Synthesis, Characterization, and Optical Response of Dipolar and Non-Dipolar Poly(phenylenevinylene) Dendrimers

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Received May 16, 2001

New dipolar and non-dipolar poly(phenylenevinylene) dendrimers bearing electron-donating and electron-withdrawing groups have been efficiently synthesized using Heck and Horner-Wadsworth-Emmons reactions. The photoluminescence of these systems may be tuned in the blue zone by choosing the appropriate peripheral groups. Despite the *meta*-substitution pattern, large Stokes shifts can be observed when π -donor and π -acceptor groups are connected by a *m*-phenylenevinylene system.

Introduction

The synthesis of new dendrimeric structures and the study of such systems in the development of new applications for dendrimers have been the focus of several research teams, particularly in the past decade. Synthetic methodologies, involving convergent¹ and divergent² methods, and applications are well established and have been reviewed.³ Other strategies have also been described and these include "hypermonomers",⁴ exponential⁵ and orthogonal⁶ growth, and "activated" monomers.⁷

Evolution from the synthesis to the application of these materials has been systematically evaluated by Vögtle.8 Electrical, optical, nonlinear optical, electroluminescent, and photophysical properties of polyconjugated dendrimers, mainly polyphenylenes, have been discussed in recent papers.⁹ The search for these kinds of properties in dendrimeric structures is based on the general properties exhibited by polyphenylvinylene, polyphenylene, polyfluorene, and other π -conjugated polymers.¹⁰

We report here a full study¹¹ regarding the synthesis of new dipolar and non-dipolar dendrimeric polyphenylenevinylenes (PPV's) bearing electron-donating and electronwithdrawing groups as well as long-chain substituents

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aimed at improving the solubility of these systems. Nondipolar dendrimeric PPV's, also called stilbenoid dendrimers, bearing either alkyl or alkoxy peripheral groups have been reported previously.¹² The new dipolar dendrimeric PPV's described here are comparable to other dendrimeric systems that contain π -donor and π -acceptor groups and have been claimed as interesting and attrac-

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tive targets.¹³ It is well established that the presence of electron-donating and electron-withdrawing groups can modify the HOMO and LUMO energies differently, thus allowing modulation of the molecular "band gap" and alteration of the redox and optical properties of the molecule.¹⁴ The ability of conjugated dendrimers to act as light-emitting diodes has also been reported.^{9i,j} Dendrimer growth has been claimed as the cause of interesting modifications in fluorescence spectra,¹⁵ although not much work has been done in this respect in the area of cross-conjugated systems. In the work described here, we also present a study of the UV and photoluminescence (PL) properties of most of the dendrons and dendrimers synthesized.

Some of the dendrons reported here have been successfully connected to binaphthyl¹⁶ and [60]-fullerene¹⁷ cores, and these routes demonstrate some of the possibilities for these systems in the field of new organic materials.

Results and Discussion

Synthesis of Cores. The convergent synthesis of dipolar and non-dipolar dendrimers bearing a 1,3,5tris(phenylenevinylene)benzene core made use of the Horner-Wadsworth-Emmons (HWE) and Heck reactions, which required different benzyl and aryl bromides as starting materials (Chart 1). Non-dipolar dendrimers were constructed from either 1,3,5-trisbromobenzene (1) or 1,3,5-tris(bromomethyl)benzene (2). While compound 1 is commercially available, intermediate 2 was obtained

in 97% yield from the corresponding triol by reaction with an excess of a 35% HBr solution in acetic acid.

On the other hand, dipolar dendrimers needed to be prepared from other basic starting units. 3,5-Bis(bromomethyl)-1-bromobenzene (3) and 5-bromomethyl-1,3-dibromobenzene (4) were obtained by reaction of 1-bromo-3,5-dimethylbenzene and 1,3-dibromo-5-methylbenzene with 2 and 1 equiv of NBS, respectively, in refluxing acetonitrile and a catalytic amount of AIBN. Although several mono- and polybrominated products appeared in the crude mixtures, the desired compounds could be easily separated and purified by column chromatography to give moderate yields (48% for 3, and 56% for 4). Undesired polybromination was a more significant problem due to the relatively large amount of NBS added to the reaction mixtures. Thus, a larger amount of byproducts was detected in the preparation of 3 than in the synthesis of 4, where only 1 equiv of NBS was required. Compounds **3** and **4** are benzyl bromides as well as aryl bromides and, therefore, could be used as starting materials in both HWE and Heck reactions. The synthesis of 1-acetyloxymethyl-3,5-bis(bromomethyl)benzene (5) and 1,3-bis(acetyloxymethyl)-5-bromomethylbenzene (6) was carried out by treatment of 2 with 1.5 equiv of sodium acetate in DMF at 100 °C to give 33% and 29% yields, respectively (62% overall). Although the presence of starting material 2 (11%) and the corresponding triacetate (27%) were also observed in the crude mixture, all the products could be easily separated by column chromatography.

The Arbuzov reaction of bromides **2–6** with triethyl phosphite at 140 °C gave the corresponding phosphonates 7-11 in quantitative yield (Chart 1).

It has recently been demonstrated that compound 12 is also a useful core for the preparation of different structures related to that described in this work.^{12b,c} An alternative method for the synthesis of acetal 12 was also developed as part of this study and is outlined in Scheme 1. Compound 12 was used in this work as a core to prepare some dendrons that are difficult to obtain by the methodologies reported here (vide infra).

Synthesis of Non-Dipolar (symmetric) First Generation Dendrimers (R)₃G1. Two strategies were

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employed for the preparation of these compounds (Scheme 2, routes a and b). The first route started with the palladium-catalyzed coupling of three molecules of parasubstituted styrene derivatives with 1,3,5-tribromobenzene (1) according to the method described by de Meijere et al.¹⁸ This method uses potassium carbonate and tetran-butylammonium bromide (TBAB) as a solid-liquidphase transfer agent. We found that when *p*-methylstyrene was used, the triple Heck reaction was successful and led to (Me)₃G1 as the major product. However, a tedious and difficult isolation and purification procedure was required, and (Me)₃G1 was obtained in only 39% yield. When p-methoxystyrene was used, only the required disubstituted product could be isolated (in 23% yield). Both purified compounds did not contain any double bonds with the Z-configuration. Overall, however, the Heck reaction proved to be unsatisfactory in terms of obtaining first generation dendrimers in good yields.

The second method involved formation of the required *E*-configured double bonds by a HWE reaction. The readily available 3-fold tris(phosphonate) **7** was used as a basic unit to form the core. When this compound was coupled with a set of *para*-substituted benzaldehydes, using KBu¹O as the base and THF as the solvent, only the all-trans isomers **(R)**₃**G1** were observed within the limits of NMR detection (Table 1). ¹H and ¹³C NMR spectroscopy confirmed the 3-fold symmetry of **(R)**₃**G1**. Compound **[CH(OMe)**₂]₃**G1** was not isolated but hydrolyzed in situ to give **(CHO)**₃**G1** under mild acid conditions.

Synthesis of Dipolar First Generation Dendrimers (\mathbf{R})₂(\mathbf{R} ')G1. To obtain the first generation of dipolar dendrimers we also conceived two different synthetic strategies: the linking of one of the branches to the core followed by the other two (identical) branches (Scheme 2, route d) or, alternatively, the coupling of two identical branches to the core and the subsequent linking of the third branch in the final reaction step (Scheme 2, routes c and e).

The initial idea was to use a combination of Heck and HWE reactions. Thus, starting from the phosphonates **8**

and **9** the dendrons $(\mathbf{R})_2\mathbf{G1}$ -**Br** and $(\mathbf{CN})\mathbf{G1}$ -**Br**₂ (*E*-isomers) were prepared as solids in moderate to good yields (Table 1).

Compound (CN)₂G1-Br, taken as a model, was coupled by a Heck reaction with *p*-methoxystyrene to afford the dipolar first generation dendrimer (CN)₂(OMe)G1 in 62% isolated yield. This system contains two electronwithdrawing groups and one electron-donating group at the periphery. The dendrimer with one cyano group and two methoxy groups at the periphery, (OMe)₂(CN)G1, was prepared in the same way from (CN)G1-Br₂ and 2 equiv of *p*-methoxystyrene. However, after column chromatography only an impure sample of this compound could be isolated, and even this was obtained in only 12% yield. Analogously, starting from (OMe)₂G1-Br, (CN)G1-Br₂, and *p*-methylstyrene, compounds (OMe)₂(Me)G1 and (Me)₂(CN)G1 were synthesized (Table 1). In all cases the crude products were difficult to purify, yields were not good and reaction times were too long (2 days minimum). These drawbacks, together with the small number of commercially available styrenes, caused us to abandon this route and focus our efforts on the synthesis of dendrimers using exclusively the HWE methodology. This reaction had proven to afford cleaner crude products, which were correspondingly easier to purify and gave better yields.

Thus, the HWE reaction of phosphonates **10** and **11** with the appropriate *p*-substituted benzaldehydes gave alcohols $(\mathbf{R})_2\mathbf{G1}$ - $\mathbf{CH}_2\mathbf{OH}$ and $(\mathbf{R})\mathbf{G1}$ - $(\mathbf{CH}_2\mathbf{OH})_2$, respectively, in good overall yields after in situ hydrolysis of the ester moiety with NaOH/H₂O (Table 1).

Some of these alcohols served as building blocks for the first generation dipolar dendrimers. Treatment of the alcohol with CBr₄/PPh₃ in acetonitrile gave the corresponding benzyl bromides. The isolation of dibromide (OMe)G1-(CH₂Br)₂ in only 25% yield prompted us to concentrate our efforts on dendrons bearing only one focal point. The use of solvents other than acetonitrile, including the use of THF, led to lower yields or intractable crude products. Bromination of derivatives (Me₂N)₂G1-CH2OH and (Me2N)G1-(CH2OH)2 proved fruitless. Although the desired products should have been generated in the reaction, attack at the dimethylamino group by the bromomethyl group of a second product molecule precludes the isolation of the target compounds. Route e was successfully completed by reaction of phosphonate (MeO)₂G1-CH₂P(O)(OEt)₂ with the appropriate aldehydes under the same experimental conditions as described above. Dendrimers (MeO)₂(CN)G1 and (MeO)₂-[CH(OMe)₂]G1 [not isolated, hydrolyzed in situ to (MeO)₂(CHO)G1] could be prepared by this method (Table 1). Once again, only the all-E isomers were detected by ¹H NMR spectroscopy. Dendritic structures that possess a C_{2v} symmetry are excellent candidates to show NLO properties¹⁹ as well as good transparencies.²⁰

Iterative Synthesis of Dendrons. Alcohols $(R)_{2n}$ Gn-CH₂OH are also precursors of the next generation dendrons, which were synthesized by a two-step iterative procedure in which the dendron is doubled in size in each iteration. The synthesis was based around the oxidation

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Scheme 2. Synthesis of First Generation Dendrimers^a



^a Reagents and conditions: (i) 3 *p*-R-C₆H₄-CH=CH₂, Pd(AcO)₂, TBAB, K₂CO₃; (ii) 3 *p*-R-C₆H₄-CHO, KBu^tO, THF; (iii) 2 *p*-R-C₆H₄-CH=CH₂, Pd(AcO)₂, TBAB, K₂CO₃; (v) *p*-R'-C₆H₄-CHO, KBu^tO, THF; (vi) 2 *p*-R-C₆H₄-CH=CH₂, Pd(AcO)₂, TBAB, K₂CO₃; (v) *p*-R'-C₆H₄-CHO, KBu^tO, THF; (vi) 2 *p*-R-C₆H₄-CH=CH₂, Pd(AcO)₂, TBAB, K₂CO₃; (vii) 2 *p*-R-C₆H₄-CHO, KBu^tO, THF; then NaOH/H₂O; (viii) CBr/PPh₃; (ix) P(OEt)₃; (x) *p*-R'-C₆H₄-CHO, KBu^tO, THF; then NaOH/H₂O.

 Table 1. Preparative Routes and Isolated Yields of Compounds Presented in Scheme 2

| compound | route | yield (%) | |
|--|---------|---------------------|--|
| (Me) ₃ G1 | (a) | 39 | |
| (OMe) ₃ G1 | (b) | 85 | |
| (NMe ₂) ₃ G1 | (b) | 60 | |
| (CN) ₃ G1 | (b) | 92 | |
| [CH(OMe) ₂] ₃ G1 | (b) | _ <i>a</i> | |
| (CHO) ₃ G1 | (b) | 86 | |
| (OMe)2G1-Br | (c) | 78 | |
| (NMe ₂) ₂ G1-Br | (c) | 42 | |
| (CN) ₂ G1-Br | (c) | 81 | |
| (NO ₂) ₂ G1-Br | (c) | 40 | |
| (CN)G1-Br ₂ | (d) | 89 | |
| (OMe) ₂ G1-CH ₂ OH | (e) | 96 | |
| (OC ₁₂ H ₂₅) ₂ G1-CH ₂ OH | (e) | 100 | |
| (NMe ₂) ₂ G1-CH ₂ OH | (e) | 80 | |
| (CN) ₂ G1-CH ₂ OH | (e) | 85 | |
| (OMe)G1-(CH ₂ OH) ₂ | - | 82 | |
| (NMe ₂)G1-(CH ₂ OH) ₂ | - | 52 | |
| (OMe)G1-(CH ₂ Br) ₂ | - | 25 | |
| (OMe) ₂ G1-CH ₂ Br | (e) | 79 | |
| (CN) ₂ G1-CH ₂ Br | (e) | 61 | |
| (OMe) ₂ G1-CH ₂ P(O)(OEt) ₂ | (e) | 100 | |
| (CN)2G1-CH2P(O)(OEt)2 | (e) | 100 | |
| (OMe) ₂ (Me)G1 | (c) | 34 | |
| (CN) ₂ (OMe)G1 | (c) | 62 | |
| (Me) ₂ (CN)G1 | (d) | 25 | |
| (OMe) ₂ (CN)G1 | (d),(e) | 12, ^b 75 | |
| (OMe) ₂ [CH(OMe) ₂]G1 | (e) | _ <i>a</i> | |
| (OMe) ₂ (CHO)G1 | (e) | 25 | |

^{*a*} Not isolated, hydrolyzed in situ with H₃O⁺. ^{*b*} Not pure.

of the alcohol group with either PCC or MnO₂ to give the corresponding aldehyde-containing dendrons (R)_{2n}Gn-**CHO**. This step was followed by coupling with the diphosphonate 10 (Scheme 3, route a). However, the oxidation reaction failed when side chains in the periphery were dialkylamino groups. Thus, we were obliged to prepare this kind of aldehyde by applying the methodology previously described by Meier et al., ^{12b,c} which makes use of compound 12 as a core. This alternative was used to obtain dendrons (Bu₂N)₂G1-CHO and (Bu₂N)₄G2-CHO, as well as (CF₃)₂G1-CHO and (CF₃)₂G2-CHO (Scheme 3, route b). Therefore, diphosphonates 10 and 12 served as the extension and branching units for the next, higher generation of dendron (Table 2). The preparation of third generation dendrons required longer reaction times; however, the molecular peaks correspond-

Scheme 3. Iterative Synthesis of Dendrons^a



 a Reagents and conditions: (i) PCC or MnO_2 ; (ii) 10, KBu^tO, THF; then NaOH/H₂O; (iii) *p*-R-C₆H₄-CHO, KBu^tO, THF; then H₃O⁺; (iv) 12, KBu^tO, THF; then H₃O⁺.

ing to the desired product and the carboxylic acid derived from the oxidation of starting material were always detected in different relative intensity by mass spectrometry. These results may be explained considering the higher steric hindrance around the reactive site.

Dialcohols **(OMe)**_n**G**_n-**(CH**₂**OH)**₂ (n = 1,2) could also be oxidized in the same way, although the yields obtained were not as good as for the monoalcohols (see Supporting Information). The resulting dialdehydes might be visualized as dendrons for the synthesis of first and second generation dendrimers (vide infra). However, this possibility was not considered because of the lower yields obtained.

Synthesis of Second Generation Dendrimers $(R)_6G2$ and $(R)_4(R')_2G2$. Compounds $(R)_{2n}Gn$ -CHO may be also regarded as the starting materials for dipolar

 Table 2.
 Preparative Routes and Isolated Yields of Compounds Presented in Scheme 3

| - | | |
|--|-------|-----------|
| compound | route | yield (%) |
| (OMe) ₂ G1-CHO | (a) | 85 |
| (OC ₁₂ H ₂₅) ₂ G1-CHO | (a) | 79 |
| (NBu ₂) ₂ G1-CHO | (b) | 91 |
| (CN) ₂ G1-CHO | (a) | 91 |
| (CF ₃) ₂ G1-CHO | (b) | 93 |
| (OMe) ₄ G2-CH ₂ OH | (a) | 97 |
| (OC ₁₂ H ₂₅) ₄ G2-CH ₂ OH | (a) | 87 |
| (OMe) ₄ G2-CHO | (a) | 92 |
| (OC ₁₂ H ₂₅) ₄ G2-CHO | (a) | 82 |
| (NBu ₂) ₄ G2-CHO | (b) | 97 |
| (CF ₃) ₄ G2-CHO | (b) | 53 |
| (OMe) ₈ G3-CH ₂ OH | (a) | <i>a</i> |
| (OC12H25)8G3-CH2OH | (a) | <i>a</i> |
| | | |

 a Not isolated, obtained as a mixture together with $(R)_4G2\text{-}$ COOH.

and non-dipolar second generation dendrimers (Scheme 4). The 3-fold reaction of $(OC_{12}H_{25})_2G1$ -CHO with the core 7 gave the compound $(OC_{12}H_{25})_6G2$. The last reaction step in the formation of the dipolar second generation dendrimers $(MeO)_4(CN)_2G2$ and $(OC_{12}H_{25})_4(CN)_2G2$ consisted of a HWE reaction between the phosphonates $(MeO)_4G2$ -CH₂P(O)(OEt)₂ or $(CN)_2G1$ -CH₂P(O)(OEt)₂ and the aldehydes $(CN)_2G1$ -CHO or $(OC_{12}H_{25})_4G2$ -CHO, respectively.

All new compounds were characterized using various analytical techniques. MS and NMR experiments proved very useful to confirm the structures of the compounds (see Experimental Section and Supporting Information). The selectivity of the HWE reaction is sufficiently high to generate all-trans isomers within the limits of NMR detection. This stereochemistry for the double bonds was established by the coupling constant of the vinylic protons in the ¹H NMR spectra (J = 16-17 Hz). It is also worth noting the line broadening observed when the ¹H NMR spectra were registered at room temperature for compounds (OC12H25)6G2 and (OC12H25)4(CN)2G2. The signals for these compounds appeared well-resolved upon heating the sample, a phenomenon that has been reported for other π -conjugated dendrimers and is probably due to a tendency for this kind of compound to aggregate.^{12c} The low solubility of the dendrimer (OMe)₄-(CN)₂G2 precluded the acquisition of any NMR spectrum, and its structure could only be confirmed by MALDI mass spectrometry. In addition to THF, chloroform, and dichloromethane were found to be very good solvents for the dendrons and dendrimers. In all cases, solubility decreased as molecular size increased. It is worth noting that NO₂, CN, and CF₃ groups at the periphery lower the solubility of the system, while compounds bearing NBu₂ and OC₁₂H₂₅ groups invariably have the highest solubility.

UV and PL Spectroscopy. The optical properties of several of the dendrimers and dendrons synthesized were investigated by UV/vis and PL spectroscopy of CH_2Cl_2 solutions and thin solid films of the compounds. The data obtained are listed in Table 3. Due to the *meta* arrangement of the dendrons, the observed absorption spectra consisted of a superposition of the absorptions due to the different stilbene chromophores. A red shift of the absorption band is observed with increasing electron-withdrawing or electron-donating strength of the peripheral groups. Only small changes are observed in the onset of absorption in the UV/Vis spectra between the different generations. As one would expect, the molar extinction

Scheme 4. Synthesis of Second Generation^a Dendrimers



^a Reagents and conditions: (i) KBu^tO, THF.

coefficients increase with increasing generation. The very high intensity of absorption can be deduced from the large extinction coefficients of these molecules at their absorption maxima. The size of the alkoxy groups has practically no influence on the absorption properties. The introduction of different groups has a negligible influence on the extinction coefficients. All of the compounds studied are absolutely transparent above 400 nm, with the exception of the dialkylamino derivatives. The fluorescence spectra also show typical bands for stilbenoid compounds. Although contributions of more than one fluorescent species cannot be excluded, we assume that in the emission spectra only the lowest energy π,π^* transition is fluorescent. The familiar crossing between absorption and emission is far from both maxima, i.e., large Stokes shifts occur. This phenomenon is particularly evident in compounds bearing both π -donor and π -acceptor groups, indicating large (vibrational, electronic, geometric) differences between the excited state reached immediately after absorption and the excited state from which the emission starts. This effect also leads to a very low degree of self-absorption of emitted light. In this sense the UV and PL spectra of compounds (OMe)₂(CN)G1, (CN)₂(OMe)G1, and (OMe)₂(CHO)G1 are significant. Stokes shifts up to 10400 cm⁻¹ are observed. Hence, these compounds are expected to perform well in organic light emitting diodes and as laser dyes. The magnitude of the Stokes shifts decreased from G1 to G2 dendrons, indicating that charge transfer

| Гable 3. | UV/Vis and | Photoluminescence | (PL) Data ^a |
|----------|------------|-------------------|------------------------|
|----------|------------|-------------------|------------------------|

| compound | UV/vis (CH ₂ Cl ₂) λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹) | PL (CH ₂ Cl ₂) λ_{max} , nm | UV/vis (thin film) $\lambda_{\rm max}$, nm | PL (thin film) λ_{max} , nm | Stokes shifts, cm ⁻¹ |
|---|---|---|---|-------------------------------------|------------------------------------|
| (Me) ₃ G1 | 319 (107300) | 396, 414 | | | 6095 |
| (OMe) ₃ G1 | 327 (103500) | 403 | 345.5 | 456, 493 | 5767 |
| (NMe ₂) ₃ G1 | 368 (117800) | 461 | | | 5482 |
| (CN) ₃ G1 | 329 (130400) | 399, 419 | | | 5332 |
| (CHO) ₃ G1 | 341.5 (80200) | 409, 425 | 367.5 | 413, 487 | 4833 |
| (OMe) ₂ (Me)G1 | 323 (103600) | 404 | | | 6207 |
| (OMe) ₂ (CN)G1 | 327.5 (79300) | 451 | | | 8361 |
| (OMe) ₂ (CHO)G1 | 331 (83800) | 505 | | | 10409 |
| (Me) ₂ (CN)G1 | 320.5 (112100) | 428 | | | 7836 |
| (CN) ₂ (OMe)G1 | 329.5 (136800) | 456 | | | 8419 |
| (OC ₁₂ H ₂₅) ₆ G2 | 327.5 (257000) | 420 | 336.5 | 430 | 6724 |
| (OMe) ₄ (CN) ₂ G2 | 325.5 (178900) | 417 | 330.5 | 410, 455 | 6741 |
| (OC ₁₂ H ₂₅) ₄ (CN) ₂ G2 | 326.5 (189200) | 424 | 340.5 | 453 | 7042 |
| (OMe)G1-(CHO) ₂ | 325.5 (18000) | 493, 426 | 354 | 490 | 10438 |
| (OMe) ₂ G1-CHO | 323.5 (49600) | 454 | 340.5 | 448 | 8885 |
| (OC ₁₂ H ₂₅) ₂ G1-CHO | 326.5 (56100) | 458 | 325 | 439 | 8794 |
| (NBu ₂) ₂ G1-CHO | 383 (50400) | 582 | 434.5 | 648 | 8927 |
| (CN) ₂ G1-CHO | 322.5 (67700) | 404 | 336.5 | 455 | 6255 |
| (CF ₃) ₂ G1-CHO | 282.5 (79000) | 412 | 340.5 | 412 | 11126 |
| (OMe) ₄ G2-CHO | 326.5 (179600) | 424, 421 | 336.5 | 457 | 7043 |
| (OC ₁₂ H ₂₅) ₄ G2-CHO | 327.5 (188900) | 427, 421 | 340.5 | 445 | 7115 |
| (NBu ₂) ₄ G2-CHO | 375.5 (138300) | 461 | 378 | 571,608 | 4939 |
| (CF ₃) ₄ G2-CHO | 316.5 (364000) | 414, 504 | 330 | 459 | 7441 |

 a All spectra were recorded at room temperature at c \simeq 3 \times 10⁻⁶ M.

processes are only effective when π -donor and π -acceptor groups are directly connected by the 1,3-phenylenevinylene system. It seems reasonable to assume that higher generations will not afford a change in this tendency. When recording PL spectra of different samples at lower concentrations (10^{-8} M) , changes in the shape and shift of the bands were detected. For instance, a red shift for (CF₃)₄G2-CHO and a blue-shift for (OC₁₂H₂₅)₂G1-CHO were observed. An explanation of these results is beyond the scope of this work and will be considered soon. A red-shift in the PL emission in the solid state was also detected. This observation may be explained by the fact that in the solid state the molecules can experience a wider distribution of conformations, including a more planar state that gives rise to a lower HOMO-LUMO energy gap.9i

Conclusions

New poly(phenylenevinylene)dendrons and dendrimers bearing π -donor and/or π -acceptor groups in the periphery were synthesized using Heck and Horner–Wadsworth–Emmons reactions. The choice of the appropriate combination of peripheral groups allows the photoluminescence to be tuned between 400 and 580 nm. Due to the *meta*-substitution pattern, all chromophores are independent and, not only do these show good transparency in a wide range of the visible region, but large Stokes shifts are observed when strong electron-donating and electron-withdrawing groups are connected through the 1,3-phenylenevinylene system.

Experimental Section

General. Unless stated otherwise, all reagents were used as received and without further purification. NBS was recrystallized from water. CBr_4 was purified by sublimation. MnO_2 was heated under vacuum at 120 °C for at least 24 h prior to use. The following solvents were distilled under positive pressure of dry argon immediately prior to use: THF and Et₂O over sodium/benzophenone ketyl; CH_2Cl_2 from CaH₂. Acetonitrile was distilled under argon from CaH₂ and stored over molecular sieves (4 Å). DMF was dried over CaH₂, filtered, distilled under reduced pressure, and stored over molecular sieves (4 Å). Column chromatography was carried out with Merck silica gel for flash columns (230–400 mesh). NMR spectra were recorded, except when stated otherwise, in CDCl₃ on a Varian FT-300 or Gemini FT-200 instrument with TMS or the solvent carbon signal as the standards. IR spectra were recorded on a Nicolet 550 spectrophotometer (FT-IR). UV/vis spectra were recorded in CH_2Cl_2 on a Jasco V-530 spectrophotometer using standard 1 cm quartz UV cells. Fluorescence spectra were recorded on a Jasco FP-750 spectrofluorimeter. Mass spectrometry and elemental analyses were performed at the Universidad Autónoma de Madrid (Servicio Interdepartamental de Investigación, S. I. D. I.). Melting points were recorded on a Gallenkamp apparatus and are uncorrected.

1-Acetyloxymethyl-3,5-bis(bromomethyl)benzene (5) and 1,3-Bis(acetyloxymethyl)-5-bromomethylbenzene (6). A stirred solution of 1,3,5-tris(bromomethyl)benzene (2) (7.2 g, 20 mmol) and sodium acetate (2.46 g, 30 mmol) in DMF (50 mL) was heated at 100 °C for 3 h. After evaporation of the solvent under vacuum, EtOAc (150 mL) was added. The solution was washed successively with water (×3) and brine (×1) and then dried (MgSO₄). After filtration and evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (hexanes/EtOAc, 9:1) to give, in sequence, 830 mg (11%) of starting material 2, 2.20 g (33%) of 5, and 1.8 g (29%) of 6. Further purification of 5 and 6 was achieved by crystallization from EtOAc/hexanes.

5. White crystals. Mp: 61.5–63 °C. ¹H NMR δ : 2.13 (s, 3H), 4.47 (s, 4H), 5.09 (s, 2H); 7.31 (d, 2H, J= 1.5 Hz), 7.39 (t, 1H, J= 1.7 Hz). ¹³C NMR and DEPT δ : 170.7 (C), 138.8 (C), 137.3 (C), 129.4 (CH), 128.6 (CH), 65.4 (CH₂), 32.4 (CH₂), 21.0 (CH₃). IR ν : 1738 (C=O) cm⁻¹. Anal. Calcd for C₁₁H₁₂Br₂O: C, 39.53; H, 3.62. Found: C, 39.50; H, 3.71.

6. White needles. Mp: 59.5-61 °C. ¹H NMR δ : 2.12 (s, 6H), 4.49 (s, 2H), 5.10 (s, 4H), 7.27 (broad s, 1H), 7.35 (broad s, 2H). ¹³C NMR and DEPT δ : 170.7 (C), 138.5 (C), 137.0 (C), 128.5 (CH), 127.8 (CH), 65.0 (CH₂), 32.6 (CH₂), 20.9 (CH₃). IR ν : 1725 (C=O) cm⁻¹. Anal. Calcd for C₁₃H₁₅BrO₄: C, 49.68; H, 4.81. Found: C, 49.67; H, 4.68.

General Procedure for the Heck Reaction. All glassware was oven-dried and cooled under Ar. To a stirred solution of TBAB (1.2 mol per mol of styrene), K_2CO_3 (0.6 mol per mol of styrene), and Pd(AcO)₂ (10 mol %) in DMF (10 mL per mol of TBAB), under argon, was added a solution of the corresponding aryl bromide and *para*-substituted styrene in DMF (10 mL per mol of aryl bromide). The mixture was immersed in an oil bath, which had been preheated to 140 °C, and stirred for the indicated period of time. The mixture was then allowed to cool, diluted with CHCl₃, and successively washed with 1 N HCl (×3), H₂O (×1), and brine (×1) and dried (MgSO₄). The solution was filtered and the solvent evaporated under reduced pressure. The residues were purified by column chromatography (hexanes/EtOAc) and/or crystallization. A representative example for the preparation of a dendrimer is described below.

1,3-Bis(*p*-cyanostyryl)-5-*p*-methoxystyrylbenzene, (CN)₂(OMe)G1. Reaction time: 48 h. Purified by column chromatography (hexanes/EtOAc, 7:3) and crystallization from CHCl₃/EtOH. Yellow solid. Yield: 62%. Mp: 234–238 °C (decomposition observed above 210 °C). ¹H NMR δ : 3.85 (s, 3H), 6.93 (A of AB_q, 2H, *J* = 8.5 Hz), 7.00 (A of AB_q, 1H), 7.17 (B of AB_q, 1H), 7.17 (A of AB_q, 2H, *J* = 16.2 Hz), 7.27 (B of AB_q, 2H, *J* = 16.3 Hz), 7.50 (B of AB_q, 2H, *J* = 8.6 Hz), 7.57 (s, 1H), 7.59 (s, 2H), 7.61 (A of AB_q, 4H, *J* = 8.9 Hz), 7.67 (B of AB_q, 4H, *J* = 8.6 Hz). ¹³C NMR δ : 159.6, 141.5, 138.8, 137.1, 132.5, 131.8, 129.6, 129.5, 127.8, 127.5, 126.9, 125.5, 124.8, 124.0, 118.9, 114.2, 110.8, 55.35. HRMS, *m/e* calcd for C₃₃H₂₄N₂O: 464.1889. Found: 464.1898.

General Procedures for Horner–Wadsworth–Emmons Reactions. Method A. All glassware was oven-dried and cooled under Ar. To a stirred solution of the corresponding phosphonate and aromatic aldehyde in THF (6-9 mL per mmol of phosphonate), under argon, was added, in small portions, potassium tert-butoxide. The deeply colored mixture was stirred for the indicated period of time at room temperature. After hydrolysis with water, the mixture was stirred for a further 20 min, and the precipitated solid was filtered off. Method B. All operations were identical to those described for method A except that, after hydrolysis with water, the mixture was extracted with CH_2Cl_2 (×3). The combined organic layers were successively washed with water and brine and then dried (MgSO₄). The solution was filtered and the solvent evaporated under reduced pressure. The crude products were purified as indicated. Method C. All operations were identical to those described for methods A and B except that hydrolysis was carried out with 1 M NaOH (10 mL) and water (50 mL per mmol of product), and the mixture was stirred for an additional 2 h at room temperature in order to remove the ester group. Method D. All operations were identical to those described for method B except that hydrolysis was carried out with 1 M HCl and the mixture was stirred for an additional 2 h at room temperature in order to remove the acetal group. Representative examples for the preparation of different dendrons and dendrimers are described below.

1,3,5-Tris(*p*-methoxystyryl)benzene, (OMe)₃G1. Method A. Reaction time: 2 h 30 min. Purification: crystallized from CHCl₃/EtOH. Colorless solid. Yield: 85%. ¹H NMR δ : 3.84 (s, 9H), 6.92 (A of AB_q, 6H, J = 8.8 Hz), 7.01 (A of AB_q, 3H, J = 16.5 Hz), 7.16 (B of AB_q, 3H, J = 16.4 Hz), 7.49 (s, 3H), 7.49 (B of AB_q, 6H, J = 8.8 Hz). ¹³C NMR δ : 159.3, 138.2, 130.1, 128.5, 127.7, 126.4, 123.1, 114.1, 55.3. IR ν : 1605, 1585, 1510 cm⁻¹. Anal. Calcd for C₃₃H₃₀O₃: C, 83.51; H, 6.38. Found: C, 83.28; H, 6.06.

5-Bromo-1,3-bis(*p*-cyanostyryl)benzene, (CN)₂G1-Br. Method B. Reaction time: 1 h. Purification: washed with EtOH. Pale yellow solid. Yield: 81%. ¹H NMR δ : 7.14 (s, 4H), 7.54–7.64 (m, 3H), 7.59 (A of AB_q, 4H, J = 8.1 Hz), 7.67 (B of AB_q, 4H, J = 8.4 Hz). ¹³C NMR δ : 141.0, 138.7, 132.6, 130.3, 129.2, 128.7, 127.0, 124.3, 123.5, 118.8, 111.2. MS (EI+), *m/e* 412.1 (100), 410.1 (97). HRMS, *m/e* calcd. for C₂₄H₁₅N₂79Br: 410.0419. Found: 410.0418. Anal. Calcd for C₂₄H₁₅N₂Br: C, 70.09; H, 3.68; N, 6.81. Found: C, 70.02; H, 3.91; N, 6.97. **3,5-Bis(p-dodecyloxystyryl)benzylalcohol,** (OC₁₂H₂₅)₂G1-CH₂OH. Method C. Reaction time: 1 h. The crude product was of sufficient purity (determined by ¹H NMR) and was used as such in the next step. White solid. Quantitative yield. Further purification could be achieved by crystallization from CHCl₃/EtOH.¹H NMR δ : 0.88 (t, 6H, J = 6.6 Hz), 1.20–1.55 (m, 36H), 1.78 (m, 4H, J = 6.9 Hz), 3.96 (t, 6H, J = 6.3 Hz), 4.72 (s, 2H), 6.89 (A of AB_q, 4H, J = 8.7 Hz), 6.96 (A of AB_q, 2H, J = 16.2 Hz), 7.10 (B of AB_q, 2H, J = 16.2 Hz), 7.35 (s, 2H), 7.44 (B of AB_q, 4H, J = 8.7 Hz), 7.48 (s, 1H). ¹³C NMR and DEPT δ : 1589 (C), 141.5 (C), 138.3 (C), 129.7 (C), 128.7 (CH), 127.7 (CH), 126.0 (CH), 123.7 (CH), 123.4 (CH), 114.7 (CH), 68.0 (CH₂), 29.4 (two signals, $2 \times CH_2$), 29.3 (CH₂), 26.0 (CH₂), 22.7 (CH₂), 14.1 (CH₃). IR ν : 3547 (OH) cm⁻¹. HRMS, m/e calcd for C₄₇H₆₈O₃: 680.5168. Found: 680.5153.

3,5-Bis(p-dibutylaminostyryl)benzaldehyde, (NBu₂)₄G2-CHO. Method D. Reaction time: 2 h. Purification: column chromatography (EtOAc/nexanes, 9:1). Yellow oil which solidified upon standing. Yield: 97%. ¹H NMR δ : 0.97 (t, 24H, J= 7.5 Hz), 1.31–1.43 (m, 16H, J = 7.5 Hz), 1.53–1.65 (m, 16H), 3.30 (m, 16H, J = 7.5 Hz), 6.65 (A of AB_q, 8H, J = 9.0 Hz), 6.93 (A of AB_q, 4H, J = 16.2 Hz), 7.14 (B of AB_q, 4H, J = 16.2 Hz), 7.25 (A of AB_q, 2H, J = 16.5 Hz) 7.43 (B of AB_q, 2H, J = 16.5 Hz) 7.43 (B of AB_q, 2H, J = 16.5 Hz) 7.43 (B of AB_q, 2H, J = 16.5 Hz) 7.43 (B of AB_q, 2H, J = 16.7 Hz), 7.45 (G, 137.4 (C), 130.9 (CH), 147.9 (C), 139.0 (C), 138.8 (C), 137.2 (C), 137.1 (C), 130.9 (CH), 130.2 (CH), 123.3 (CH), 122.6 (CH), 111.6 (CH), 50.8 (CH₂), 29.5 (CH₂), 20.4 (CH₂), 14.0 (CH₃). MS (MALDI), m/e 1227.7

1,3-Bis(p-methoxystyryl)-5-*p***-cyanostyrylbenzene, (OMe)**₂ **(CN)G1.** Method B. Reaction time: 2 h 30 min. Purified by column chromatography (hexanes/EtOAc, 1:1). Further purification could be achieved by crystallization from CHCl₃/EtOH. Pale yellow solid. Yield: 75%. ¹H NMR δ : 3.84 (s, 6H), 6.92 (A of AB_q, 4H, *J* = 8.7 Hz), 6.98 (A of AB_q, 2H, *J* = 16.2 Hz), 7.13 (B of AB_q, 2H, *J* = 16.2 Hz), 7.11–7.25 (m, 2H), 7.46–7.53 (m, 7H), 7.58 (A of AB_q, 2H, *J* = 8.7 Hz), 7.63 (B of AB_q, 2H, *J* = 8.7 Hz). ¹³C NMR and DEPT δ : 159.4 (C), 141.7 (C), 138.4 (C), 136.8 (C), 132.5 (CH), 132.2 (CH), 129.8 (CH), 124.3 (CH), 127.8 (CH), 127.0 (CH), 126.8 (CH), 125.9 (CH), 124.3 (CH), 123.6 (CH), 119.0 (C), 114.2 (CH), 110.6 (C), 55.3 (2 × CH₃). HRMS, *m/e* calcd for C₃₃H₂₇NO₂: 469.2042. Found: 469.2042.

 $(OC_{12}H_{25})_4(CN)_2G2.$ Method B. Reaction time: 4 h 30 min. Purified by crystallization from CHCl₃/EtOH. Pale yellow solid. Yield: 66%. ¹H NMR (70 °C) δ : 0.89 (t, 12H, J= 6.6 Hz), 1.10–1.55 (m, 72H), 1.79 (m, 8H), 3.98 (t, 8H, J= 6.6 Hz), 6.87–7.24 (m, 26H), 7.41–7.68 (m, 28H). 13 C NMR δ : 159.0, 141.4, 138.3, 138.0, 137.5, 137.1, 132.5, 131.7, 129.7, 129.1, 128.7, 128.3, 127.8, 127.4, 126.9, 126.0, 125.0, 123.8, 123.3, 118.9, 114.7, 110.8, 68.1, 31.9, 29.7 (four signals), 29.5, 29.4, 29.3, 26.1, 22.7, 14.1. IR (KBr) ν : 2224 (CN) cm⁻¹. MS (MALDI), m/e 1784.0.

Acknowledgment. Financial support from the Spanish DGES (PB97-0425 and 1FD97-0167) is gratefully acknowledged.

Supporting Information Available: Additional experimental procedures, compound characterization data, and copies of ¹H NMR and ¹³C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO015764R