Metallodendrimers containing both ruthenium (internal layer) and rhenium (external layer)†

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The reaction of [Re(bipy)$(CO)_3$(C≡Cpy)] with two carbosilane dendrimers containing terminal (*p*-cymene)Ru$(triflate)_2$ units gives bimetallic dendrimers functionalised with (*p*-cymene) Ru(triflate)(pyC≡C)Re(bipy)$(CO)_3$ units. Dendrimers of this kind can be envisaged as formed by two metal layers: the internal, constituted by ruthenium atoms, and the external, by rhenium metals. The luminescent properties of these species are only attributed to the rhenium moieties.

Introduction

Dendrimers incorporating organometallic units at the periphery or within the framework have been extensively investigated in recent years due to their attractive electrochemical, optical and catalytic properties.[1] Indeed, metallodendrimers of all transition metals are now known.[2] Likewise, a good number of polypyrydine-based dendrimers containing two and even three different metal centers have been obtained by using the known "complexes as ligands and complexes as metals" synthetic strategy.[3] However, carbosilane dendrimers containing two or more metals are rare due to the lack of synthetic strategies. With the exception of some heteronuclear cluster-terminated dendrimers,[4] the only examples reported include the heterogeneously peripherally substituted dendrimers containing cobaltocene and ferrocene units.[5] Very recently, we have described a specific method for the synthesis of ruthenium-terminated dendrimers which allows the addition of a new shell of metallic fragments onto the surface of the dendrimer.[6] The method involves the grafting of a ditopic ligand, such as 4-pyPPh_2, to peripheral ruthenium atoms through the pyridine group. In order to enlarge the applicability of this strategy we have now explored the possibility of obtaining Ru–Re dendrimers, taking advantage of our recent synthesis of [Re(bipy)$(CO)_3$(C≡Cpy)],[7] which displays a pendant pyridine ring. The interest of this research is underlined by the fact that rhenium dendrimers have received little attention,[8] in spite of their potential in medical[9] and photophysical applications.[10]

Results and discussion

Preparation of the Ru–Re dendrimers

The starting ruthenium-containing carbosilane dendrimers **1** and **2** are represented in Chart 1 and were obtained as previously described.[11]

The synthesis of the bimetallic ruthenium–rhenium dendrimers required the abstraction of the chloride ligands attached to the ruthenium atoms by the use of AgOTf. After AgCl filtration, the rhenium derivative was added to the solution (Scheme 1) in a 1 (Ru) : 1 (Re) molar ratio and the reaction was instantaneous.

As can be seen from Scheme 1, the rhenium complex displaces only one of the two triflate ligands bonded to the ruthenium centers, giving, as a result, two kinds of triflate anions.

Workup of the resulting solution rendered a deep orange air-stable solid in good yields. **3** and **4** are relatively soluble in CH_2Cl_2, acetone and other common polar organic solvents, and they were characterized by using IR and ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy and 2D-COSY and HSQC ^1H–^{13}C experiments. No parent ion was observed either in the MALDI-TOF or in the ES mass spectra in any case, as observed in a vast number of carbosilane metallodendrimers.[12] The IR spectra for **3** and **4** are practically superimposable and show a strong sharp band at 2006 cm^{-1} and a broad intense absorption in the 1900–1907 cm^{-1} range, attributed to ν_{CO} of the $Re(CO)_3$ units.[13] The $\nu_{C\equiv C}$ vibration shifted slightly to higher wave numbers from the 2084 cm^{-1} of the starting rhenium precursor. The NMR spectra for **3** and **4** were almost identical so they will be discussed together. The ^{31}P NMR spectra showed only one signal at about δ 28 ppm and no traces of the ruthenium starting dendrimer were detected, indicating that complete functionalisation of the dendrimers was achieved. The ^{19}F NMR spectra contained two signals for the triflate group at δ −78.2 and −79.0 ppm, corresponding to the coordinated and to the free anion, respectively. In the ^1H NMR spectra, two methyl resonances of the isopropyl group were seen at about δ 1.03 and 0.92 ppm, as a result of the loss of the symmetry plane passing through the ruthenium. In addition, this feature makes the four protons of the *p*-cymene ring different. Thus, although only two broad signals appeared at δ 5.72 and 5.20 ppm for **3**, an HSQC ^1H-^{13}C experiment revealed that each resonance correlated with two carbon nuclei. The ^1H NMR spectrum of **4** was more sharply defined and permitted direct identification of the four signals at δ 5.73, 5.68, 5.41 and 5.29 ppm. The methyl, methylene, and ethylene

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† This paper is dedicated to Dr Antonio Abad on the occasion of his retirement.

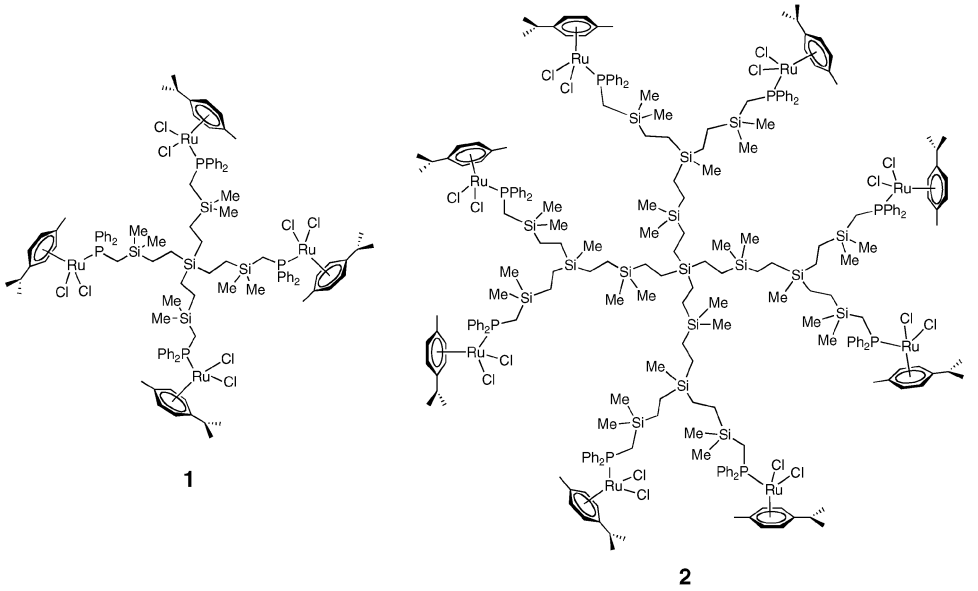
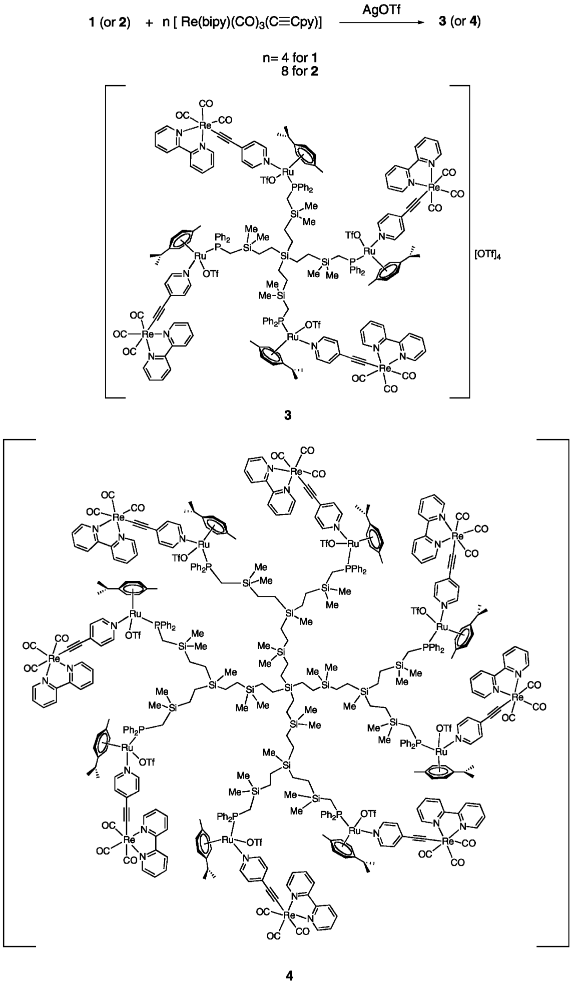


Chart 1

protons, as well as the signals due to the bipyridine ligands, were present with the correct proton integration. Interestingly, the α-protons of the pyridine ring shifted upfield after coordination of the rhenium ligand to the ruthenium center, and this shift can be used to monitor the course of the reaction. The ^{13}C NMR spectra of **3** confirmed the presence of both free and coordinated CF_3SO_3 anions at δ 121.1 and 118.1 ppm, respectively, along with two resonances in the carbonyl region at about δ 198 and 192 ppm. In addition, the four signals for the carbon ring of the *p*-cymene appeared in the 80–90 ppm region, while those of the two remaining quaternary carbons appeared at δ 104 and 114 ppm. The two signals expected for the methyl groups of the isopropyl unit resonated at δ 22.1 and 21.6 ppm. Note that the coordination of the rhenium ligand to the ruthenium dendrimer induces the methyl groups bonded to silicon to be diastereotopic. Thus, the signals for **3** at δ −0.36 and −0.60 ppm in the ^{1}H NMR spectrum and those at δ −2.2 and −2.7 ppm in the ^{13}C NMR spectrum were assigned unambiguously by means of an HSQC ^{1}H-^{13}C experiment. All these data are consistent with the structure proposed and confirm that pure species **3** and **4** were obtained within the limits of the NMR spectroscopic detection.



Scheme 1

Photoluminescence studies

Given that we have recently described the photoluminescent behaviour of [Re(bipy)(CO)$_3$(C≡Cpy)] and other analogous rhenium derivatives,[7] we examined the effect of ruthenium fragments on the luminescent properties of the rhenium units grafted onto the periphery of the dendrimer. Few rhenium-containing dendrimers have been studied from this perspective.[10]

Absorption spectra for the complexes were obtained in CH_2Cl_2 (Fig. 1). Spectra of compounds **1** and **2** showed three bands at 290, 365 and 480 nm, the lowest energy band (480 nm) appearing as a shoulder of the 365 nm band. These compounds are not luminescent in CH_2Cl_2 at 298 K upon excitation at any of the three absorption maxima. Compound **2** presented extinction coefficients that are roughly double those of compound **1**, as expected from the relative number of chromophores.

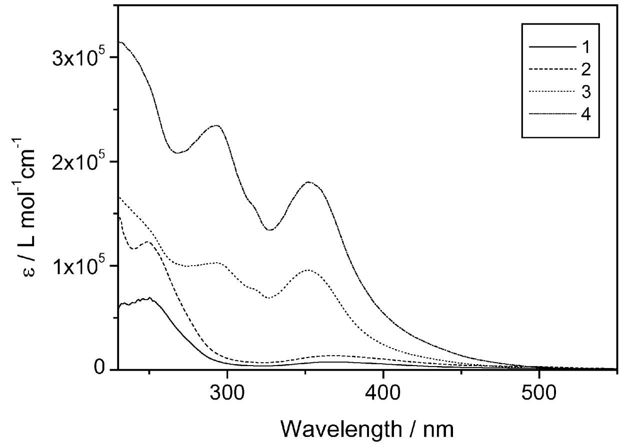


Fig. 1 Absorption spectra of compounds **1**, **2**, **3** and **4** in CH_2Cl_2 at 298 K.

The absorption spectra of compounds **3** and **4** are dominated by a new band at ~350 nm. This band is not present in the simulated spectra constituted by the sum of the spectrum of **1** with the spectrum of [Re(bipy)(CO)$_3$(C≡Cpy)] (in 1 : 4 proportion) or the spectrum of **2** and the spectrum of [Re (bipy)(CO)$_3$(C≡Cpy)] (in 1 : 8 proportion) (Fig. 2), and it can consequently be assigned to a new MLCT band from ruthenium to the pyridine ligand in the bimetallic dendrimer. The low-energy MLCT transition corresponding to [Re(bipy) (CO)$_3$(C≡Cpy)][14] (~408 nm) is buried under the new transition and is not observed in the absorption spectra.

Excitation of the bimetallic dendrimers at ~350 nm gave rise to a broad emission band, typical of MLCT-based luminescence of rhenium or ruthenium complexes.[15] Excitation spectra collected at the maximum of the emission band, however, do not match the ~350 nm band observed in the absorption spectrum. This implies that the broad emission originates from the dπ(Re(I)) → π*(L–L), of the rhenium complex[15], buried under the dominant ruthenium MLCT absorption at 350 nm. The dπ(Re(I)) → π*(L–L) MLCT transition in the dendrimer at ~373 nm, (Fig. 3) is blue shifted with respect to the same transition in [Re(bipy)(CO)$_3$ (C≡Cpy)] (~408 nm).

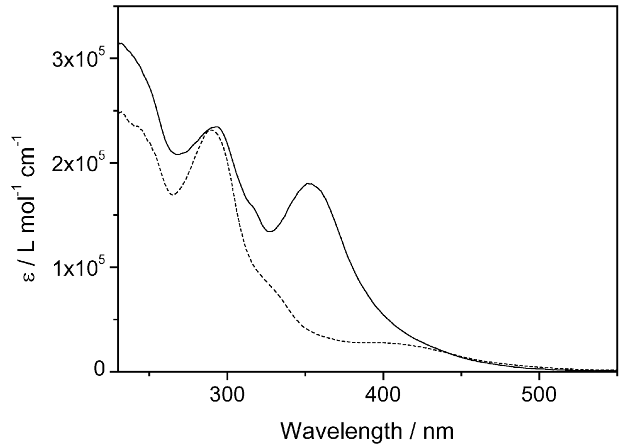


Fig. 2 Absorption spectrum of **4** (solid line) superimposed to the sum of the spectrum of **2** and [Re(bipy)(CO)$_3$(C≡Cpy)] (1 : 8 proportion, dashed line) in CH_2Cl_2 at 298 K.

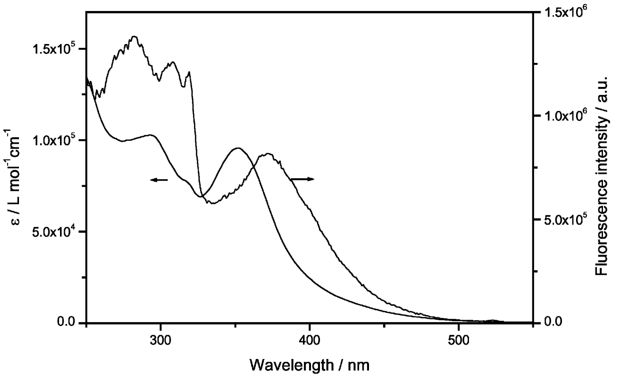


Fig. 3 Absorption (light line) and excitation spectra (λ_{em} = 630 nm) of **3** (dark line) in CH_2Cl_2 at 298 K.

The apparent emission quantum yields (Table 1) are similar for compounds **3** and **4**, but are one order of magnitude lower than that measured for [Re(bipy)(CO)$_3$(C≡Cpy)]. In part this could be due to the competition for light absorption of the new MLCT band at 350 nm, which does not contribute to the luminescence.

Hence, the fluorescence quantum yield of the dπ(Re(I)) → π*(L–L) MLCT transition in the dendrimer cannot be determined. However, it is interesting to note that the decay times are progressively shortened in the series [Re(bipy) (CO)$_3$(C≡Cpy)], **3** and **4**.

This implies that the decrease in apparent quantum yield observed when [Re(bipy)(CO)$_3$(C≡Cpy)] is incorporated in **3** and **4** is not solely due to the light absorbed by the non-emitting MLCT band at ~350 nm. An additional quenching effect must exist upon incorporation in the dendrimer, that accounts for the observed decrease in the decay times. The quenching increases with the number of ruthenium units, but, since the increase in ruthenium units is accompanied by the increase in the number of branches, quenching by the dendrimeric silane branches cannot be discarded at this point, despite this ruthenium is a better candidate for the quenching. The observed quenching could be associated to energy transfer from rhenium to ruthenium, as previously reported in binuclear complexes of these metals[16] but since the ruthenium complex is not emissive, in this case energy transfer cannot be confirmed through the enhancement of ruthenium based emission. We have measured the decay times of compounds **3**, **4** and [Re(bipy)(CO)$_3$(C≡Cpy)] in CH_2Cl_2 at 77 K. The decays were fitted perfectly with a single exponential function and the retrieved lifetimes are identical within the experimental error (50–60 μs), thus the quenching mechanism observed at room temperature is blocked at 77 K.

In summary, we report in this paper the synthesis and luminescence properties of the first bimetallic ruthenium and rhenium-containing dendrimers.

Experimental

General methods

All manipulations were performed under prepurified nitrogen using standard Schlenk techniques. All solvents were distilled

Table 1 Electronic absorption and emission data for compounds **1–4** and [Re(bipy)(CO)$_3$(C$\equiv$Cpy)] at 298 K in CH$_2$Cl$_2$

Compound	Absorption spectra λ_{max}/nm ($\varepsilon \times 10^{-3}$/M^{-1} cm^{-1})	Emission λ_{exc}/nm	λ_{max}/nm	$\phi \times 10^{-3}$	τ/ns
1	290 (69.4); 365 (7.6); 480 (1.9)	—		—	—
2	290 (122.4); 365 (13.7); 480 (3.6)	—	—	—	—
3	290 (102.5); 314 (78.9); 352 (95.6)	352	615	0.5^a	81
4	290 (233.7); 314 (161.8); 350 (180.3)	352	630	0.7^a	56
[Re(bipy)(CO)$_3$(C$\equiv$Cpy)]	291 (28.6); 330 (9.6); 408 (283)	358	627	4.3	119

^{a} These are apparent quantum yields with λ_{exc} = 336 nm (see text).

from appropriate drying agents. Infrared spectra were recorded on an FT-IR 520 Nicolet spectrophotometer. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectra were obtained on Bruker DXR 250 and Varian Mercury 400 spectrometers. Chemical shifts are reported in ppm relative to external standards (SiMe$_4$ for ^{1}H and ^{13}C; 85% H$_3$PO$_4$ for ^{31}P and CF$_3$COOH for ^{19}F) and coupling constants are given in Hz.

Absorption spectra were recorded on a Shimadzu UV-2510 PC, UV-Vis spectrophotometer. The concentrations used for the absorption measurements were >**1**] = 6.0×10^{-5} M, [**2**] = 2.5×10^{-5} M, [**3**] = 9.6×10^{-6} M and [**4**] = 3.2×10^{-6} M.

Fluorescence emission was recorded on an SPEX Jobin-Yvon Fluorolog 3 spectrofluorimeter. The absorbance at the excitation wavelength was maintained lower than *ca.* 0.15. The fluorescence quantum yields were obtained in the presence of air with excitation at 336 nm; an aqueous solution of Ru (bipy)$_3$Cl$_2$ (ϕ_1 = 0.028) was used as a reference standard.[17]

For fluorescence decay measurements the samples were excited at 337 nm using a coaxial flash lamp (IBH, 5000 system) filled with nitrogen. The lamp pulses were monitored using a synchronization photomultiplier; the PM signal was shaped in a constant fraction discriminator (Canberra 2126) and directed to a time-to-amplitude converter (TAC, Canberra 2145) as start pulses. Emission wavelength was selected with a monochromator (Oriel 77250) imaged in a fast photomultiplier (9814B Electron Tubes Inc.) and the PM signal was shaped as described above, and delayed before entering the TAC as stop pulses. The analogue TAC signals were digitized (ADC, ND582) and stored on a PC. Decays were analysed by the method of modulating functions, extended by global analysis, as implemented by Striker.[18] The starting dendrimers **1** and **2** were prepared following published procedures [11], as was the rhenium complex, [Re(bipy)(CO)$_3$(C$\equiv$Cpy)].[7]

Emission decays at 77 K were measured in a Perkin Elmer LS 45 luminescence spectrometer, with excitation at 358 nm and collecting the emission spectrum between 500 and 700 nm at different delays after flash up to 300 µs (50 µs increments).

Syntheses

3. To a solution of **1** (38 mg, 0.016 mmol) in 10 ml of CH$_2$Cl$_2$, AgOTf (66 mg, 0.256 mmol) was added. The mixture was stirred for 2 h and the AgCl formed and the excess of AgOTf were removed by filtration through celite. To this solution, the rhenium complex (34 mg, 0.064 mmol) was added. After stirring for 30 min, the solvent was evaporated to dryness. The residue was washed in toluene. The product was obtained as an orange solid (59 mg, 82%). IR (KBr, cm^{-1}): 2094 (w, $\nu_{C\equiv C}$), 2033 (w, $\nu_{C\equiv O}$), 2005 (s, $\nu_{C\equiv O}$), 1907 (s, $\nu_{C\equiv O}$). ^{1}H NMR (298 K, CD$_2$Cl$_2$): δ 9.03 (s (br), 8H, H$_6$, H$_{6'}$ bipy), 8.45 (d, J = 8.0 Hz, 8H, H$_3$, H$_{3'}$ bipy), 8.22 (m, 8H, H$_4$, H$_{4'}$ bipy), 8.00–6.80 (m, 56H, phenyl, H$_5$, H$_{5'}$ bipy and H$_{\alpha py}$), 6.61 (s (br), 8H, H$_{\beta py}$), 5.72 (s (br), 8H, C$_6$H$_4$), 5.20 (s (br), 8H, C$_6$H$_4$), 1.95 (m, 4H, C*H*(CH$_3$)$_2$), 1.90–1.40 (m, 20H, CH$_2$P and C*H*$_3$–C$_6$H$_4$), 1.03 (s (br), 12H, CH(C*H*$_3$)$_2$), 0.92 (s (br), 12H, CH(C*H*$_3$)$_2$), 0.40–(−0.35) (m, 16H, CH$_2$Si), −0.36 (s, 12H, CH$_3$Si), −0.60 (s, 12H, CH$_3$Si). ^{13}C NMR (298 K, CD$_2$Cl$_2$): δ 198.0 (s, CO), 196.2 (s, CO), 153.2 (s (br), C$_{\alpha py}$), 153.1 (s, C$_6$, C$_{6'}$ bipy), 139.3 (s, C$_4$, C$_{4'}$ bipy), 133.0–127.0 (m, phenyl), 128.6 (s, C$_{\beta py}$), 127.2 (s, C$_5$, C$_{5'}$ bipy), 124.0 (s, C$_3$, C$_{3'}$ bipy), 121.1 (q, J = 319.3 Hz, OTf), 118.1 (q, J = 319.3 Hz, OTf), 104.0 (s, *C*–CH$_3$), 114.0 (s (br), *C*–CH(CH$_3$)$_2$), 90.3 (s (br), C$_6$H$_4$), 88.4 (s (br), C$_6$H$_4$), 84.2 (s (br), C$_6$H$_4$), 80.6 (s (br), C$_6$H$_4$), 30.6 (s, *C*H(CH$_3$)$_2$), 22.1 (s, CH(*C*H$_3$)$_2$), 21.6 (s, CH(*C*H$_3$)$_2$), 17.9 (s, *C*H$_3$–C$_6$H$_4$), 8.7 (s (br), CH$_2$Si), 2.0 (s (br), CH$_2$Si), −2.2 (s, CH$_3$Si), −2.7 (s, CH$_3$Si). ^{31}P NMR (298 K, CD$_2$Cl$_2$): δ 28.6. ^{19}F NMR (298 K, CD$_2$Cl$_2$): δ −78.2 (s (br)), −79.0 (s).

4. It was prepared in the same way as **3**. In the workup, diethyl ether was used instead of toluene. The product was obtained as an orange solid (35 mg, 73%). IR (KBr, cm^{-1}): 2090 (w, $\nu_{C\equiv C}$), 2033 (w, $\nu_{C\equiv O}$), 2006 (s, $\nu_{C\equiv O}$), 1900 (s, $\nu_{C\equiv O}$). ^{1}H NMR (298 K, CD$_2$Cl$_2$): δ 9.02 (d, J = 6.4 Hz, 16H, H$_6$, H$_{6'}$ bipy), 8.55 (s, 16H, H$_3$, H$_{3'}$ bipy), 8.16 (m, 16H, H$_4$, H$_{4'}$ bipy), 8.00–6.90 (m, 112H, phenyl, H$_5$, H$_{5'}$ bipy and H$_{\alpha py}$), 6.64 (s (br), 16H, H$_{\beta py}$), 5.73 (s (br), 8H, C$_6$H$_4$), 5.68 (s (br), 8H, C$_6$H$_4$), 5.41 (s (br), 8H, C$_6$H$_4$), 5.29 (s (br), 8H, C$_6$H$_4$), 2.00 (m, 8H, C*H*(CH$_3$)$_2$), 1.90–1.40 (m, 40H, CH$_2$P and C*H*$_3$–C$_6$H$_4$), 1.04 (d, J = 5.2 Hz, 24H, CH(C*H*$_3$)$_2$), 0.93 (d, J = 5.2 Hz, 24H, CH(C*H*$_3$)$_2$), 0.50–(−0.70) (m, 148H, CH$_3$Si and CH$_2$Si). ^{13}C NMR (298 K, CD$_2$Cl$_2$): δ 153.1 (s (br), C$_{\alpha py}$), 141.0–122.0 (m, Ar), 30.5 (s, *C*H(CH$_3$)$_2$), 22.0 (s, CH(*C*H$_3$)$_2$), 21,2 (s, CH(*C*H$_3$)$_2$), 17.7 (s, *C*H$_3$–C$_6$H$_4$), 8.8–2.5 (m, CH$_2$Si), −2.3–(−4.7) (m, CH$_3$Si). ^{31}P NMR (298 K, CD$_2$Cl$_2$): δ 28.7. ^{19}F NMR (298 K, CD$_2$Cl$_2$): δ −78.2 (s (br)), −79.0 (s).

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