

# Novel Fluorescent (*p*-Phenylene ethynylene)-Calix[4]arene-based Polymer: Design, Synthesis, and Properties

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**ABSTRACT:** A novel fluorescent (*p*-phenylene ethynylene)-calix[4]arene-based polymer (**CALIX-PPE**) has been successfully synthesized by cross-coupling polymerization of bis-calix[4]arene **1** with 1,4-diethynylbenzene. The polycondensation was carried out in toluene/NEt<sub>3</sub> at 35 °C for 24 h, using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI as the catalytic system, furnishing **CALIX-PPE** in excellent isolated yields (higher than 95%, several runs). The yellow polymer is freely soluble in several nonprotic organic solvents. The GPC trace of the isolated polymer showed a monomodal distribution and a number-average molecular weight of 23,300 g mol<sup>-1</sup> ( $M_w/M_n = 2.05$ ). No evidence was found in the structural analysis (FTIR and <sup>1</sup>H/<sup>13</sup>C NMR) regarding the formation of alkyne homocoupled segments along the polymer chain. For comparative purposes, the synthesis of an analogous poly(*p*-phenylene ethynylene) containing *p*-*t*-butyl-phenoxy-methyl side chains (**TBP-PPE**) was also undertaken. A great similarity was found between the photophysical properties of **CALIX-PPE** and **TBP-PPE** in solution (UV-vis and laser induced luminescence), clearly demonstrating their unique dependence on the structure and conformation of the conjugated PPE backbone. The fluorescence spectra of polymers are of nearly identical shape, displaying their maximum emission around 420 nm. The calculated solution photoluminescence quantum yields of **CALIX-PPE** and **TBP-PPE** are of similar magnitude ( $\phi_F(\text{CALIX-PPE}) = 0.43$ ;  $\phi_F(\text{TBP-PPE}) = 0.51$ ). © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 6477–6488, 2008

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## INTRODUCTION

Macrocyclic receptors linked to conjugated polymers have been continuously screened as chemical and biological sensors.<sup>1–3</sup> For instance, crown and aza-crown ethers,<sup>4</sup> cyclodextrins,<sup>5</sup> and calixarenes<sup>6</sup> have been used for this purpose. In comparison to single receptor molecules, conjugated polymer-based sensors show higher sensitivity

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leading to a higher transduction signal amplification.<sup>7,8</sup> Considering the use of calixarenes as building blocks for this type of supramolecular assemblies, only a few studies have so far tackled the potential use of these cyclic oligomeric units as structural components of larger polymeric entities.<sup>6,9,10</sup> The construction of such systems has been based on the association of a molecular recognition element (the calix[4]arene unit), which should be ideally capable of selective interactions with a given guest, and a conjugated polymer, to which it is covalently linked, responsible for the transduction of the signal to the sensory device by means of measurable changes in its photo/electroluminescence or magnetic properties after a host-guest interaction had taken place.

Our prior synthetic approach toward these systems was based on calix[4]arene side- and main-chain conjugated poly(phenylacetylene) type polymers, where mono and bifunctional calix[4]arenes possessing lower rim phenylethynyl substituents were smoothly polymerized with Rh-based binary<sup>11</sup> and ternary<sup>12</sup> catalytic systems. Unfortunately, these type of conjugated polymers were devoid of significant luminescence,<sup>13</sup> limiting its potential use as a fluorescent material for sensing. We report herein the synthesis and properties of a new calixarene-based *p*-phenylene ethynylene polymer (**CALIX-PPE**), as well as its polymer analogue poly((2,5-bis(*p*-*t*-butyl-phenoxy)methyl)-*p*-phenylene)ethynylene-*p*-phenyleneethynylene (**TBP-PPE**), both displaying high fluorescence quantum yields.

## EXPERIMENTAL

### Materials and Methods

Melting points were measured in sealed capillaries on a Büchi 530 apparatus and are reported uncorrected. Infrared spectra (FTIR) were measured on a Bruker Vertex 70 as KBr pellets (transmission mode) or thin films at a resolution of 2 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz) and H-decoupled <sup>13</sup>C NMR (100 MHz) spectra were recorded on Bruker AVANCE II<sup>+</sup> spectrometers (300 and 400 MHz) and reported chemical shifts ( $\delta$ , ppm) are internally referenced to tetramethylsilane (<sup>1</sup>H) and CD<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub> (<sup>13</sup>C; 53.8 and 77.0 ppm relative to Me<sub>4</sub>Si); *J* values are given in Hz. <sup>13</sup>C-<sup>1</sup>H Heteronuclear Single Quantum Coherence (HSQC) NMR experiments were used for spectral assignments. Elemental analyses were performed at the Laboratorio Análisis Instrumental, C.A.C.T.I., of Uni-

versidad de Vigo. High-resolution mass spectra (HRMS) were obtained at the Servicio de Determinación Estructural e Proteómica, C.A.C.T.I., of Universidad de Vigo on a Fourier Transform-Ion Cyclotron Resonance (FT-ICR) mass spectrometer (Bruker Daltonics, APEX Qe FT-ICR, equipped with a 7-Tesla superconducting magnet using  $\alpha$ -cyano-4-hydroxycinnamic acid (4-HCCA) as the matrix-assisted laser desorption/ionization (MALDI) matrix, positive ion mode). UV-vis spectra were recorded on a Nicolet Evolution 300 and on a Camspec M501 spectrophotometers at  $5.0 \times 10^{-5}$  M in CHCl<sub>3</sub>. Gel permeation chromatography (GPC) analysis was performed on a Jasco Liquid Chromatograph system equipped with a Jasco Refractive Index Detector 2031 Plus and a Jasco UV Absorption Detector 1575 (selected to 270 nm), using PSS SDV columns (10<sup>3</sup> and 10<sup>5</sup> Å) and THF as eluent at 35 °C. Calibration was done with monodisperse polystyrene standards. The polymeric, oligomeric, or dimeric contents of the polymerization mixtures, the degrees of conversion, and the final composition of the isolated materials, as well as the number-average (*M*<sub>n</sub>) and weight-average (*M*<sub>w</sub>) molecular weights were estimated from the GPC traces based on UV response. The polymerization yields were determined gravimetrically. Polymer concentrations were based on the molecular weight of the repeating unit.

Analytical thin-layer chromatography (TLC) was performed on E. Merck kieselgel 60, F-254 silica-gel 0.2-mm thick plates.

Laser-induced luminescence (LIL) experiments were performed with a N<sub>2</sub> laser (PTI model 2000, ca. 600 ps FWHM, ~ 1.1 mJ per pulse) at an excitation wavelength of 337 nm. A schematic diagram of the LIL system was previously reported.<sup>14</sup> An integrating sphere (Sphere Optics Integrating Sphere, model Zenith RT6Z, with baffle) was used for fluorescence quantum yield determinations.

9,10-Diphenylanthracene (scintillation grade, Nuclear Enterprises.), covering the emission range (400–500 nm),<sup>15,16</sup> was used as reference standard. 1,4-Diiodo-2,5-bis(bromomethyl)benzene **3**<sup>17</sup> and calix[4]arene **4**<sup>18</sup> were synthesized according to reported methods and characterized by FTIR, <sup>1</sup>H NMR, and microanalysis. *p*-*Tert*-butylphenol (97%, Fluka), 1,4-diethynylbenzene (96%, Aldrich), copper(I) iodide (98%, Aldrich), dichlorobis(triphenylphosphine)palladium (II) (98%, Aldrich) were used as received. Triphenylphosphine (98%, Merck) was recrystallized from hexane, triethylamine (99%, Riedel-de-Haën) was previously dried from CaH<sub>2</sub> and distilled under N<sub>2</sub> prior to use, and toluene

was distilled from CaH<sub>2</sub>. All other reagents and solvents were reagent grade and were purified and dried by standard methods. Organic extracts were dried over anhydrous magnesium sulfate.

### Synthesis of Monomeric Compounds

#### 1,4-Bis-[5,11,17,23-tetrakis(1,1-dimethylethyl)-25-(oxymethyl)-26,27,28-tripropoxy]calix[4]arene]-2,5-diiodo-benzene (1)

To a clear solution of tri-*O*-propyl-*p*-*tert*-butylcalix[4]arene **4** (1.96 g, 2.53 mmol) in dry CH<sub>3</sub>CN (187 mL) at rt, K<sub>2</sub>CO<sub>3</sub> (1.33 g, 9.60 mmol) and 1,4-diiodo-2,5-bis(bromomethyl)benzene **3** (0.652 g, 1.26 mmol) were added in portions. The resulting white suspension was refluxed with stirring under argon for 72 h, having the TLC control (CHCl<sub>3</sub>:hexane; 1:2) revealed the consumption of **4** after that period. After cooling to rt, the beige suspension was filtered and washed thoroughly with CH<sub>3</sub>CN, H<sub>2</sub>O, and again CH<sub>3</sub>CN, yielding 1.94 g of a fine beige powder after vacuum drying at 65 °C (crude yield: 81%). Recrystallization of the crude product from CH<sub>2</sub>Cl<sub>2</sub>:MeOH furnished 1.12 g (46.5%) of **1** as colorless crystals.

mp 237–238 °C;  $\nu_{\max}$  (cm<sup>-1</sup>) 3042, 2963, 2906, 2874, 1603, 1585, 1485, 1205, 1126, 1047, 1012, 872;  $\lambda_{\max}$  (nm) [ $\epsilon_{\max}$ ] ( $\times 10^{-3}$  M<sup>-1</sup> cm<sup>-1</sup>) 274 (9.0), 282 (8.5);  $\delta_{\text{H}}$  (ppm) (CDCl<sub>3</sub>; 300 MHz) 0.86 (18H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.87 (12H, t, —CH<sub>2</sub>—CH<sub>3</sub>, *J* 7.5; partially overlapped), 0.87 (18H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.05 (6H, t, —CH<sub>2</sub>—CH<sub>3</sub>, *J* 7.5), 1.30 (36H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.92 (4H, m, —CH<sub>2</sub>—CH<sub>3</sub>), 2.01 (8H, m, —CH<sub>2</sub>—CH<sub>3</sub>, *J* 7.5), 3.08 (4H, d, ArCH<sub>2</sub>Ar, *J* 12.6), 3.11 (4H, d, ArCH<sub>2</sub>Ar, *J* 12.6), 3.65 (4H, t, —O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>, *J* 7.2), 3.97 (8H, m, —O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>), 4.41 (4H, d, ArCH<sub>2</sub>Ar, *J* 12.6), 4.44 (4H, d, ArCH<sub>2</sub>Ar, *J* 12.6), 4.82 (4H, s, ArOCH<sub>2</sub>Ar), 6.49 (4H, s, ArH), 6.50 (4H, s, ArH), 7.06 (8H, s, ArH), 8.035 (2H, s, ArH(I<sub>2</sub>));  $\delta_{\text{C}}$  (ppm) (CD<sub>2</sub>Cl<sub>2</sub>; 100 MHz) 10.2, 10.6 (—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>, ratio 2:1), 23.3, 23.65 (—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>, ratio 2:1), 31.11, 31.13, 31.6 (C(CH<sub>3</sub>)<sub>3</sub>, ~ ratio 1:1:2), 31.3 (—CH<sub>2</sub>—), 33.6, 33.7, 34.0 (C(CH<sub>3</sub>)<sub>3</sub>, ~ ratio 1:1:2), 76.7, 77.5, 80.3 (—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>, —O—CH<sub>2</sub>—Ar, ratio 2:1:1), 98.9 (Ar—C—I), 124.6, 124.9, 125.5, 125.6 (calix-ArC—H, ratio 1:1:1:<1), 132.4, 135.4, 135.7, 140.8 (I—C—Ar(C—H)—C—I), 142.0, 144.0, 144.6, 144.8, 151.8, 153.0, 154.5 (ArC) [fewer carbon signals than expected in the region 30–33 ppm (bridged CH<sub>2</sub>) due to accidental isochrony; running the <sup>13</sup>C spectrum in CDCl<sub>3</sub>, the signals corresponding to

—CH<sub>2</sub>— appeared at 31.5 and 31.6 ppm; <sup>13</sup>C-<sup>1</sup>H HSQC NMR experiment (CD<sub>2</sub>Cl<sub>2</sub>) was used for the spectral assignments]. HR-MS (FT-ICR-MALDI-MS) *m/z*: 1925.94258 ([M-Na]<sup>+</sup>, C<sub>114</sub>H<sub>152</sub>I<sub>2</sub>NaO<sub>8</sub> requires 1925.94688). Anal. Calcd. for C<sub>114</sub>H<sub>152</sub>I<sub>2</sub>O<sub>8</sub>: C, 71.90; H, 8.05. Found: C, 71.43; H, 8.21. GPC data (THF solution at 35 °C against polystyrene standards):  $M_{\text{p(GPC)}}$  = 1291 g mol<sup>-1</sup>; Calcd.  $M_{\text{w}}$  = 1904.23 g mol<sup>-1</sup>.

#### 1,4-Bis-(4-*tert*-butyl-phenoxymethyl)-2,5-diiodo-benzene (2)

To a suspension of *p*-*tert*-butylphenol (0.500 g, 3.33 mmol) in dry CH<sub>3</sub>CN (250 mL) at rt was added K<sub>2</sub>CO<sub>3</sub> (1.75 g, 12.65 mmol) and 1,4-diiodo-2,5-bis(bromomethyl)benzene **3** (0.858 g, 1.66 mmol). The resulting white suspension was refluxed with stirring under argon for 24 h at which time the TLC control (CHCl<sub>3</sub>:hexane; 1:1) showed the completion of the reaction. Upon cooling, the solvent was removed in a rotary evaporator and the white-yellowish residue was partitioned with CH<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O. The organic extract was washed twice with H<sub>2</sub>O, dried and the solvent evaporated. After drying under vacuum at 50 °C, 1.07 g (98.5%) of crude product was obtained, which upon recrystallization from CH<sub>2</sub>Cl<sub>2</sub>:MeOH afforded 0.937 g (86.3%) of **2** as yellowish crystals.

mp 124–125 °C;  $\nu_{\max}$  (cm<sup>-1</sup>) 3042, 2959, 2906, 2871, 1607, 1581, 1515, 1485, 1241, 1202, 1190, 1054, 1035, 1011, 821, 549;  $\lambda_{\max}$  (nm) [ $\epsilon_{\max}$ ] ( $\times 10^{-3}$  M<sup>-1</sup> cm<sup>-1</sup>) 274 (5.3), 282 (shoulder);  $\delta_{\text{H}}$  (ppm) (CDCl<sub>3</sub>) 1.32 (18H, s, —C(CH<sub>3</sub>)<sub>3</sub>), 4.96 (4H, s, ArOCH<sub>2</sub>Ar), 6.93 and 7.34 (4H each, d each, *t*-butyl—Ar(*H*)—O—; *J* 9.0), 7.98 (2H, s, ArH(I<sub>2</sub>));  $\delta_{\text{C}}$  (ppm) (CDCl<sub>3</sub>) 31.9 (C(CH<sub>3</sub>)<sub>3</sub>), 34.5 (2 C(CH<sub>3</sub>)<sub>3</sub>), 73.5 (—O—CH<sub>2</sub>—Ar), 97.1 (Ar—C—I), 114.8 (*t*-butyl—Ar—C—H), 126.7 (*t*-butyl—Ar—C—H), 138.9 (Ar(I<sub>2</sub>)—C—H), 141.1, 144.6 (ArC), 156.3 (ArC—O—) [<sup>13</sup>C-<sup>1</sup>H HSQC NMR experiment (CD<sub>2</sub>Cl<sub>2</sub>) was used for the spectral assignments]. HR-MS (FT-ICR-MALDI-MS) *m/z*: 693.01106 ([M-K]<sup>+</sup>, C<sub>28</sub>H<sub>32</sub>I<sub>2</sub>KO<sub>2</sub> requires 693.01232). Anal. Calcd. for C<sub>28</sub>H<sub>32</sub>I<sub>2</sub>O<sub>2</sub>: C, 51.39; H, 4.93. Found: C, 51.06; H, 4.94. GPC data (THF solution at 35 °C against polystyrene standards):  $M_{\text{p(GPC)}}$  = 505 g mol<sup>-1</sup>; Calcd.  $M_{\text{w}}$  = 654 g mol<sup>-1</sup>.

### General Procedure for the Cross-Coupling Polymerizations Using Pd/Cu Catalysts

Poly(*p*-phenylene ethynylene) (PPE) type polymers here described were synthesized by

standard methods. All the polymerizations were carried out in septum-sealed dry glass flasks under an argon atmosphere. Typical procedures are described below.

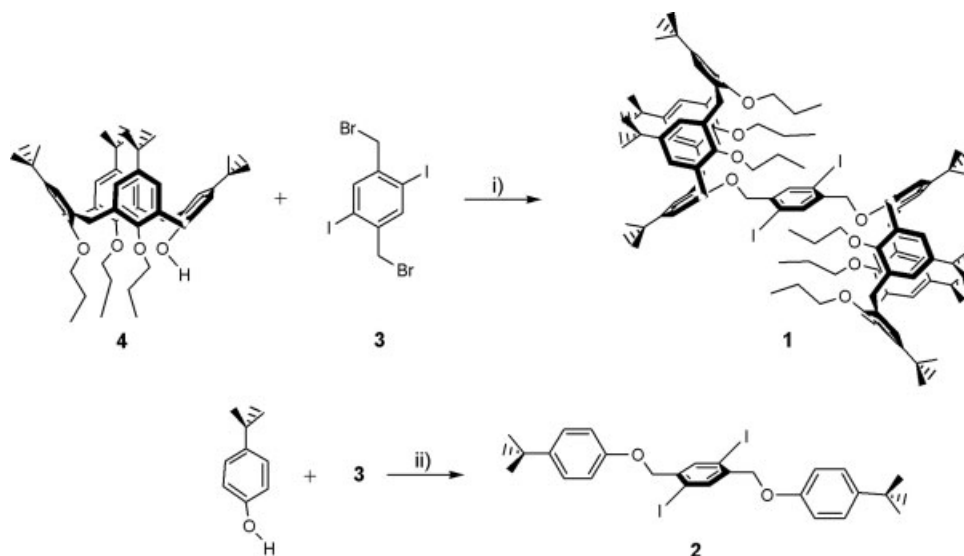
**CALIX-PPE** (poly((2,5-bis[5,11,17,23-tetrakis(1,1-dimethylethyl)-25-(oxymethyl)-26,27,28-tripropoxy-calix[4]arene]-*p*-phenylene)ethynylene-*p*-phenyleneethynylene). To an argon degassed solution containing 100 mg (52.5  $\mu\text{mol}$ ) of **1** in dry toluene (2.1 mL) and freshly distilled  $\text{NEt}_3$  (2.1 mL) was added 1,4-diethynylbenzene (7.28 mg, 57.8  $\mu\text{mol}$ ),  $\text{PdCl}_2(\text{PPh}_3)_2$  (2.6 mg, 3.7  $\mu\text{mol}$ ) and  $\text{CuI}$  (0.7 mg, 3.7  $\mu\text{mol}$ ) under argon. After sealing the flask, the contents were stirred in a preheated bath at 35  $^\circ\text{C}$ . The mixture acquired a yellow color that rapidly turned to brownish with turbidity. After a certain time ( $\sim 2$  h), an intense yellow-orange color developed within the reaction mixture and a precipitate formed. GPC control after 24 h revealed a conversion higher than 98% based on **1**. Solvents were removed by evaporation and the residue taken in  $\text{CH}_2\text{Cl}_2$  (20 mL) and washed successively with 2% aq.  $\text{HCl}$  and  $\text{H}_2\text{O}$ . The extract was dried and evaporated to dryness. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and poured into  $\text{MeOH}$ . The yellow precipitate was filtered and dried in a vacuum oven at 65  $^\circ\text{C}$ , yielding 89.9 mg (96.4%) of a yellow solid.

$\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 3042, 2963, 2906, 2874, 2201, 1603, 1585, 1483, 1202, 1123, 1043, 1010, 871, 836;  $\lambda_{\text{max}}$  (nm) [ $\epsilon_{\text{max}}$ ] ( $\times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ ) 276 (3.03), 282 (2.95), 382 (5.87) cutoff 450 nm;  $\delta_{\text{H}}$  (ppm) ( $\text{CDCl}_3$ ; 300 MHz) 0.80 (12H, b t,  $-\text{CH}_2-\text{CH}_3$ ,  $J$  7.5), 0.88 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 0.90 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.04 (6H, b t,  $-\text{CH}_2-\text{CH}_3$ ,  $J$  7.5), 1.26, 1.27, 1.31 (36H, s,  $\text{C}(\text{CH}_3)_3$ ; ratio  $\sim 9:1:1$ ), 1.96 (12H, m,  $-\text{CH}_2-\text{CH}_3$ ), 3.11 (8H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J$  11.1), 3.69 (4H, m,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 3.92 (8H, m,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 4.41 (4H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J$  11.4), 4.55 (4H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J$  11.4), 4.875, 5.05, 5.10 (4H, b s,  $\text{ArOCH}_2\text{Ar}$ ; ratio  $\sim 1:1:7.5$ ), 6.50, 6.54 (with a shoulder at  $\sim 6.535$ ), 6.56 (8H, s, calix-ArH; ratio  $\sim 1:(1)10:10$ ), 7.00 (s, calix-ArH) and 7.07 (m, calix-ArH) [8H; ratio:  $\sim 8:1$ , respectively], 7.33–7.45 and 7.45–7.57 (4H, m,  $\equiv\text{C}-\text{Ph}(\text{H})_4-\text{C}\equiv$ ), 7.85, 7.965, 8.19 [2H, b s, *ortho*-H-ArI (chain ends),  $\text{H}-\text{Ar}(-\text{C}\equiv\text{C})_2-\text{H}$  (middle chain) and *meta*-H-ArI (chain ends), respectively; ratio  $\sim 1:9.5:1$ ];  $\delta_{\text{C}}$  (ppm) ( $\text{CD}_2\text{Cl}_2$ ; 100 MHz) 10.5, 11.1 ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 23.8, 24.1 ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , ratio  $\sim 2:1$ ), 31.65 ( $\text{C}(\text{CH}_3)_3$ ), 31.9 ( $-\text{CH}_2-$ ), 32.0 ( $\text{C}(\text{CH}_3)_3$ ), 34.2, 34.4 ( $\text{C}(\text{CH}_3)_3$ ), 75.2 ( $-\text{O}-\text{CH}_2-\text{Ar}$ ), 77.3, 77.9 ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 123.8, 125.2, 125.5, 125.8 (calix-ArC-H), 132.1 ( $\equiv\text{C}-\text{Ph}(\text{C}-\text{H})-\text{C}\equiv$ ), 133.0,

133.3, 133.4 134.9, 135.6 ( $\equiv\text{C}-\text{Ar}(\text{C}-\text{H})-\text{C}\equiv$ ), 135.7 ( $\equiv\text{C}-\text{Ar}(\text{C}-\text{H})-\text{C}\equiv$ ), 139.8, 144.6, 145.0, 153.0, 153.6, 154.9 (ArC) [no carbon signals for  $-\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-$  could be firmly detected, although a dispersed signal around 90.5 ppm, just slightly above the spectrum noise, was noticed]. Anal. Calcd. for  $\text{C}_{1354}\text{H}_{1712}\text{I}_2\text{O}_{88}$  (DP = 11; NMR based end-group analysis): C, 82.75; H, 8.79. Found: C, 81.64; H, 8.46. GPC data (THF solution at 35  $^\circ\text{C}$  against polystyrene standards):  $M_n = 23,300 \text{ g mol}^{-1}$ ;  $M_w/M_n = 2.05$ ; degree of polymerization (DP, based on  $M_n$ ) = 13.

An identical procedure was followed for the polymerization of compound **2**. **TBP-PPE** (poly((2,5-bis(*p*-*t*-butyl-phenoxy)methyl)-*p*-phenylene)ethynylene-*p*-phenyleneethynylene). To an argon degassed solution of **2** (400 mg, 0.61 mmol) in dry toluene (25 mL) and freshly distilled  $\text{NEt}_3$  (25 mL) was added 1,4-diethynylbenzene (80.3 mg, 0.61 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (30.0 mg, 42.8  $\mu\text{mol}$ ) and  $\text{CuI}$  (8.15 mg, 42.8  $\mu\text{mol}$ ) under argon. The mixture was stirred in a preheated bath at 35  $^\circ\text{C}$  during 10h and then kept at 65  $^\circ\text{C}$  for 13 h. During that period, the reaction mixture turned orange and the formation of a copious precipitate was observed. After removal of the solvents, the residue was taken in  $\text{CH}_2\text{Cl}_2$  (20 mL) and washed successively with 2% aq.  $\text{HCl}$  and  $\text{H}_2\text{O}$ . The extract was dried and evaporated to dryness. Dissolution in  $\text{CH}_2\text{Cl}_2$  and precipitation into  $\text{MeOH}$  furnished 255.9 mg (79.5%) of a yellow solid, after it has been dried in vacuum at 65  $^\circ\text{C}$ .

$\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 3042, 2959, 2902, 2867, 2204, 1607, 1581, 1511, 1244, 1183, 1040, 1016, 899, 829;  $\lambda_{\text{max}}$  (nm) [ $\epsilon_{\text{max}}$ ] ( $\times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ ) 276 (1.76), 283 (1.73), 380 (5.77) cutoff 450 nm;  $\delta_{\text{H}}$  (ppm) ( $\text{CDCl}_3$ ; 300 MHz) 1.32 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 5.01, 5.23, 5.285 (4H, s,  $\text{ArOCH}_2\text{Ar}$ ; ratio  $\sim 1:1:2.1$ ), 6.96 (4H, m,  $\text{Ar}(\text{H})_2-\text{OCH}_2-$ ), 7.35 (m, 4H, *t*-butyl-Ar(H) $_2-$  and 2.5H,  $\equiv\text{C}-\text{Ph}(\text{H})-\text{C}\equiv$ ), 7.47 (1.5H, d,  $\equiv\text{C}-\text{Ph}(\text{H})-\text{C}\equiv$ ,  $J$  8.7 Hz), 7.70, 7.78, 8.09 [2H, s, *ortho*-H-ArI (chain ends),  $\text{H}-\text{Ar}(-\text{C}\equiv\text{C})_2-\text{H}$  (middle chain) and *meta*-H-ArI (chain ends), respectively; ratio  $\sim 1:2:1$ ];  $\delta_{\text{C}}$  (ppm) ( $\text{CD}_2\text{Cl}_2$ ; 100 MHz) 31.3, 31.4, 34.10, 67.5, 67.8, 73.6, 97.5, 114.3, 114.4, 121.8, 123.1, 126.5, 131.0, 131.5, 131.6, 131.7, 132.6, 138.2, 138.3, 138.8, 139.5, 140.2, 144.1, 144.2, 144.3, 156.2, 156.5, 156.6. Anal. Calcd. for  $\text{C}_{142}\text{H}_{140}\text{I}_2\text{O}_8$  (DP = 4; NMR based end-group analysis): C, 76.53; H, 6.33. Found: C, 77.32; H, 5.97. GPC data (THF solution at 35  $^\circ\text{C}$  against polystyrene standards):  $M_n = 3550 \text{ g mol}^{-1}$ ;  $M_w/M_n = 1.56$ ; degree of polymerization (DP, based on  $M_n$ ) = 7.



**Scheme 1.** Synthesis of 1,4-bis[5,11,17,23-tetrakis(1,1-dimethylethyl)-25-oxomethyl-26,27,28-tripropoxy]calix[4]arene]-2,5-diiodo-benzene (**1**) and 1,4-bis(4-*tert*-butylphenoxy)methyl-2,5-diiodo-benzene (**2**): (i)  $\text{K}_2\text{CO}_3$  (3.8 eq.),  $\text{CH}_3\text{CN}$ , reflux, 72 h; (ii)  $\text{K}_2\text{CO}_3$  (3.8 eq.),  $\text{CH}_3\text{CN}$ , reflux, 24 h.

## RESULTS AND DISCUSSION

### Monomer Synthesis

1,4-Diiodo-2,5-bis(bromomethyl)benzene (**3**) was prepared by a recent described route<sup>17</sup> starting from 1,4-bis(hydroxymethyl)benzene in four steps (16% overall yield). Treatment of **3** with tri-*O*-propyl-*p*-*tert*-butylcalix[4]arene **4** in dry  $\text{CH}_3\text{CN}$  at reflux for 72 h in the presence of  $\text{K}_2\text{CO}_3$  furnished the desired bis-calix[4]arene compound **1** as colorless crystals in 47% yield after recrystallization (Scheme 1). Longer reaction times (up to 120 h) did not improve the yield. Performing the reaction in refluxing THF, using NaH as base, larger amounts (up to 40%) of the monosubstituted calixarene derivative (1-bromomethyl-4-[5,11,17,23-tetrakis(1,1-dimethylethyl)-25-(oxomethyl)-26,27,28-tripropoxy]calix[4]arene]-2,5-diiodo-benzene) were retrieved under a variety of conditions. The monosubstituted derivative was isolated by preparative TLC ( $\text{CHCl}_3$ :hexane; 1:2) and was briefly characterized by  $^1\text{H}$  NMR (characteristic signals at 8.01 and 7.99 ( $2 \times 1\text{H}$ , s,  $\text{ArH}(\text{I})_2$ ) and at 4.78 and 4.61 ( $2 \times 2\text{H}$ , s,  $\text{ArOCH}_2\text{Ar}$ )).

The  $^1\text{H}$  NMR analysis of **1** clearly pointed to the proposed structure, showing the benzylic resonances ( $\text{ArOCH}_2\text{—Ar}(\text{I})_2\text{—CH}_2\text{OAr}$ ) as a singlet at 4.82 ppm along with the four sets of doublets of the bridged methylene protons resonating at 3.08

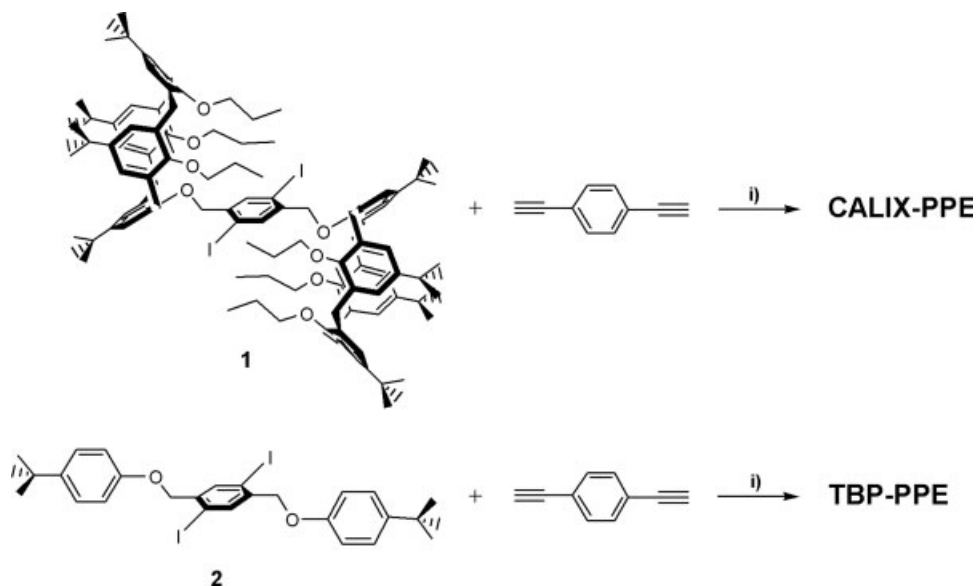
and 3.11 ppm and 4.41 and 4.44 ppm, with a  $\Delta\delta$  between the *exo* and *endo* protons around 1.3 ppm, which unambiguously indicate that a cone conformation was secured for the calixarene units in **1** (Fig. S1). In addition, a singlet for the diiodo moiety's protons appears at 8.035 ppm.  $^{13}\text{C}$  NMR spectrum (Fig. S2) revealed a resonance for the bridged methylene carbon at 31.3 ppm ( $\text{CD}_2\text{Cl}_2$ ), which is in agreement with the expected chemical shift for a cone conformation. Other representative signals, and their assignments based on  $^{13}\text{C}$ - $^1\text{H}$  HSQC NMR experiments (Fig. S3), may be found in the Experimental Section.

Compound **2**, used as a model compound in the subsequent study toward the synthesis of the corresponding *p*-phenylene ethynylene type polymer (TBP-PPE), was prepared in a similar fashion in 86% (Scheme 1).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Figs. S4 and S5, respectively), which were also correlated ( $^{13}\text{C}$ - $^1\text{H}$  HSQC NMR; Fig. S6), showed full agreement with the expected structure for **2** (see detailed data and assignments on Experimental Section).

### Polymer Synthesis

#### Polymerization of Bis-calixarene 1

Cross-coupling polymerizations of bis-calix[4]arene **1** with 1,4-diethynylbenzene were typically

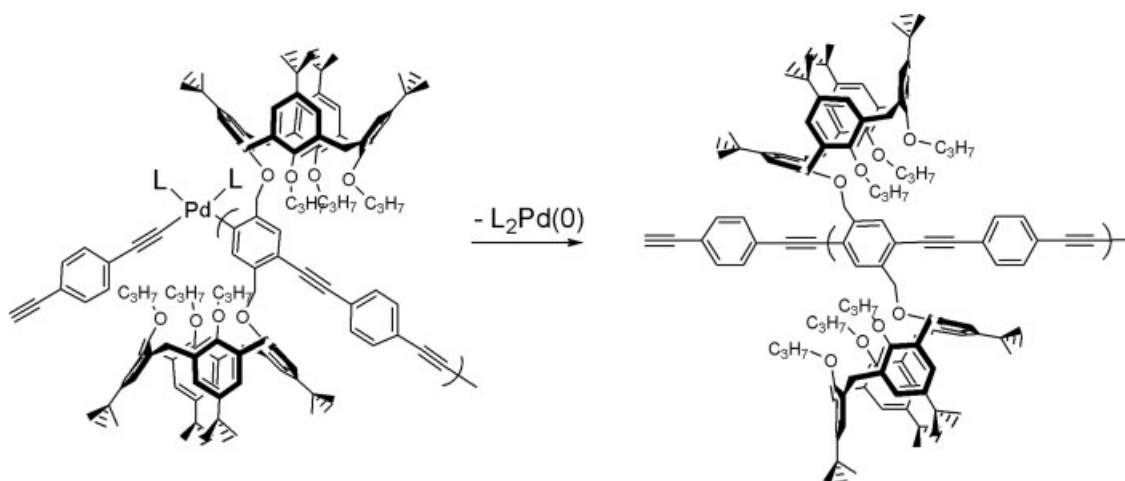


**Scheme 2.** Synthesis of **CALIX-PPE** and **TBP-PPE** conjugated polymers: (i)  $\text{PdCl}_2(\text{PPh}_3)_2$  and  $\text{CuI}$  (catalytic amounts),  $\text{NEt}_3/\text{toluene}$ , 35–65 °C, 24 h.

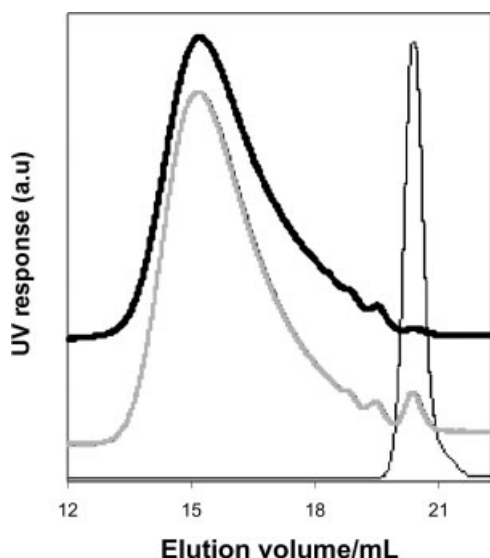
carried out in toluene/ $\text{NEt}_3$  at 35 °C for 24 h, using  $\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI}$  as the catalytic system (Scheme 2). Performing the polycondensation at a higher reaction temperature (60 °C) and monomers concentration (0.025 M) resulted in gelation of the reaction mixture after 16 h, leading to the isolation of a large amount of an insoluble material (Pd and Cu catalysts used at 5 and 10 mol % respectively, in addition to 10 mol % of  $\text{PPh}_3$ ).

The expected polymerization reaction was fully accomplished in spite of the crowded environment imparted by the calixarene units near the electrophilic reaction centers. This is especially relevant if one takes into account the structures of the probable intermediates and transition states that develop during the catalytic cycle of the Sonogashira-Hagihara reaction (Chart 1).<sup>19</sup>

Under the best-tested conditions, high conversions and excellent isolated yields of **CALIX-PPE**



**Chart 1.** Idealized structures of the  $\text{Pd(II)}$ -intermediate (left) and the resulting eneyne product (right) generated during the catalytic cycle of the cross-coupling polymerization.



**Figure 1.** GPC traces of cross-coupling polymerization of bis-calix[4]arene **1** with 1,4-diethynylbenzene: (a) polymerization mixture after 24 h (gray line), (b) isolated **CALIX-PPE** (solid line). For comparison, the chromatogram of bis-calixarene **1** is also shown (thin line).

were normally achieved, being the polymers freely soluble in common nonprotic organic solvents (e.g., THF,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , toluene). The GPC traces of the polymerization mixtures revealed that after 24 h of reaction the conversion of **1** was higher than 98% and only a presumable dimeric species ( $M_{\text{p(GPC)}} \approx 2624 \text{ g mol}^{-1}$ ), roughly corresponding to two units of the bis-calixarene **1** ( $M_{\text{p(GPC)}} \approx 1291 \text{ g mol}^{-1}$ ), could in addition be detected (1.8%). **CALIX-PPE** was isolated as a yellow solid in yields higher than 95% (several runs) showing by GPC a monomodal distribution (Fig. 1); the lower molecular weight product assigned to the dimer accounted for less than 1.5% of the isolated polymer. The degree of polymerization (DP) based on the  $M_n$  (GPC) was 13.

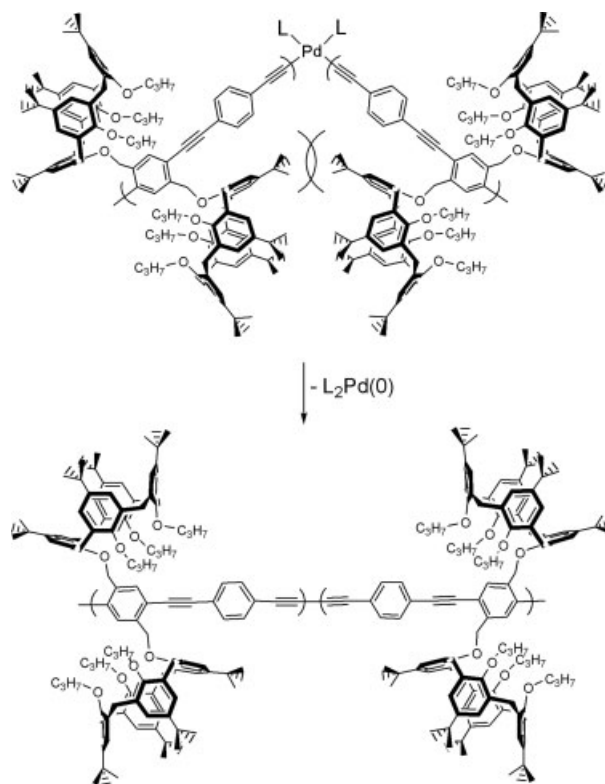
It is well known that alkyne homocoupling is a recurrent side reaction in the course of the Sonogashira coupling. In the present case, this would mean that the polymer chain might contain some segments resulting from the oxidative coupling of ethynyl-terminated intermediates generated during the polymerization, leading to an irregular sequence of the repeating units along the polymer. To prevent the oxidative homocoupling, practical measures normally involve thorough degassing of the reaction mixtures and/or addition of radical inhibitors.<sup>20</sup> In our case it was found that, in addition

to careful degassing, the use of freshly distilled solvents ( $\text{NEt}_3$  and toluene) was of utmost importance for the final outcome of the polymerization.

We reasoned, however, that in the polymerization of **1** this side reaction do not occur to any appreciable extent because of the high steric hindrance, which would develop in the  $\text{Pd(II)}$ -acetylide complex generated from  $(\text{PPh}_3)_2\text{Pd(0)}$  and ethynyl terminated bis-calixarene-derived intermediates (Chart 2), since a *cis* relationship should be attained between them in order for the reaction to proceed.<sup>19,20</sup>

In the case of monomer **2**, such steric constraints should not occur because the intervening partners are much less sterically demanding.

Of course the above reasoning does not exclude the presence of diynyl segments along the polymer chain as the homodimer resulting from the oxidative coupling of 1,4-diethynylbenzene during the formation of the active  $\text{Pd(0)}$  catalytic species,



**Chart 2.** Idealized structures in the homocoupling of terminal ethynyl derivatives: dialkynylpalladium (II)-intermediate (above) and the polymer segment containing the 1,3-butadiyne moiety (below) that would result after reductive elimination.

is available in the reaction mixture and thus could participate in subsequent cross-coupling reactions.

### Polymerization of 1,4-Bis(4-tert-butyl-phenoxymethyl)-2,5-diiodo-benzene 2

The polymerization of **2** was effected under similar conditions of those described for the polymerization of **1**. Some comments are, however, in order. When the polymerization was carried out at 35 °C for 24 h, conversion only reached 85% (based on **2**). The GPC trace of the reaction mixture was multimodal showing a  $M_{p(\text{GPC})}$  of 9200 g mol<sup>-1</sup> for the highest peak. During the work-up an insoluble material persisted at the interface when the residue from evaporation was taken in CH<sub>2</sub>Cl<sub>2</sub>/aq. HCl; after filtration, attempts to get it dissolved (prolonged sonication in a large excess of CH<sub>2</sub>Cl<sub>2</sub> or toluene or hot toluene) proved ineffective. This insoluble fraction, obtained as a dark orange solid, accounted for 72% of total weight of isolated materials. The soluble fraction, obtained as a yellow powder, was composed by dimers, trimers, and higher oligomers with a  $M_n$  of 3700 g mol<sup>-1</sup> ( $M_{p(\text{GPC})}$  of 5200 g mol<sup>-1</sup> for the highest peak). Both fractions presented identical FTIR spectra, which revealed the similarity of polymeric structures obtained, differing only on their molecular weights.

Performing the cross-coupling of **2** at a higher temperature (10 h at 35 °C followed by 13 h at 65 °C), a soluble yellow polymer was obtained in 79.5% yield, with a number-average molecular weight of 3550 g mol<sup>-1</sup> ( $M_w/M_n = 1.56$ ; DP, based on  $M_n = 7$ ; GPC trace: Fig. S7). The amount of insolubles in this case was negligible.

### Structural Characterization of Polymers

The FTIR spectrum of **CALIX-PPE** resembles, in general, that of bis-calix[4]arene **1**. The characteristic frequencies, revealing the main structural differences between them, can be found at 2201 cm<sup>-1</sup>, which identifies the ethynyl stretching vibration of the disubstituted acetylene ( $-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}-$ ) and the bands attributable to the newly introduced 1,4-disubstituted benzene moiety with the stretching vibration appearing at 1511 cm<sup>-1</sup> and the corresponding C—H deformation vibration of the benzene ring at 836 cm<sup>-1</sup>. The presence of  $-\text{Ph}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Ph}-$  segments in the polymer backbone, possible origi-

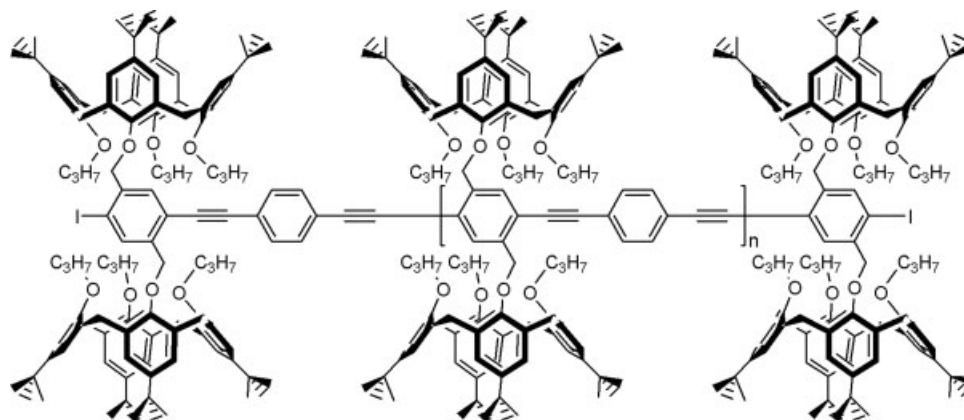
nated from the homocoupling of end-terminated acetylenic functionalities, were not found; however, their existence could not be excluded by this analysis because their stretching bands fall in the same region, with similar low intensity, as that described above for the cross-coupled product. In addition, no triple-bond nor ethynyl  $\text{C}\equiv\text{C}-\text{H}$  stretching vibrations (which should appear around 2100 cm<sup>-1</sup> and 3250–3300 cm<sup>-1</sup>, respectively) were discernible in the spectrum.

For **TBP-PPE** polymer, characteristic bands appear at 2204 cm<sup>-1</sup> (ethynyl stretching vibration,  $-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}-$ ), at 1511 cm<sup>-1</sup> due to the 1,4-disubstituted benzene moiety, with the corresponding PhC—H deformation vibration appearing at 829 cm<sup>-1</sup>. The ethynyl  $\text{C}\equiv\text{C}-\text{H}$  and  $\text{C}\equiv\text{C}-\text{H}$  stretching vibrations were not present in the spectrum.

The <sup>1</sup>H and <sup>13</sup>C NMR analysis of **CALIX-PPE** and **TBP-PPE** gave a full account of the structure of each polymer. As a distinctive feature in both polymers, no terminal acetylenic C—H protons were found in their spectra, corroborating the FTIR data. Therefore, both polymers seem to be end-terminated by an aryl-iodide functionality.

The <sup>1</sup>H NMR spectrum (Fig. S8) of **CALIX-PPE** shows, at high field, three signals for the *t*-butyl groups of the two distal *O*-propylated-phenol subunits at 1.26, 1.27 (partially overlapped), and 1.31 ppm, at an approximate 9:1:1 ratio (integrating for 36 H). This could be tentatively explained by the three distinct types of environment surrounding each subunit (terminal outward, terminal inward and middle chain *t*-butyl groups; see Chart 3).

The remaining resonances in this part of the spectrum do not deserve any special comment (see Experimental Section for assignments). The *exo*-bridging methylene protons resonate at 3.11 ppm ( $J = 11.1$  Hz) and those of the *endo*-CH<sub>2</sub> at 4.41 and 4.55 ppm ( $J = 11.4$  Hz) as should be expected for the embedded calix[4]arene cone conformer units. The benzylic protons appear as three distinct broad singlets at 4.875 and 5.05 ppm, assigned to  $-\text{CH}_2-\text{Ar}(\text{ortho-I})$  and  $-\text{CH}_2-\text{Ar}(\text{meta-I})$  of the terminal units of **CALIX-PPE**, respectively, (cf. Chart 3), and the remaining at 5.10 ppm corresponding to the middle chain units' benzylic protons; their relative integrals were computed to 1:1:7.5. The aromatic calixarene protons, integrating overall to 16H, appear as singlets at 6.54, 6.56, and 7.00 ppm with additional resonances in the nearby attributable to those of the terminal units. Two sets of



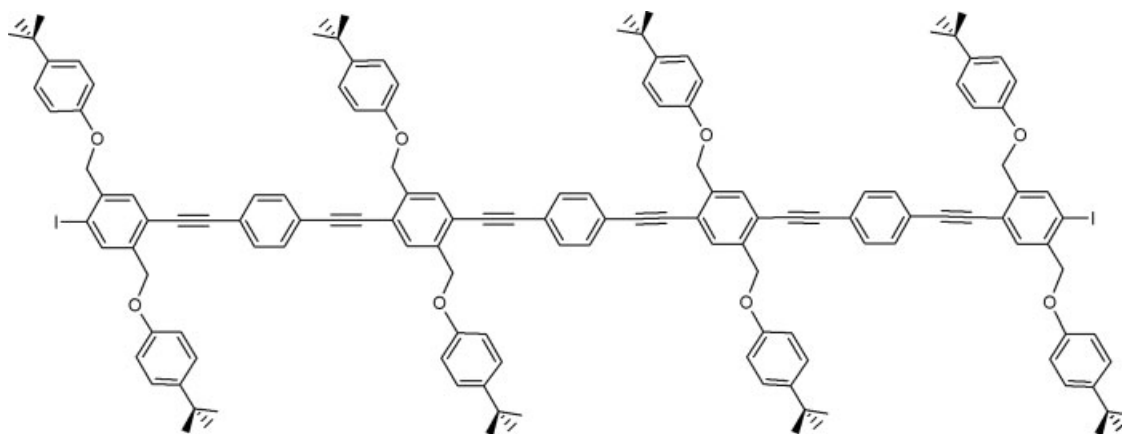
**Chart 3.** Proposed structure of **CALIX-PPE** polymer based on  $^1\text{H}$  NMR end-group analysis ( $n = 9$ ).

broad multiplets emerge at 7.33–7.45 and 7.45–7.57 ppm which were assigned to the 1,4-disubstituted benzene repeat unit (at the middle of the polymer chain and at its ends, respectively). At last, three broad singlets could also be detected in the low field region (7.85, 7.965, and 8.19 ppm), with a  $\sim 1:9.5:1$  ratio, attributed respectively, to *ortho*-H-ArI, middle chain  $\text{H-Ar}(-\text{C}\equiv\text{C-})_2\text{-H}$  and *meta*-H-ArI 1,2,4,5-tetrasubstituted benzene protons.

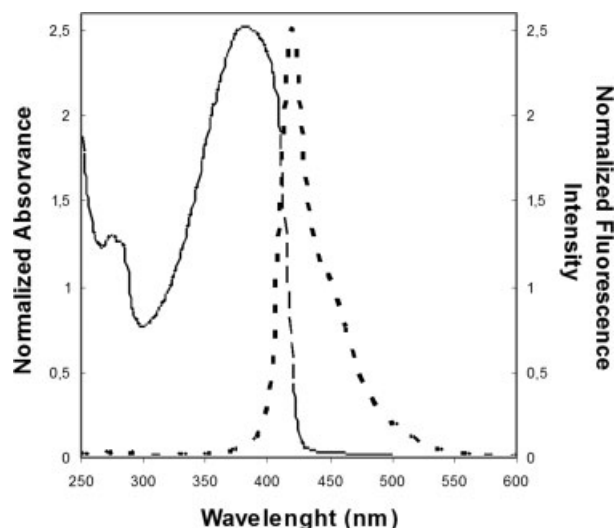
The foregoing data, showing fairly close integration ratios between different sets of considered protons, seems to clearly point to a polymer comprising about nine middle repeat units and two iodide-terminated units. This end-group analysis correlates reasonable well with the GPC data, where the calculated DP based on  $M_n$  was 13. It is

worth mentioning that for rigid-rod-type polymers, for instance those of alkyl-substituted *p*-phenylene ethynylene and thiophene ethynylene type, the computed  $M_n$  based on polystyrene standards (which are randomly coiled) are normally inflated relative to the actual molecular weights.<sup>21</sup>

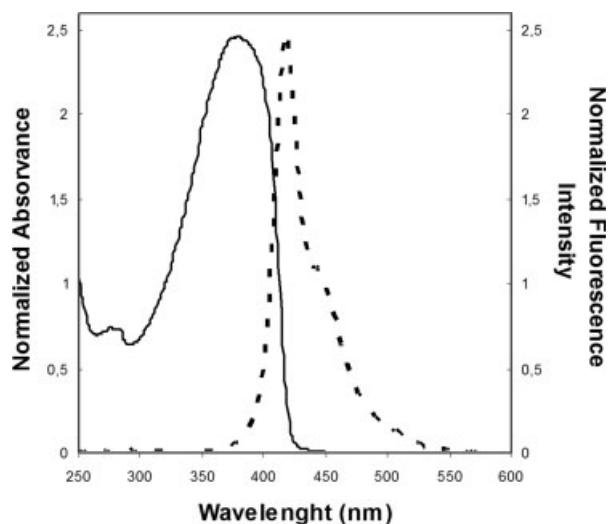
Analysis of **TBP-PPE**  $^1\text{H}$  NMR spectrum (Fig. S9) revealed that for this polymer the overestimation of its molecular weight by GPC was particularly high. Indeed, the GPC analysis point to a DP of 7, whereas the NMR end-group calculations furnishes only four repeat units (DP = 4). Thus, integration of the peaks assigned to benzylic protons (5.01, 5.23 and 5.285 ppm; ratio  $\sim 1:1:2$ ) and that of the end-chain *ortho*-H-ArI, middle chain  $\text{H-Ar}(-\text{C}\equiv\text{C-})_2\text{-H}$  and end-chain *meta*-H-ArI



**Chart 4.** Proposed structure of **TBP-PPE** polymer.



**Figure 2.** Absorption (solid line) and fluorescence (dotted line) spectra of **CALIX-PPE** in chloroform ( $5 \times 10^{-5}$  M). The laser induced luminescence spectrum (argon-deaerated equilibrated solution, room temperature) was recorded immediately after laser pulse, at an excitation wavelength of 337 nm.



**Figure 3.** Absorption (solid line) and fluorescence (dotted line) spectra of **TBP-PPE** in chloroform ( $5 \times 10^{-5}$  M). The laser induced luminescence spectrum (argon-deaerated equilibrated solution, room temperature) was recorded immediately after laser pulse, at an excitation wavelength of 337 nm.

1,2,4,5-tetrasubstituted benzene protons, respectively, at 7.70, 7.78, 8.09 (ratio  $\sim 1:2:1$ ), strongly suggests that **TBP-PPE** has the structure depicted in Chart 4.

The  $^{13}\text{C}$  NMR spectra of **CALIX-PPE** and **TBP-PPE** are shown on Figs. S10 and S11, respectively.

### Photophysical Properties

**UV-vis and Fluorescence.** The absorption and the laser induced luminescence spectra of **CALIX-PPE** and **TBP-PPE** are illustrated in

Figures 2 and 3. Absorption bands peaking at 382 and 380 nm were observed for **CALIX-PPE** and **TBP-PPE**, respectively. From the low energy onset of the absorption bands, similar optical HOMO–LUMO energy gaps ( $E_g$ ) were found for the two polymers ( $E_{g(\text{CALIX-PPE})} = 2.91$  eV;  $E_{g(\text{TBP-PPE})} = 2.93$  eV). These data suggest that the polymers have analogous conjugation lengths, in spite of the higher DP attained for **CALIX-PPE**, as calculated from the GPC and NMR end-group analysis, probably implying that significant steric hindrance effects are imparted by the calixarene units, which limits a more extended coplanarity of the conjugated backbone.

**Table 1.** Photophysical Properties of **CALIX-PPE** and **TBP-PPE** Polymers

Polymer	$M_n$ ( $\times 10^{-3}$ g mol $^{-1}$ ) [ $M_w/M_n$ ] <sup>a</sup>	$E_g^b$ (eV)	$\lambda_{\text{max, abs}}$ (nm) ( $\text{CHCl}_3$ ) [ $\epsilon_{\text{max}}$ ] ( $\times 10^{-4}$ M $^{-1}$ cm $^{-1}$ )	$\lambda_{\text{max, em}}$ (nm) ( $\text{CHCl}_3$ )	Stokes shift <sup>c</sup> (nm)	$\phi_F^d$ in $\text{CHCl}_3$ (THF)
<b>CALIX-PPE</b>	23.3 [2.05]	2.91	382 [5.87]	420	38	$0.43 \pm 0.03$ ( $0.37 \pm 0.03$ )
<b>TBP-PPE</b>	3.5 [1.56]	2.93	380 [5.77]	419	39	$0.51 \pm 0.03$ ( $0.42 \pm 0.03$ )

<sup>a</sup>The  $M_n$  and polydispersity ( $M_w/M_n$ ) were determined by GPC (THF, 35 °C, polystyrene standards).

<sup>b</sup>The energy gaps ( $E_g$ ) were calculated from the low energy onset of the absorption bands.

<sup>c</sup>The Stokes shifts were calculated from  $\lambda_{\text{max, em}} - \lambda_{\text{max, abs}}$ .

<sup>d</sup>Fluorescence quantum yields determined by the absolute method (see text); by this method, 9,10-DPA (EtOH) gave a  $\phi_F = 0.72 \pm 0.03$  (lit.:<sup>16</sup>  $0.69 \pm 0.03$ ; air-equilibrated conditions).

Similar and large molar absorptivities ( $\epsilon$ , Table 1) were found for the two polymers, clearly showing that the  $\pi \rightarrow \pi^*$  electronic transitions of polymers' main chain are strongly allowed.

The fluorescence spectra of polymers are of nearly identical shape, displaying their maximum emission around 420 nm. Spectra were obtained both with air-equilibrated conditions and in argon-deaerated samples and no differences were found within experimental error.

The similitude of the photophysical properties of **CALIX-PPE** and **TBP-PPE** polymers (Table 1) in solution clearly demonstrate that they are uniquely dependent on the structure and conformation of the conjugated PPE backbone.

**Photoluminescence Quantum Yield.** Several methods have been proposed for the measurement of the absolute photoluminescence efficiency, using an integrating sphere to collect the emitted light (hollow sphere, coated in the inside with a diffuse reflecting material, typically, barium sulfate, magnesium oxide, or thermoplastic resins).<sup>22,23</sup> Photoluminescence quantum yield (PLQY) calculations here described have followed a literature procedure based on an absolute method.<sup>23</sup> Using this method, the PLQY determination of a standard fluorophore, 9,10-diphenylanthracene (9,10-DPA), with a known quantum yield, was also performed for validation purposes. It was found that a very good agreement exists between the  $\phi_F$  calculated for this compound by the absolute method and that reported in the literature<sup>16</sup> (see Table 1), thus validating the polymer photoluminescence quantum yields here determined. The luminescence quantum yields of the polymers were measured in dilute  $\text{CHCl}_3$  and THF solutions in which an optical density of 0.16 was set at the excitation wavelength (337 nm); an identical procedure was used for 9,10-DPA in dilute EtOH solution. The fluorescence quantum yields were obtained by the use of the following equations:

$$\phi_F = P_c - (1 - A)P_b / AL_a \quad A = (1 - L_c / L_b)$$

where  $A$  is the absorption coefficient,  $P_b$  is the light emitted by the sample after absorption of scattered excitation light,  $P_c$  is the light emitted by the sample after absorption of total laser light,  $L_a$  is the total amount of excitation laser light,  $L_b$  is the scattered laser light, and  $L_c$  is excitation light spectrum. The results are shown in Table 1 along with other photophysical properties of the polymers.

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## CONCLUSIONS

Cross-coupling polymerization of bis-calix[4]arene **1** with 1,4-diethynylbenzene was successfully accomplished leading to a novel fluorescent (*p*-phenylene ethynylene)-calix[4]arene-based polymer (**CALIX-PPE**). The conjugated PPE-type polymer, obtained in excellent yield, showed high solubility in several common organic solvents, having the collected spectroscopic data analyses allowed its full structural characterization. The design and synthetic methodology here disclosed, using **CALIX-PPE** as an example, open new opportunities for the development of a diversity of other differently functionalized calixarene-based PPE polymers, which can be structurally tailored to match various application targets. The exploitation of this type of materials for sensing devices is currently underway.

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