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Efficient Electron Delocalization Mediated by Aromatic Homoconjugation in 7,7-Diphenylnorbornane Derivatives[†]

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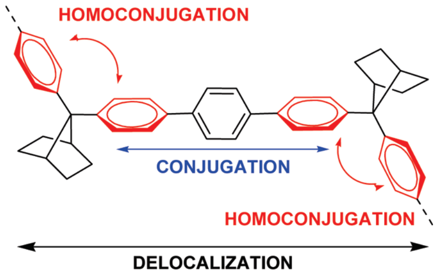

Efficient electron delocalization by aromatic homoconjugated 7,7-diphenylnorbornane (DPN) in alternated homoconjugated−conjugated block copolymers and reference compounds is revealed by photophysical and electrochemical measurements. The synthesis of the polymers was achieved by Suzuki polycondensation reaction. Effective electron delocalization by DPN is demonstrated by the significant red shifts observed in the absorption and emission spectra and the variation of the energy band gap of the polymers and monomeric model compounds in comparison to a series of oligophenylenes used as references (*p*-quaterphenyl, *p*-terphenyl, and biphenyl). The electron delocalization is also clearly demonstrated by the lower oxidation potential measured for homoconjugated model compound in comparison to *p*-terphenyl. The results show that the electron delocalization caused by two homoconjugated aryl rings is comparable to the effect produced by one conjugated aryl ring.

Introduction

Electron delocalization in covalently linked molecules is one of the most important and widely studied phenomena in organic chemistry.[1] During the last decades, conjugated polymers[2] and oligomers[3] have attracted great interest in material science due to their fascinating semiconducting and NLO properties, among others. Orbital overlap in these systems is the basis of their potential applications in the emerging areas of molecular electronics and nanotechnology,[4] as organic semiconductors,[5] light-emitting diodes (OLEDs),[6] organic field effect transistors (OFEDs),[7] polymer lasers,[8]

[†] Dedicated to Prof. Antonio García Martínez on the occasion of his partial retirement.

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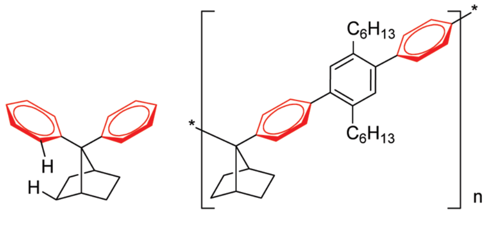
organic photovoltaic and solar cells,[9] and biological and chemical sensors.[10] It is well-known that the nature of the interactions between the π systems in these oligomers and polymers governs their properties and that small variations in their structures can modify the characteristics and, as a result, the applications of these materials. Therefore, the study of structure−property relationships to develop new applications is of great importance.[2−4,11] A very interesting way to achieve structure−property studies is by incorporating nonconventional methods of electronic communication in electron-delocalized molecules. In that respect, the search for alternative modes of interaction between organic π systems has recently led to a variety of new structures with promising electronic features: aromatic derivatives with toroidal delocalization,[12−15] spiro compounds,[16−18] cross-conjugated molecules,[19−21] and π-stacked systems.[22−29] In particular, π-stacked systems are very interesting as model compounds in the study of electron-transfer processes mediated by DNA oligonucleotides.[27,30,31]



1 (DPN) 2

FIGURE 1. Structures of 7,7-diphenylnorbornane (**1**) (DPN) and polymer **2**.

In recent years, we have focused our attention on aromatic homoconjugated systems derived from 7,7-diphenylnorbornane (**1**, DPN, Figure 1).[32] DPN is an easily accessible homoconjugated and preorganized system that can be considered as an example of an open-chain cyclophane (protophane, according to the definition by Vögtle)[33,34] since the H-*exo* atoms of the norbornane skeleton hinders the rotation of the aryl rings, resulting in a cofacial aromatic π-system bridged by a sp^3-hybridized spacer (homoconjugated), with barriers to rotation of the aryl rings in DPN′s in the range of 12.5−17.5 kcal/mol.[32,35] On the basis of these characteristics, DPN has shown to be a good model system for the study of aromatic face-to-face[35] and edge-to-face[36] interactions, the design of homoconjugated NLO-active chromophores,[37] and the synthesis of preorganized macrocycles able to act as molecular clocks.[38]

On the other hand, organic oligomers and polymers in which electron delocalization takes place through aromatic homoconjugation remain almost unexplored, despite their potential interest due to the similar properties that these nonconventional delocalized systems could exhibit in comparison to conjugated oligomers and polymers. In previous works, we have described the first examples of a soluble polymer with alternating conjugation−homoconjugation[39]

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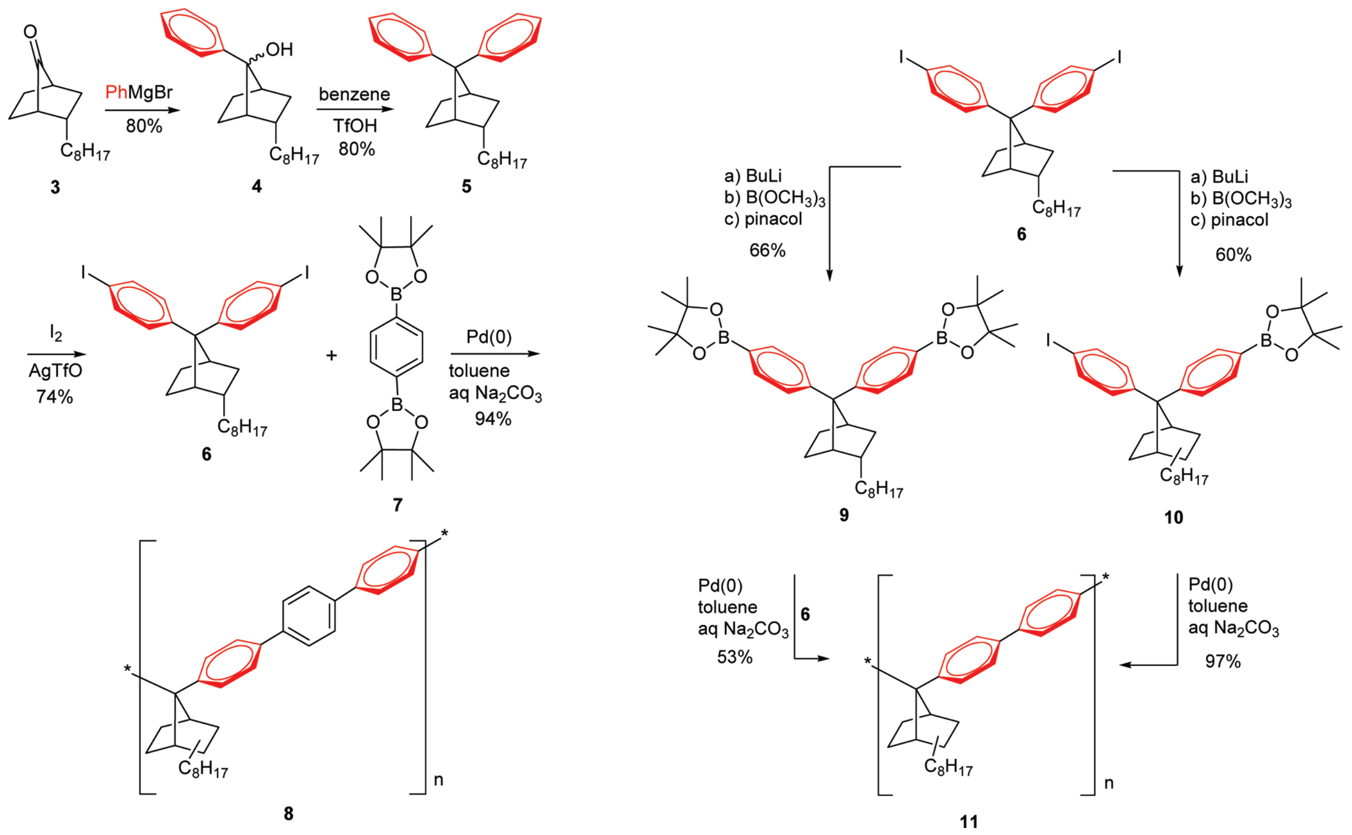
SCHEME 1. Synthetic Route for the Preparation of Polymers 8 and 11



as well as homoconjugated oligomers[40] based on DPN. In both cases, the cofacial DPN subunits contribute effectively to the electronic delocalization along the structures of the molecules. In the case of homoconjugated oligomers derived from DPN, we have shown that the effective length of homoconjugation is in the range of five to six phenyl rings.[40] Some examples of systems that include diphenylmethane (DPM) subunits in their structure have been described, but in these cases, noncofacial DPM acts mainly as conjugation interrupter or barrier.[4b,41−44] In conjugated polymeric systems, block copolymers are obtained by the introduction of nonconjugative interrupters in the main chain. The strategy of including conjugated sequences separated by nonconjugated spacers or fragments is an important tool in order to tailor the morphology, processability, and stability as well as optical and electrical properties of the corresponding materials since such polymers are expected to retain the electronic and optical properties of the conjugated oligomeric chromophores.[2,4,45] In the present work we gain further insight into the synthesis and properties of a new class of fluorescent polymers with alternated homoconjugated−conjugated backbone structure. Unlike similar block copolymers, cofacial DPN′s contribute efficiently to electron delocalization along the polymer chain.

Results and Discussion

Synthesis of Polymers and Reference Compounds. In a previous paper,[39] we have described the synthesis of the alternating homoconjugated−conjugated polymer **2** (Figure 1) by Suzuki polycondensation reaction.[46] Hexyl alkyl chains were introduced in the *p*-terphenyl segment in order to increase the solubility of the polymer. However, the steric hindrance caused by these chains increases the torsional angle between the aryl rings, and as a consequence, the conjugation in the *p*-terphenyl subunit and the electronic delocalization in the polymer decreased. Now we report the syntheses of two new block-copolymers with alternating homoconjugation−conjugation **8** and **11** (Scheme 1) and compare their electronic properties with those found in polymer **2**. Alkyl chains (n-C_8H_{17}), necessary to ensure the solubility of the polymers, are now introduced as

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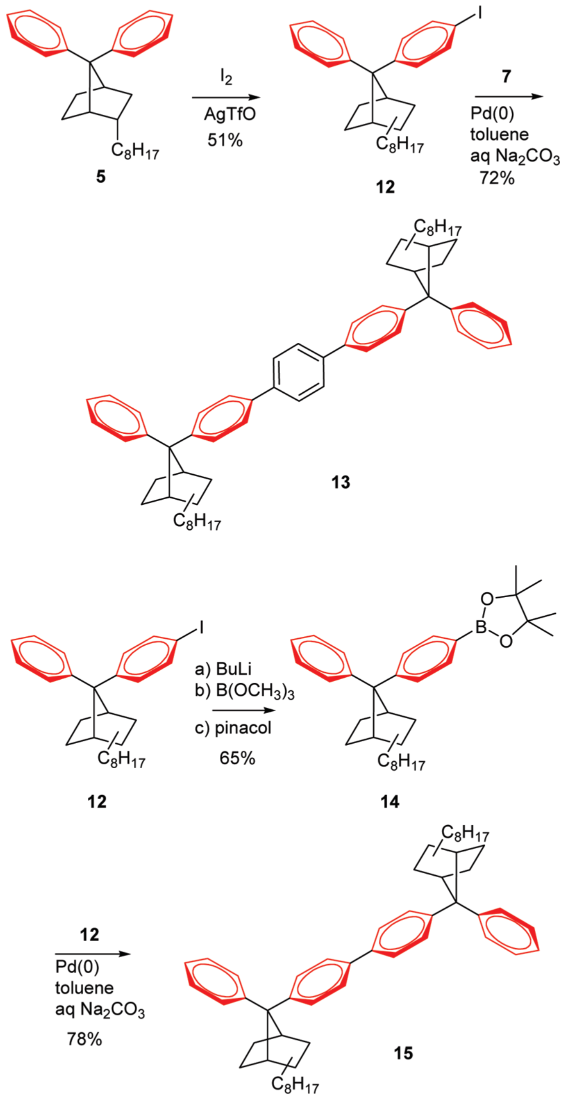
SCHEME 2. Synthetic Route for the Preparation of Reference Compounds 13 and 15



substituents in the norbornane skeleton with the idea of increasing the conjugation in the *p*-terphenyl and biphenyl subunits. As can be seen, the main difference between **8** and **11** is the relative contribution of homoconjugation vs conjugation to the backbone structure of the polymers, since **8** can be described as a series of DPN subunits bridged by *p*-phenylene rings, while in the case of **11**, the DPN's are linked together, yielding a polymer with a higher degree of homoconjugation than **8**.

Polymers **8** and **11** were prepared starting from 2-*endo*-octyl-7-norbornanone (**3**)[40] according to the synthetic procedure described in Scheme 1 employing the Suzuki polycondensation methodology followed previously by us in the case of **2**.[39] In order to facilitate the elucidation of the structures of polymers **8** and **11** as well as the study of their properties, we have also synthesized the corresponding monomeric reference compounds **13** and **15** by Suzuki coupling reactions of iodide **12** and boronates **7** or **14** (Scheme 2). Although boronic acids have been often directly used as reagents in poly-Suzuki couplings, boronic esters like **9**, **10**, or **14** have proven to be more advantageous in this kind of reactions, since the presence of the 1,1,2,2-tetramethylethylene glycol units has a protective effect on the labile boronic acid precursor. Simultaneously to the polymerization, a hydroxylation deprotection process takes place in which the removal of such protecting groups as ethylene glycol does not affect the couplings.[46f,g]

TABLE 1. Properties of Polymers 8, 11, and 2

compd	yield (%)	M_w[a]	M_n[a]	PDI[a]	λ_{abs}[b]	λ_{em}[b]	Stokes shift[b]	λ_{onset}[b]	E_g^{opt} (eV)
8	94	3470	2600	1.3	298	366	68	342	3.62
11	97	6440	4650	1.4	283	337	54	319	3.89
2	94	21600	8820	2.4	268	348	80	308	4.02

[a] Determined by GPC in THF by using a calibration curve of polystyrene standards. [b] In nm.

Polymer **8** is obtained in almost quantitative yield by Pd(0)-catalyzed reaction of diiodide **6** with diboronate **7** (Scheme 1). If benzene-1,4-diboronic acid is used instead of **7**, the yield of polymer **8** diminishes considerably. As shown in Scheme 1, two different protocols were followed for the synthesis of polymer **11**: (i) condensation of two different monomers **9** and **6** (AA-type monomer + BB-type monomer) and (ii) condensation of bifunctional monomer **10** (AB-type monomer). The best results (97%) were obtained by polycondensation reaction of iodoboronate **10** catalyzed by $[Pd(PPh_3)_4]$.

Both polymers were obtained as white solids, soluble in common organic solvents (toluene, THF, $CHCl_3$) and show the expected spectroscopic (^1H and ^{13}C NMR) signals. We have shown that one of the main advantages of Suzuki polycondensation reactions is the high regioselectivity of the catalytic process that allows the synthesis of structurally well-defined polymers.[39,46] The structures of **8** and **11** were confirmed by comparison of their NMR spectra with those of reference compounds **13** and **15**.

Gel permeation chromatography (GPC) revealed the following degrees of polymerization and polydispersities (PDI): **8**: M_w = 3470, M_n = 2600, PDI = 1.3; **11**: M_w = 6440, M_w = 4650, PDI = 1.4 (Table 1). The degrees of polymerization of **8** and **11** are lower than the obtained previously for the analogous polymer **2** under the same reaction conditions. The reason is probably their lower solubility due to the fact that only one alkyl chain has been introduced in the structure of norbornane.

Optical and Electrochemical Properties. The most relevant information from polymers **8** and **11** in relation to the extension of electron delocalization is obtained from their absorption spectra (Table 1) and the electrochemical behavior of reference compound **13** (Table 2). It is well established that a convenient way to study electron delocalization in polymers is by means of absorption spectroscopy, comparing the spectra of the polymers and monomeric model compounds.[47] Extension of π-conjugation causes bathochromic shifts of the $\pi-\pi^*$ bands of the polymers relative to the absorption of the reference compounds. The λ_{max} values of **8** and **11** as well as of polymer **2** are shown in Table 1. The λ_{max} values of reference compounds **13** and **15** as well as those of *p*-quaterphenyl, *p*-terphenyl, and biphenyl

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TABLE 2. Properties of Reference Compounds 13 and 15 and *p*-Quaterphenyl, *p*-Terphenyl, and Biphenyl

compd	$\lambda_{abs}{}^{a,b}$	$\lambda_{em}{}^{a,b}$	Stokes shift^b	$\lambda_{onset}{}^b$	$E_g{}^{opt}$ (eV)	$E_{oxd}{}^{1/2}$(V)	E^{HOMO} (eV)	E^{LUMO} (eV)
13	295	361	66	335	3.70	1.11^c 1.18, 1.43^d	−5.37	−1.67
15	272	325	53	310	4.00			
p-quaterphenyl	292	364	72	334	3.71	1.09^c	−5.41	−1.70
p-terphenyl	274	338	64	312	3.97	1.44^d(1.5^e)	−5.56	−1.59
biphenyl	247	315	68	278	4.46			

^{a}In CH_2Cl_2. ^{b}In nm. ^{c}In CH_2Cl_2 containing 0.1 M $n\mathrm{Bu_4NClO_4}$ as supporting electrolyte; potentials were recorded using Ag/AgCl as reference electrode, and values are given vs Fc/Fc$^+$. ^{d}In CH_3CN containing 0.1 M $n\mathrm{Bu_4NClO_4}$ as supporting electrolyte; potentials were recorded vs Ag/AgCl and calibrated with Fc/Fc$^+$. ^{e}See ref 50b.

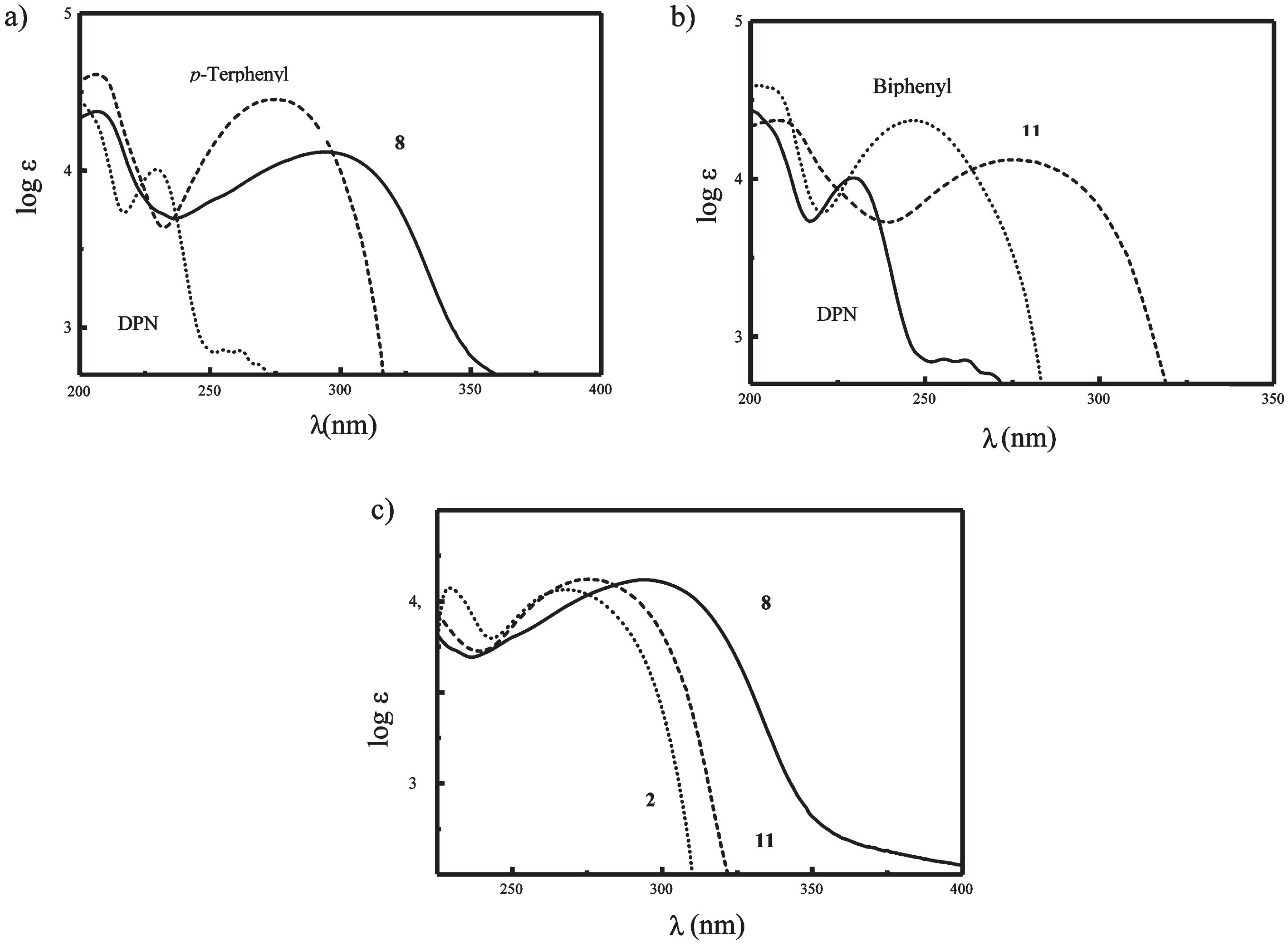

FIGURE 2. (a) Absorption spectra of polymer **11**, 7,7-diphenylnorbornane (DPN), and biphenyl. (b) Absorption spectra of polymer **8**, 7,7-diphenylnorbornane (DPN), and *p*-terphenyl. (c) Absorption spectra of polymers **8**, **11**, and **2**.

are also included in Table 2 for comparison. The corresponding absorption spectra are displayed in Figure 2: (a) polymer **8**, DPN, and *p*-terphenyl; (b) polymer **11**, DPN, and biphenyl; (c) polymers **8**, **11**, and **2**.

In previous works we shown that, as a result of aromatic homoconjugation, the absorption spectrum of cofacial DPN shows an additional band centered at 228 nm (Figure 2).[32,35,40] In DPN oligomers, this band shows a red shift on going from the monomer to the tetramer (250 nm), pointing to effective electron delocalization in aromatic homoconjugated systems. When DPN subunits are attached at the end of *p*-terphenyl (reference compound **13**) or biphenyl (reference compound **15**), the characteristic absorption bands of these hydrocarbons[48] are bathochromically shifted from 274 to 295 nm in the case of *p*-terphenyl (Δλ = 21 nm) and from 247 to 272 nm in the case of biphenyl (Δλ = 25 nm) (Table 2), showing the effect that the addition of homoconjugated subunits exerts on the electronic properties of the corresponding systems. On the other hand, the corresponding spectra of polymers **8** and **11** are red-shifted in

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(48) For a study on absorption spectra and effective conjugation length of oligo-*p*-phenylenes, see: Grimme, J.; Kreyenschmidt, M.; Uckert, F.; Müllen, K. *Adv. Mater.* **1995**, *7*, 292–295.

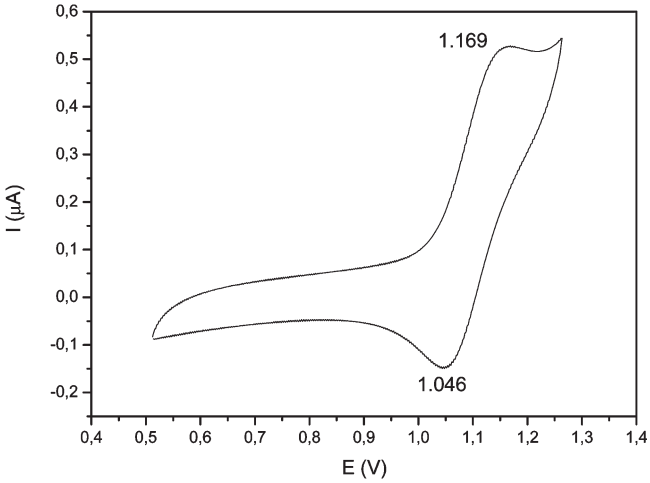

FIGURE 3. Cyclic voltammogram of compound **13** in 0.1 M n-$Bu_4NClO_4-CH_2Cl_2$.

comparison to reference compounds **13** and **15**, which further evidence the effect of homoconjugation on the electronic properties of these materials. Figure 2a shows the spectra of DPN, **8**, and p-terphenyl, and as can be seen, the spectrum of **8** shows a broad absorption between 235 and 350 nm, centered at 298 nm and red-shifted in comparison to p-terphenyl (24 nm). Polymer **11** (Figure 2b) also shows a broad band centered at 283 nm and bathochromically shifted in comparison to biphenyl (36 nm) and **15** (11 nm). Finally, Figure 2c shows the spectra of polymers **8**, **11**, and **2**. The higher value of λ_{max} is observed for the polymer containing the longest conjugated subunit (polymer **8**, p-terphenyl).

As expected, introduction of alkyl chains, needed to ensure the solubility of the materials, in the structure of norbornane instead of in the p-terphenyl subunit (polymers **8** and **2**) increases the conjugation, and as a consequence, a bathochromic shift (30 nm) of the corresponding absorption band is observed (Table 1). It should be noted that the λ_{max} of polymer **11**, with biphenyl instead of p-terphenyl subunits, is red-shifted in comparison to polymer **2**, also because of the distorting influence of the alkyl chains in the case of **2**.

The optical band gap (E_g^{opt}) of polymers **8**, **11**, and **2** (Table 1) and reference compounds **13** and **15** (Table 2) can be obtained from the edge of the absorption spectra (λ_{onset}) using the equation $E_g^{opt} = 1240/\lambda_{onset}$. The smaller band gap is obtained for polymer **8** (3.62 eV), which shows higher electron delocalization than polymers **11** (3.89 eV) and **2** (4.02 eV). Comparison of the band gaps of compounds **13** (3.70) and **15** (4.00 eV) with those of p-terphenyl (3.97 eV) and biphenyl (4.46 eV), respectively, indicates again an extension of the electron delocalization via homoconjugation with the DPN subunits. Therefore, the band gap of **13** (3.70 eV) is almost the same as that obtained for p-quaterphenyl (3.71 eV) and the corresponding band gap obtained for **15** (4.00 eV) very similar to the value measured for p-terphenyl (3.97 eV). These results, as well as the data obtained from the emission spectra (vide infra), suggest that the homoconjugative effect of two DPNs is comparable to the delocalization caused by an additional conjugated phenyl ring. In summary, the results obtained from the absorption spectra of all the compounds described in this work clearly show that the homoconjugated subunits of DPN contribute significantly to electron delocalization and, hence, to the electronic properties of the polymers. This situation differs from the described for other poly(biphenylmethylene)s in which the methylene group interrupts the conjugation between the aromatic groups.[49]

We have also used cyclic voltammetry to prove the electronic delocalization caused by the homoconjugated DPN subunits. The compounds described in this work are relatively difficult to oxidize and reduce and, for this reason, we have limited the study to model compound **13** as well as p-terphenyl and p-quaterphenyl.[50] We have determined the oxidation potentials both in CH_2Cl_2 and acetonitrile due to the different solubility of p-terphenyl and p-quaterphenyl. The results are summarized in Table 2. In CH_2Cl_2, **13** exhibited one reversible oxidation potential at 1.11 V (Figure 3) (two irreversible oxidation processes at 1.18 and 1.43 V were recorded in acetonitrile). As can be seen, the oxidation potential of **13** (1.11 V, CH_2Cl_2) is almost the same than the oxidation potential of p-quaterphenyl (1.09 V, CH_2Cl_2), but considerably lower than the oxidation potential of p-terphenyl (1.18 vs 1.44 V, both measured in acetonitrile), which further supports the previously mentioned similar effect of two DPNs and one phenyl ring on electron delocalization. On the other hand, the difference between the first and the second oxidation potentials in **13** (0.25 V, acetonitrile) points to efficient radical cation delocalization along the homoconjugated backbone.

The corresponding HOMO energy values (Table 2) have been calculated from the onset of the oxidation potentials (**13**: 1.03 eV; p-quaterphenyl: 1.07 eV; p-terphenyl: 1.22 eV) using the equation $-E^{HOMO} = E_{oxd}^{onset} + 4.44$ eV.[51] Unfortunately, we were not able to measure the reduction potential of **13**, and therefore, the corresponding LUMO energy level as well of those of p-quaterphenyl and p-terphenyl could only be estimated from the HOMO energy levels and the optical band gaps ($E^{LUMO} = E^{HOMO} + E_g^{opt}$) (Table 2). These results show that linking two DPN subunits to p-terphenyl increases the energy of the HOMO orbital of p-terphenyl from -5.56 eV to -5.37 eV, a value slightly higher than the HOMO orbital of p-quaterphenyl (-5.41 eV). A similar situation is observed for the LUMO energy values, pointing to the effective electronic delocalization caused by the homoconjugated DPN subunits.

Fluorescent Properties. The fluorescence emission spectra of polymers **8**, **11**, and **2** as well as of those of reference model compounds **13** and **15** (Tables 1 and 2) measured in CH_2Cl_2 are shown in Figure 4. The emission peaks of all the compounds studied are observed in the UV region, between 366 and 337 nm in the case of the polymers and at 361 and 325 nm in models **13** and **15**, respectively, as expected for compounds with p-phenylenes as chromophores. The

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(49) Only a few examples of poly(biphenylmethylene)s have been described: (a) Del Rosso, P. G.; Almassio, M. F.; Antollini, S. S.; Garay, R. O. *Opt. Mater.* **2007**, *30*, 478–485. (b) Beinhoff, M.; Bozano, L. D.; Scott, J. C.; Carter, K. R. *Macromolecules* **2005**, *38*, 4147–4156. (c) Havelka-Rivard, P. A.; Nagai, K.; Freeman, B. D.; Sheares, V. V. *Macromolecules* **1999**, *32*, 6418–6424. See also: (d) Del Rosso, P. G.; Almassio, M. F.; Aramendia, P.; Antollini, S. S.; Garay, R. O. *Eur. Polym. J.* **2007**, *43*, 2584–2593. (e) Fáber, R.; Staško, A.; Nuyken, O. *Macromol. Chem. Phys.* **2001**, *202*, 2321–2327.

(50) (a) Bohnen, A.; Räder, H. J.; Müllen, K. *Synth. Met.* **1992**, *47*, 37–63. (b) Eiras, C.; Foschini, M.; Faria, R. M.; Gonçalves, D. *Mol. Cryst. Liq. Cryst.* **2002**, *374*, 493–496.

(51) Bredas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555–6559.

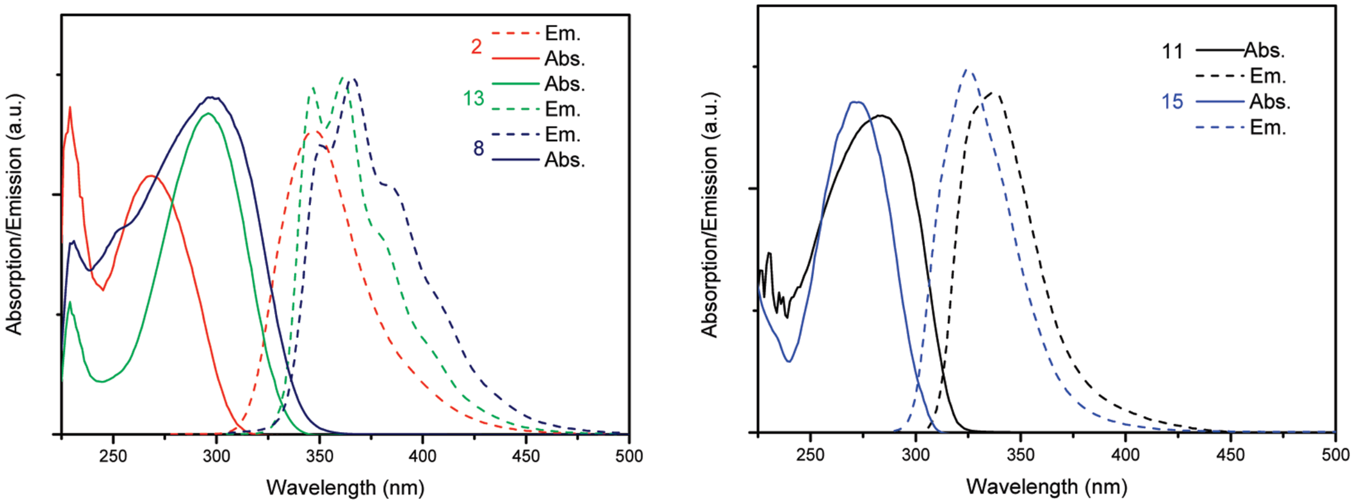

FIGURE 4. Absorption and emission spectra of polymers **8**, **11**, and **2** and reference compounds **13** and **15** in CH_2Cl_2 excited at their respective longest wavelength absorption maximum.

influence of including homoconjugated DPN subunits in the backbone structure of the polymers is again very clear by comparing the λ_{em} values of polymer **8** (366 nm), model compound **13** (361 nm), *p*-terphenyl (338 nm), and *p*-quaterphenyl (364 nm). The same trend is observed for the case of polymer **11** (337 nm), model compound **15** (325 nm), and biphenyl (315 nm).

The shapes of the absorption and emission spectra of polymers **11** and **2** and model compound **15** follow the mirror image rule, although in the cases of the emission spectra of **11** additional shoulders in the emission band start to be appreciable. On the contrary, the shapes of **8** and **13** do not follow the mirror image rule and resemble the shape observed for *p*-quaterphenyl. The breakdown of the mirror image symmetry in the optical/emission spectra of oligo(*p*-phenylene)s has been extensively studied,[52] and a clear correlation between the phenylene ring librations and the violation of the mirror symmetry rule has been be established. Therefore, the different shapes observed for the emission of polymers **8** and **2** can be attributable to the lower degree of torsional freedom of the *p*-terphenyl subunit of **2** caused by the alkyl chains, while in polymer **8**, as well as in **13**, the librations of the unsubstituted aryl rings are responsible of the unsymmetrical shapes observed in the emission spectra. It should be mentioned that the librational barrier of the aryl rings in DPN is considerably high (12.5 kcal/mol).[32,35]

The Stokes shifts of polymers **8** (68 nm) and **11** (54 nm) (Table 1) are relatively large and very similar to the values of the corresponding reference compounds **13** (66 nm) and **15** (53 nm) (Table 2). Therefore, the overlap of the absorption and emission spectra is weak. It should be noted that the Stokes shift in the case of polymer **2** (80 nm) is considerably higher than in polymer **8** (68 nm). Both polymers have a similar structural backbone of poly(terphenylmethylene), but in the case of **2** the alkyl chains linked to the central aryl ring diminish the electronic conjugation in the terphenyl subunit. In this case, the larger Stokes shift is mainly due to the pronounced blue shift of the absorption spectra of **2** (30 nm) caused by its limited conjugation rather than to the red-shift of **8** that places its λ_{max} value even at lower wavelengths than the λ_{max} of polymer **11**, a poly(biphenylmethylene), while the differences in the emission spectra are not so pronounced (18 nm) and the λ_{em} follow the order **8** (366 nm) > **2** (348 nm) > **11** (337 nm).

Conclusion

Suzuki polycondensation reaction has been used for the synthesis of block copolymers with alternating homoconjugation−conjugation derived from 7,7-diphenylnorbornane (DPN) ((poly(biphenylmethylene)s and poly(terphenylmethylenes)s). The special topology of homoconjugated DPN allows the preparation of conjugated biphenyls or *p*-terphenyls separated by a spacer with geometry halfway between conjugated and π-stacked aryl rings, which contribute to the delocalization of the electrons along the backbone structure of the polymers. The absorption and emission spectra of the polymers and model compounds demonstrate that the introduction of homoconjugated subunits leads to an extension of the delocalization that modify the electronic properties of the polymers in comparison to other systems in which the conjugated subunits are separated by saturated carbon atoms that act as interrupters of the conjugation. Also cyclic voltammetry studies, carried out on model compound **13**, shows that homoconjugation enhances the degree of electron delocalization since lower oxidation potentials are observed upon increasing the molecular length by linking two DPN subunits to *p*-terphenyl. Our results show that the delocalization effect caused on oligo *p*-phenylenes by two homoconjugated aryl rings is in the same range than the effect produced by one additional conjugated aryl ring. The electron delocalization mediated by aromatic homoconjugation observed in our systems differs from the situation observed in homoconjugated acetylenes in which no significant homoconjugative stabilization is observed.[53]

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(52) Heimel, G.; Daghofer, M.; Gierschner, J.; List, E. J. W.; Grimsdale, A. C.; Müllen, K.; Beljonne, D.; Brédas, J.-L.; Zojer, E. *J. Chem. Phys.* **2005**, *122*, 54501.

(53) For a review on homoconjugated acetylenes, see: de Meijere, A.; Kozhushkov, S. I. Macrocyclic Structurally Homoconjugated Oligoacetylenes: Acetylene- and Diacetylene-Expanded Cycloalkanes and Rotanes. *Top. Curr. Chem.* **1999**, *201*, 1-42.

In summary, the polymers described by us can be considered as a new class of delocalized structures with a degree of delocalization between all-conjugated block copolymers[54] and block copolymers with conjugated segments separated by interrupters. The introduction of homoconjugated subunits in these materials may be an efficient method to modulate and control some important properties such as the band gap of the polymers, the dielectric constant,[55] or their optical and electrochemical properties. The synthesis of new polymers with alternating homoconjugation−conjugation and the study of their optical and electronic properties are currently in progress.

Experimental Section

2-*endo*-Octyl-7-(4-iodophenyl)-7-phenylnorbornane (12). A solution of 0.25 g (1.00 mmol) of I_2 in 25 mL of $CHCl_3$ was slowly added at 25 °C with vigorous stirring and protected from light to 0.36 g (1.00 mmol) of 2-*endo*-octyl-7,7-diphenylnorbornane (**5**) and 0.26 g (1.00 mmol) of AgOTf in 20 mL of $CHCl_3$. After disappearance of iodine, silver iodide was separated by filtration, and the organic solution was washed with saturated $NaHCO_3$ (1 × 20 mL), 10% $Na_2S_2O_3$ (2 × 20 mL), and water (1 × 20 mL) and dried over $MgSO_4$. After evaporation of the solvent under vacuum, the mixture of *syn*- and *anti*-**12** was purified by flash chromatography (silica gel, hexane/dichloromethane 80:20): yield 51%, colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.53 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.35 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.23−7.02 (m, 5H), 2.97−2.92 (m, 2H), 1.90−1.75 (m, 2H), 1.69−1.42 (m, 4H), 1.40−1.10 (m, 14H), 0.88 (t, ^3J(H,H) = 6.8 Hz, 3H), 0.81−0.72 (m, 1H) ppm; ^{13}C NMR (50 MHz $CDCl_3$, 25 °C, TMS) δ 146.1, 145.7, 145.2, 137.4, 137.3, 129.6, 129.4, 128.5, 128.4, 127.3, 127.0, 125.5, 90.5, 65.7, 45.1, 41.8, 37.1, 35.9, 32.8, 31.9, 30.0, 29.6, 29.3, 28.7, 22.7, 20.7, 14.1 ppm. FTIR (film) ν 3059, 3028, 2926, 2872, 2854, 1601, 1580, 1551, 1483, 1460, 1391, 1005, 908, 785, 715, 698 cm^{-1}; MS (EI, 70 eV) *m*/*z* 486 (M^+, 100), 361 (39), 360 (70), 332 (53), 293 (41), 206 (80), 205 (94), 193 (58), 192 (86), 191 (51), 167 (45), 166 (29), 165 (48), 115 (43), 91 (75). Anal. Calcd for $C_{27}H_{35}I$: C, 66.66; H, 7.25. Found: C, 66.32; H, 7.32.

General Procedure for the Synthesis of Boronates 9, 10, and 14. A 1.2 mmol portion of *n*-BuLi in hexanes (or 2.4 mmol for the preparation of **9**) was slowly added to a solution of 1.15 mmol of iodides **6** or **12** under argon atmosphere at −78 °C. The reaction mixture was stirred for 2 h at −78 °C, and then 2.30 mmol (or 4.60 mmol) of trimethyl borate was added. After the mixture was stirred for 3 h at room temperature, the reaction was quenched with water (20 mL) and extracted with Et_2O (3 × 25 mL). The organic solution was washed with saturated aqueous NaCl (1 × 20 mL) and dried over $MgSO_4$, and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (50 mL), and 1.4 mmol (or 2.8 mmol) of pinacol was added. After the solution was refluxed for 3 days using a Dean−Stark, the solvent was evaporated under vacuum and the boronates purified by flash chromatography (silica gel, hexane/diethyl ether 20:1).

Boronate 9: yield 66%; mp 217−220 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.64 (d, ^3J(H,H = 6.9 Hz, 4H), 7.40 (d, ^3J(H,H = 6.9 Hz, 4H), 3.12−2.98 (m, 2H), 1.96−1.83 (m, 2H), 1.70−1.45 (m, 4H), 1.35−1.17 (m, 38H), 0.92−0.84 (m, 3H), 0.81−0.75 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS) δ 149.2, 148.8, 134.9, 126.9, 126.3, 83.5, 66.5, 44.9, 41.7, 37.1, 35.9, 32.8, 31.9, 30.0, 29.6, 29.3, 28.7, 24.8, 22.7, 20.7, 14.1 ppm; FTIR (film) ν 2980, 2924, 2852, 1604, 1458, 1362, 1325, 1271, 1144, 1091, 908, 858, 734 cm^{-1}. MS (EI, 70 eV) *m*/*z* 612 (M^+, 19), 486 (18), 442 (45), 427 (22), 419 (19), 101 (56), 91 (20), 83 (94), 73 (100), 57 (32), 55 (45). Anal. Calcd for $C_{39}H_{58}B_2O_4$: C, 76.48; H, 9.54. Found: C, 76.39; H, 9.61.

Boronate 10: yield 60%; mp 128−130 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.65 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.50 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.37 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.12 (d, ^3J(H,H) = 8.4 Hz, 2H), 3.15−2.95 (m, 2H), 1.93−1.82 (m, 2H), 1.75−1.40 (m, 4H), 1.38−1.10 (m, 26H), 0.93−0.75 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS) δ 149.0, 148.5, 145.7, 137.5, 135.1, 129.6, 129.4, 126.7, 126.5, 90.6, 83.6, 65.9, 45.0, 41.7, 37.2, 35.9, 32.8, 31.9, 29.9, 29.6, 29.3, 28.7, 28.5, 24.8, 22.7, 20.7, 14.1 ppm; FTIR (film) ν 2922, 2851, 1608, 1400, 1361, 1323, 1271, 1143, 1092, 1005, 858, 825, 804, 650 cm^{-1}; MS (EI, 70 eV) *m*/*z* 612 (M^+, 22), 486 (29), 485 (31), 419 (19), 217 (25), 101 (35), 83 (35), 73 (100), 72 (28), 57 (25), 55 (27). Anal. Calcd for $C_{33}H_{46}BIO_2$: C, 64.72; H, 7.57. Found: C, 64.78; H, 7.60.

Boronate 14: yield 65%; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.67 (d, ^3J(H,H) = 8 Hz, 2H), 7.47−7.34 (m, 4H), 7.18−7.02 (m, 2H), 7.00−6.89 (m, 1H), 3.01−2.88 (m, 2H), 1.96−1.83 (m, 2H), 1.72−1.45 (m, 4H), 1.41−1.10 (m, 26H), 0.95−0.84 (m, 3H), 0.82−0.75 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS) δ 149.2, 145.9, 134.9, 128.3, 127.4, 127.2, 126.9, 126.6, 125.3, 83.5, 65.2, 45.1, 41.8, 37.2, 36.0, 32.9, 31.9, 30.0, 29.6, 29.3, 28.7, 24.8, 22.7, 20.7, 14.1 ppm; FTIR (film) ν 2959, 2928, 2852, 1711, 1608, 1398, 1362, 1261, 1144, 1090, 1020, 908, 808, 735, 650 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 487 ($[M + H]^+$, 40), 486 (M^+,100), 485 (27), 386 (16), 332 (13), 204 (18), 101 (22), 91 (13), 83 (23), 55 (17). Anal. Calcd for $C_{33}H_{47}BO_2$: C, 81.47; H, 9.74. Found: C, 81.53; H, 9.80.

4,4″-Bis(2-*endo*-octyl-7-phenyl-7-norbornyl)-*p*-terphenyl (13). A mixture of 0.83 g (1.72 mmol) of **12** and 0.42 g (0.86 mmol) of **7** in 20 mL of toluene and 70 mL of 1 M solution of $NaCO_3$ was degassed three times using the freeze−pump−thaw technique. A 0.01 g (0.0086 mmol) portion of $[Pd(PPh_3)_4]$ was added, and the reaction was heated under argon for 24 h, extracted with CH_2Cl_2 (3 × 25 mL), and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (silica gel, hexane) yielded 72% of **13** as a white solid: mp 62−64 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.53 (s, 4H), 7.50−7.40 (m, 12H), 7.27−7.15 (m, 4H), 7.10−7.00 (m, 2H), 3.10−2.95 (m, 4H), 2.03−1.82 (m, 4H), 1.75−1.45 (m, 4H), 1.42−1.06 (m, 32H), 0.95−0.73 (m, 8H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS) δ 146.2, 145.8, 145.4, 145.0, 139.4, 137.5, 128.3, 127.8, 127.6, 127.2, 127.0, 126.9, 125.3, 65.8, 45.2, 41.9, 37.2, 36.0, 32.9, 31.9, 31.6, 30.0, 29.6, 29.3, 28.7, 22.7, 20.8, 14.1 ppm; FTIR (film) ν 3082, 3059, 3028, 2926, 2852, 1601, 1488, 1460, 1445, 1004, 812, 762, 711, 698 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ε) 295 nm (29800 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV) *m*/*z* 795 ($[M + H]^+$, 64), 794 (M^+, 100), 601 (38), 206 (20), 169 (19), 149 (17), 143 (20), 97 (16), 91 (55), 85 (34), 83 (25), 81 (23), 71 (34), 69 (40), 67 (35), 57 (55), 56 (16), 55 (43). Anal. Calcd for $C_{60}H_{74}$: C, 90.62; H, 9.38. Found: C, 90.60; H, 9.35.

4,4′-Bis(7-phenyl-2-*endo*-octyl-7-norbornyl)biphenyl (15). A mixture of 0.42 g (0.86 mmol) of **12** and 0.42 g (0.86 mmol) of **14** in 20 mL of toluene and 70 mL of 1 M solution of $NaCO_3$ was degassed three times using the freeze−pump−thaw technique. A 0.01 g (0.0086 mmol) portion of $[Pd(PPh_3)_4]$ was added, and the reaction was heated under argon for 24 h, extracted with CH_2Cl_2 (3 × 25 mL), and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (silica gel, hexane) yielded 78% of **15** as colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.45−7.30 (m, 12H), 7.25−7.14 (m, 4H), 7.10−6.98 (m, 2H), 3.05−2.93 (m, 4H), 2.00−1.82 (m, 4H), 1.70−1.43 (m, 4H), 1.40−1.02 (m, 32H), 0.98−0.76 (m, 8H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C,

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(55) Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3–65.

TMS) δ 146.3, 145.8, 145.0, 144.6, 137.8, 128.3, 127.7, 127.4, 127.2, 126.8, 125.3, 65.7, 45.2, 41.9, 37.2, 36.1, 32.9, 31.9, 31.6, 30.0, 29.7, 29.3, 28.7, 22.7, 20.8, 14.1 ppm; FTIR (film) ν 3028, 2926, 2854, 1711, 1599, 1493, 1460, 1379, 908, 814, 735, 700, 650 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ε) 270 nm (26000 mol^{-1} dm^3 cm^{-1}); MS (EI, 70 eV) *m*/*z* 719 ($[M + H]^+$, 65), 718 (M^+, 100), 564 (11), 526 (21), 525 (45), 143 (16), 91 (15), 55 (8). Anal. Calcd for $C_{54}H_{70}$: C, 90.19; H, 9.81. Found: C, 90.10; H, 9.88.

General Procedure for the Synthesis of Polymers 8 and 11 by Suzuki Policondensation Reaction. A mixture of 0.86 mmol of boronate **7** or **9** and 0.86 mmol of iodide **6** in 20 mL of toluene and 70 mL of 1 M solution of $NaCO_3$ was degassed three times using the freeze−pump−thaw technique. A 0.01 g (0.0086 mmol) portion of $[Pd(PPh_3)_4]$ was added, and the reaction was heated under argon for 3 days. The organic solution was separated and concentrated to a volume of 10 mL. Methanol (150 mL) was then added dropwise with vigorous stirring. The white precipitate was separated and purified by repeating the precipitation with methanol. Polymer **11** was also obtained by reaction of 1.76 mmol of **10** and 0.01 g (0.0086 mmol) of $[Pd(PPh_3)_4]$ under the same reaction conditions.

Polymer 8: yield 94%; ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.60−7.10 (m, 12H), 3.20−2.90 (m, 2H), 2.00−1.90 (m, 2H), 1.85−1.10 (m, 18H), 0.90−0.80 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS) δ 145.3, 144.9, 139.4, 137.6, 128.6, 127.8, 127.6, 127.1, 126.9, 65.5, 45.3, 42.0, 37.2, 36.1, 33.0, 31.9, 31.2, 30.0, 29.7, 29.3, 28.8, 22.7, 20.8, 14.1 ppm; FTIR (film) ν 2922, 2851, 1261, 1101, 1022, 806 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ε) 298 nm (14400 mol^{-1} dm^3 cm^{-1}), Anal. Calcd for $(C_{33}H_{38})_n$: C, 91.19; H, 8.81. Found: C, 91.23; H, 8.79. Weight-average molecular weight (M_w): 3470. Polydispersity index (PDI): 1.3.

Polymer 11: yield 97%; ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.60−7.10 (m, 8H), 3.10−2.95 (m, 2H), 2.00−1.80 (m, 2H), 1.70−1.00 (m, 18H), 0.95−0.75 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS) δ 144.9, 144.5, 137.8, 128.6, 128.3, 127.7, 127.4, 126.8, 65.4, 45.3, 42.0, 37.2, 36.0, 32.9, 31.9, 31.6, 30.0, 29.6, 29.3, 28.7, 22.7, 20.8, 14.1 ppm; FTIR (film) ν 2922, 2851, 1261, 1101, 1022, 806 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ε) 283 nm (12400 mol^{-1} dm^3 dm^{-1}). Anal. Calcd for $(C_{27}H_{34})_n$: C, 90.44; H, 9.56. Found: C, 90.45; H, 9.60. Weight-average molecular weight (M_w): 6440. Polydispersity index (PDI): 1.4.

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Supporting Information Available: ^1H/^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.