

Polyanionic Aryl Ether Metallodendrimers Based on Cobaltabisdicarbollide Derivatives. Photoluminescent Properties

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ABSTRACT: Fluorescent Fréchet-type poly(aryl ether) dendrimers that incorporate the 1,3,5-triphenylbenzene as core molecule and 3, 6, 9, or 12 terminal allyl ether groups have been prepared in very good yield by following the Fréchet convergent approach. Regiospecific hydrosylilation reactions on the allyl ether functions with the cobaltabisdicarbollide derivative $Cs[1,1'-\mu$ -SiMeH-3,3'-Co(1,2-C₂B₉H₁₀)₂] lead to different generations of Féchet-type polyanionic metallodendrimers decorated with 3, 6, and 9 cobaltabisdicarbollide units. Starting dendrimers exhibit photoluminescence properties at room temperature under ultraviolet irradiation; nevertheless, after functionalization with cobaltabisdicarbollide derivatives, the fluorescence properties are quenched. Products are fully characterized by FTIR, NMR, and UV–vis spectroscopies. For metallodendrimers, the UV–vis absorptions have been a good tool for estimating the experimental number of cobaltabisdicarbollide units peripherally attached to the dendrimeric structure and consequently to corroborate the unified character of the dendrimers. Because of the anionic character of these compounds and the boron-rich content, we actually focus our research on biocompatibility studies and potential applications.

Introduction

In the past years, the incorporation of boron clusters in the interior or on the periphery of hydrocarbon,¹ poly(lysine)² and aliphatic polyester dendrimers,³ and other macromolecules and dendrimeric systems⁴ has become an area of great attention. The design of water-soluble boron-rich macromolecules is of significance for boron neutron capture therapy (BNCT) or for drug delivery. Recently, we have been interested in the use of different types of dendrons and dendrimers as platforms for the incorporation of boron-based clusters in order to obtain high boron content molecules.⁵ However, closo-carboranes are extremely lipophilic, generating water-insoluble structures with limited bioavailability and preventing their application in BNCT. Thus, with the aim of preparing boron-rich anionic systems, we have developed different synthetic strategies for the incorporation of nido-carboranes into dendrimeric structures.⁶ Cobaltabisdicarbollide, $[(3,3'-Co-(1,2-C_2B_9H_{11})_2]^{-,7}$ is a boron-rich monoanionic cluster that possesses extraordinary chemical and thermal stability, hydrophobicity,8 weakly coordinating character,9 and low nucleophilicity.¹⁰ These features make it suitable for a wide range of applications, such as the extraction of radionuclides,¹¹ doping agent in conducting polymers,¹² or in ion selective PVC membrane electrodes for medical drug analysis,¹³ among others.^{14,15} Cobaltabisdicarbollide derivatives have also been considered promising agents as boron-rich carriers for cancer treatment and diagnosis in boron neutron capture therapy (BNCT).¹⁶ These boron compounds can be delivered into tumor cells using

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different strategies for tumor targeting or can be used as building blocks for the synthesis of boron-containing biomolecules. For that reason, this metallacarborane has been bonded to different organic groups and biomolecules, such as nucleosides¹⁷ and porphyrins.¹⁸

Fréchet-type poly(aryl ether) dendrimers¹⁹ are of current interest because of their properties and multiple applications.²⁰ More recently, it has been reported that Frèchet-type dendrimers are biocompatibles and have been used for biomedical applica-tions, such as drug delivery.^{20d} On the other hand, Fréchet-type dendrimers with homoallyl and allyl ether end groups, similar to those prepared in this work, have been previously reported by Zimmerman et al. to produce cross-linking dendrimers via ring-closing metathesis reactions.²¹ In other examples, dendrimers containing allyl ether groups were chosen for their selective removal with Pd catalysts in order to obtain dendrimers with peripheral hydroxyl groups.²² In this work, the terminal allyl ether groups will be active groups for hydrosilylation reactions. In our continuing investigation of structure/properties relationship in cobaltabisdicarbollide-containing dendrimers,²³ we now report the synthesis and characterization of a new family of starshaped molecules and dendrimers. These dendrimers consist of a 1,3,5-triphenylbenzene unit as fluorescent core, Fréchet-type poly(aryl ether) fragments as connecting groups, and 3, 6, 9, and 12 terminal allyl ether groups that will be hydrosilylated by $[1,1'-\mu$ -SiMeH-3,3'-Co $(1,2-C_2B_9H_{10})_2]^{-24}$ Our fluorescence core molecule, 1,3,5-triphenylbenzene (TPB), is a class of C3-symmetry compound important in electrodes and electroluminescent devices. The 1,3,5-triphenylbenzene core has been used to develop organic light emitting diodes (OLEDS)²⁵ and has also been used in the synthesis of dendrimers and fullerene fragments.²⁶



Scheme 2. Preparation of Dendrimers 5a and 5b



In this work we study the photoluminescent properties of dendrimers, before and after functionalization with cobaltabisdicarbollide derivatives.

Results and Discussion

Synthesis of Poly(aryl ether) Star-Shaped Molecules and Dendrimers with Fluorescent Cores. In this work we have prepared dendrimers with 1,3,5-triarylbenzene as core and 3, 6, 9, and 12 terminal allyl ether groups by using the Fréchet convergent strategy. These dendrimers have been used as precursors to attach metallacarborane derivatives at the periphery via hydrosilylation reactions.

The synthesis of 1,3,5-triarylbenzene can be carried out using Suzuki cross-coupling or cyclocondensation reactions from substituted acetophenones.²⁷ The cyclocondensation allows the synthesis of many chemical species, such as multimetallic pincer,²⁸ star-shaped thiophenes,²⁹ and organic–inorganic hybrid mesoporous materials,³⁰ which can be carried out with triflic acid,²⁹ sulfuric acid–sodium pirosulfate,³⁰ perfluorinated resins,³¹ and tetrachlorosilane in ethanol.²⁸

The sequence of reactions used for the preparation of 1,3,5-tris(4-allyloxyphenyl)benzene, **2**), is shown in Scheme 1. 4-Allyloxyacetophenone, **1**, was first synthesized in quantitative yields from 4-hydroxyacetophenone and allyl bromide in the presence of potassium carbonate under reflux of acetone; the spectroscopic data of **1** were compared with those reported in the literature.^{32a} Triple condensation of **1** in absolute ethanol using tetrachlorosilane led to **2** in 80% yield.

Next generation dendrimers—1,3,5-(4-(3,5-bis(allyloxy)benzyloxy)phenyl)benzene, **5a**; 1,3,5-(4-(3,4,5-tris(allyloxy)benzyloxy)phenyl)benzene, **5b**; and 1,3,5-(4-(3,5-bis(3,5-bis-(allyloxy)benzyloxy)benzyloxy)phenyl)benzene, **7**, were prepared using a convergent approach. In a first step the allyl groups of compound **2** were removed using a procedure previously described in the literature, with Pd(OAc)₂ in the presence of PPh₃,³³ to give 1,3,5-(4-hydroxyphenyl)benzene, 3^{34} (see Scheme 1). Benzyl chloride derivatives **4a** and **4b** were prepared using procedures described in the literature,^{21d,22} and the spectral data of **4a** were compared with that already published.³³ The reaction of **4a** and **4b** with **3** at reflux of acetonitrile in the presence of K₂CO₃ and catalytic amounts of 18-crown-6 ether^{34,35} gave **5a** and **5b** as amber oils, in 95% and 92% yield, respectively (see Scheme 2).

Finally, the reaction of (3,5-hydroxy)benzyl alcohol with 3,5-bis(allyloxy)benzyl chloride gave 3,5-bis(3,5-bis(allyloxy)benzyloxy)benzyl alcohol which was reacted with SOCl₂ and Et₃N in CH₂Cl₂ to give **6**. Subsequent reaction of **6** with **3** under reflux of acetone in the presence of K₂CO₃ and catalytic amounts of Bu₄NF³⁵ gave **7** as amber oil in 53% yield (Scheme 3).

General Procedure for Peripheral Functionalization with Cobaltabisdicarbollide Units. To decorate the periphery of the fluorescent star-shaped molecule 2 and dendrimers 5a,b and 7 with cobaltabisdicarbollide units, hydrosilylation reactions of the allyl ether end groups with Cs[1,1'-µ-SiMeH- $3,3'-Co(1,2-C_2B_9H_{10})_2$], 8 (see Figure 1),²⁴ in the presence of Karstedt catalyst in THF at 50 °C, were carried out. The reaction of 3 equiv of 8 with 1 equiv of 2 afforded the cesium salt of the anionic three-functionalized compound 10, in 54% yield (Scheme 4). When compound 8 reacts with dendrimers 5a and 7, using the ratios 6:1 and 12:1, respectively, under the same conditions, a complete hydrosilylation of dendrimers was observed to obtain polyanionic metallodendrimers 11 and 12 (Schemes 4 and 5). These metallodendrimers were precipitated as orange solids by addition of hexane and isolated as cesium salts, 11 and 12, in 63 and 51%

Scheme 3. Preparation of Dendrimer 7



yield, respectively. Nevertheless, all attempts for the complete hydrosilylation of compound **5b**, which contains nine terminal allyl ether functions, were unsuccessful even using a large excess of **8**, changing the catalyst, reaction times, and temperatures (Scheme 5). The Supporting Information contains a Monte Carlo simulation study about the steric hindrance for these metallodendrimers. In all cases, the binding of the cobaltacarborane anion **8** to the allyl ether functions was monitored by IR and ¹H NMR spectroscopy, following the disappearance of the Si-H signal in both spectra and, above all, the absence of allyl protons in the ¹H NMR.

The increase of the number of cobaltabisdicarbollide fragments in a dendrimeric structure provides the increase of boron content in the molecule, which is capital in producing a useful drug delivery agent. Compound **12**, with 12 cobaltabisdicarbollide units, is the molecule with highest content of these metallacarboranes described in the literature, which possesses about 30 wt % boron. These boronenriched molecules possess a great potential as boron drug delivery compounds; however, due to the presence of 1,3, 4-phenylene core, these dendrimeric structures could be potentially useful in materials science to form structures for liquid crystal materials and develop materials with photoelectric and luminescent properties.³⁶

Characterization of Star-Shaped Molecules and Dendrimers before and after Functionalization. The starting compounds 1–7 were characterized on the basis of FT-IR, ¹H NMR, ¹³C NMR, and UV-vis spectroscopy and mass spectrometry, whereas compounds 10, 11, and 12 were also characterized by ¹¹B and ²⁹Si NMR and elemental analyses. All compounds show resonances between 7.80 and 7.00 ppm attributed to the aromatic protons at 1, 4, and 5 positions of the central phenyl ring of the 1,3,5-triphenylbenzene core in the ¹H NMR spectra. Dendrimers 2, 5a, 5b, and 7 show resonances in the range δ 6.20 and 5.20 ppm attributed to the allyl protons, which have been assigned according to the area and coupling constants. These signals disappear after hydrosilvlation reaction, indicating the anti-Markovnikov addition of the $-\mu$ -Si-H function of 8 to the double bonds and subsequently the formation of complete functionalized metallodendrimers 10, 11, and 12. In the latter compounds, the presence of $-CH_2$ - proton resonances around 4.00 (-OCH₂-), 1.90 (-CH₂), and 1.00 ppm (-SiCH₂-) corroborates their formation (Figure 2). Broad resonances at



Figure 1. Representation of cobaltabisdicarbollide derivatives 8 and 9.

 \sim 4.50 ppm attributed to the C_c-H protons of the cobaltabisdicarbollide are also observed in metallodendrimers. The ¹H NMR spectra also exhibit resonances at low frequencies, in the range 0.32-0.38 ppm for C_c -SiCH₃ protons. The $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectra show different resonances in the aromatic region, from 160.5 to 100.5 ppm for all compounds. Depending on the metallodendrimer, different resonances attributed to the carbon atoms of the ether groups $(-OCH_2-)$ are observed between 65.00 and 78.50 ppm for 10, 11, and 12. After functionalization with cobaltabisdicarbollide, dendrimers 10-12 show resonances around 55.25 and 40.50 ppm attributed to the C_c -H and C_c -Si atoms, respectively. The resonances for the Si-CH₃ units bonded to the C_c appear between -6.03 and -7.09 ppm, whereas the $-CH_2$ - carbons are displayed in the range 22.3-8.41 ppm.

The ¹¹B NMR spectra of **10–12** exhibit an identical 2:2:4:2:2:2:2 pattern in the range from +8.40 to -22.30 ppm, typical of cobaltabisdicarbollide derivatives.³⁷ Because of the similarity of these spectra with that of Cs[1,1'- μ -SiMe₂-3,3'-Co(1,2-C₂B₉H₁₀)₂],²⁴ **9**, in which the μ -Si(Me)₂ group is bridging the dicarbollide ligands (Figure 1), it has been possible to confirm the formation of these metallodendrimers. The boron resonance with a relative intensity of 4 is due to a coincidental overlap of two resonances with a 2:2 relative intensity. All three cobaltabisdicarbollide-functionalized compounds **10**, **11**, and **12** show only one peak about 12.0 ppm in the ²⁹Si NMR spectra, corresponding to the - μ -SiMeCH₂-. This resonance is shifted about 8.5 ppm downfield with respect to the starting compound **8** ($\delta_{Si} = 2.94$ ppm)²⁴ but is very close to that shown for **9** at 13.98 ppm, which always proves the formation of the expected

metallodendrimers. The IR spectra of 10–12 present typical v(B-H) strong bands for *closo* clusters around 2550 cm⁻¹ and intense bands near 1257 cm⁻¹ corresponding to the δ (Si–CH₃).

Different mass spectrometry techniques have been used for the characterization of compounds: high-resolution mass spectrometry (HMRS), ESI-MS, and MALDI-TOF-MS. The formula of the star-shaped compound 10 was well established by using ESI-MS mass spectrometry, and the molecular ion peak appears at m/z = 1837.1 (M-Cs), in concordance with the calculated pattern (Figure 3). The MALDI-TOF mass spectra of dendrimers 11 and 12 were recorded in the ion mode without matrix, where a big fragmentation was observed. This fragmentation phenomenon was previously observed for cobaltabisdicarbollidecontaining carbosilane and carbosiloxane dendrimers.²³ Thus, this technique cannot be used to fully characterize this type of dendrimer. Hypothetically, the reason could be due to the relative strong UV absorption of these metallodendrimers at 337 nm, which corresponds precisely to the λ of the laser used in the MALDI experiment. A similar behavior was already observed by Caminade et al. in the case of phosphorus-containing dendrimers.³

Absorption and Emission Measurements. The UV-vis absorption measurements for compounds 2, 5a, 5b, 7, 10, 11, and 12 were performed in acetonitrile. Tables 1 and 2 list the spectroscopic and photophysical data obtained for these compounds. Starting dendrimers 2, 5a,b, and 7 display a significant solvatochromic shift and exhibit bands of absorption maxima in the region 269–272 nm, which correspond

to the π to π^* transitions in the aromatic core, similar to the maximum at 254 nm reported for 1,3,5-triphenyl-substituted benzene compounds (Figure 4).^{26b} Cobaltabisdicarbollide-functionalized dendrimers show two maxima absorption bands, one in the region 271–276 nm attributed to the dendrimeric core and the second band between 307 and 310 nm, which corresponds to the [1,1'- μ -CH₂Si(CH₃)-1,2-Co(C₂B₉H₁₁)₂]⁻ fragment (Figure 5), due to the similarity with the previously reported Cs[1,1'- μ -Si(CH₃)₂-1,2-Co(C₂B₉H₁₁)₂], 9.²⁴

As was already reported for metallocene-containing dendrimers,³⁹ in our case the UV-vis spectroscopy has been a suitable method to estimate the number of terminal cobaltabisdicarbollide units and corroborate the level of functionalization for metallodendrimers 10-12. The silyl-containing cobaltabisdicarbollides show absorption bands at 310 and 462 nm in the UV-vis spectra that follow the Lambert-Beer law.²³ This method consists of the UV-vis absorption's measurement of solutions that contain the functionalized dendrimer and study the trend of the molar absorptivity (ε). The molar absorptivities (ε_{max}) of the cobaltabisdicarbollide-containing dendrimers must be proportional to the number of metallacarboranes attached to the periphery.²³ The number of cobaltabisdicarbollide fragments for each dendrimer can be estimated by comparing the absorptivity (ε) of the dendrimers with that obtained for monomer 9 (ε_0). The spectra do not show well-defined peaks, which made calculating the molar absorptivities at $\lambda = 309$ nm difficult, to overcome this problem a line-fitting analysis was performed (Figures S3-S5 in the Supporting Information).







Thus, the deconvolution with Gaussians permitted accurate discernment of the band positions and the retrieval of λ and ε data with more accuracy. Table 2 shows the molar absorptivity values (ε) for all metallodendrimers and the calculated number of cobaltabisdicarbollide units using the Lambert–Beer law. The number of metallacarboranes calculated fits quite well with the theoretical numbers, corroborating the well functionalization and the unified character of the different metallocarborane-containing dendrimers.

It is worth noting that compounds **2**, **5a**, **5b**, and **7** exhibit blue emission with λ_{max} around 364 nm after excitation at 270 nm in acetonitrile. Nevertheless, dendrimers **10**, **11**, and **12** do not show appreciable fluorescence emission. Table 1 collects the data, and Figure 4 shows the photoluminescent (PL) normalized spectra for compounds **2**, **5a**, **5b**, and **7**.

Fluorescence lifetimes (the time lag between the absorption and emission of photons) for compounds 2, 5a, 5b, and 7 were measured to give values around 9.4 ns, and their decay is described by a single exponential. The fluorescence quantum yield, Φ , is defined as the ratio of the total number of photons emitted within the total number of absorbed photons. The four samples have a quantum yield around 20%. However, metallodendrimers 10, 11, and 12 do not show any fluorescence can be rationalized as a quenching

after functionalization with the cobaltabisdicarbollide moieties. As a control experiment, PL measurements of a solution containing 1 equiv of compound 2 and 3 equiv of $Cs[1,1'-\mu-Si(CH_3)_2-Co(1,2-C_2B_9H_{10})_2]$, 9, were performed, resulting in a quantum yield of $\Phi = 14\%$. This fact indicates that the quenching by the cobaltabisdicarbollide moiety is more effective when it is chemically bonded to the fluorescent core. Furthermore, this fact confirms that the intermolecular effects are not significant. Two possible mechanisms, electron exchange and dipole-dipole, can be invoked to account for the aromatic core dendrimer to cobaltabisdicarbollide energy transfer. Electron exchange can be discarded because saturated units connecting the respective parts behave like insulators toward electronic communication because the HOMO-LUMO energy separation is large. On this basis, we propose that the occurrence of energy transfer is due possibly to the dipole-dipole mechanism.

The starting dendrimers exhibit photoluminescence at room temperature under ultraviolet irradiation due to the core molecule. However, after functionalization with C-substituted cobaltabisdicarbollide, the fluorescence properties are quenched. By using steady-state and time-resolved luminescence measurements, we show that for these metallodendrimers a mechanism different than photon emission



Figure 2. 1 H NMR spectra of (a) dendrimer 5a and (b) metalloden-drimer 11.



Figure 3. Simulated and experimental ESI spectra for compound 10.

could be available to go from excited singlet state to the ground electronic state due mainly to peripheral functionalization.

Simulation of UV–Vis and Fluorescence Spectra. Excited states of 2 were calculated using a semiempirical method PM6 implemented in MOPAC⁴⁰ to simulate its absorption spectra with the effect of a solvent model (COSMO) surrounding the molecule.⁴¹ The ground state (S_0) and the first singlet excited state (S_1) have been optimized, allowing to do a direct comparison of calculated results with experimental data for the fluorescence spectrum of 2. The computed absorption and fluorescence wavelength in acetonitrile for 2 is represented in Figure 6.

The calculated wavelengths and general pattern are in very good agreement with experimental data, with a theoretical error on the Stokes shift around 16%. The computed fluorescence wavelength (355 nm) is in very good agreement with the one measured (363 nm). Furthermore, the calculated relative energy difference between $S_1 \rightarrow S_0$ is 4.29 eV and the calculated Stokes shift is 1.34 eV, which would represent about 30% of quantum yield. If the experimental Stokes shift is very close to the experimental value of 20%. Unfortunately, parametrization for the semiempirical optimization of cobaltabisdicarbollide-containing compounds is not available, and therefore, insight into the quenching mechanism of the

Table 1. UV–Vis Spectroscopic and Photophysical Data for Dendrimers 2, 5a,b, and 7

		absorption	emission		
	$\lambda_{\max}(nm)$	$\varepsilon (10^{-3} \mathrm{dm^3 mol^{-1} cm^{-1}})$	λ_{\max} (nm)	$\Phi\left(\%\right)$	μ (ns)
2	269	127	364	20	9.3
5a	270	66	364	21	9.5
5b 7	270 272	65 78	364 363	21 22	9.5 9.5
'	212	10	505		

Table 2. Number of Cobaltabisdicarbollide Units Calculated of the Metallocarborane-Terminated Dendrimers Using the Lambert-Beer Law

dendrimer	λ_{\max} (nm)	theoretical number of cobalta- bisdicarbollides	ε^{a}	calculated ^a number of cobalta- bisdicarbollides
monomer ^b	310	1	$\varepsilon_0 = 12687$	
10	310	3	35 328	2.8 ± 0.3
11	309	6	67 1 63	5.3 ± 0.5
12	307	12	159485	12.6 ± 0.7

^{*a*} ε/ε₀ represents the experimental cobaltabisdicarbollide units number calculated according to Lambert–Beer law. ^{*b*}Cs[1,1'-μ-Si(CH₃)₂-Co(1,2-C₂B₉H₁₀)₂]²⁴ is used as monomer.

fluorescence cannot be envisaged. It is our opinion, however, that when these moieties are bonded to the dendrimeric surface, the Jablowsky diagram changes from an emissive system A to a nonemissive system B (Figure 7).

Conclusions

A new family of star-shaped molecules and dendrimers, which consist of 1,3,5-triphenylbenzene unit as fluorescent core, Fréchet-type poly(aryl ether) fragments as connecting groups, and 3, 6, 9, and 12 terminal allyl ether groups have been prepared by a convergent approach to be used as scaffold for incorporating cobaltabisdicarbollide derivatives. Thus, the hydrosylilation reaction of the allyl ether groups with [1,1'-µ-SiMeH-3,3'- $Co(1,2-C_2B_9H_{10})_2$ using optimal reaction conditions leads to Féchet-type polyanionic metallodendrimers (whith 3, 6, and 9 negative charges) decorated with cobaltabisdicarbollide units. UV-vis spectroscopy was used to estimate the number of peripheral cobaltabisdicarbollide units by using the Lambert-Beer law. Concerning the photoluminescent properties, the starting dendrimers exhibit fluorescence at room temperature under ultraviolet irradiation; nevertheless, after functionalization with cobaltabisdicarbollide derivatives, the fluorescence was quenched. By using steady-state and time-resolved luminescence measurements, it is shown that for metallodendrimers 10-12 a mechanism different than photon emission could be available to go from excited singlet state to the ground electronic state, mainly due to peripheral functionalization. Because of the anionic character of these compounds and the boron-rich content, we are actually focusing our research on biocompatibility studies and potential applications in medicine as antiviral or BNCT agents.

Experimental Section

Instrumentation. The melting point of **2** was recorded on an Electrothermal 9200 apparatus and is uncorrected. Microanalyses were performed in the analytical laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets or NaCl on a Shimadzu FTIR-8300 spectrophotometer. UV-vis spectroscopy was carried out with a Shimadzu UV-vis 1700 spectrophotometer, at 23 °C temperature, using 1 cm quartz cuvettes. Fluorescence spectra were measured on Cary Eclipse fluorescence spectrophotometer. The electrospray-ionization mass spectra (ESI-MS) were recorded on a Bruker Esquire 3000

Figure 4. UV-vis and normalized fluorescence spectra for starting dendrimers 2, 5a, 5b, and 7.

Figure 5. UV-vis spectra for metallacarborane-containing poly-(aryl ether) dendrimers 10-12.

spectrometer using a source of ionization and a ions trap analyzer. MALDI-TOF-MS mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF [N₂ laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. Mass spectra were recorded on a Hewlett-Packard 5989A spectrometer using electron ionization; HRMS (high-resolution mass spectroscopy) spectra were obtained on an Agilent Technologies G1969A and APCI (atmospheric pressure chemical ionization) ionization time-of-flight spectrometer, coupled to a HPLC model 1100. The ¹H, ¹H{¹¹B} NMR (300.13, 300 and 400 MHz), ¹¹B, ¹¹B{¹H} NMR (96.29 MHz), ¹³C{¹H} NMR (75.47 and 100 MHz), and ²⁹Si{¹H} NMR (59.62 MHz) spectra were recorded on a Bruker DPX 300, a Bruker ARX 300 and a Jeol Eclipse 400 spectrometers equipped with the appropriate decoupling accessories at room temperature in deuterated chloroform or acetone-d₆ solutions. Chemical shift values for ¹¹B NMR and ¹¹B{¹H} spectra were referenced to external BF₃·OEt₂, and those for ¹H, ¹H $\{^{11}B\}$, ¹³C $\{^{1}H\}$ NMR, and ²⁹Si $\{^{1}H\}$ NMR spectra were referenced to SiMe₄. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in hertz.

Materials. All manipulations were carried out under a dinitrogen atmosphere using standard Schlenck techniques. Solvents were reagent grade and were purified by distillation from appropriate drying agents before use. 3,5-Hydroxybenzyl alcohol, 4-hydroxyacetophenone, SiCl₄, allyl bromide, potassium carbonate, 18-crown-6 ether, palladium(II) acetate, tetrabutylammoniun, tetramethylammonium, and fluoride hydrate were purchased from Aldrich. Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex, 2.1-2.4% platinum in vinyl terminated polydimethylsiloxane) was obtained from ABCR and used as received. Compounds $1,^{32a}, 3,^{34}, 4a,^{33}, 6,^{42}$ 3,4,5-trisallyloxy(benzyloxy)benzene,⁴³ 8, and 9^{24} were prepared according to the literature procedures.

Preparation of 1,3,5-Tris(4-allyloxyphenyl)benzene (2). Compound **2** was prepared from **1** (4.80 g, 27.27 mmol) and tetrachlorosilane (12.5 mL, 109.08 mmol) in absolute ethanol at room temperature for 24 h. The precipitate was filtered and washed with methanol to give **2** as a white powder. Yield: 80% (3.44 g, 7.26 mmol); mp 83–85 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.68 (3H, s, H-1), 7.64 (6H, d, J^3 (H,H) = 8.7, H-4), 7.04 (6H, d, J^3 (H,H) = 8.7, H-5), 6.11 (3H, ddt, $J_{trans} = 17.2$, $J_{cis} = 10.4$, $J^3_{allylic} = 5.3$, H-8), 5.48 (3H, dd, $J_{trans} = 17.2$, J^2 (H,H) = 1.3, H-9a), 5.34 (3H, dd, $J_{cis} = 10.4$, J^2 (H,H) = 1.3, H-9b), 4.62 (6H, d, $J^3_{allylic} = 5.3$, H-7). ¹H NMR (300 MHz, acetone- d_6): δ 7.75 (9H, m, H-1, H-4), 7.07 (6H, m, H-5), 6.10 (3H, m, H-8), 5.45 (3H, d, J(HH) = 17.3, H-9a), 5.27 (3H, d, J(HH) = 10.6, H-9b), 4.64 (6H, d, $J^3_{allylic} = 5.1$, H-7). ¹³C NMR (75.47 MHz, CDCl₃): δ 158.5 (C-6), 142.0 (C-2), 134.2 (C-3), 133.4 (C-8), 128.5 (C-4), 124.1 (C-1), 118.0 (C-9), 115.2 (C-5), 69.1 (C-7); MS [*m*/*z*], 475 ([M + H]⁺, 35), 474 (M⁺, 100), 434 (27), 433 (81), 292 (42), 351 (21). IR (ν_{max}/cm^{-1}): 3130, 1642, 1608, 1511, 1400, 1325, 1234, 1180, 996, 833, 777. HRMS C₁₃H₃₁O₃ [M + H]⁺, calculated 475.2268; found 475.2266, with an error of 0.361 ppm.

Preparation of 3,4,5-Tris(allyloxy)benzyl Chloride (4b). To a solution of 3,4,5-trisallyloxy(benzyloxy)benzene (0.91 g, 3.29 mmol) in dry CH₂Cl₂ were added 5 mL (3.62 mmol) of Et₃N under a nitrogen atmosphere. The solution was cooled to 0 °C, and SOCl₂ (0.262 mmol) was added slowly. The reaction mixture was stirred for 24 h at RT, and after, water was added and the organic phase extracted with CH₂Cl₂, dried and evaporated under vacuum to give 4b as an amber oil. Yield: 95% (0.92 g). ¹H NMR (300 MHz, CDCl₃): δ 6.60 (2H, s, H-3), 6.18-5.98 (3H, m, H-7, H-7'), 5.44 (2H, dd, $J_{\text{trans}} = 17.2$, $J_{\text{gem}} = 17.2$ 1.5 Hz, H-8), 5.35 (1H, dd, $J_{\text{trans}} = 17.2$, $J_{\text{gem}} = 1.5$ Hz, H-8'), $5.27 (2H, dd, J_{cis} = 10.4, J_{gem} = 1.5 Hz, H-8), 5.19 (1H, d, J_{cis} = 1.5 Hz, H-8)$ 10.4, J = 1.5, H-8', 4.55 (6H, d, J = 5.4, H-6), 4.47 (2H, s, H-1). ¹³C NMR (75.47 MHz, CDCl₃): δ 152.8 (C-4), 138.1 (C-5), 134.6 (C-7'), 133.3 (C-7), 132.7 (C-2), 117.4 (8'), 117.2 (8), 107.6 (C-3), 73.9 (C-6'), 69.6 (C-6), 46.6 (C-1). IR (NaCl, v_{max}/cm⁻¹): 3080, 1825, 2868, 1590, 1502, 1440, 1422, 1332, 1234, 1128, 1111, 989, 926, 708. MS [m/z], 296 (M⁺ + 2, 8), 294 (M⁺, 22), 255 (16), 253 (46), 81 (29), 41 (100). HRMS C₁₆H₂₀O₃Cl 295.1095, with an error of 0.1055 ppm.

Preparation of 1,3,5-Tris[4-(3,5-bis(allyloxy)benzyloxy)phenyl]benzene (5a). Compound 5a was synthesized from 1,3,5 tris(4-hydroxyphenyl)benzene (3) (0.625 g, 1.76 mmol) and 3,5bis(allyloxy)benzyl chloride (4a) (1.50 g, 5.30 mmol) under reflux of acetonitrile for 48 h, in the presence of K_2CO_3 and

Figure 6. Computed absorption and fluorescence wavelength in acetonitrile for 2.

Figure 7. Jabloswky diagram for emissive (system A) and nonemissive (system B) systems.

catalytic amounts of 18-crown-6 ether. The solid residue was removed by filtration, and the solvent was evaporated under vacuum to give an oily residue. The crude oil product was percolated on silica get eluting with hexane/EtOAc (8:2) to give **5a** as an amber oil. Yield: 95% (1.61 g, 1.67 mmol). ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: δ 7.67 (3H, s, H-1), 7.61 (6H, d, $J_0 = 8.8$, H-4), 7.08 (6H, d, $J_0 = 8.8$, H-5), 6.68 (6H, d, $J_m = 2.2$, H-9), 6.48 $(3H, t, J_m = 2.2, H-11), 6.14-6.00 (6H, m, H-13), 5.46 (6H, dd, dd)$ $J_{\text{trans}} = 17.3, J = 1.5, \text{H-14a}, 5.31 (6\text{H}, \text{dd}, J_{\text{cis}} = 10.5, J = 1.5)$ Hz, H-14b), 5.08 (6H, s, H-7), 4.56 (12H, dt, J(HH) = 5.3, J(HH) = 1.4, H-12). ¹H NMR (300 MHz, acetone- d_6): 7.74 (t, J = 4.4, H-1, H-5, 7.12 (6H, d, J = 8.7, H-5), 6.70 (6H, s, H-9), 6.50 (3H, s, H-11), 6.10 (6H, m, H-13), 5.41 (6H, d, J(HH) = 17.3, H-14a), 5.24 (6H, d, *J*(HH) = 10.5, H-14b), 5.12 (6H, s, H-7), 4.57 (12H, d, J(HH) = 3.7, H-12). ¹³C NMR (75.47 MHz, CDCl₃): δ 160.2 (C-10), 158.6 (C-6), 142.0 (C-2), 139.5 (C-8), 134.3 (C-3), 133.3 (C-13), 128.6 (C-4), 124.1 (C-1), 118.0 (C-14), 115.4 (C-5), 106.3 (C-9), 101.5 (C-11), 70.2 (C-7), 69.1 (C-12). IR (NaCl, $\nu_{\text{max}}/\text{cm}^{-1}$): 3128, 2924, 1643, 1601, 1510, 1400, 1324, 1168, 1016, 828. HRMS $C_{63}H_{61}O_9$ [M + H]⁺, calculated 961.4310; found 961.4331, with an error of 2.173 ppm.

Preparation of 1,3,5-Tris[4-(3,4,5-tris(allyloxy)benzyloxy)phenyl]benzene (5b). The procedure was the same as for 5a using 3 (0.70 g, 1.97 mmol) and 4b (1.90 g, 5.58 mmol), to obtain compound 5b as an amber oil. Yield: 90% (2.05 g, 1.81 mmol). ¹H NMR (400 MHz; CDCl₃): δ 7.67 (3H, s, H-1), 7.63 (6H, d, $J_{O} = 8.6, H-4$), 7.07 (6H, d, $J_{O} = 8.6, H-5$), 6.69 (6H, s, H-9), 6.12–6.04 (9H, m, H-13, H-13'), 5.43 (6H, dd, $J_{trans} = 17.2, J =$ 3.3, H-14a), 5.33 (3H, dd, $J_{trans} = 17.2, J = 3.3$ H-14a'), 5.28 (6H, d, $J_{cis} = 12.0, H-14b$), 5.21 (3H, d, $J_{cis} = 12, H-14b'$), 4.64–4.59 (18H, m, H-12, H-12'), 4.99 (6H, s, H-7). ¹³C NMR (100 MHz, CDCl₃): δ 158.9 (C-6), 153.2 (C-10), 142.2 (C-2), 137.9 (C-11), 135.1 (C-3), 134.5 (C-13'), 133.8 (C-13), 132.7 (C-8), 128.8 (C-4), 124.3 (C-1), 118.0 (C-14'), 117.9 (C-14), 115.7 (C-5), 107.2 (C-9), 74.6 (C-12'), 70.7 (C-7), 70.4 (C-12). IR (NaCl, ν_{max}/cm^{-1}): 3126, 2926, 2838, 1643, 1594, 1509, 1439, 1329, 1232, 1112, 992, 926, 828.

Preparation of 1,3,5-Tris[4-(3,5-bis(3,5-bis(allyloxy)benzyloxy)benzyloxy)phenyl]benzene (7). Compound 7 was synthesized from 3 (0.78 g, 0.28 mmol) and 3,5-bis[3,5-bis-(allyloxy)benzyloxy]benzyl chloride (6) (0.50 g, 0.88 mmol) under reflux of acetone for 56 h, in the presence of K₂CO₃ and catalytic amounts of Bu₄NF hydrate. The solid residue was removed by filtration; the organic phase was washed with H₂O, dried with Na₂SO₄, and evaporated under vacuum to give a residue. The crude product was percolated over silica get eluting with hexane/EtOAc (7:3) and washed with pentane to give 7 as an amber oil. Yield: 53% (0.350 g, 1.67 mmol). ¹H NMR (400 MHz; CDCl₃): δ 7.68 (3H, s, H-1), 7.63 (6H, d, $J_0 = 8.9$, H-4), 7.07 (6H, d, $J_0 = 8.9$, H-5), 6.72 (6H, d, $J_m = 1.8$, H-9), 6.62 $(12H, d, J_m = 1.5, H-14), 6.58 (3H, t, J_m = 1.8 Hz, H-11), 6.48$ $(6H, t, J_m = 1.5, H-16), 6.10-6.00 (12H, m, H-18), 5.42 (12H, m)$ dd, $J_{\text{trans}} = 17.4$, $J_{\text{gem}} = 1.5$, H-19a), 5.27 (12H, dd, $J_{\text{cis}} = 11.9$, $J_{\text{gem}} = 1.5, \text{H-19b}$, 5.06 (6H, s, H-7), 4.99 (12H, s, H-12), 4.53 (24H, d, J = 5.4 Hz, H-17). ¹³C NMR (100 MHz, CDCl₃): δ 160.2 (C-10), 160.0 (C-15), 158.5 (C-6), 141.8 (C-2), 139.5 (C-8), 139.3 (C-13), 134.2 (C-3), 133.2 (C-18), 128.4 (C-4), 123.9 (C-1), 117.8 (C-19), 115.3 (C-5), 106.5 (C-9), 106.3 (C-14), 101.8 (C-11), 101.5 (C-16), 70.1 (C-12, 7), 69.0 (C-17). IR (NaCl, ν_{max} / cm⁻¹): 3135, 1642, 1597, 1400, 1324, 1167, 1052, 830.

Preparation of Metallodendrimer 10. In a Schlenk flask, 2 (63.1 mg, 0.133 mmol), 10 µL of Karstedt catalyst, and 2 mL of THF were stirred for 10 min at room temperature. To this solution, Cs[1,1'-µ-Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂], 8 (200.0 mg, 0.401 mmol), was added, and the mixture was stirred overnight at 50 °C. After, 10 mL of Et₂O was added to produce two phases. The Et₂O phase was discarded by decantation. To the other oily dark orange phase, 10 mL of hexane was added to precipitate 10 as an orange solid. Yield: 54% (142.1 mg). ¹H NMR (300 MHz, acetone- d_6): δ 7.77 (m, 9H, C-H_{aryl}), 7.06 $(d, 6H, {}^{3}J(HH) = 8.5, C-H_{aryl}), 4.56 (brs, 6H, C_{c}-H), 4.07 (t, t)$ 6H, ${}^{3}J(HH) = 6.4$, $-O-CH_{2}-$), 1.92 (m, 6H, $-CH_{2}-CH_{2}-$), 1.07 (300 MHz, acetone, 6H, $-CH_{2}-Si$), 0.38 (s, 9H, Si-CH₃). ${}^{1}H{}^{1}B{}$ NMR (96.29 MHz, acetone-d₆): δ 7.77 (m, 9H, $C-H_{aryl}$, 7.06 (d, 6H, ³J(HH) = 8.5, $C-H_{aryl}$), 4.56 (br s, 6H, $C_c - H$, 4.07 (t, 6H, ${}^{3}J$ (HH) = 6.4, $-O - CH_2 -$), 3.43 (brs, 2H, B-H), 3.30 (br s, 2H, B-H), 3.10 (br s, 2H, B-H), 2.38 (br s, 2H, B-H), 2.22 (br s, 2H, B-H), 1.94 (br s, 2H, B-H), 1.92 (m, 6H, -CH₂-CH₂-), 1.69 (br s, 6H, B-H), 1.07 (m, 6H, -CH2-Si), 0.38 (s, 9H, Si-CH3). ¹¹B NMR (96.29 MHz, acetone- d_6): δ 8.26 (d, 2B, ${}^{1}J(BH) = 118$), 2.84 (d, 2B, ${}^{1}J(BH) = 136$, -1.68 (d, 4B, ${}^{1}J(BH) = 140$), -3.47 (2B), -4.68 (d, 2B, $^{1}J(BH) = 130$), -14.34 (d, 2B, $^{1}J(BH) =$ 180), -16.62 (d, 2B, ${}^{1}J(BH) = 148$), -22.10 (d, 2B, ${}^{1}J(BH) =$ 147). ¹³C NMR (75.47 MHz, acetone- d_6): δ 157.2–114.6 (C_{aryl}), 69.50 (O-CH₂), 55.31 (C_c-H), 41.29 (C_c-Si), 22.3 (-CH₂-), 12.01 (Si-CH₂), -6.03 (Si-CH₃). ²⁹Si NMR (59.62 MHz, acetone- d_6): δ 11.96. IR (KBr, ν_{max}/cm^{-1}): 3059 (pI, $\nu(C_c-H)$, 3030 (pI, v(C-H)_{aryl}), 2874 (pI, v(C-H)_{alkyl}), 2546 (mI, v(B-H)), 1257 (I, δ(Si-CH₃)), 1234 (I, vas(C_{arvl}-O-C)), 1041 (I, $vs(C_{aryl}-O-C)$), 829 (I, $\gamma(Si-CH_3)$). Anal. Calcd for $C_{48}H_{102}B_{54}$ Co₃Cs₃O₃Si₃: C, 29.26; H, 5.22. Found: C, 29.32; H 5.34. ESI-MS: (m/z) calcd 1837.8; found 1837.1 (M-Cs).

Preparation of Metallodendrimer 11. In a Schlenk flask, 5a (68.0 mg, 0.071 mmol), $10 \,\mu\text{L}$ of Karstedt catalyst, and 2 mL of THF were stirred for 10 min at room temperature. To the solution Cs[1,1'-µ-Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂], 8 (211.7 mg, 0.424 mmol), was added, and the mixture was stirred overnight at 50 °C. After, 10 mL of Et₂O was added to produce two phases. The Et₂O was discarded by decantation. To the other oily dark orange phase, 10 mL of hexane was added to precipitate 11 as an orange solid. Yield: 63% (176.2 mg). In other attempts, the addition of an aqueous solution of [NMe4]Cl to the residue gives the corresponding tetramethylammonium salt of the metallodendrimer as an orange solid. Yield: 55%. ¹H NMR (300 MHz, acetone-d₆): δ 7.77 (m, 9H, H_{aryl}), 7.15 (d, 6H, ${}^{3}J(\text{HH}) = 12.0, \text{ C}-H_{\text{arvl}}), 6.69 \text{ (s, 6H, C}-H_{\text{arvl}}), 6.50 \text{ (s, 3H,}$ $C-H_{arvl}$, 5.12 (s, 6H, $-OCHH_2-$), 4.56 (brs, 12H, C_c-H), 4.00 $(t, 12H, {}^{3}J(HH) = 6.4, -OCHH_2-), 1.87 (m, 12H,$ $-CH_2-CH_2-$), 1.04 (m, 12H, $-CH_2-Si$), 0.37 (s, 18H, Si-CH₃). ${}^{1}H{}^{11}B{}$ NMR (300 MHz, acetone- d_6): δ 7.77 (m, 9H,C- H_{aryl}), 7.15 (d, 6H, ³J(HH) = 12.0, C- H_{aryl}), 6.69 (s, 6H, $C-H_{aryl}$, 6.50 (s, 3H, $C-H_{aryl}$), 5.12 (s, 6H, $-OCHH_2-$), 4.56 (brs, 12H, C_c-H), 4.00 (t, 12H, ${}^{3}J(HH) = 6.4$, $-OCHH_2-$), 3.40 (br s, 12H, B-H), 3.29 (br s, 12H, B-H), 3.09 (br s, 12H, B-H), 2.38 (br s, 12H, B-H), 2.20 (br s, 12H, B-H), 1.88 (br s, 12H, B-H), 1.87 (m, 12H, -CH₂-CH₂-), 1.66 (br s, 72H, B-H), 1.04 (m, 12H, -CH₂-Si), 0.37 (s, 18H, Si-CH₃). ¹¹B NMR (96.29 MHz, acetone- d_6): δ 8.35 (d, 2B, ${}^{1}J(BH) = 120$), $2.86 (d, 2B, {}^{1}J(BH) = 135), -1.72 (d, 4B, {}^{1}J(BH) = 146), -3.50$ (2B), -4.76 (d, 2B, ${}^{1}J(BH) = 130$), -14.59 (d, 2B, ${}^{1}J(BH) = 189$), -16.79 (d, 2B, ${}^{1}J(BH) = 140$), -22.30 (d, 2B, {}^{1}J(BH) = 140), -22.30 (d, 2B, {}^{1}J(BH) = 140), -22.30 (d, 2 166). ${}^{13}C{}^{1}H{}$ NMR (75.47 MHz, acetone- d_6): δ 160.4–100.3 (C_{aryl}) , 69.70 (O-CH₂), 55.21 (C_c -H), 40.7 (C_c -Si), 22.3 (-CH₂-), 8.03 (Si-CH₂), -7.09 (Si-CH₃). ²⁹Si NMR (59.62 MHz, acetone- d_6): δ 12.04. IR (KBr, v_{max}/cm^{-1}): 3061 (pI, v(C_c-H), 2976 (pI, v(C-H)_{aryl}), 2874 (pI, v(C-H)_{alkyl}), 2554 (mI, v(B-H)), 1257 (I, $\delta(Si-CH_3)$), 1233 (I, $vas(C_{aryl}-O-C)$), 1053 (I, vs(Caryl-O-C)), 828 (I, γ(Si-CH₃)). Anal. Calcd for C₁₁₇H₂₇₆B₁₀₈Co₆N₆O₉Si₆: C, 39.02; H, 7.73; N, 2.33. Found: C, 38.08; H, 7.77; N, 2.09. MALDI-TOF-MS: (m/z) 530.5 ((M + H₂O)/6, 37%), 1051.6 (M/2, 3%).

Preparation of Metallodendrimer 12. The procedure was the same as for 10 using 7a (41.2 mg, 0.021 mmol), 10μ L of Karstedt catalyst, and 2 mL of THF to give 12 as an orange solid. Yield: 51% (86.0 mg). ¹H NMR (300 MHz, acetone- d_6): δ 7.77 (m, 6H, $C-H_{aryl}$, 7.12 (m, 6H, H_{aryl}), 6.78 (s, 6H, C_6H_5), 6.69 (s, 12H, C_6H_5), 6.54 (s, 6H, C_6H_5), 6.45 (s, 6H, $C-H_{aryl}$), 6.37 (s, 3H, $C-H_{arvl}$, 5.11 (s, 6H, $-OCHH_2-$), 5.06 (s, 12H, $-OCHH_2-$), 4.50 (brs, 24H, C_c-H), 3.99 (s, 24H, $-OCHH_2$ -), 1.85 (m, 24H, -CH₂-CH₂-), 1.01 (m, 24H, -CH₂-Si), 0.32 (s, 36H, Si- \tilde{CH}_3). ¹¹B NMR (96.29 MHz, acetone- d_6): δ 8.40 (d, 2B, ${}^{1}J(BH) = 121$, 3.03 (d, 2B, ${}^{1}J(BH) = 130$), -1.59 (d, 4B, ${}^{1}J(BH) = 140), -3.38 (2B), -4.54 (d, 2B, {}^{1}J(BH) = 120), -14.22 (d, 2B, {}^{1}J(BH) = 170), -16.46 (d, 2B, {}^{1}J(BH) = 141), -21.90 (d, 2B, {}^{1}J(BH) = 160). {}^{13}C{}^{1}H{}NMR (75.47 MHz, acetone-d_6): \delta$ 160.6-106.3 (Caryl), 78.36 (O-CH₂), 69.60 (O-CH₂), 65.11 $(O-CH_2)$, 55.24 (C_c-H) , 40.6 (C_c-Si) , 22.3 $(-CH_2-)$, 14.9, 8.41 $(Si-CH_2)$, 3.70, -1.01, -7.04 $(Si-CH_3)$. ²⁹Si NMR (59.62) MHz, acetone- d_6): δ 12.40. IR (KBr, v_{max}/cm^{-1}): 3056 (pI, $v(C_c-H)_{arvl}$, 2963 (pI, $v(C-H)_{arvl}$), 2872 (pI, $v(C-H)_{alkyl}$), 2535 (mI, v(B-H)), 1258 (I, $\delta(Si-CH_3)$), 1226 (I, vas- $(C_{aryl}-O-C))$, 1040 (I, $vs(C_{aryl}-O-C))$, 834 (I, $\gamma(Si-CH_3))$. Anal. Calcd for C₁₈₃H₄₀₈B₂₁₆Co₁₂Cs₁₂O₂₁Si₁₂: C, 27.75; H, 5.19. Found: C, 27.26; H, 5.47. MALDI-TOF-MS: (m/z) 530.4 ((M/12 + H₂O, 19%).

UV-Vis and Fluorescence Measurements. UV-vis, stationary state fluorescent spectra, and fluorescent lifetime measurements have been done at room temperature using the following procedure: stock solutions of compounds were obtained by preparing solutions of several milligrams, in the range of 1-10 mg, of the compounds 2, 5a, 5b, 7a, and 10-12 and the quantum yield reference tryptophan⁴⁴ in acetonitrile. From

stock solutions, three different concentrations ranging between 1.92×10^{-5} and 1.95×10^{-7} M for each compound are prepared. Fluorescent measurements are developed in two situations, with degassed solutions with N₂ and with ambient oxygen atempered, and no significance difference in wavenumber has been noted. Lifetime fluorescence measurements were performed on a EasyLife V. The excitation was performed with a 278 pulsed LED, and the emission was measured at 364 nm.

Computational Methods. All calculations have been carried out with PM6 implemented in MOPAC.⁴⁰ The bulk solvent effects on the geometries are evaluated by means of the conductor-like screening model (COSMO) continuum approach using as EPS 37.5 for acetonitrile.⁴¹

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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