On the Tacticity of Polynorbornenes with 5,6-endo Pendant Groups That Contain Substituted Aryl Chromophores


In memory of Yoshihiko Ito

Introduction

We recently reported an unprecedented approach for the synthesis of DNA-like double-stranded polymer 2 by Grubbs I catalyst (1)-promoted ring-opening metathesis polymerization (ROMP) of bisnorbornene derivative 3 (Scheme 1). [1] The key to the success of this strategy lies in the rigid rodlike structure and stereochemical homogeneity of the polymer. It has been shown that the single-stranded polynorbornenes 4 with dipolar pendant groups at the C5 and C6 positions [2] may adopt rigid rod structures. [3] The stereoregularity of simple polynorbornenes has been extensively examined, and it appears that the nature of the catalyst and the structure of the monomeric norbornenes may influence the tacticity and the double-bond configurations of the polymers. [4–11] To illustrate this, molybdenum-catalyzed ROMP of norbornenes gives mainly cis double bonds and isotactic selectivity. [7] Recently, ROMPs of norbornadiene diester and exo,exo-2,3-dicarbomethoxy-5-norbornene with a ruthenium catalyst reportedly gave isotactic polymers with mainly trans double bonds. [8] It has been shown that catalyst 1 yields predominantly trans double bonds in polynorbornenes. [9] However, the tacticity of the polymers varies with substrate. [4–11] 13C NMR spectra have been widely used for the elucidation of the tacticity of these polymers. [10] Thus, polymer 4 was shown to assume mainly isotactic stereochemistry, whereas 5 is atactic. In a preliminary communication, we showed that 6 exhibits molecule-dependent nonlinear optical β values, [10] which may imply that 6 may adopt homogeneous stereochemistry and conformation. Although 5 and 6 are structurally similar with pendant endo nitrogen heterocycles, the imide ring in 5 and the pyrrolidine moiety in 6 may behave differently under these ruthenium-

Abstract: Two dimers and a series of polymers with 5,6-endo pendant aryl groups that contain different substituents at the para positions were synthesized. The conformation and stereochemistry of the dimers and polymers were determined by nonlinear optical analysis (EFISH) as well as UV/Vis and 13C NMR spectroscopy. The chemical shifts of C7 for the polymers appeared as two peaks in the 13C NMR spectra when the substituents are electron-drawing substituents. The percentage decrease in the relative extinction coefficient of the polymers, eπ, was linearly related to the Hammett constant σ. Polynorbornenes with electron-drawing substituents may adopt isotactic stereochemistry with all pendant groups aligned in one direction. The nature of the interactions between neighboring chromophores may be one of the most important factors in directing the stereoregularity and conformation of these polymers. The corresponding polymers derived from the exo isomers appeared to be less stereoregular.

Keywords: chromophores · pendant groups · polynorbornenes · ring-opening polymerization · tacticity
catalyzed conditions. Furthermore, the presence of the N-aryl pendant groups in 6 may be an important factor because they may interact with the neighboring aryl pendant group. It is envisaged that such interaction may depend on the nature of the aromatic rings. Hence, the substituent on these aryl pendant groups may influence the mode of these interactions. More recently, we found that single-stranded polymer 7 can serve as a template to accommodate monomeric norbornene moiety 8, leading to 9. ROMP of 9 followed by hydrolysis and esterification yields the corresponding complementary polymer 10 with an isotactic structure (Scheme 2). This finding indicates that polynorbornenes such as 7 should adopt homogeneous tacticity. We now report a systematic investigation into the tacticity of 6 and its related polymers, which have a range of different aryl pendant groups.

Results and Discussion

Dimers

To begin, dimers 11 were synthesized according to Scheme 3. Notably, the Grubbs II catalyst was necessary to promote the cross-metathesis leading to 11. The two stereoisomers (11a: 46%; 11b: 25%) were separated and their photophysical properties were measured (Table 1). The absorption maxima for the dimers 11 and monomer 12 are similar. Interestingly, the μμ values obtained by the EFISH (electric-field-induced second harmonic) method for both 11a and 11b were significantly enhanced (Table 1). These results indicate that the pendant groups in 11a and 11b may align essentially toward a similar direction or adopt syn conformations. The IR absorption band at around 960 cm⁻¹ suggests that the double bonds in both 11a and
11b has $C_2$ symmetry and, hence, is syndiotactic.$^{[15]}$ These results provide a useful hint for the elucidation of the tacticity of the polymers as described later.

X-ray analysis of 14 suggested that the distance between the two olefinic moieties is 5–6 Å.$^{[18]}$ and STM of 2 showed that the Fe–Fe distance is 5–5.5 Å.$^{[1]}$ It is therefore envisaged that each of the monomeric units in 2 and its related polymers may also occupy a similar amount of space. Rotation along the carbon–nitrogen bond in 11 may bring two neighboring arene moieties closer so that interaction between these chromophores might take place.

**Polymer 6**

We previously showed that 6 may adopt homogeneous tacticity based on its spectroscopic data and nonlinear optical properties.$^{[3]}$ As described above, the stereochemistry of dimers 11 were established with the help of $^{13}$C NMR spectroscopy. Interestingly, two peaks of equal intensity at 35.46 and 35.95 ppm attributed to $C_7$ were observed in the $^{13}$C NMR spectrum of 6 (Figure 1). This observation suggests that there are two types of nonequivalent $C_7$ atoms in 6.

As described previously, polynorbornenes obtained by ROMP with the Grubbs I catalyst have double bonds in trans configurations.$^{[3,9]}$ The dipolar pendant groups are coherently aligned in the syn configuration.$^{[3]}$ Scheme 4 shows the possible structures of the isotactic and syndiotactic polymers. 6. For syn conformations, the syndiotactic structure has a $C_2$ symmetry axis bisecting the carbon–carbon double bond. As such, the environments for each of the neighboring monomeric units are the same, and only one set of $^{13}$C NMR signals would be expected. In the isotactic structure, on the other hand, there is a plane of symmetry perpendicular to the polymeric backbone and bisecting each monomeric unit. However, the two planes of symmetry ($\sigma$ and $\sigma'$) in two neighboring units are different; therefore, two sets of $^{13}$C NMR signals would be anticipated. For anti conformations, the isotactic structure has the center of inversion ($i$) at

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**Table 1. Absorption maxima and EFISH data of 11a, 11b, and 12.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\mu_\beta$ [D]</th>
<th>$\mu_\beta$ [10$^{-4}$ esu]</th>
<th>$\mu_\beta$ [10$^{-4}$ esu (12)]</th>
<th>$\mu_\beta$(11)/$\mu_\beta$(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>441 (28.0)</td>
<td>3.8</td>
<td>2.7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>11a</td>
<td>440 (27.4)</td>
<td>6.1</td>
<td>4.3</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>11b</td>
<td>400 (27.5)</td>
<td>5.3</td>
<td>3.8</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

[a] All $\mu_\beta$ values were measured in chloroform at 1907 nm. [b] $\mu_\beta$ values were deduced from the experimental values by using a two-level dispersion model.$^{[3,9]}$

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**11b** have a trans configuration. The large $^1$H NMR coupling constant ($J = 15.1$ Hz) for the two olefinic protons of 11a further supports this argument. The $^{13}$C NMR spectrum for 11a has seven pairs of signals at high field, whereas that for 11b has only seven peaks. These results suggest that 11a has $C_1$ symmetry and, therefore, is isotactic. On the other hand,
the center of the carbon–carbon double bond, whereas the syndiotacti
cform has the $C_2$ rotation axis perpendicular to the polymeric
backbone and orthogonal to the correspond-
ing $C_2$ axis of the syn confor-
mation. One might expect that
both structures with anti confor-
mation would show only
one set of $^{13}$C NMR signals.

On the basis of this analysis,
it seems likely that polymer 6
adopts isotactic stereochemis-
try. It is believed that interac-
tions between pendant chro-
mophores may play an impor-
tant role in dictating the ste-
reochemistry of the polynor-
bornenes. Interaction between
these chromophores may
depend on the relative elec-
tron demand of the aromatic
rings. The substituents on
these aryl pendant groups may
influence the mode of such in-
teractions, which may result in
changes in the stereochemistry
of the polymer. Accordingly, a
series of polymers 17 with dif-
f erent substituents at the para
position of the pendant phenyl
groups were synthesized
(Scheme 5). Different number-
average molecular weights ($M_n$)
for 17 were obtained [4,5].

Table 2 summarizes the selec-
ted photophysical properties of
these polymers.

Absorption Properties of 17
As is the case with the polynor-
bornenes 6 with azo penda-
tant groups, [3] the $\lambda_{max}$ values
of 17 also consistently ap-
peared at shorter wavelengths relative to those of the corre-
sponding monomers 18, and the UV/Vis absorption profiles
remained unchanged with changes in concentration. In gen-

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**Scheme 4. Possible conformations of isotactic and syndiotactic polymers 6.**

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**Figure 1. $^{13}$C NMR spectrum of polymer 6.**
eral, with the exception of 17b and 18b, monomers 18 and polymers 17 exhibited both E and B bands at 250–270 and 310–330 nm, respectively. These two bands, however, merged into one for 17b and 18b at around 313 nm. In all cases, the extinction coefficients ($\varepsilon / C_0$) of 17 decreased with an increase in the degree of polymerization. The percentage decrease in the relative extinction coefficient of the polymer, $\varepsilon_d$, is defined in [Eq. (1)]:

$$\varepsilon_d = \left[1 - \left(\varepsilon_p / \varepsilon_m\right)\right] \times 100$$  \hspace{1cm} (1)

in which $\varepsilon_p$ and $\varepsilon_m$ are the extinction coefficients ($g^{-1}cm^2$)

for 17 and the corresponding monomer 18, respectively. The $\varepsilon_d$ values at 250–270 nm for 17a–f were thus obtained, and the results are summarized in Table 2.\cite{16} A plot of these $\varepsilon_d$ values of 17 for a given substituent against the average number of repeating units, $n$ (15 < $n$ < 99), is shown in Figure 2.\cite{16} Interestingly, the $\varepsilon_d$ values are larger for polymers with electron-withdrawing substituents and smaller for those with electron-donating substituents. From these plots, a series of $\varepsilon_d$ values for 17a–f with 40 repeating units were estimated by intra- or extrapolations (Figure 2, dotted line). As shown in Figure 3, the Hammett plot of these $\varepsilon_d$ values gave a good linear relationship ($R^2 = 0.992$). These results indicate that interchromophore interactions among the pendant groups of 17 are more important for those with electron-withdrawing rather than electron-donating substituents.

The pyrrolidine moiety in 17 is a strongly electron donating group. When the other substituent on the aromatic ring in 17 is also an electron-donating group, the aromatic rings would be highly electron-rich. As such, the modes of interaction between such electron-rich chromophores may be different from those with electron-withdrawing substituents. Such differences may lead to discrepancies in the $\varepsilon_d$ values due to the nature of the substituents.

It is known that substituents on phenylene ethynylene macrocycles and related cyclic conjugated systems may have

![Scheme 5. Synthesis of saturated polymer 19. Ts = tosyl.](image)

Table 2. Absorption data of monomers 18a–f and polymers 17a–f of different molecular weights.

<table>
<thead>
<tr>
<th>Compound $^{[a]}$</th>
<th>$M_n$</th>
<th>PDI $^{[b]}$</th>
<th>$n$</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\varepsilon$</th>
<th>$\varepsilon_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18a</td>
<td>279</td>
<td>1</td>
<td>1</td>
<td>273</td>
<td>83.1</td>
<td></td>
</tr>
<tr>
<td>17a–1</td>
<td>6990</td>
<td>1.17</td>
<td>25</td>
<td>270</td>
<td>43.5</td>
<td>47.6</td>
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<tr>
<td>17a–2</td>
<td>10901</td>
<td>1.18</td>
<td>39</td>
<td>270</td>
<td>27.7</td>
<td>66.7</td>
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<td>18114</td>
<td>1.31</td>
<td>65</td>
<td>270</td>
<td>16.0</td>
<td>80.7</td>
</tr>
<tr>
<td>18b</td>
<td>283</td>
<td>1</td>
<td>317</td>
<td>270</td>
<td>122.5</td>
<td></td>
</tr>
<tr>
<td>17b–1</td>
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<td>1.20</td>
<td>35</td>
<td>313</td>
<td>103.7</td>
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<td>98.8</td>
<td>19.3</td>
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<td>99</td>
<td>313</td>
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<tr>
<td>18c</td>
<td>289</td>
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<td>268</td>
<td>270</td>
<td>64.3</td>
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<tr>
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<td>5531</td>
<td>1.13</td>
<td>19</td>
<td>265</td>
<td>41.8</td>
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<tr>
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<td>9593</td>
<td>1.35</td>
<td>25</td>
<td>265</td>
<td>36.1</td>
<td>43.8</td>
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<td>17c–3</td>
<td>21421</td>
<td>1.05</td>
<td>74</td>
<td>265</td>
<td>32.6</td>
<td>49.3</td>
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<tr>
<td>18d</td>
<td>211</td>
<td>1</td>
<td>260</td>
<td>75.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17d–1</td>
<td>7669</td>
<td>1.13</td>
<td>36</td>
<td>256</td>
<td>61.1</td>
<td>18.6</td>
</tr>
<tr>
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<td>9958</td>
<td>1.25</td>
<td>47</td>
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<td>59</td>
<td>256</td>
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<td>18e</td>
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<td>1</td>
<td>257</td>
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<td>23</td>
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<td>55.6</td>
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<td>17e–3</td>
<td>12985</td>
<td>1.06</td>
<td>58</td>
<td>255</td>
<td>55.5</td>
<td>13.0</td>
</tr>
<tr>
<td>18f</td>
<td>241</td>
<td>1</td>
<td>253</td>
<td>61.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17f–1</td>
<td>10041</td>
<td>1.52</td>
<td>42</td>
<td>251</td>
<td>55.7</td>
<td>9.2</td>
</tr>
<tr>
<td>17f–2</td>
<td>13048</td>
<td>1.42</td>
<td>54</td>
<td>251</td>
<td>54.9</td>
<td>10.7</td>
</tr>
<tr>
<td>17f–3</td>
<td>16253</td>
<td>1.33</td>
<td>67</td>
<td>251</td>
<td>54.3</td>
<td>11.5</td>
</tr>
</tbody>
</table>

[a] Numbers after the dashes denote polymers of different $M_n$. [b] PDI = polydispersity index ($M_w/M_n$).

![Figure 2. Plots of the $\varepsilon_d$ values of 17 against the average number of repeating units $n$. Substituents: $\triangledown$ = CF$_3$, $\triangle$ = Br, $\square$ = H, $\blacksquare$ = Me, $\bullet$ = OMe.](image)
favor π-stacking interactions, whereas such aggregation may become less favorable in those substrates with electron-donating substituents such as alkoxy groups.[19] Although the quantitative relationship remains to be clarified, our results on polynorbornenes may be compatible with those in the literature[18,19] in which interactions between the chromophores may be substituent-dependent. For electron-withdrawing substituents, such interactions may be more important. Therefore, the pendant chromophores in these polymers (e.g., 17a-c) may align coherently in similar directions. Powder X-ray analysis of 17b suggested that the polymer is amorphous, with a broad peak at 2θ = 18.76°.

**Effect of Substituent on the 13C NMR Spectrum of 17**

Figure 4 shows the 13C NMR spectra of 17b and the corresponding hydrogenated polymer 19b. The simplicity of the spectrum for 19b suggests that this polymer may adopt a single tacticity.[10,11] As with the spectrum of 6, the high-field signals assigned to C7[12] for 17b occur as two peaks of equal

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**Figure 3.** Hammett plot of the $\rho_e$ values of 17.

**Figure 4.** 13C NMR spectra of a) 17b and b) 19b. Insets: Corresponding expanded high-field region.
intensity at 35.75 and 36.21 ppm. These signals are independent of the degree of polymerization. In a similar manner, the signal for this carbon atom of 17a (35.63 and 36.12 ppm) and 17c (35.56 and 35.80 ppm) also show two peaks at high field. Interestingly, the separation of these two peaks (Δδ) is substituent-dependent. The more strongly electron withdrawing group gave a larger Δδ value. On the other hand, the 13C NMR signals of C7 for 17d-f with electron-donating substituents or hydrogen appeared as a single peak (Δδ = 0 ppm).

The change in Δδ with substituents is interesting. For polymers 17a-c with electron-withdrawing substituents, π-stacking interactions between neighboring aromatic chromophores may be significant. Accordingly, on the basis of the structures shown in Scheme 4, it seems likely that these polymers may adopt the isotactic structure with syn conformation. As the substituents become more electron-donating, such π-stacking tendencies would become less important. Interactions between two neighboring aromatic rings in such polymers (those with electron-donating substituents) may, therefore, be unfavorable. These tendencies may lead to conformational changes or even perturbation of the stereoregularities in polynorbornenes.

Polymers from exo-Norbornene Derivatives

Polymers 20 and 21, derived from the corresponding exo isomer 22a and the corresponding furan adduct 23a, respectively, were prepared for comparison. Interestingly, both 20 and 21 may contain both cis and trans double bonds. Furthermore, the extinction coefficients of 20 and 21 are essentially the same as those of 22a and 23a, respectively. These results indicate that the stereochemistry for polymerization of the exo derivatives of norbornene and related skeletons may not be as good as those of the corresponding endo isomers.

Conclusions

A series of polynorbornenes with aryl substituents on the 5,6-end Re pendant groups has been synthesized by Grubbs I catalyst mediated ROMP of the corresponding norbornene monomers. The tacticity of these polymers and the related dimers has been examined by UV/Vis and 13C NMR spectroscopy, and their nonlinear optical properties have been probed. The results suggest that polynorbornenes that contain aryl groups with electron-withdrawing substituents may adopt isotactic stereochemistry with all the pendant groups aligned in one direction. Interaction between these chromophores may take place in these polymers. Such interaction may also be important in directing the stereochemistry of the polymer during the course of the ROMP process of norbornenes with aryl pendant groups. More importantly, the present work echoes our previous successful synthesis of double-stranded polymers[1] because of the nice coherent alignment of the pendant groups and the homogeneous tacticity in the polymerization of norbornene derivatives. The corresponding polymers derived from the exo isomers appeared less stereoregular.

Experimental Section

General

Gel permeation chromatography (GPC) was performed on a Waters GPC machine with an isocratic HPLC pump (1515) and a refractive-index detector (2414). THF was used as the eluent (flow rate = 1.0 mL/min). Waters Styragel HR2, HR3, and HR4 columns (7.8 × 300 mm) were employed for determination of relative molecular weight with polystyrene as standard (Mw values ranged from 375 to 3.5 × 10⁵).

EFISH Measurements

EFISH measurements were taken with a nonlinear optical spectrometer from SOPRA. The fundamental wavelength at about 1907 nm is the first Stokes peak of a hydrogen Raman cell pumped by the 1064-nm light from a Q-switched Nd:YAG laser (Quantel YG 781, 10 ppw, 8 ns, pulse). That light was passed through a linear polarizer and focused onto the EFISH cell. The polarizing dc voltage (parallel to the light polarization) used in this cell was 10 kV. The output light from the cell was passed through an interference filter to select the second harmonic (954 nm), which was detected with an R642 photomultiplier from Hamamatsu. Static μp values were deduced from the experimental values by using a two-level dispersion model. Each sample was measured with chloroform (CHCl₃) as solvent, and the concentration was about 10⁻⁸ m for monomers.

Syntheses

15: Compound 14 (1.03 g, 3.0 mmol) in CH₂Cl₂ (50 mL) was added slowly to a slurry of LiAlH₄ (0.68 g, 18 mmol) in Et₂O (100 mL), and the mixture was stirred at room temperature for 1 h. Ethyl acetate (5 mL) was carefully added, water (1 mL) was then introduced, the resulting suspension was filtered, and the organic layer was evaporated in vacuo to give the residue, which was triturated repeatedly with CH₂Cl₂. The solution in CH₂Cl₂ was dried (MgSO₄) and filtered. The solvent was removed in vacuo to give 15 as a colorless liquid (0.79 g, 84%). IR (KBr): ν = 3023, 2958, 2912, 2848, 1774, 1706, 1594, 1491, 1455, 1384, 1322, 1291, 1192, 1167, 107, 961, 921, 873, 815, 772, 755, 692, 622, 586 cm⁻¹; 1H NMR (400 MHz, CDCl₃): δ = 1.70 (q, J = 12.0 Hz, 1H), 1.96 (dt, J = 12.0, 5.9 Hz, 1H), 2.83–3.10 (m, 4H), 5.11 (dd, J = 17.2, 1H), 5.93 (add, J = 17.2, 1H, 3.5 Hz, 1H, 6.30 (dd, J = 16.0, 7.2 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 6.76 (t, J = 8.8 Hz, 1H), 7.23–7.36 ppm (m, 8H); 13C NMR (100 MHz, CDCl₃): δ = 35.3, 45.5, 46.1, 46.2, 46.7, 50.3, 50.4, 113.4, 115.3, 116.8, 126.1, 127.1, 128.5, 129.1, 130.5, 131.1, 137.5, 139.1, 148.6 ppm; GPC machine with an isocratic HPLC pump (1515) and a refractive-index detector (2414). THF was used as the eluent (flow rate = 1.0 mL/min). Waters Styragel HR2, HR3, and HR4 columns (7.8 × 300 mm) were employed for determination of relative molecular weight with polystyrene as standard (Mw values ranged from 375 to 3.5 × 10⁵).

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9.0Hz, 2H), 7.19–7.32 (m, 5H), 8.16 ppm (d, J = 15.8Hz, 1H), 6.43 (d, J = 8.4Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 7.19–7.32 (m, 5H), 8.16 ppm (d, J = 9.0 Hz, 2H).

3076, 2822, 1711, 1597, 1539, 1522, 1384, 1255, 1200, 1181, 808, 790 cm⁻¹;

137.2, 143.5, 150.9, 166.0 ppm; HRMS (FAB+): m/z calculated for C₁₃H₁₇N₃O: 295.1113 [M+H]+; found: 295.1111.

18a: 4-(4-Fluorophenyl)-4-azaisoquinoline (8g, 0.10 mmol) in CCl₄ (250 mL) was added slowly to a suspension of LiAlH₄ (13 g, 0.34 mmol) in THF (200 mL) and the mixture was stirred at room temperature for 2 h. Ethyl acetylate (5 mL) was added dropwise to the mixture, which was cooled to 0°C. The residue was triturated with CHCl₃, the solution in CHCl₃ was dried (MgSO₄) and filtered. The solvent was removed in vacuo to give 18a as a white solid (1.7 g, 71%). M.p.: 57–58°C; IR (KBr): v = 3076, 2923, 2874, 2844, 1594, 1493, 1374, 1344, 1255, 1200, 1181, 808, 790 cm⁻¹;

29c: nmbrBuLi (13 mL, 2.55 in hexane, 30 mmol) was added dropwise under argon to a solution of 22b (580 g, 20 mol) in dry THF (140 mL) cooled to –78°C. After stirring at –78°C for 1 h, excess CO₂ gas was bubbled into the solution until the white solid (∼2 h) was precipitated. The mixture was gradually warmed to room temperature, poured into a mixture of EtO₂ (200 mL) and H₂O (200 mL), and filtered to give the filter cake and filtrate I. The filter cake was washed with 1 mol/L NaOH (2×1 L) and the solution was washed with aq. HCl (10%) until pH 6 to give a precipitate, which was filtered. Additional solid was obtained from neutralization of filtrate I (10% HCl until pH 6). The combined solid was washed with EtO₂ (2×100 mL) to give 22c as a white solid (459.9%, M.p.: 278°C C; IR (KBr): v = 3076, 2923, 2874, 2844, 1594, 1493, 1374, 1344, 1255, 1200, 1181, 808, 790 cm⁻¹;

3H NMR (500 MHz, CDCl₃): δ = 1.52 (d, J = 8.2 Hz, 1H), 1.62 (d, J = 8.2 Hz, 2H), 7.24–7.49 (m, 10H), 7.79–8.01 (m, 8H), 8.10 ppm (d, J = 8.8 Hz, 4H); 13C NMR (125 MHz, CDCl₃): δ = 141.3, 35.8, 44.5, 46.6, 46.9, 49.8, 49.9, 66.2, 121.8, 125.0, 127.1, 128.2, 128.3, 128.5, 128.7, 130.1, 130.4, 131.7, 137.0, 137.4, 138.9, 150.9, 161.0 ppm; HRMS (FAB+): m/z calculated for C₁₃H₁₇N₃O: 295.1113 [M+H]+; found: 295.1111.

18c: In a manner similar to that described for the preparation of 18a, the reaction of 11a with 11b (239 mg, 25 µmol) and 16 (169 mg, 0.2 mmol in CCl₄ (4 mL) was heated under reflux for 24 h, cooled to room temperature, and the mixture was quenched with ethyl vinyl ether (10 mL).

11a: M.p.: 210–213°C; IR (KBr): v = 2923, 2874, 2844, 1594, 1493, 1374, 1344, 1255, 1200, 1181, 808, 790 cm⁻¹; 1H NMR (500 MHz, CDCl₃): δ = 1.47 (t, J = 7.0 Hz, 6H), 1.67–1.70 (m, 2H), 2.39–2.43 (m, 16H), 4.42 (q, J = 7.0 Hz, 4H), 5.45 (s, 2H), 6.15–6.17 (m, 12H), 6.40–6.52 (m, 2H), 6.71–6.80 (m, 4H), 7.22–7.49 (m, 10H), 7.79–8.01 (m, 8H), 8.10 ppm (d, J = 8.8 Hz, 4H); 13C NMR (125 MHz, CDCl₃): δ = 141.3, 35.8, 44.5, 46.6, 46.9, 49.8, 49.9, 66.2, 121.8, 125.0, 127.1, 128.2, 128.3, 128.5, 128.7, 130.1, 130.4, 131.7, 137.0, 137.4, 138.9, 150.9, 161.0 ppm; HRMS (FAB+): m/z calculated for C₁₃H₁₇N₃O: 295.1113 [M+H]+; found: 295.1111.
(decomp.); IR (KBr): ν = 3060, 2962, 2850, 1664, 1554, 1552, 1477, 1420, 1384, 1268, 1180, 827, 775, 702, 670 cm⁻¹; ¹H NMR (300 MHz, CDCl₃ [dimethyl sulfoxide]): δ = 1.27 (d, J = 9.0 Hz, 1H), 1.41 (d, J = 9.0 Hz, 1H), 2.35 (m, 2H), 2.75 (br, 2H), 3.06-3.10 (m, 2H), 3.39-3.50 (m, 2H), 4.12 (br, 2H), 4.57 (s, 1H), 5.56 (s, 1H), 6.19 (s, 1H), 6.71 (s, 1H), 7.55 (s, J = 9.0 Hz, 2H), 12.09 ppm (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 42.4, 44.3, 47.5, 52.6, 111.8, 117.5, 134.0, 151.1, 160.8 ppm; HRMS (MALDI): m/z: calcd for C₉H₉NO₂⁺: 256.1338; found: 256.1332; elemental analysis: calcld (%): for C₉H₉NO₂: C, 75.27; H, 6.71; N, 5.49; found: C, 75.24; H, 6.68; N, 5.41.

22a: Oxadyl chloride (7.2 mL, 80 mmol) and NaN₃-dimethylformamide (DMF, 3 mmol) were added to a suspension of 22c (10.20 g, 40 mmol) in CHCl₃ (150 mL) at 0°C. The mixture was gradually warmed to room temperature and then stirred for 3 h. The solvent was removed in vacuo to give the corresponding acid chloride, which was dissolved in CHCl₃ (70 mL). EtOH (15 mL) was added to this solution, and the mixture was stirred at room temperature for 5 h. Water was introduced, and the organic layer was separated and washed with water and brine (200 mL) and then dried (MgSO₄). The solvent was removed in vacuo to give 22a as a white solid (10.30, 90%). M.p.: 123–124°C; UV/Vis (CHCl₃): λₐ₅₅₄ (e) = 313 nm (10.80, 10 g); IR (KBr): ν = 3053, 2974, 2978, 2958, 2875, 1701, 1691, 1612, 1556, 1527, 1436, 1369, 1280, 1208, 1184, 771, 699, 680 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 1.36 (t, J = 7.2 Hz, 3H), 1.38 (dd, J = 9.0, 1.5 Hz, 1H), 1.50 (d, J = 9.0 Hz, 1H), 2.41–2.44 (m, 2H), 2.75 (s, J = 8.3 Hz, 2H), 3.00–3.10 (m, 2H), 4.31 (q, J = 9.0 Hz, 1H), 7.04 (t, J = 10.2 Hz, 1H), 7.30 ppm (d, J = 9.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ = 14.5, 24.3, 44.3, 47.7, 60.1, 111.2, 117.2, 131.2, 137.6, 150.9, 167.1 ppm; HRMS (MALDI): m/z: calcd for C₂₂H₁₉NO₃⁺: 318.1651; found: 318.1645; elemental analysis: calcld (%): for C₂₂H₁₉NO₃: C, 76.49, H, 7.47, N, 5.94; found: C, 76.02; H, 7.26, N, 4.67.

22b: 4-(4-(Bromophenyl)-4-aza-10-oxaoxiracyclo[5.2.1.0²,6]tricyclo[3.5.5.0⁻³⁻,⁻⁴⁰]dodec-8-ene-8-carboxylic acid (2933, 2750, 1620, 1594, 1377, 1374, 1334, 1183, 967, 808 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 1.36 (t, J = 7.2 Hz, 3H), 1.38 (dd, J = 9.0, 1.5 Hz, 1H), 1.50 (d, J = 9.0 Hz, 1H), 2.41–2.44 (m, 2H), 2.75 (s, J = 8.3 Hz, 2H), 3.00–3.10 (m, 2H), 4.31 (q, J = 9.0 Hz, 1H), 7.04 (t, J = 10.2 Hz, 1H), 7.30 ppm (d, J = 9.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ = 14.5, 24.3, 44.3, 47.7, 60.1, 111.2, 117.2, 131.2, 137.6, 150.9, 167.1 ppm; HRMS (MALDI): m/z: calcd for C₂₂H₁₉NO₃⁺: 318.1651; found: 318.1645; elemental analysis: calcld (%): for C₂₂H₁₉NO₃: C, 76.49, H, 7.47, N, 5.94; found: C, 76.02; H, 7.26, N, 4.67.

17c: In a manner similar to that described for the preparation of 17a.

22c: In a manner similar to that described for the preparation of 22b.

23a: In a manner similar to that described for the preparation of 22a.

23b: In a manner similar to that described for the preparation of 23a.

19a: A solution of 17a (200 mg, 0.77 mmol) and p-tosyhydrazide (2 g, 10.9 mmol) in PhCH₃ (10 mL) was stirred under argon at 120°C for 2 h and then filtered. The filtrate was poured into methanol (50 mL). The mixture was centrifuged to collect the precipitate, which was washed several times with methanol and dried under vacuum to yield 19a (30 mg, 49%) as a solid. IR (KBr): ν = 2924, 1700, 1700, 1596, 1505, 1455, 1375, 1320, 1177, 1020 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 0.99–1.96 (m, 8H), 2.86 (br, 2H), 3.20 (br, 4H), 4.27 (br, 2H), 6.59 (br, 2H), 7.41 ppm (br, 2H); ¹³C NMR (125 MHz, CDCl₃): δ = 30.7, 37.0, 41.6, 45.1, 48.7, 111.7, 124.3, 126.5, 131.6, 149.3 ppm; elemental analysis: calcld (%): for C₈H₈F₂NO: C, 68.31, H, 6.45, N, 4.99; found: C, 67.88, H, 6.64, N, 4.99.

19c: In a manner similar to that described for the preparation of 19a.

19d: In a manner similar to that described for the preparation of 19a.
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[2] The numbering of the monomeric unit in the polynorbornene backbone used in this paper are based on the numbering of norbornenes.


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