Synthesis and Electronic Properties of Covalent Assemblies of Oligophenylenevinylene Units Arising from a Calix[4]arene Core

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Assemblies of four oligophenylenevinylene moieties arising from a calix[4]arene core, i.e., calix[4]-oligophenylenevinylenes, have been prepared by Heck-type cross-coupling reactions of styrene derivatives with a tetraiodinated cone-calix[4]arene precursor. Photophysical studies in solution have revealed that there are electronic ground state interactions between the covalently bonded OPV moieties. The absorption spectra of the calix[4]oligophenylenevinylenes are significantly different from those obtained by summing the spectra of four model units and their emission is red-shifted when compared to the corresponding model compounds. Electrochemical studies have shown that the redox processes of the four OPV subunits do not take place at the same potentials indicating also a strong electronic interaction among them in the calix[4]oligophenylenevinylenes.

Introduction

Conjugated organic materials such as oligophenylenevinylenes (OPV) have attracted considerable attention in recent years.[1] Thanks to their special electronic properties, they appear as promising new materials for light emitting diodes (LEDs)[2] or photovoltaic cells.[3,4] In such devices, the morphology of the organic films plays a fundamental role in the functional characteristics of the device[5] and a challenging task appears to be the understanding of the chromophore−chromophore interactions in solid samples. However, studies that clearly relate electroluminescence or charge transport properties with molecular morphology appear difficult due to the many possible environments present in a solid sample. An alternative approach to gaining insight into interchromophore interactions is the investigation of well-defined molecules combining several chromophores.[6−8] They can be considered as representative isolated models of chromophore aggregates in the solid and studied in the absence of intermolecular interactions. In recent years, these considerations have led to substantial efforts in the synthesis and optical characterization of new molecules that bring together two π-conjugated chromophores into close proximity.[6] As part of this research, we now report the synthesis and electronic properties of assemblies of four OPV moieties arising from a calix[4]arene core, i.e., calix[4]OPVs. We found that the four OPV fragments constituting the calix[4]OPVs **1** and **2** are neither equivalent nor even directly related to the corresponding OPV model compounds **3** and **4**, respectively.

Results and Discussion

Synthesis. The synthetic approach to prepare the calix[4]OPVs relies upon Heck type cross-coupling[9] reactions of styrene derivatives on the upper rim of the tetraiodinated calix[4]arene **6**. Compound **6** was prepared in two steps from the commercially available calix[4]-

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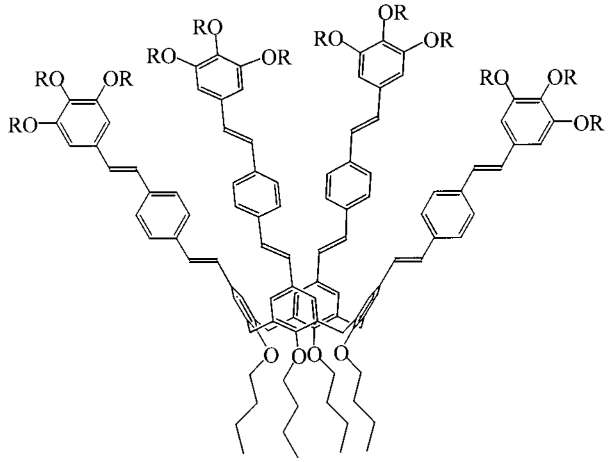
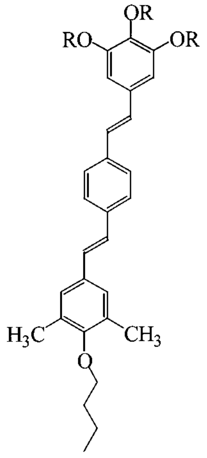


1 $R = C_{12}H_{25}$



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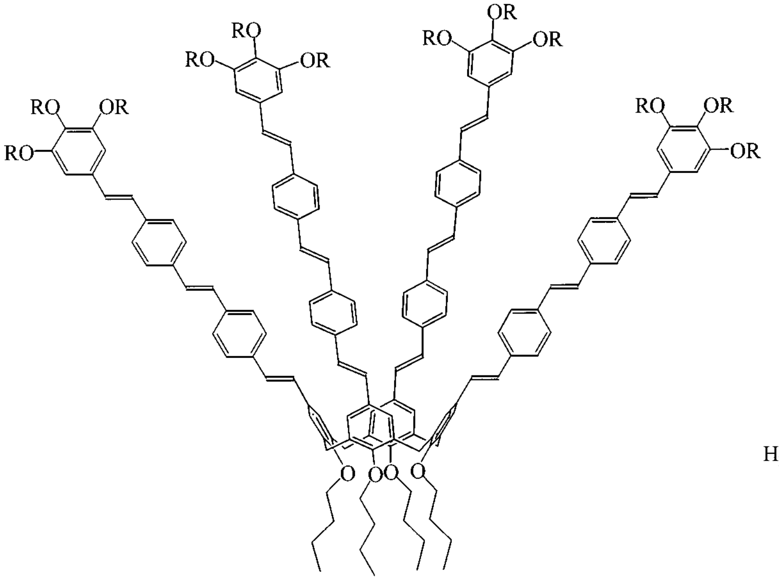
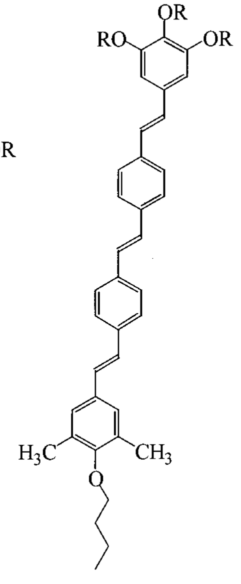


2 $R = C_{12}H_{25}$



4 $R = C_{12}H_{25}$

arene (Scheme 1). The tetra-*O*-alkylated cone-calix[4]arene **5** was obtained in 62% yield by treatment of calix[4]arene with 1-bromobutane in DMF at 60 °C in the presence of NaH as previously reported.[10] Subsequent iodination under the conditions developed by Reinhoudt, Pochini, Ungaro and co-workers[11] yielded **6** in 91% yield. The cone conformation of **6** was deduced from the ^{1}H- and ^{13}C NMR spectra. In particular, the ^{13}C NMR chemical shift of the methylene groups connecting the aromatic rings (δ 31.98 ppm) was in good agreement with a cone conformation as previously shown in the literature.[12]

The conditions for the Heck-type cross-coupling reactions involving the tetraiodinated calix[4]arene **6** were first adjusted with a commercially available styrene derivative, namely 4-methylstyrene. The best results were obtained with $Pd(OAc)_2$ as catalyst in the presence of tri-*o*-tolylphosphine (POT) in xylene-Et_3N at 120−140 °C. Under these conditions, reaction of **6** with a slight excess of 4-methylstyrene (4.5 equiv) afforded compound **7** in 78% yield. The ^{1}H NMR spectrum of **7** in CD_2Cl_2 recorded at room temperature shows all the expected signals. The coupling constant of ca. 17 Hz for the AB signal corresponding to the vinylic protons confirmed the *E* stereochemistry of the double bonds in **7**. The cone conformation of **7** was deduced from the ^{1}H and ^{13}C NMR spectra. Effectively, the characteristic AB quartet is observed for the calix[4]arene methylene groups in the ^{1}H NMR spectrum. Furthermore, the resonance of the methylene groups connecting the aromatic rings is observed at δ 31.14 ppm in the ^{13}C NMR spectrum. It is worth noticing that the isomerization of the tetra-*O*-alkylated cone-calix[4]arene into other conformers (partial-cone, 1,2- and 1,3-alternate) does not take place under the Heck coupling reaction conditions. The latter observation is consistent with previous studies.[13] Effectively, it has been shown that *n*-propyl groups are bulky enough to inhibit oxygen-through-the-annulus rotation in tetra-*O*-alkylated cone-calix[4]arene even at high temperature.[13] The structure of **7** is also confirmed by FAB-mass spectrometry showing the expected molecular ion peak at *m*/*z* 1112.8 (M^+, calcd for $C_{80}H_{88}O_4$: 1112.67).

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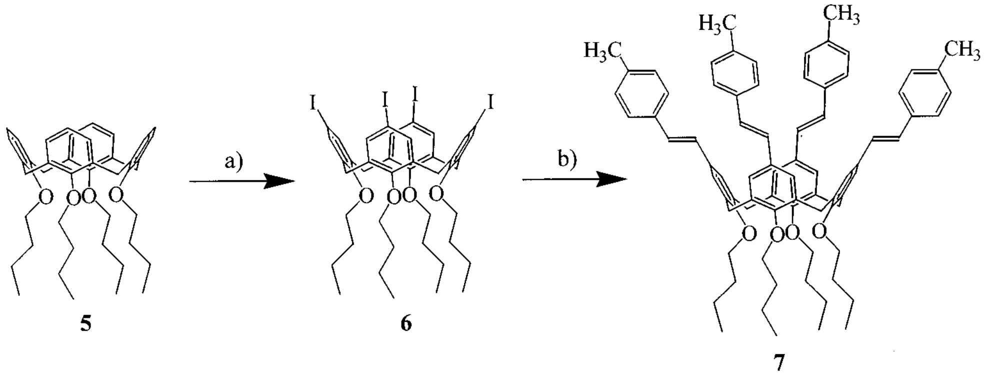
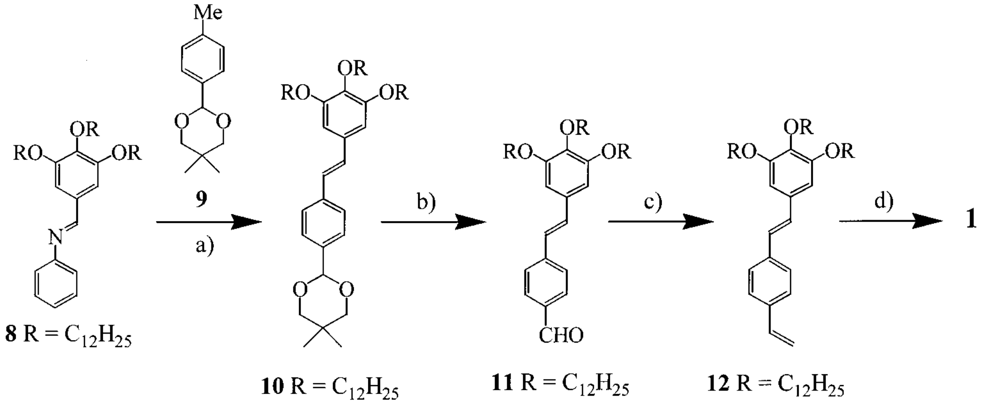
Scheme 1[a]



[a] Reagents and Conditions: (a) CF_3CO_2Ag, I_2, $CHCl_3$, Δ (91%); (b) 4-methylstyrene, $Pd(OAc)_2$, POT, Et_3N, xylene, Δ (78%).

Scheme 2[a]



[a] Reagents and Conditions: (a) *t*-BuOK, DMF, 80 °C (55%); (b) CF_3CO_2H, CH_2Cl_2, H_2O, rt (94%); (c) methyl triphenylphosphonium bromide, *t*-BuOK, THF, rt (86%); (d) **6**, $Pd(OAc)_2$, POT, Et_3N, xylene, Δ (75%).

The preparation of calix[4]OPV **1** is depicted in Scheme 2. Benzaldimine **8** was prepared in four steps from methyl 3,4,5-trihydroxybenzoate as previously reported.[14] Treatment of **8** with **9**[4b] under Siegrist conditions gave stilbene **10** in 55% yield. In the ^1H NMR spectrum of **10**, the signal corresponding to the vinylic protons appears as a singlet, thus the stereochemistry of the double bond could not be unambiguously determined. However, after deprotection with CF_3CO_2H in CH_2Cl_2/H_2O, the ^1H NMR spectrum of the resulting aldehyde **11** exhibits an AB signal with a coupling constant of ca. 16 Hz for the ethylenic protons confirming the *E* stereochemistry of the double bond. Reaction of aldehyde **11** with methyl triphenylphosphonium bromide under Wittig conditions gave **12** in 83% yield. Calix[4]OPV **1** was then obtained in 75% yield from **6** and **12** under Heck type cross-coupling conditions. The corresponding higher homologue **2** was prepared in a similar manner from compound **13**[15] (Scheme 3). Deprotection with CF_3CO_2H in CH_2Cl_2/H_2O followed by reaction of the resulting **14** with methyl triphenylphosphonium bromide under Wittig conditions afforded **15** in an overall 62% yield. Subsequent Heck coupling with **6** gave calix[4]OPV **2** in 38% yield.

Both **1** and **2** gave complicated ^1H NMR spectra. For example, the ^1H NMR spectrum of calix[4]OPV **2** is shown in Figure 1. As seen by comparison with the ^1H NMR spectra of **4** and **6**, all the anticipated signals are present but some of them are large. The broadening observed in the spectra of **1** and **2** suggests the existence of several conformers. Indeed, the OPV moieties in **1** and **2** are not perpendicular to the calixarene core and free rotation of the four substituents on the upper rim of the calix[4]arene core is necessary to produce a NMR spectrum with sharp signals corresponding to a C_{4v} symmetrical structure. When compared to **7** for which a C_{4v} symmetric structure is deduced from the ^1H NMR spectrum at room temperature, restricted rotation in **1** and **2** can easily be explained by steric reasons resulting from the increased size of the upper-rim substituents. For both **1** and **2**, the NMR spectra recorded at high temperature show only little differences when compared to the spectra taken at room temperature. Actually, simple inspection of CPK models shows that free rotation of the

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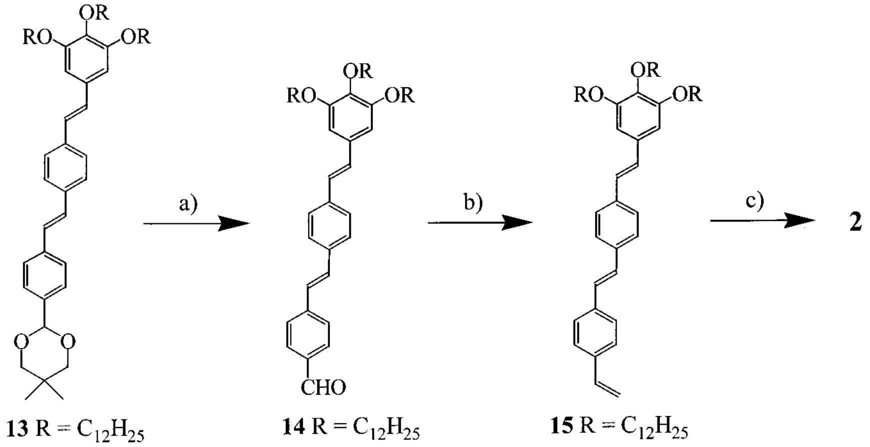
Scheme 3[a]



[a] Reagents and Conditions: (a) CF_3CO_2H, CH_2Cl_2, H_2O, rt (97%); (b) methyl triphenylphosphonium bromide, *t*-BuOK, THF, rt (64%); (c) **6**, $Pd(OAc)_2$, POT, Et_3N, xylene, Δ (38%).

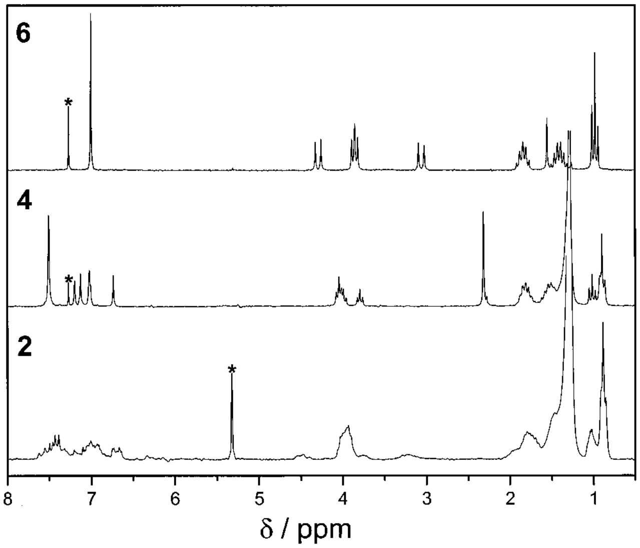


Figure 1. ^{1}H NMR spectra of **2** (200 MHz, CD_2Cl_2, * = $CHDCl_2$), **4** (200 MHz, $CDCl_3$, * = $CHCl_3$) and **6** (200 MHz, $CDCl_3$, * = $CHCl_3$). All the spectra have been recorded at 25 °C.

four substituents on the upper-rim of the calix[4]arene core is obviously not possible. The dynamic exchange allowing the obtention of NMR spectra with sharp signals corresponding to C_{4v} symmetrical structures cannot occur and the calix[4]OPVs must adopt C_1 symmetrical conformations leading to the observed NMR spectra. The ^{13}C NMR spectra of both **1** and **2** are also complicated. It is however worth noting that the C atoms of the methylene groups connecting the aromatic rings resonate around δ 31 ppm in the ^{13}C NMR spectra of both calix[4]OPVs in good agreement with the proposed cone conformations. The structure of both **1** and **2** is finally confirmed by their MALDI-TOF mass spectra showing as base peak the expected molecular ion peaks [**1**: 3679 (MH$^+$, calculated for $C_{252}H_{393}O_{16}$: 3678.88); **2**: 4087 (MH$^+$, calculated for $C_{284}H_{417}O_{16}$: 4087.42)].

Model compounds **3** and **4** were prepared as depicted in Scheme 4. Reaction of commercially available 4-bromo-2,6-dimethylphenol with 1-bromobutane in the presence of NaH afforded **16** in 87% yield. Subsequent reaction with **12** under Heck coupling conditions gave **3** in 23% yield. Model compound **4** could not be obtained by treatment of **16** with styrene **15** under similar conditions. Bromide **16** was found to be poorly reactive under the Heck cross-coupling conditions and it was necessary to prepare the more reactive iodine derivative **18** in order to obtain model compound **4**. Reaction of 2,6-dimethylphenol with 1-bromobutane in DMF at 70 °C in the presence of NaH, followed by iodination of the resulting **17**, yielded **18** in an overall yield of 40%. Subsequent Heck coupling with **15** gave model compound **4** in 54% yield.

Photophysical Properties. The absorption spectra of **10**, **3** and **4** (Figures 2-3, Table 1) show a strict similarity with that of the parent unit *trans*-stilbene,[16] that exhibits a band with $\lambda_{max} = 310$ nm (of B_u^+ symmetry) mainly due to a vinylic transition mixed with a benzenic one, along with an absorption feature ($\lambda_{max} = 220$ nm, B_u^-) more localized on the aromatic rings.[16] For the band peaked at 310 nm, upon addition of an extra styrenic unit to the *trans*-stilbene molecule, the calculated (ZINDO/S) absorption maximum shifts to the red by ca. 20 nm and the oscillator strength increases by ca. 20%; this is a consequence of the increased π-conjugation, as shown by the HOMO−LUMO transition density plots. Importantly, subsequent disruption of the conjugation, for example by rotating of 90° the terminal ring, causes a decrease of intensity and a blue-shift of the same amount, thus leading back a spectrum very similar to that of *trans*-stilbene. In **10**, **3** and **4**, the effect of increased conjugation is quite evident for the lower-energy band, but hardly observable for that centered at ca. 250 nm. This suggests that the latter band is of purely benzenic character and is scarcely affected by the double bond conjugation, in line with the *trans*-stilbene behavior (see above).

The absorption spectra of **1** and **2** are significantly different (both in shape and intensity) from those obtained by summing the spectra of four model units **3** and **4**, respectively (Figure 2). The blurring of the absorption bands that leads to the unexpected spectral shapes of the calix[4]OPVs could be a consequence of an exciton contribution resulting from intramolecular interchromophore interactions in good agreement with data reported by Shinkai and co-workers for fluorescent calix[4]arene derivatives.[17]

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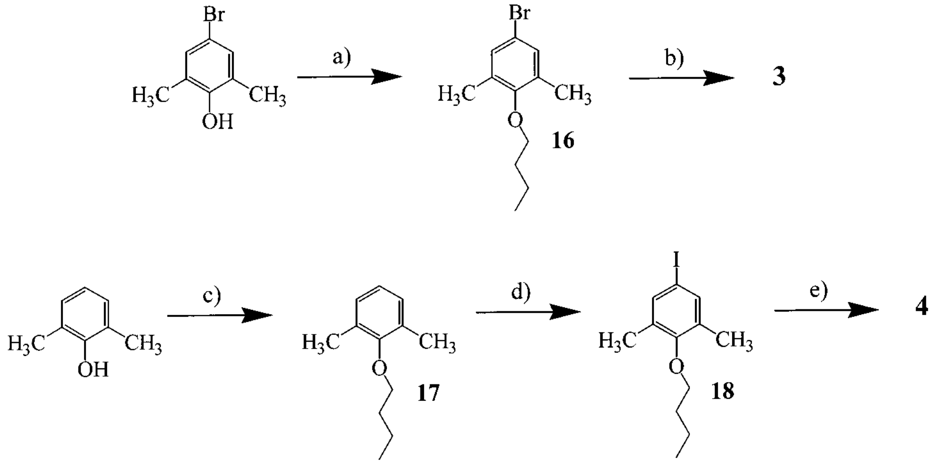
Scheme 4[a]



[a] Reagents and Conditions: (a) 1-bromobutane, NaH, DMF, 70 °C (87%); (b) **12**, Pd(OAc)$_2$, POT, Et$_3$N, xylene, Δ (23%); (c) 1-bromobutane, NaH, DMF, 70 °C (44%); (d) CF$_3$CO$_2$Ag, I$_2$, CHCl$_3$, Δ (91%); (e) **15**, Pd(OAc)$_2$, POT, Et$_3$N, xylene, Δ (54%).

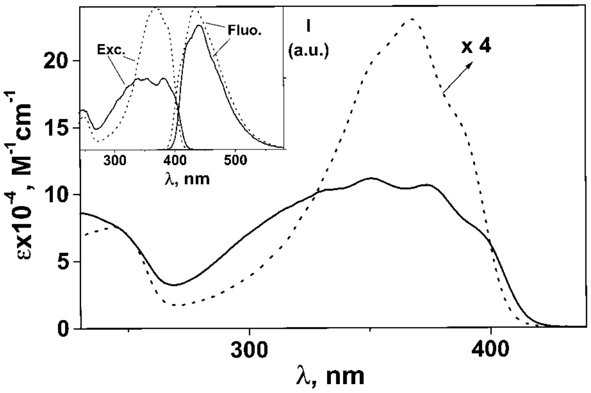


Figure 2. Absorption spectra of **1** (full line) and **3** (multiplied by a factor of 4, dotted line); inset: excitation and fluorescence spectra of **1** (solid line) and **3** (dotted line). All the spectra are recorded in CH$_2$Cl$_2$ solution.

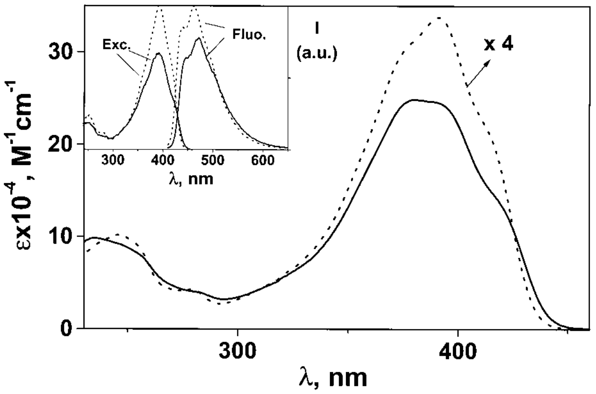


Figure 3. Absorption spectra of **2** (full line) and **4** (multiplied by a factor of 4, dotted line); inset: excitation and fluorescence spectra of **2** (solid line) and **4** (dotted line). All the spectra are recorded in CH$_2$Cl$_2$ solution.

Table 1. Absorption Properties of Compounds 10 and 1−4

	λ_{max} nm	ϵ (M^{-1}cm^{-1})
10	243	15 000
	324	29 000
1	248 (sh.)	73 000
	351	111 000
3	244	19 000
	367	57 500
2	258 (sh.)	75 000
	380	249 000
4	246	25 000
	391	84 000

Table 2. Luminescence Data in CH$_2$Cl$_2$[a]

	298 K			77 K	
	λ_{max} (nm)	τ^b (ns)	Φ_{em}	λ_{max} (nm)	τ^b (ns)
10	410	<0.5	0.18	400	2.0 18.1
1	440	1.1	0.67	431	1.9 14.9
3	434	1.1	0.77	405	1.1 9.2
2	472	0.9	0.49	466	1.7 11.5
4	462	1.0	0.61	442	1.1 8.5

[a] The fluorescence spectra and quantum yields were obtained upon excitation on the absorption maxima. [b] λ_{exc} = 337 nm.

The luminescence properties of **1-4** and **10** in CH$_2$Cl$_2$ (298 and 77 K) are summarized in Table 2. All these molecules exhibit intense fluorescence bands and their excitation spectra match their absorption profiles. For **10**, **3**, and **4**, as expected, the fluorescence maxima shift to longer wavelengths when the π-conjugated chain lengths are increased. The excited-state lifetimes of **3** and **4** at 298 K are in the typical 0.5−1.0 ns range, with a strictly monoexponential decay. On the contrary, at 77 K, biexponential decays are recorded, probably as a consequence of the presence of different "frozen" rotameric forms in the solid matrix.[4b]

Qualitatively, the luminescence properties of **1** and **2** are similar to those of **3** and **4** however, relative to the model compounds, the fluorescence maxima of the calix[4]OPVs are slightly red-shifted and the emission quantum yields lower. The observed red-shift is consistent with an exciton contribution, brought about by the face-to-face arrangements of two OPV units in a pinched-cone conformation.[13] It is well-known that tetra-*O*-alkylated cone calix[4]arenes do not adopt regular C_{4v} symmetry but C_{2v} symmetry with a pinched conformation. This fits with the calculated structure (MM+ Molecular Mechan-

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Table 3. Electrochemical Properties of Compounds 1−4[a]

compound	solvent	II_{ox}	I_{ox}	I_{red}	II_{red}
1	CH_2Cl_2	%	$+1.10^b$		%
	THF	%	$+1.03^c$ $(+1.01^c)$	$-2.11^{b,d}$ (-2.17^d)	%
3	CH_2Cl_2	$+1.23^b$	$+1.06^b$	−1.97	%
	THF	$+1.31^c$	$+0.98^c$	−2.11 (−2.15)	−2.44 (−2.54)
2	CH_2Cl_2	+1.02	+0.90	%	%
	THF	%	$(+1.0^c)$	$-2.0^{b,d}$ (-1.98^d)	$-2.2^{b,d}$ (-2.18^d)
4	CH_2Cl_2	$+1.25^b$	$+1.04^b$	%	%
	THF	$+1.27^c$	$+1.03^c$ (+0.87)	−1.95 (−1.98)	−2.10 (−2.16)

[a] Cyclic voltammetry measurements at 298 and, in parentheses, at 208 K in degassed CH_2Cl_2 or THF, nBu$_4$PF$_6$ (0.1 M) as supporting electrolyte. [b] The reported half-wave potentials were estimated by digital simulation (EC mechanism) at scan rates in the range: 0.1−10 Vs^{-1}. [c] Chemically irreversible process, E_p value at 0.2 V s^{-1}. [d] Bielectronic process.

ics) in which two OPV chromophores are facing to each other in close proximity (nearly $\pi-\pi$ contact) whereas the two others are far apart. In addition to the blurring of the absorption bands of calix[4]OPVs, the observed redshift in the emission is a clear indication of interchromophoric interactions in the calix[4]OPVs capable of lowering the lowest excited singlet state relative to the model compounds. Finally, it should also be mentioned that the UV/Vis and emission spectra were taken at different concentrations and were unchanged, thus confirming that the observed interactions are intramolecular and not caused by intermolecular aggregation.

Electrochemical Properties. The electrochemical properties of compounds **1-4** are summarized in Table 3.

In THF/nBu$_4$NPF calix[4]OPV **2** shows two 2-electron processes in the cathodic region, while **1** only exhibits a 2-electron transfer. These electron transfers are Nernstian, but chemical reversibility can be attained only at scan rates higher than 2 V/s at 298K or by decreasing the temperature to 208 K. Both model compounds **3** and **4** show two Nernstian and chemically reversible 1-electron reductions under the same experimental conditions (Table 3). Considering the OPV moieties as noninteracting in the calix[4]OPVs, one would have expected, for **1** and **2**, two 4-electron peaks at the potential values observed for **3** and **4**, respectively. Indeed, the observed electrochemical behavior shows a strong electronic interaction between the OPV units in the calix[4]OPVs. The first reduction process of both **1** and **2** is due to the simultaneous 1-electron reduction of two OPV moieties at potential values close to those observed for the corresponding model compounds **3** and **4**, respectively. The second reduction process observed for **2** can be assigned to the 1-electron reduction of the remaining two OPV units. The reduction of the remaining two OPV moieties in **1** is shifted beyond the available potential window, as well as the second reduction of each OPV unit in both **1** and **2**. The observed electrochemical behavior shows that two OPV units of each calix[4]OPVs behave very similarly to the corresponding model compounds while the other two units show a strong perturbation within the calixarene framework, which results in a substantial negative shift of their reduction potentials. The latter observation is consistent with a pinched-cone conformation of the calix[4]OPVs. In such a conformation, two chromophores are in rather close proximity, whereas the two others are fairly apart. Therefore a 2-electron transfer is expected for the decoupled pair. Clearly, after bringing two electrons on the molecule, further stabilization is expected for the pinched-cone conformation which then determine the subsequent redox behavior of the other two OPV moieties.

The anodic region of the cyclic voltammograms performed in CH_2Cl_2/nBu$_4$NPF$_6$ shows two 1-electron processes for **2** and only a single 1-electron process for **1**. Both model compounds **3** and **4** present two 1-electron processes (Table 3). As observed for the reduction, the oxidation of the four OPV subunits of both **1** and **2** do not take place at the same potential indicating a strong electronic interaction among them in the calix[4]OPVs. Interestingly, the calix[4]OPVs are unable to easily accommodate many positive charges since only one 1-electron oxidation could be observed for **1** and two for **2** in the available potential range.

Conclusion

New strongly luminescent calix[4]arene derivatives combining four OPV moieties have been synthesized by Heck-type cross-coupling reactions of styrene derivatives on the upper rim of a tetraiodinated cone-calixarene precursor. Both electrochemical and photophysical studies in solution have revealed that there are electronic ground state interactions between the covalently bonded OPV moieties. Interestingly, the comparison of the electronic properties of a chromophore in dilute solutions and in thin films generally shows a broadening of the absorption spectrum and a red-shift of the photoluminescence.[5] This is in line with the difference observed between the OPV model derivatives and the corresponding Calix[4]OPVs. Compounds **1** and **2** can thus be considered as good models for chromophore aggregates in the solid and further studies are under way for a better understanding of the observed electronic properties. In particular, better insight will be obtained by the investigations of related optically active chiral calix[4]OPV derivatives, for instance by using circular dichroism spectroscopy.[18] Finally, the calix[4]OPV derivatives are strongly luminescent compounds and therefore good candidates for optoelectronic applications. In addition, by taking advantage of the binding properties of the calix[4]arene core,[17,19] related calix[4]OPVs appears to be potentially interesting sensors for host−guest chemistry.

Experimental Section

General Methods. Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **5**,[10] **8**,[14] **9**,[4b] and **13**[15] were prepared according to previously reported procedures. All the reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel *60* (230−400 mesh, 0.040−0.063 mm) was purchased from *E. Merck*. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel *60 F*$_{254}$ purchased from *E. Merck*, visualization by UV light. Melting

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points were measured on an *Electrothermal Digital Melting Point* apparatus and are uncorrected. UV/Vis spectra (λ_{max} in nm (ϵ))were measured on a *Hitachi U-3000* spectrophotometer. IR spectra (cm^{-1}) were measured on an *ATI Mattson Genesis Series FTIR* instrument. NMR spectra were recorded on a *Bruker AC 200* (200 MHz) or a *Bruker AM 400* (400 MHz) with solvent peaks as reference. FAB-mass spectra (*m*/*z*) were taken on a *ZA HF* instrument with 4-nitrobenzyl alcohol as matrix. MALDI-TOF mass spectra were taken on a on a Brucker BIFLEX matrix-assisted laser desorption time-of-flight mass spectrometer (MALD-TOF) equipped with the SCOUT High-Resolution Optics with a X−Y multi-sample probe and a gridless reflector, a saturated solution of 1,8,9-trihydroxyanthracene (dithranol Aldrich EC: 214−538−0) in CH_2Cl_2 was used as a matrix. Elemental analysis were performed by the analytical service at the Institut Charles Sadron (Strasbourg, France).

Compound 6. I_2 (313 mg, 1.23 mmol) was added in portions to a mixture of CF_3CO_2Ag (272 mg, 1.23 mmol) and **5** (200 mg, 0.31 mmol) in refluxing $CHCl_3$ (10 mL). The resulting mixture was refluxed for 15 min, then cooled to room temperature, filtered over Celite and evaporated to dryness. The residue was taken up with AcOEt. The organic layer was washed with an aqueous solution of $Na_2S_2O_5$ and water (3x), dried ($MgSO_4$), filtered and evaporated. Recrystallization from $CHCl_3$/MeOH afforded **6** (320 mg, 91%) as colorless crystals (mp 217 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.00 (s, 8H), 4.28 (d, J = 13.5 Hz, 4H), 3.85 (t, J = 7.5 Hz, 8H), 3.05 (d, J = 13.5 Hz, 4H), 1.84 (m, 8H), 1.40 (m, 8H), 0.98 (t, J = 7 Hz, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): 156.28, 137.00, 136.76, 86.06, 75.14, 31.98, 30.28, 19.19, 13.97.

Compound 7. A mixture of **6** (305 mg, 0.26 mmol), 4-methylstyrene (140 mg, 1.18 mmol), $Pd(OAc)_2$ (3 mg), and POT (7 mg) in xylene/Et_3N 2:1 (15 mL) was stirred under Ar at 130 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated. The brown residue was taken up in CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 7:3) followed by recrystallization from $CHCl_3$/MeOH gave **7** (230 mg, 78%) as colorless crystals (mp 97 °C). ^{1}H NMR (200 MHz, CD_2Cl_2): 7.17 (d, J = 7 Hz, 8H), 6.95 (d, J = 7 Hz, 8H), 6.85 (s, 8H), 6.74 (AB, J = 17 Hz, 8H), 4.48 (d, J = 13 Hz, 4H), 3.94 (t, J = 7.5 Hz, 8H), 3.21 (d, J = 13 Hz, 4H), 2.32 (m, 12H), 1.94 (m, 8H), 1.48 (m, 8H), 1.01 (t, J = 7 Hz, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): 156.49, 136.32, 134.98, 134.87, 131.76, 129.07, 127.96, 126.68, 126.36, 126.07, 74.94, 32.26, 31.14, 21.16, 19.36, 14.06. FAB-MS: 1112.8 (M^+, calcd for $C_{80}H_{88}O_4$: 1112.67).

Compound 10. *t*-BuOK (2.28 g, 19.70 mmol) was added to a solution of **8** (4.00 g, 5.45 mmol) and **9** (1.12 g, 5.45 mmol) in dry DMF (30 mL) under argon at 80 °C. The mixture was stirred for 1 h at 85 °C and, after cooling, it was poured into an aqueous 0.5 M HCl solution (200 mL). The mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$) and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/hexane 1:1) gave **10** (2.56 g, 55%) as pale yellow crystals (mp 62 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.49 (s, 4H), 7.00 (s, 2H), 6.71 (s, 2H), 5.40 (s, 1H), 4.03 (t, J = 6.5 Hz, 4H), 3.92 (t, J = 6.5 Hz, 2H), 3.79 (d, J = 11 Hz, 2H), 3.67 (d, J = 11 Hz, 2H), 1.81 (m, 6H), 1.56−1.27 (m, 57H), 0.88 (t, J = 6.5 Hz, 9H), 0.81 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): 153.25, 138.27, 137.96; 137.54, 132.40, 129.18, 127.32, 126.44, 126.28, 105.12, 101.55, 73.50, 69.12, 31.93, 30.32, 30.24, 29.67, 29.40, 26.11, 23.05, 22.68, 21.88, 14.12. Anal. Calcd for $C_{56}H_{94}O_5$ (847.36): C 79.38, H 11.18. Found: C 79.32 H 11.31.

Compound 11. A mixture of **10** (2.0 g, 2.36 mmol) and CF_3CO_2H (28 mL) in CH_2Cl_2/H_2O 2:1 (75 mL) was stirred at room temperature for 5 h. The organic layer was then washed with water (3 x), dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) gave **8** (1.70 g, 94%) as a pale yellow solid (mp 49 °C). IR (CH_2Cl_2): 1700 (C=O). ^{1}H NMR (200 MHz, $CDCl_3$): 8.60 (s, 1H), 7.87 (d, J = 7 Hz, 2H), 7.64 (d, J = 7 Hz, 2H), 7.18 (d, J = 16.0 Hz, 1H), 7.00 (d, J = 16.0 Hz, 1H), 6.75 (s, 2H), 4.04 (t, J = 6.5 Hz, 4H), 3.99 (t, J = 6.5 Hz, 2H), 1.82 (m, 6H), 1.57−1.27 (m, 54H), 0.89 (t, J = 6.5 Hz, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): 191.43, 153.35, 143.51, 139.01, 135.12, 132.44, 131.70, 130.19, 126.69, 126.21, 105.55, 73.53, 69.17, 31.94, 30.36, 29.68, 29.43, 26.14, 22.70, 14.12. Anal. Calcd for $C_{51}H_{84}O_4$ (761.23): C 80.47, H 11.12. Found: C 80.68 H 11.29.

Compound 12. A mixture of **10** (1.50 g, 1.97 mmol), *t*-BuOK (243 mg, 2.16 mmol) and methyltriphenylphosphonium bromide (774 mg, 2.16 mmol) in dry THF (10 mL) was stirred at room temperature for 1 h. A saturated aqueous NH_4Cl solution was then added and the resulting mixture was concentrated. The aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 7:3) gave **12** (1.24 g, 83%) as a pale yellow solid (mp 43 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.44 (AB, J = 7 Hz, 4H), 7.03 (AB, J = 16 Hz, 2H), 6.73 (dd, J = 17 and 11 Hz, 1H), 6.72 (s, 2H), 5.76 (dd, J = 17 and 2 Hz, 1H), 5.25 (dd, J = 11 and 2 Hz, 1H), 4.03 (t, J = 6.5 Hz, 4H), 3.98 (t, J = 6.5 Hz, 2H), 1.79 (m, 6H), 1.56−1.43 (m, 54H), 0.89 (t, J = 6.5 Hz, 9H).

Compound 14. A mixture of **13** (3.50 g, 3.69 mmol) and CF_3CO_2H (35 mL) in CH_2Cl_2/H_2O 2:1 (105 mL) was stirred at room temperature for 5 h. The organic layer was then washed with water (3x), dried ($MgSO_4$), filtered and evaporated to dryness. Recrystallization from $CHCl_3$/MeOH gave **14** (3.10 g, 97%) as yellow crystals (mp 83 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 8.59 (s, 1H), 7.89 (d, J = 7 Hz, 2H), 7.67 (d, J = 7 Hz, 2H), 7.53 (s, 4H), 7.21 (AB, J = 16 Hz, 2H), 7.01 (AB, J = 16 Hz, 2H), 6.73 (s, 2H), 4.03 (t, J = 6.5 Hz, 4H), 3.97 (t, J = 6.5 Hz, 2H), 1.80 (m, 6H), 1.56−1.27 (m, 54H), 0.89 (t, J = 6.5 Hz, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): 191.51, 153.32, 143.42, 138.49, 137.68, 135.60, 135.25, 132.36, 131.73, 130.23, 129.41, 127.27, 126.99, 126.81, 105.24, 73.54, 69.16, 31.96, 30.37, 29.70, 29.46, 29.41, 26.15, 22.71, 14.14.

Compound 15. A mixture of **14** (3.07 g, 3.556 mmol), *t*-BuOK (439 mg, 3.91 mmol) and methyltriphenylphosphonium bromide (1.397 g, 3.91 mmol) in dry THF (20 mL) was stirred at room temperature for 1 h. A saturated aqueous NH_4Cl solution was then added and the resulting mixture was concentrated. The aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 7:3) gave **15** (1.96 g, 64%) as a yellow solid (mp 90 °C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.50 (s, 4H), 7.45 (AB, J = 7 Hz, 4H), 7.11 (s, 2H), 7.01 (AB, J = 16 Hz, 2H), 6.75 (dd, J = 17 and 11 Hz, 1H), 6.73 (s, 2H), 5.77 (dd, J = 17 and 2 Hz, 1H), 5.26 (dd, J = 11 and 2 Hz, 1H), 4.04 (t, J = 6.5 Hz, 4H), 3.98 (t, J = 6.5 Hz, 2H), 1.80 (m, 6H), 1.56−1.27 (m, 54H), 0.89 (t, J = 6.5 Hz, 9H).

Compound 16. A mixture of 4-bromo-2,6-dimethylphenol (1.00 g, 5 mmol), NaH (2.00 g, 50 mmol) and 1-bromobutane (5.5 mL) in dry DMF (25 mL) was heated at 70 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated to dryness. The brown residue was taken up in CH_2Cl_2. The organic layer was washed with a saturated aqueous NaCl solution, then with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 4:1) gave **16** (1.12 g, 87%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): 7.14 (s, 2H), 3.73 (t, J = 6.5 Hz, 2H), 2.24 (s, 6H), 1.76 (m, 2H), 1.54 (m, 2H), 0.99 (t, J = 7 Hz, 3H).

Compound 17. A mixture of 2,6-dimethylphenol (4.00 g, 32.6 mmol), NaH (3.00 g, 75 mmol) and 1-bromobutane (9 mL, 83 mmol) in dry DMF (60 mL) was heated at 70 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated to dryness. The brown residue was taken up in CH_2Cl_2. The organic layer was washed with a saturated aqueous NaCl solution, then with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 3:2) gave **17** (2.59 g, 44%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): 7.01 (B from AB_2, J = 7 Hz, 2H), 6.92 (A from AB_2, J = 7 Hz, 1H), 3.77 (t, J = 6.5 Hz, 2H), 2.29 (s, 6H), 1.80 (m, 2H), 1.55 (m, 2H), 1.00 (t, J = 7 Hz, 3H).

Compound 18. I_2 (1.84 g, 7.27 mmol) was added in portions to a mixture of CF_3CO_2Ag (1.60 g, 7.27 mmol) and **17** (1.30 g, 7.26 mmol) in refluxing $CHCl_3$ (10 mL). The resulting mixture was refluxed for 15 min, then cooled to room temperature, filtered over Celite and evaporated to dryness. The residue was taken up with AcOEt. The organic layer was washed with an aqueous solution of $Na_2S_2O_5$ and water (3x), dried ($MgSO_4$), filtered and concentrated to afford **18** (2.01 g, 91%) as a colorless liquid. ^1H NMR (200 MHz, $CDCl_3$): 7.34 (s, 2H), 3.73 (t, $J = 6.5$ Hz, 2H), 2.22 (s, 6H), 1.80 (m, 2H), 1.55 (m, 2H), 0.99 (t, $J = 7$ Hz, 3H).

Compound 1. A mixture of **6** (180 mg, 0.16 mmol), **12** (522 mg, 0.69 mmol), $Pd(OAc)_2$ (1 mg), and POT (3 mg) in xylene/Et_3N 1:1 (4 mL) was stirred under Ar at 125 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated. The brown residue was taken up in CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Two successive column chromatographies (SiO_2, hexane/CH_2Cl_2 7:3 to 1:1) gave **1** (430 mg, 75%) as a yellow glassy product. ^1H NMR (200 MHz, CD_2Cl_2): 7.28−6.57 (m, 48H), 4.50 (broad d, 4H), 3.95−3.74 (m, 32H), 3.25 (broad d, 4H),1.94−1.71 (m, 32H), 1.51−1.27 (m, 224H), 0.97 (t, $J = 7.0$ Hz, 12H), 0.87 (t, $J = 7$ Hz, 36H). MALDI-TOF MS: 3679 (MH^+, calcd for $C_{252}H_{393}O_{16}$: 3678.88). Anal. Calcd for $C_{252}H_{392}O_{16}$ (3677.87): C 82.30, H 10.74. Found: C 82.44 H 10.91.

Compound 2. A mixture of **6** (400 mg, 0.35 mmol), **15** (1.315 mg, 1.53 mmol), $Pd(OAc)_2$ (2.5 mg), and POT (6 mg) in xylene/Et_3N 3:1 (20 mL) was stirred under Ar at 125 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated. The brown residue was taken up in CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Two successive column chromatographies (SiO_2, hexane/CH_2Cl_2 7:3 to 1:1) gave **2** (540 mg, 38%) as a yellow glassy product. ^1H NMR (200 MHz, CD_2Cl_2): 7.60−6.66 (m, 72H), 4.50 (broad d, 4H), 4.1−3.8 (m, 32H), 3.20 (broad, 4H), 2.1−1.6 (m, 32H), 1.51−1.27 (m, 224H), 1.1−0.95 (m, 12H), 0.87 (t, $J = 6.5$ Hz, 36H). MALDI-TOF MS: 4087 (MH^+, calcd for $C_{284}H_{417}O_{16}$: 4087.42). Anal. Calcd for $C_{284}H_{416}O_{16}$ $CHCl_3$ (4205.80): C 81.39, H 9.99. Found: C 81.45 H 10.04.

Compound 3. A mixture of **16** (130 mg, 0.50 mmol), **12** (422 mg, 0.56 mmol), $Pd(OAc)_2$ (4 mg), and POT (10 mg) in xylene/Et_3N 1:1 (12 mL) was stirred under Ar at 140 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated. The brown residue was taken up in CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 4:1 to 3:2) gave **3** (110 mg, 23%) as a yellow solid (mp 85 °C). ^1H NMR (200 MHz, $CDCl_3$): 7.48 (s, 4H), 7.19 (s, 2H), 7.01 (s, 2H), 6.99 (s, 2H), 6.72 (s, 2H), 4.03 (t, $J = 6.5$ Hz, 4H), 3.98 (t, $J = 6.5$ Hz, 2H), 3.78 (t, $J = 6.5$ Hz, 2H), 2.31 (s, 6H), 1.80 (m, 8H), 1.57−1.28 (m, 56H), 1.01 (t, $J = 7$ Hz, 3H), 0.89 (t, $J = 6$ Hz, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): 155.96, 153.28, 138.31, 136.81, 136.43, 132.54, 131.18, 128.58, 128.19, 127.31, 126.95, 126.62, 105.16, 73.52, 72.17, 69.17, 32.48, 31.92, 30.33, 29.67, 29.43, 26.12, 22.67, 19.35, 16.37, 14.11, 13.99. Anal. Calcd for $C_{64}H_{102}O_4$ (935.51): C 82.17, H 10.99. Found: C 81.81 H 11.02.

Compound 4. A mixture of **18** (230 mg, 0.76 mmol), **15** (567 mg, 0.66 mmol), $Pd(OAc)_2$ (4.5 mg), and POT (12 mg) in xylene/Et_3N 2:1 (12 mL) was stirred under Ar at 125 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated. The brown residue was taken up in CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 7:3 to 1:1) gave **4** (370 mg, 54%) as a yellow solid (mp 103 °C). ^1H NMR (200 MHz, $CDCl_3$): 7.50 (s, 8H), 7.19 (s, 2H), 7.12 (s, 2H), 7.02 (m, 4H), 6.73 (s, 2H), 4.04 (t, $J = 6.5$ Hz, 4H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.78 (t, $J = 6.5$ Hz, 2H), 2.31 (s, 6H), 1.80 (m, 8H), 1.56−1.27 (m, 56H), 1.01 (t, $J = 7$ Hz, 3H), 0.89 (t, $J = 6.5$ Hz, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): 156.02, 153.31, 138.40, 137.03, 136.74, 136.55, 136.37, 132.63, 132.53, 131.16, 128.79, 128.71, 128.61, 128.32, 128.12, 127.95, 127.27, 126.98, 126.79, 126.68, 126.21, 105.24, 73.54, 72.17, 69.19, 32.50, 31.93, 30.34, 29.67, 29.44, 29.38, 26.12, 22.68, 19.35, 16.38, 14.09, 13.99. Anal. Calcd for $C_{72}H_{108}O_4$ (1037.65): C 83.34, H 10.49. Found: C 83.43 H 10.61.

Spectroscopic and Photophysical Measurements. The solvent used for the photophysical investigations is spectrofluorimetric grade CH_2Cl_2 (Carlo Erba). Absorption spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer. Emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter eqipped with a continuous 150 W Xe lamp as excitation source and a Hamamatsu R-928 photomultiplier tube as detector. Fluorescence quantum yields were measured with the method described by Demas and Crosby[20] using as standards quinine sulfate in 1 N H_2SO_4 ($\Phi = 0.546$).[21] To record the 77 K luminescence spectra the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz dewar, filled up with liquid nitrogen. When needed, spectra of pure dichloromethane solvent were recorded and then subtracted as background signal, to eliminate the contribution of the light scattered by the rigid matrix. Corrected excitation spectra were recorded with a Perkin-Elmer LS-50B spectrofluorimeter (pulsed Xe lamp).

Emission lifetimes were determined with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working at 40 kHz ($\lambda_{exc} = 337$ nm, 0.5 ns time resolution after deconvolution of the flash profile); the detector was a red-sensitive (185−850 nm) Hamamatsu R-3237−01 photomultiplier tube.

Experimental uncertainties are estimated to be ± 7% for lifetime determination, ± 15% for quantum yields, and ± 3 nm for emission and absorption peaks.

Electrochemistry. The electrochemical experiments were carried out in argon-purged CH_2Cl_2 or THF solutions at room temperature or 208 K (by employing a liquid N_2/EtOH low-temperature bath) with an EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.08 cm^2, Amel); its surface was routinely polished with a 0.05 μm alumina-water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and a silver wire was employed as a quasi-reference electrode(AgQRE). The potentials reported are referred to SCE by measuring the AgQRE potential with respect to ferrocene. The concentration of the compounds examined was of the order of 8×10^{-4} M; 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was added as supporting electrolyte. Cyclic voltammograms were obtained with scan rates in the range 0.05−10 V s^{-1}. The number of electrons exchanged in each process was estimated by comparing the current intensity of the corresponding CV wave with that observed for the monoelectronic oxidation of ferrocene, after correction for differences in the diffusion coefficients.[22] The experimental error on the potential values was estimated to be ±10 mV. The CV simulations were carried out by the program Antigona developed by Dr. L. Möttier.[23] All the electron-transfer processes were considered fast in the simulation and the chemical rate constants were chosen so as to obtain a visual best fit over 100-fold range of scan rate (0.1−10 V s^{-1}).

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