and pyrene) as end groups of several types and generations of phosphorus-containing dendrimers, and the tentative use of one series for the elaboration of organic light-emitting diodes (OLEDs).

2. Results and discussion

2.1. Grafting of fluorescent derivatives on the surface of phosphorus dendrimers

In a first attempt, we decided to use our classical series of phosphorus dendrimers, synthesized by the repetition of two steps (a nucleophilic substitution of hydroxybenzaldehyde on $P(S)Cl_2$ groups and a condensation reaction of a phosphorhydrazide with the aldehydes),[29,30] starting from hexafunctional cyclotriphosphazene core.[31] The simplest way to graft functional groups on the surface of phosphorus-containing dendrimers having $P(S)Cl_2$ end groups consists of using functional phenols in basic conditions, generally as their sodium salts. The grafting of naphthol on the surface of the second generation dendrimer **1-G$_2$** possessing 12 $P(S)Cl_2$ end groups (Scheme 1) is easily monitored by ^{31}P

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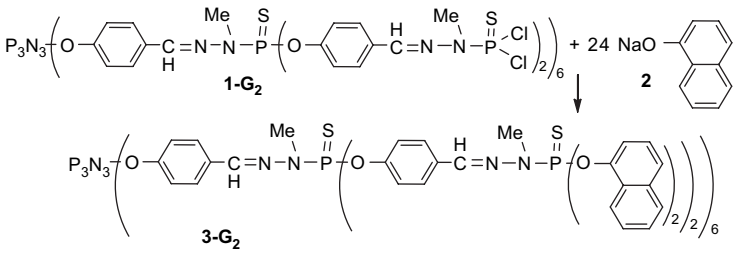


Scheme 1.

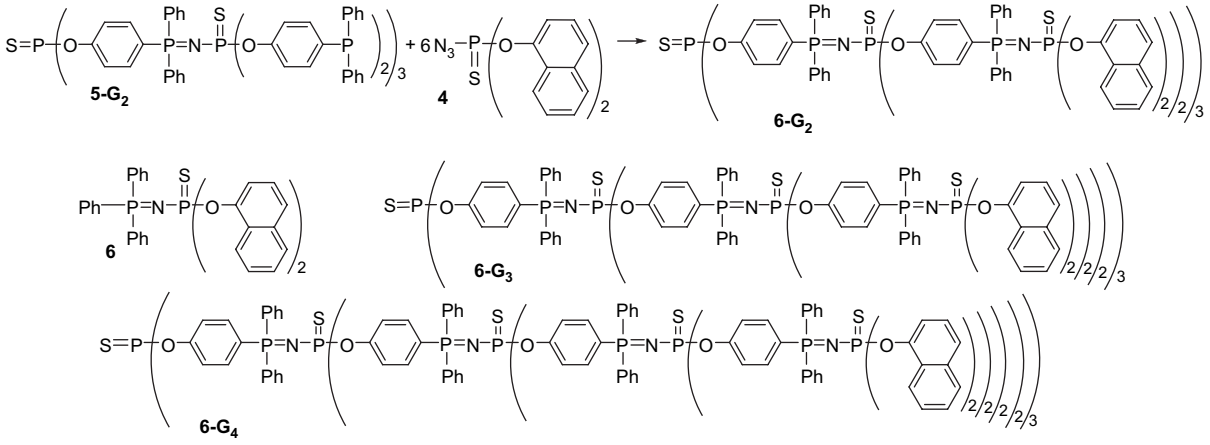
NMR. An intermediate signal at δ=67.5 ppm corresponding to the monosubstitution on each end group is first observed, replaced after the completion of the reaction by a singlet at 61.9 ppm, in addition to the signals corresponding to the core in the first generation. This dendrimer **3-G$_2$** is also characterized by ^{1}H and ^{13}C NMR.

Surprisingly, despite the presence of 24 fluorophores on the surface of dendrimer **3-G$_2$**, this compound is not fluorescent. In order to determine whether the skeleton of the dendrimer could be responsible for this astonishing result, we decided to try to graft naphthol on the surface of another type of phosphorus dendrimers, based on P═N–P═S linkages.[32] This series of dendrimers has free or protected phosphines as end groups at each step. Thus, naphthol cannot be directly linked to these end groups, and we decided to synthesize first the azide **4**, obtained by the reaction of 2 equiv of naphthol on $P(S)Cl_3$, followed by the substitution of the remaining Cl by N_3. The reactivity of this azide toward phosphines was first tested with PPh_3 as a model and with the second generation dendrimer **5-G$_2$**. The Staudinger reactions occur as expected, creating P═N linkages in the model compound **6** and the dendrimer **6-G$_2$** (Scheme 2).

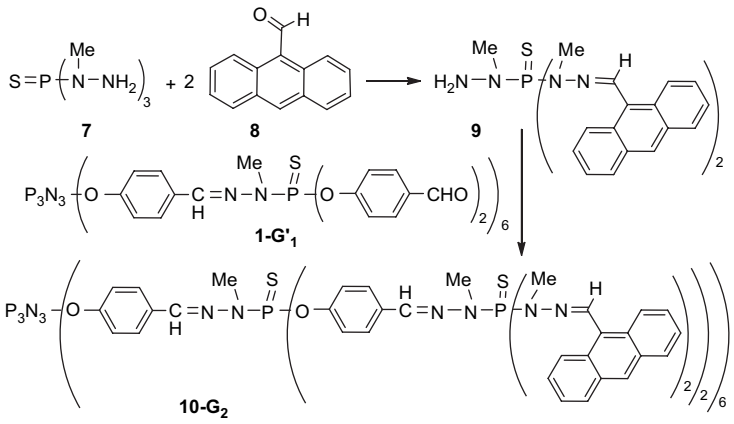
The Staudinger reaction is characterized by ^{31}P NMR, which displays both the disappearance of the singlet corresponding to the phosphine end groups (δ=−6 ppm) and the singlet corresponding to the azide **4** (δ=59.3 ppm), on behalf of the appearance of two doublets at δ=12 ppm (P═N) and 51 ppm (P═S), with $^{2}J_{PP}$=32 Hz. These signals are obtained in addition to two other doublets corresponding to the internal P═N–P═S linkages, and one singlet corresponding to the core of the dendrimer **6-G$_2$**. The azide **4** was also reacted with the third and fourth generations of the dendrimer **5-G$_n$**, to afford dendrimers **6-G$_3$** and **6-G$_4$**, respectively.

The presence of numerous conjugated Ph–P═N–P═S linkages incited us to test the electrochemical behavior of this series of dendrimers. The cyclic voltammogram of the first generation displays a single wave characteristic of an irreversible oxidation. This assumption is supported by the ^{31}P NMR spectrum obtained after electrolysis: the doublets characteristic of **6-G$_2$** disappeared on behalf of a multitude of signals between −10 and +60 ppm. This observation implies the occurrence of an EC process, that is, an electronic transformation followed by a chemical transformation. Such instability under current is incompatible with the use of this series of dendrimers **6-G$_n$** for the elaboration of OLEDs, thus we decided to move back to the first type of dendritic skeleton (shown in Scheme 1), and to modify the type of fluorophore end groups.

In a first attempt, we decided to use the sodium salt of anthracen-9-ol to react with $P(S)Cl_2$ end groups. The reaction is monitored by ^{31}P NMR, which shows the appearance of an intermediate signal at δ=68.8 ppm, corresponding to the substitution of one Cl on each end groups, slowly followed by the appearance of a signal at 63.3 ppm, corresponding to the di-substitution. However, the fully substituted dendrimer could not be isolated, presumably due to a [2+2] photochemical cycloaddition reaction, which induces the precipitation of insoluble compounds. Such behavior has been already observed when two 9-anthryl groups are linked through three atoms,[33] such as the O–P–O linkage in our case.



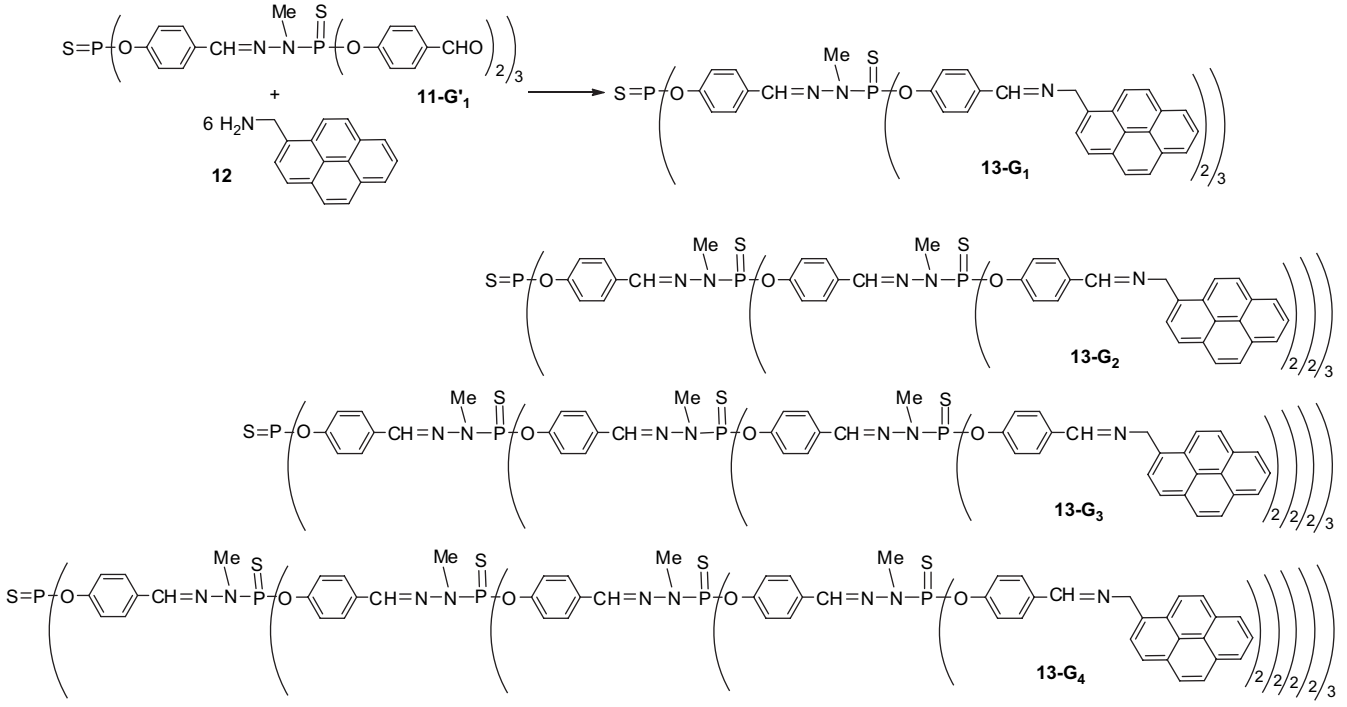
Scheme 2.



Scheme 3.

Thus, we designed another strategy, in order to have a longer linker between both anthryl groups. For such purpose, 2 equiv of 9-anthraldehyde **8** was reacted with 1 equiv of the phosphotrihydrazide **7**, to afford compound **9**, which is isolated in 73% yield. No trace of dimerization is observed for this compound, in which both anthryl groups are separated by seven atoms. The unreacted NH_2 group of compound **9** is used in condensation reactions with the aldehyde end groups of the first generation dendrimer **1-G$_1$′**,[31] to afford the second generation dendrimer **10-G$_2$** (Scheme 3). The completion of the condensation reaction is easily shown by the disappearance of the signals corresponding to the aldehydes by ^{1}H and ^{13}C NMR and by IR spectroscopy.

Unfortunately, this dendrimer also is not fluorescent. In view of all the problems we encountered concerning fluorescence, we reasoned that the presence of several heteroatoms in close proximity to the fluorophores might be the reason, by inducing non-radiative relaxations, in particular due to $n \rightarrow \pi^*$ transitions. Thus, we decided to introduce an alkyl linker to isolate the chromophore from the electronic effects of the dendrimer. Our choice was made on the simplest linker, a CH_2 group, present for instance in 1-pyrenemethylamine **12**. This compound was used in condensation reactions on aldehyde end group of the dendrimer **11-G$_1$′**,[29,30] which differs from **1-G$_1$′** only by the type of core, and the number of end groups. The condensation reactions induce the total disappearance of the signals corresponding to the aldehydes in ^{1}H and ^{13}C NMR and IR spectra. We did not observe hydrolysis of the imine bonds, neither in solution in organic solvents nor when kept as a powder in air. The same condensation reactions were carried out with generations two, three, and four of dendrimer **11-G$_n$′**, to afford dendrimers **13-G$_2$**, **13-G$_3$**, and **13-G$_4$**, respectively (Scheme 4 and Fig. 1).



Scheme 4.

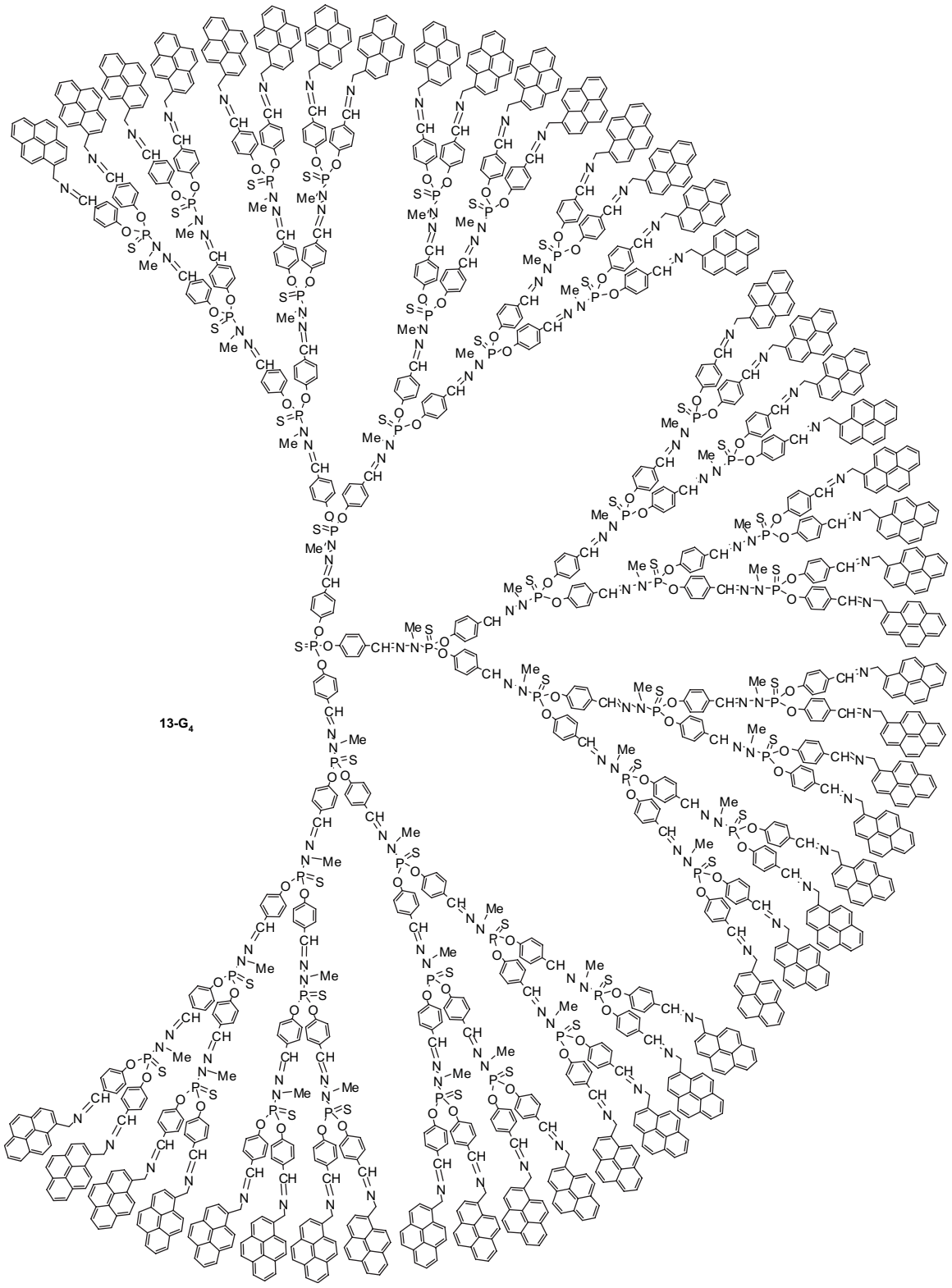


Figure 1. Structure of dendrimer **13-G$_4$**.

Our assumption concerning the negative influence of heteroatoms on the fluorescence properties appears right: the series of dendrimers **13-G$_n$** is fluorescent. Thus, we have carried out a series of tests with these dendrimers, in view of the elaboration of OLEDs. Most of the tests were carried out on the first generation as a model, then on generations three and four to compare with large compounds.

2.2. Photo-physical properties of dendrimers 13-G$_n$

The first property we checked concerns the thermal stability. Thermogravimetric analyses of all compounds display a slight loss of mass (2–7%) between 80 and 180 °C, corresponding to the evaporation of residual solvents, as identified by GC mass. The real decomposition of dendrimers

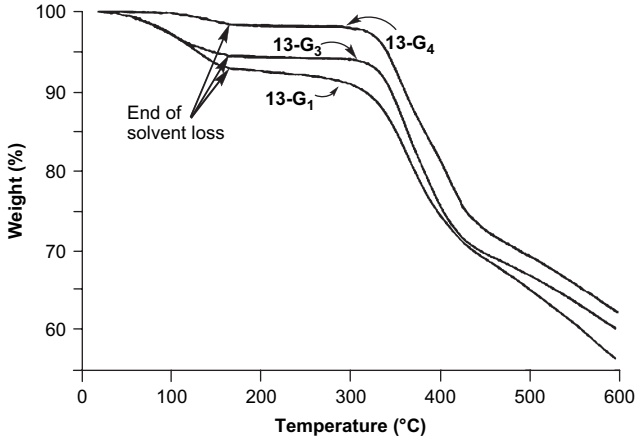


Figure 2. Thermogravimetric analyses of dendrimers **13-G$_n$** (n=1, 3, and 4).

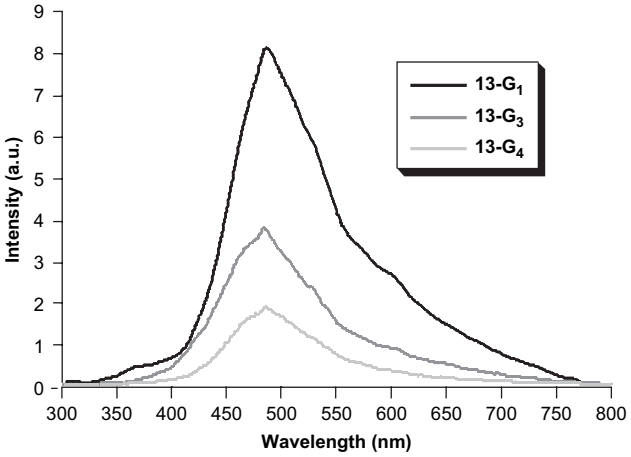


Figure 3. Emission spectra of pyrene excimers of thin films of **13-G$_1$**, **13-G$_3$**, and **13-G$_4$** (intensities in arbitrary units).

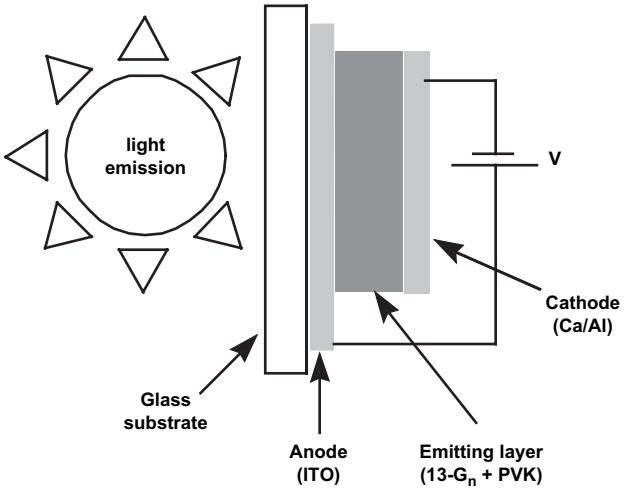


Figure 4. OLED device structure elaborated for electroluminescence experiments.

begins at about 320 °C for all generations (Fig. 2); thus this series of dendrimers is thermally stable enough to be used for the elaboration of OLEDs. The insensitivity of the thermal stability toward generations was already observed for other series of dendrimers having the same skeleton but different end groups.[34]

The second point to be verified concerns the glass transition temperature (T_g). Indeed, the T_g value must be higher than the temperature of the OLED; if not, crystalline microdomains can be formed, inducing a degradation of the performances of the OLED. No glass transition temperature could be detected for **13-G$_1$** between 20 and 300 °C; this result is surprising in view of the value found for the parent compound **11-G$_1$′** (74 °C).[35] The T_g value is 153 °C for **13-G$_3$** and 243 °C for **13-G$_4$**. Thus, OLEDs created from both dendrimers must be used at temperatures lower than 150 and 240 °C, respectively.

The photoluminescence properties of these dendrimers were measured on thin films of **13-G$_1$**, **13-G$_3$**, and **13-G$_4$**. The UV–visible absorption spectra display the bands characteristic of pyrene at 335 and 352 nm, in addition to a very broad band between 230 and 330 nm, corresponding to the aromatic groups of the dendrimers.[36] The fluorescence measured after excitation at 250 nm displays a single emission band in the blue at 484 nm for all three dendrimers. This very broad band corresponds to the emission of excimers of pyrene (Fig. 3). No emission of monomeric pyrene could be detected, in accordance with our previous experiments concerning pyrene derivatives included within the interior of dendrimers.[20]

Electroluminescence was measured on diodes elaborated from a glass substrate covered by a thin film of indium tin oxide (ITO), constituting the transparent anode. The emitting organic layer is deposited by spin coating on the anode of a solution in trichloroethane of dendrimer **13-G$_n$** (5 g/L) in a matrix of poly(vinylcarbazole) (PVK, 20 g/L); then the solvent is eliminated by slow evaporation. The PVK polymer acts as hole transporter and prevents crystallization. The inorganic refractive cathode is constituted by a layer of Ca/Al (Fig. 4).

Application of a voltage between the electrodes should induce the injection of charges into the organic layer (holes from the anode and electrons from the cathode); their recombination will create excitons; a fraction of them will decay radiatively. In the case of the materials elaborated from dendrimers **13-G$_n$**, the threshold tension (V_t) is very high (18 V for **13-G$_1$** and **13-G$_3$**, 20 V for **13-G$_4$**) (Fig. 5). This high value might be due to the trapping of electrons by the dendritic structure, a phenomenon that we already observed.[37] Such high working voltage precludes any practical applications of such devices; however, we decided to determine their brightness.

In all devices, electroluminescence emission peaks are in the blue at about 484 nm, as observed for the photoluminescence spectra of the corresponding dendrimers in thin films. Figure 6 displays the current–luminance characteristics of these OLEDs. The best results are obtained with the fourth generation dendrimer, but even in this case the emission of light is low, only 3.5 cd/m^2. The inset in Figure 6 shows that the threshold voltage for both current and light is similar, indicating a fairly balanced charge injection and transport; furthermore, the luminance is approximately proportional to the current density, indicating that the quantum efficiency is constant over a relatively large range of current.

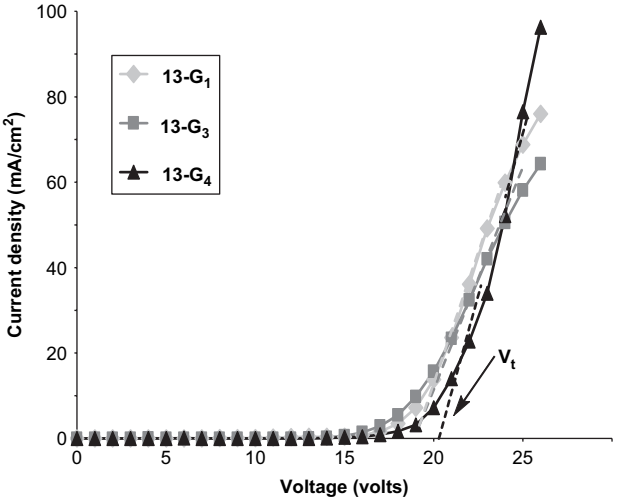


Figure 5. Current–voltage characteristics of **13-G$_n$** (n=1, 3, and 4) dendrimer-based OLEDs with structure of (ITO/**13-G$_n$**:PVK/Ca,Al; V_t: threshold tension).

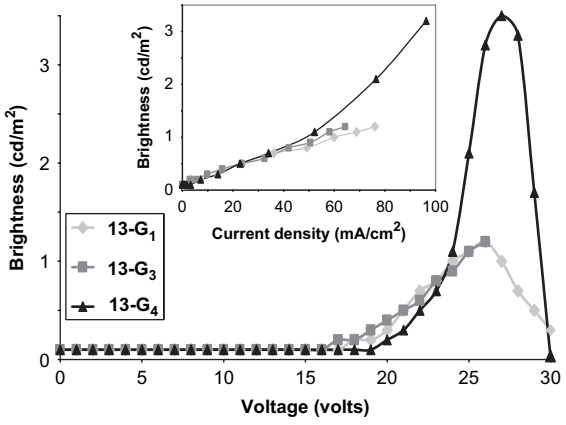


Figure 6. Light–voltage characteristics of **13-G$_n$** (n=1, 3, and 4) dendrimer-based OLEDs with structure of (ITO/**13-G$_n$**:PVK/Ca,Al). Inset: light–current correlation.

3. Conclusion

We have synthesized several series of phosphorus dendrimers bearing potential fluorescent entities as end groups (naphthalene, anthracene, and pyrene). However, the loss of fluorescence observed in several cases led us to the unexpected conclusion that the fluorophore must not be linked to the dendrimer through a heteroelement (oxygen or nitrogen) but through an alkyl linkage. The condensation of 1-pyrenemethylamine with the aldehyde end groups of the dendrimer led to a series of compounds fluorescent even in the solid state, and thermally very stable (up to 320 °C). This series of dendrimers has been tested for the elaboration of organic light-emitting diodes. These OLEDs have a threshold voltage for emission of light that is too high for practical purposes (18–20 V), but they do possess electroluminescent properties.

4. Experimental

4.1. General

All compounds were protected against light by wrapping the vessel in aluminum film. All manipulations were carried out with standard high vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and ether over sodium/benzophenone, pentane and CH_2Cl_2 over phosphorus pentoxide). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, or DPX 300 spectrometer. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, and $SiMe_4$ for ^{1}H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using J_{mod}, two-dimensional HMBC, and HMQC, Broad Band or CW ^{31}P decoupling experiments when necessary (br s means broad singlet). The number scheme used for NMR assignments is shown in Figure 7. Compounds **1-G$_n$**,[31] **1-G$_n$′**,[31] **5-G$_n$**,[32] and **11-G$_n$′**[29,30] were synthesized according to published procedures. The OLEDs are elaborated and characterized according to published procedures.[9,38,39]

4.1.1. Synthesis of dendrimer 3-G$_2$. A solution of dendrimer **1-G$_2$** (0.1 g. 20.9 μmol) in THF (30 mL) was added to a suspension of sodium salt of 1-naphthol **2** prepared with 0.1 g (0.69 mmol) of 1-naphthol and 17 mg of sodium hydride in THF (50 mL). The resulting mixture was stirred for 16 h at room temperature, then centrifuged, and the solution was evaporated to dryness to afford a powder, which was washed twice with ether (2×30 mL) to afford dendrimer **3-G$_2$** as a pale beige powder in 96% yield.

^{31}P {^{1}H} NMR ($CDCl_3$): δ=7.8 (s, P_0), 60.7 (s, P_2), 61.9 (s, P_2) ppm. ^{1}H NMR ($CDCl_3$): δ=3.1 (d, $^3J_{HP1}$=10.1 Hz, 18H, Me_1), 3.3 (d, $^3J_{HP2}$=10.6 Hz, 36H, Me_2), 6.9 (d, $^3J_{HH}$=8.5 Hz, 12H, H-C_0^2), 7.1 (d, $^3J_{HH}$=8.1 Hz, 24H, H-C_1^2), 7.2–7.6 (m, 174H, H Arom), 7.7 (d, $^3J_{HH}$=7.5 Hz, 24H, H-C^5), 8.1 (d, $^3J_{HH}$=7.8 Hz, 24H, H-C^8) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ=32.9 (d, $^2J_{CP1-2}$=13.8 Hz, Me_1, Me_2), 116.0 (d, $^3J_{CP2}$=3.9 Hz, C^2), 121.3 (br s, C_0^2), 121.5 (d, $^3J_{CP1}$=3.9 Hz, C_1^2), 122.5 (s, C^4), 125.2, 125.3 (2s, C^7, C^8), 126.0 (s, C^3), 126.5 (s, C^6), 127.0 (s, C_0^3), 127.1 (s, C_1^3), 127.6 (s, C^5), 128.2 (s, C^9), 132.1 (s, C_0^4), 132.2 (s, C_1^4), 134.7 (s, C^{10}), 138.6 (d, $^3J_{CP1-2}$=13.8 Hz, C_0^5, C_1^5), 147.0 (d, $^2J_{CP2}$=9.8 Hz, C^1), 151.1 (d, $^2J_{CP0-1}$=6.0 Hz, C_0^1, C_1^1) ppm. Anal. Calcd for $C_{384}H_{312}N_{39}O_{66}P_{21}S_{18}$ (7757): C, 59.46; H, 4.05; N, 7.04. Found: C, 59.19; H, 3.88; N, 6.85.

4.1.2. Synthesis of the azide 4. A solution of 1-naphthol (0.94 g, 6.5 mmol) and triethylamine (1 mL, 7.2 mmol) in THF (20 mL) was added dropwise at room temperature to a solution of trichlorothiophosphine (0.33 mL, 3.25 mmol) in THF (30 mL). After stirring for 24 h, the solution was filtered, and then concentrated. Acetone (20 mL) and sodium azide (0.23 g, 3.5 mmol) were added, and the resulting mixture was stirred for 3 days at room temperature, then concentrated and centrifuged. The solution was evaporated to dryness to afford the azide **4** without further purification as maroon oil in 88% yield.

^{31}P {^{1}H} NMR ($CDCl_3$): δ=59.3 (s) ppm. ^{1}H NMR ($CDCl_3$): δ=7.30–7.90 (m, 12H, H_{Ar}), 8.2 (m, 2H, H-C_8) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ=116.6 (d, $^3J_{CP1}$=4.1 Hz, C^2), 122.0 (s, C^8), 125.4 (d, $^5J_{CP}$=1.0 Hz, C^7), 125.8 (d, $^5J_{CP}$=1.0 Hz, C^4), 126.6 (s, C^3), 126.7 (s, C^6), 126.8 (d, $^3J_{CP}$=5.6 Hz, C^9), 127.8 (s, C^5), 134.8 (s, C^{10}), 146.8 (d, $^2J_{CP}$=10.0 Hz, C^1) ppm. IR (THF): 2160 (ν_{N3}) cm^{-1}.

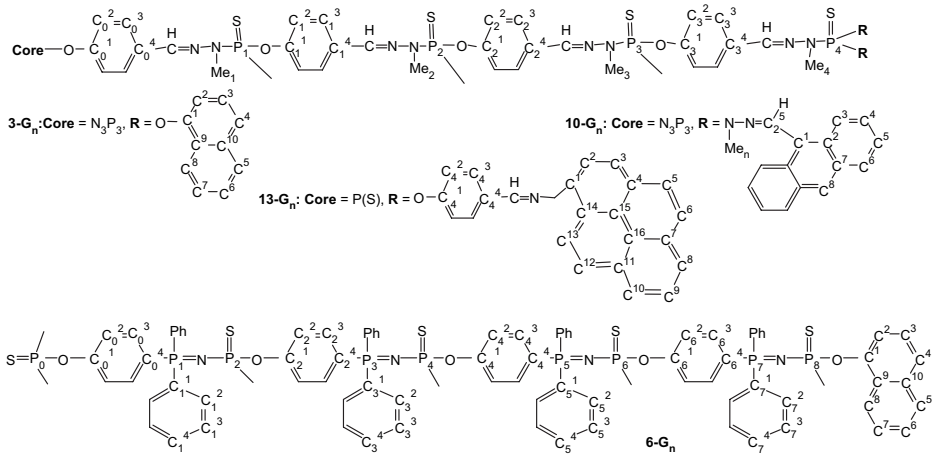


Figure 7. Numbering used for NMR assignments.

4.1.3. Synthesis of the model compound 6. A solution of the azide **4** (100 mg, 0.26 mmol) in THF (10 mL) was added to a solution of triphenylphosphine (70 mg, 0.26 mmol) in THF (10 mL) and stirred at room temperature for 1 h. The resulting solution was evaporated to dryness to afford a powder, which was washed three times with a diethylether/pentane mixture (1/9) to afford **6** as a white powder in 95% yield.

^{31}P {^{1}H} NMR ($CDCl_3$): δ=12.6 (d, $^{2}J_{PP}$=32.0 Hz, P_0), 51.0 (d, $^{2}J_{PP}$=32.0 Hz, P_1) ppm. ^{1}H NMR ($CDCl_3$): δ=7.30–7.39 (m, 10H, H-C^3, H-C^7, H-C$_0^3$), 7.40–7.47 (m, 2H, H-C^6), 7.47–7.57 (m, 9H, H-C$_0^2$, H-C$_0^4$), 7.65 (m, 2H, H-C^4), 7.71 (m, 2H, H-C^2), 7.83 (m, 2H, H-C^5), 8.15 (m, 2H, H-C^8) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ=117.2 (d, $^{3}J_{CP1}$=4.5 Hz, C^2), 123.8 (s, C^8), 124.4 (d, $^{5}J_{CP1}$=2.0 Hz, C^4), 126.0 (br s, C^3, C^7), 126.6 (s, C^6), 127.8 (s, C^5), 128.3 (d, $^{3}J_{CP1}$=5.0 Hz, C^9), 128.9 (d, $^{3}J_{CP0}$=13.0 Hz, C$_0^3$), 129.1 (dd, $^{3}J_{CP1}$=4.0 Hz, $^{1}J_{CP0}$=107 Hz, C$_0^1$), 132.8 (d, $^{4}J_{CP0}$=3.0 Hz, C$_0^4$), 133.1 (d, $^{2}J_{CP0}$=11.0 Hz, C$_0^2$), 135.2 (s, C^{10}), 148.9 (d, $^{2}J_{CP1}$=10.0 Hz, C1) ppm. Anal. Calcd for $C_{38}H_{29}NO_2P_2S$ (25,618): C, 72.95; H, 4.67; N, 2.24. Found: C, 71.74; H, 4.36; N, 1.99.

4.1.4. General method for the synthesis of the series of dendrimers 6-G$_n$ (n=2, 3, and 4). A stoichiometric amount of azide **4** in dissolved in THF (10 mL) was added dropwise to a solution of dendrimer **5-G$_{n-1}$** (typically 100 mg) in THF (20 mL) and stirred at room temperature for 1 h. The resulting solution was evaporated to dryness to afford a powder, which was washed three times with a diethylether/pentane mixture (1/1) to afford dendrimers **6-G$_n$** as white powders.

4.1.4.1. Compound 6-G$_2$. Yield 89%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=11.3 (d, $^{2}J_{PP}$=32.5 Hz, P_3), 13.0 (d, $^{2}J_{PP}$=30.5 Hz, P_1), 49.2 (s, P_0), 49.3 (d, $^{2}J_{PP}$=30.5 Hz, P_2), 51.0 (d, $^{2}J_{PP}$=32.5 Hz, P_4) ppm. ^{1}H NMR ($CDCl_3$): δ=7.0–7.6 (m, 186H, C_6H_5, C_6H_4, naphthyl), 7.63 (d, $^{3}J_{H5H6}$=7.9 Hz, 12H, H-C^5), 7.96 (d, $^{3}J_{H7H8}$=8.1 Hz, 12H, H-C^8) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ=116.7 (d, $^{3}J_{CP6}$=3.6 Hz, C^2), 121.5–121.8 (m, C$_0^2$, C$_2^2$), 123.2 (s, C^8), 123.2 (br d, $^{1}J_{CP}$=111 Hz, C$_2^4$), 123.9 (br s, C^4), 125.5 (br s, C^3, C^7), 126.1 (s, C^6), 127.3 (s, C^5), 127.7 (br d, $^{1}J_{CP1}$=106 Hz, C$_1^1$), 128.2 (br d, $^{1}J_{CP}$=106 Hz, C$_3^1$), 128.4 (d, $^{3}J_{CP4}$=13.5 Hz, C^9), 128.7 (d, $^{3}J_{CP}$=13.1 Hz, C$_1^3$, C$_3^3$), 132.4 (s, C$_1^4$, C$_3^4$), 132.5 (d, $^{2}J_{CP}$=11.3 Hz, C$_1^2$, C$_3^2$), 134.3 (d, $^{2}J_{CP}$=12.1 Hz, C$_0^3$, C$_2^3$), 134.6 (s, C^{10}), 148.3 (d, $^{2}J_{CP4}$=9.7 Hz, C^1), 153.4 (br d, $^{2}J_{CP0}$=8 Hz, C$_0^1$), 155.2 (dd, $^{4}J_{CP3}$=3.69 Hz, $^{2}J_{CP2}$=7.63 Hz, C$_2^1$) ppm. Anal. Calcd for $C_{282}H_{210}N_9O_{21}P_{19}S_{10}$ (4970): C, 68.15; H, 4.26; N, 2.54. Found: C, 67.77; H, 3.92; N, 2.18.

4.1.4.2. Compound 6-G$_3$. Yield 93%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=11.3 (d, $^{2}J_{PP}$=33.4 Hz, P_5), 13.0 (br d, $^{2}J_{PP}$=31.0 Hz, P_1, P_3), 49.2 (s, P_0), 49.3 (br d, $^{2}J_{PP}$=31.0 Hz, P_2, P_4), 51.0 (d, $^{2}J_{PP}$=33.4 Hz, P_6) ppm. ^{1}H NMR ($CDCl_3$): δ=7.0–7.6 (m, 414H, C_6H_5, C_6H_4, naphthyl), 7.60 (d, $^{3}J_{H5H6}$=7.9 Hz, 24H, H-C^5), 7.95 (d, $^{3}J_{H7H8}$=8.1 Hz, 24H, H-C^8) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ=116.7 (d, $^{3}J_{CP6}$=3.6 Hz, C^2), 121.5–121.8 (m, C$_0^2$, C$_2^2$, C$_4^2$), 123.2 (s, C^8), 123.2 (br d, $^{1}J_{CP}$=111 Hz, C$_2^4$, C$_4^4$), 123.9 (br s, C^4), 125.5 (br s, C^3, C^7), 126.1 (s, C^6), 127.3 (s, C^5), 127.7 (br d, $^{1}J_{CP1}$=106 Hz, C$_1^1$), 128.2 (br d, $^{1}J_{CP}$=106 Hz, C$_3^1$, C$_5^1$), 128.4 (d, $^{3}J_{CP6}$=13.5 Hz, C^9), 128.7 (d, $^{3}J_{CP}$=13.1 Hz, C$_1^3$, C$_3^3$, C$_5^3$), 132.4 (s, C$_1^4$, C$_3^4$, C$_5^4$), 132.5 (d, $^{2}J_{CP}$=11.3 Hz, C$_1^2$, C$_3^2$, C$_5^2$), 134.3 (d, $^{2}J_{CP}$=12.1 Hz, C$_0^3$, C$_2^3$, C$_4^3$), 134.6 (s, C^{10}), 148.3 (d, $^{2}J_{CP6}$=9.8 Hz, C^1), 153.4 (br m, C$_0^1$), 155.1–155.3 (m, C$_2^1$, C$_4^1$) ppm. Anal. Calcd for $C_{618}H_{462}N_{21}O_{45}P_{43}S_{22}$ (10,940): C, 67.85; H, 4.26; N, 2.69. Found: C, 67.32; H, 3.90; N, 2.25.

4.1.4.3. Compound 6-G$_4$. Yield 93%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ=11.3 (d, $^{2}J_{PP}$=33.7 Hz, P_7), 13.0 (br d, $^{2}J_{PP}$=30.6 Hz, P_1, P_3, P_5), 49.1 (br d, $^{2}J_{PP}$=30.6 Hz, P_2, P_4, P_6), 49.6 (s, P_0), 50.9 (d, $^{2}J_{PP}$=33.7 Hz, P_8) ppm. ^{1}H NMR ($CDCl_3$): δ=7.1–7.5 (m, 822H, C_6H_5, C_6H_4, naphthyl), 7.60 (d, $^{3}J_{H5H6}$=7.9 Hz, 48H, H-C^5), 7.95 (d, $^{3}J_{H7H8}$=8.1 Hz, 48H, H-C^8) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ=116.7 (d, $^{3}J_{CP8}$=3.8 Hz, C^2), 121.5–121.8 (m, C$_0^2$, C$_2^2$, C$_4^2$, C$_6^2$), 123.2 (s, C^8), 123.2 (br d, $^{1}J_{CP}$=111 Hz, C$_2^4$, C$_4^4$), 123.7 (br d, $^{1}J_{CP7}$=109.7 Hz, C$_6^4$), 123.9 (br s, C^4), 125.5 (br s, C^3, C^7), 126.0 (s, C^6), 127.3 (s, C^5), 127.7 (br d, $^{1}J_{CP1}$=106 Hz, C$_1^1$), 128.2 (br d, $^{1}J_{CP}$=106 Hz, C$_3^1$, C$_5^1$), 128.4 (d, $^{3}J_{CP8}$=13.5 Hz, C^9), 128.7 (br d, $^{1}J_{CP}$=105.7 Hz, C$_7^1$), 128.7 (d, $^{3}J_{CP}$=13.1 Hz, C$_1^3$, C$_3^3$, C$_5^3$, C$_7^3$), 132.4 (s, C$_1^4$, C$_3^4$, C$_5^4$, C$_7^4$), 132.5 (d, $^{2}J_{CP}$=11.0 Hz, C$_1^2$, C$_3^2$, C$_5^2$, C$_7^2$), 134.2 (d, $^{2}J_{CP}$=12.1 Hz, C$_0^3$, C$_2^3$, C$_4^3$, C$_6^3$), 134.6 (s, C^{10}), 148.3 (d, $^{2}J_{CP8}$=10.0 Hz, C^1), 153.4 (br m,

C_0^1), 155.1–155.7 (m, C_2^1, C_4^1, C_6^1) ppm. Anal. Calcd for $C_{1290}H_{918}N_{45}O_{93}P_{91}S_{46}$ (22,831): C, 67.86; H, 4.05; N, 2.76. Found: C, 67.29; H, 3.92; N, 2.37.

4.1.5. Synthesis of compound 9. A solution of 9-anthraldehyde **8** (2.80 g, 13.6 mmol) in THF (10 mL) was added to a solution of tris(1-methylhydrazino)thiophosphine **7** (1.1 g, 5.55 mmol) in THF (20 mL) at room temperature and stirred overnight. A precipitate was obtained; it was separated from the solution by filtration. The solution was recovered, and the precipitate was partly dissolved in 40 mL of THF (the trisubstitution product is insoluble). The resulting solution was combined with the previous one, and the solvent was removed under vacuum to afford **9** as a yellow powder in 73% yield.

^{31}P {^1H} NMR ($CDCl_3$): δ=75.5 (s) ppm. ^1H NMR ($CDCl_3$): δ=1.6 (br s, 2H, NH_2), 3.1 (d, $^3J_{HP}$=10 Hz, 3H, Me), 3.5 (d, $^3J_{HP}$=9 Hz, 6H, Me), 7.9, 7.95 (2s, 4H, CH=N, H anthryl), 7.1–7.4, 8.2–8.5 (m, 16H, H anthryl) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ=33.2 (d, $^2J_{CP}$=8.5 Hz, Me), 41.6 (d, $^2J_{CP}$=11.5 Hz, Me), 125.6 (s, C^3), 126.5 (s, C^5), 128.0 (s, C^2), 128.5 (s, C^6), 129.1 (s, C^4), 130.3 (s, C^1), 131.9 (s, C^7), 135.8 (s, C^8), 136.5 (s, CH=N) ppm. Anal. Calcd for $C_{33}H_{31}N_6PS$ (574.7): C, 68.97; H, 5.44; N, 14.62. Found: C, 68.60; H, 4.17; N, 14.48.

4.1.6. Synthesis of dendrimer 10-G_2. A solution of dendrimer **1-G_1′** (2.80 g, 13.6 mmol) in THF (10 mL) was added to a solution of compound **9** (1.10 g, 5.55 mmol) in THF (20 mL). After stirring for 4 days at room temperature, the solvent was removed under reduced pressure to afford a powder, which was purified by column chromatography on silica gel with ethyl acetate as eluent. Dendrimer **10-G_2** was isolated as a yellow powder in 73% yield.

^{31}P {^1H} NMR ($CDCl_3$): δ=8.5 (s, P_0), 62.5 (s, P_1), 74.0 (s, P_2) ppm. ^1H NMR ($CDCl_3$): δ=3.0 (d, $^3J_{HP1}$=10.6 Hz, 18H, Me_1), 3.1 (d, $^3J_{HP}$=9.8 Hz, 36H, Me_2), 3.4 (d, $^3J_{HP}$=8.3 Hz, 72H, Me_3), 6.8–8.5 (m, 330H, CH=N, H Ar) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ=32.7 (br d, $^2J_{CP}$=9.8 Hz, Me_{1-2-3}), 121.3 (s, C_0^2, C_1^2), 125.6 (s, C^3), 126.5 (s, C^5), 127.7 (s, C_0^3), 128.0 (s, C_1^3), 128.2 (s, C^2), 128.4 (s, C^6), 129.6 (s, C^4), 130.9 (s, C_0^4), 131.0 (s, C^1), 132.1 (s, C^7), 133.0 (s, C_1^4), 135.7 (d, $^3J_{CP1}$=10.2 Hz, C_1^5, C_2^5), 135.8 (s, C^8), 136.6 (d, $^3J_{CP1}$=10.4 Hz, C_0^5), 150.4 (d, $^2J_{CP1}$=7.9 Hz, C_0^1, C_1^1) ppm. Anal. Calcd for $C_{528}H_{456}N_{87}O_{18}P_{21}S_{18}$ (9536): C, 66.51; H, 4.82; N, 12.78. Found: C, 66.33; H, 4.67; N, 12.48.

4.1.7. General method for the synthesis of the series of dendrimers 13-G_n (n=1, 2, 3, and 4). A stoichiometric amount of pyrenemethylamine (freshly prepared from its chlorohydrate by reaction with KOH) in MeOH (10 mL) was added dropwise at room temperature to a solution of dendrimer **11-G_n′** (typically 100 mg) in THF (20 mL). The resulting solution was stirred at room temperature for 1 day (**G_1′**), 3 days (**G_2′**), 5 days (**G_3′**), or 7 days (**G_4′**) until the disappearance of the signal corresponding to the aldehydes in ^1H NMR. The solvent was evaporated to dryness to afford dendrimers **13-G_n** as white powders.

4.1.7.1. Compound 13-G_1. Yield 91%. ^{31}P {^1H} NMR ($CDCl_3$): δ=52.3 (s, P_0), 61.7 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ=3.3 (d, $^3J_{HP1}$=10.6 Hz, 9H, Me_1), 5.2 (s, 12H, CH_2), 7.2 (br d, $^3J_{HH}$=8.5 Hz, 18H, H-C_0^2, H-C_1^2), 7.5 (s, 3H, C_0^5), 7.6 (d, $^3J_{HH}$=8.6 Hz, 6H, H-C_0^3), 7.7 (d, $^3J_{HH}$=8.6 Hz, 12H, H-C_1^3), 7.8–8.30 (m, 60H, CH=N, pyrene) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ=33.0 (d, $^2J_{CP1}$=13.1 Hz, Me_1), 62.2 (s, CH_2-Pyr), 121.5 (d, $^3J_{CP0}$=5.9 Hz, C_0^2), 121.6 (d, $^3J_{CP1}$=4.9 Hz, C_1^2), 123.3 (s, C^{13}), 124.8–125.2 (m, C^2, C^8, C^{10}, C^{15}, C^{16}), 125.9 (s, C^3), 126.7 (s, C^9), 127.0 (s, C^5), 127.4, 127.7 (2s, C^6, C^{12}), 128.4 (s, C_0^3), 128.8 (s, C^{14}), 129.5 (s, C_1^3), 130.7, 130.8 (2s, C^7, C^{11}), 131.2 (s, C^4), 132.5 (s, C_0^4), 132.6 (s, C^1), 133.6 (s, C_1^4), 138.6 (d, $^3J_{CP1}$=14.1 Hz, C_0^5), 151.2 (d, $^2J_{CP0}$=8.2 Hz, C_0^1), 152.4 (d, $^2J_{CP1}$=7.1 Hz, C_1^1), 160.6 (s, CH=N) ppm. Anal. Calcd for $C_{168}H_{120}N_{12}O_9P_4S_4$ (2703): C, 74.65; H, 4.47; N, 6.22. Found: C, 74.54; H, 4.19; N, 6.07.

4.1.7.2. Compound 13-G_2. Yield 93%. ^{31}P {^1H} NMR ($CDCl_3$): δ=52.0 (s, P_0), 61.3 (s, P_2), 61.6 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ=3.2 (m, 27H, Me_1, Me_2), 5.2 (br s, 24H, CH_2), 7.1–8.3 (m, 213H, pyrene, C_6H_4, CH=N) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ=32.9 (d, $^2J_{CP1-2}$=12.8 Hz, Me_1, Me_2), 62.2 (s, CH_2-Pyr), 121.5 (d, $^3J_{CP0-1-2}$=3.4 Hz, C_0^2, C_1^2, C_2^2), 123.2 (s, C^{13}), 124.7–125.1 (m, C^2, C^8, C^{10}, C^{15}, C^{16}), 125.8 (s, C^3), 126.7 (s, C^9), 127.0 (s, C^5), 127.4, 127.6 (2s, C^6, C^{12}), 128.2 (s, C_0^3, C_1^3), 128.7 (s, C^{14}), 129.5 (s, C_2^3), 130.7, 130.8 (2s, C^7, C^{11}), 131.2 (s, C^4, C_1^4), 132.0 (s, C_0^4), 132.6 (s, C^1), 133.5 (s, C_2^4), 138.8 (d, $^3J_{CP0-1}$= 13.0 Hz, C_0^5, C_1^5), 151.3 (d, $^2J_{CP0-1}$=6.9 Hz, C_0^1, C_1^1), 152.3 (d, $^2J_{CP2}$=7.2 Hz, C_2^1), 160.6 (s, CH=N) ppm. Anal. Calcd for $C_{360}H_{264}N_{30}O_{21}P_{10}S_{10}$ (5977): C, 72.35; H, 4.45; N, 7.03. Found: C, 71.98; H, 4.32; N, 7.09.

4.1.7.3. Compound 13-G_3. Yield 94%. ^{31}P {^1H} NMR ($CDCl_3$): δ=51.7 (s, P_0), 61.2 (s, P_3), 61.5 (s, P_2), 61.8 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ=3.1 (m, 63H, Me_1, Me_2, Me_3), 5.2 (br s, 48H, CH_2), 7.1–8.3 (m, 441H, pyrene, C_6H_4, CH=N) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ=32.9 (d, $^2J_{CP1-2-3}$=12.6 Hz, Me_1, Me_2, Me_3), 62.2 (s, CH_2-Pyr), 121.5 (d, $^3J_{CP0-1-2-3}$=3.4 Hz, C_0^2, C_1^2, C_2^2, C_3^2), 123.2 (s, C^{13}), 124.6–125.1 (m, C^2, C^8, C^{10}, C^{15}, C^{16}), 125.8 (s, C^3), 126.6 (s, C^9), 127.0 (s, C^5), 127.4, 127.6 (2s, C^6, C^{12}), 128.2 (s, C_0^3, C_1^3, C_2^3), 128.7 (s, C^{14}), 129.5 (s, C_3^3), 130.7, 130.8 (2s, C^7, C^{11}), 131.2 (s, C^4, C_2^4), 132.0 (s, C_0^4, C_1^4), 132.6 (s, C^1), 133.5 (s, C_3^4), 138.8 (d, $^3J_{CP0-1-2}$=12.5 Hz, C_0^5, C_1^5, C_2^5), 151.3 (d, $^2J_{CP0-1}$=6.1 Hz, C_0^1, C_1^1, C_2^1), 152.3 (d, $^2J_{CP3}$=7.3 Hz, C_3^1), 160.6 (s, CH=N) ppm. Anal. Calcd for $C_{744}H_{552}N_{66}O_{45}P_{22}S_{22}$ (12,524): C, 71.35; H, 4.44; N, 7.38. Found: C, 71.10; H, 4.17; N, 7.57.

4.1.7.4. Compound 13-G_4. Yield 93%. ^{31}P {^1H} NMR ($CDCl_3$): δ=51.7 (s, P_0), 61.2 (s, P_4), 61.5 (s, P_3), 61.9 (s, P_2), 62.2 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ=3.0 (m, 135H, Me_1, Me_2, Me_3, Me_4), 5.2 (br s, 96H, CH_2), 7.0–8.0 (m, 897H, pyrene, C_6H_4, CH=N) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ=32.7 (d, $^2J_{CP1-2-3-4}$=13.8 Hz, Me_1, Me_2, Me_3, Me_4), 62.2 (s, CH_2-Pyr), 121.5 (d, $^3J_{CP4}$=4.0 Hz, C_4^2), 121.8 (d, $^3J_{CP0-1-2-3}$=4.0 Hz, C_0^2, C_1^2, C_2^2, C_3^2), 123.2 (s, C^{13}), 124.7 (s, C^2, C^{15}, C^{16}), 125.0 (br s, C^8, C^{10}), 125.8 (s, C^3), 126.5 (s, C^9), 127.0 (s, C^5), 127.3, 127.5 (2s, C^6, C^{12}), 128.2 (br s, C_0^3, C_1^3, C_2^3, C_3^3), 128.6 (s, C^{14}), 129.5 (s, C_4^3), 130.5, 130.6 (2s, C^7, C^{11}), 131.1 (s, C_3^4), 131.2 (s, C^4), 132.0 (s, C_0^4, C_1^4, C_2^4), 132.6 (s, C^1), 133.5 (s, C_4^4), 138.6–139.5 (m, C_0^5, C_1^5, C_2^5, C_3^5), 150.3 (d, $^2J_{CP0-1-2-3}$=7.4 Hz,

C_0^1, C_1^1, C_2^1, C_3^1), 151.3 (d, $^2J_{CP4}$=7.4 Hz, C_4^1), 160.5 (s, CH=N) ppm. Anal. Calcd for $C_{1512}H_{1128}N_{138}O_{93}P_{46}S_{46}$ (25,618): C, 70.89; H, 4.44; N, 7.54. Found: C, 70.64; H, 4.19; N, 7.38.

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