On the Rigidity of Polynorbornenes with Dipolar Pendant Groups

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Abstract: A range of polynorbornenes (PNBs) with fused dipolar pendant groups at C-5,6 positions was synthesized by ring-opening metathesis polymerization catalyzed by a ruthenium carbene complex (Grubbs I). Photophysical studies, EFISH measurements, and atomic force microscopy images have been used to investigate the structures and morphology of these polymers. These results suggest that the polymers may adopt rigid rod-like structures. The presence of the double bonds in PNBs appeared to be indispensable for the rigidity of the polymers. Interaction between unsaturated pendant groups may result in coherent alignment leading to a rod-like structure.

Keywords: atomic force microscopy · EFISH · poly(norbornene)s · polymerization · rigid rod polymers · ring-opening metathesis

Introduction

Arranging organic dipolar chromophores as pendants onto a supramolecular backbone leads to an enhancement of second-order nonlinear optical (NLO) properties.[1–4] For example, when chromophores are organized as the side groups of poly(isocyanide)s, the first hyperpolarizabilities β_o of the polymers are increased.[1] The key to the success of this strategy relies on the helical conformation of the polymer backbone,[1–4] which leads to a strong orientational correlation of the side groups. In a preliminary communication, we reported that polynorbornenes (PNBs) derived from the ring-opening metathesis polymerization (ROMP)[5,6] of norbornene derivatives with dipolar pendant groups[7] exhibit molecular-weight-dependent β_o values as measured by hyper-Rayleigh scattering (HRS) methods.[8] Each of the non-centrosymmetric chromophores in these PNBs may contribute coherently to the hyperpolarizability of the polymers. It is worthy to note that PNBs having a variety of pendant groups have also been used in light-harvesting,[9] liquid-crystal,[10] and third-order nonlinear optical[11] applications. One of the advantages of using PNB polymers may hinge on the relative rigidity of the backbones,[8–11] which may not only provide a coherent array of the pending groups along the polymeric chain but also serve as insulating spacers.[8–11] Interestingly, photo-induced electron transfer may take place efficiently among chromophores from one end to the other along the PNB polymeric chain. Presumably, the pendant chromophores in these polymers may be in close proximity.[9] Although extensive studies have been carried out on the stereochemistry of PNBs by using ^{13}C NMR spectroscopy,[6c,12] and the parent PNB has been shown to exhibit spherical morphology,[13] the morphology of these important polymers having different kinds of pendants has not been explored in detail. It is known that the morphology of a polymer may dependent on, inter alia, the nature of the substituents on the polymeric backbone.[14] It is therefore envisaged that the presence of pendant groups on PNBs may alter the three-dimensional conformation. Herein we report the design, synthesis, morphological studies of a series of PNBs having a range of pendant moieties.

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Results and Discussion

Synthesis: Monomer **1** was designed because not only can this compound be easily made, but also the *endo*-fused pyrrolidene ring with aromatic substituents may generate a favorable environment for the π–π interactions, which may lead to a coherent array of the pendant groups during the course of polymerization. The details of the synthesis of monomer **1** and the corresponding polymer **2** were reported previously [Eq. (1)].[8] The more rigid monomer **3** with a propellane skeleton and the corresponding polymer **4** were synthesized according to Scheme 1. The stereochemistry of **7**
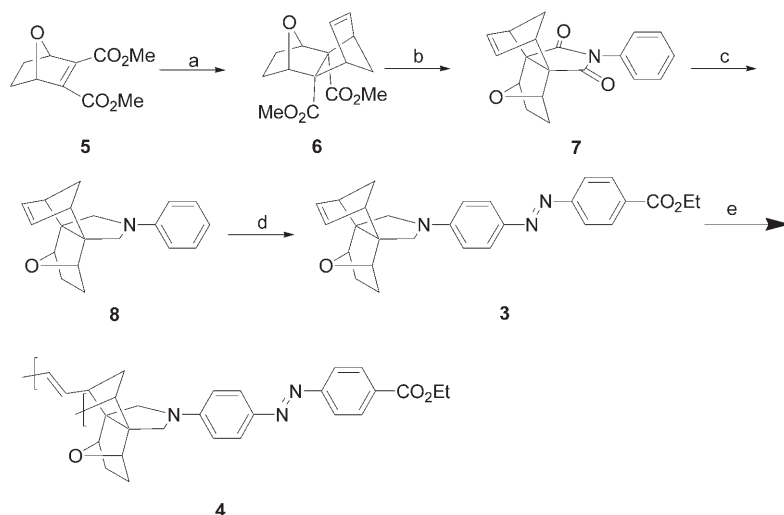
Scheme 1. a) cyclopentadiene, PhH, reflux, 12 h, 73 %; b) aniline, Me₃Al, benzene, reflux, 12 h, 90 %; c) LAH, toluene, reflux, 40 %; d) ethyl 4-aminobenzoate, HNO₂, 48 %; e) [(Cy₃P)₂Cl₂Ru=CHPh], ClC₂H₄Cl.

was confirmed by X-ray crystallography. Grubbs I catalyst was employed for the polymerization of norbornene monomers **1** and **3** (see [Eq. (1)] and Scheme 1). Only *trans* double bonds were found in all of these polymers **2** and **4** as revealed by the ¹H and ¹³C NMR spectra as well as IR spectra. These polymers were stable up to about 280 °C as revealed by thermal gravimetric analyses (TGAs). Differential scanning calorimetry (DSC) studies indicated that polymers **2** and **4** exhibited neither T_g nor T_m points. These results suggested that these polymers might adopt a rigid structure.
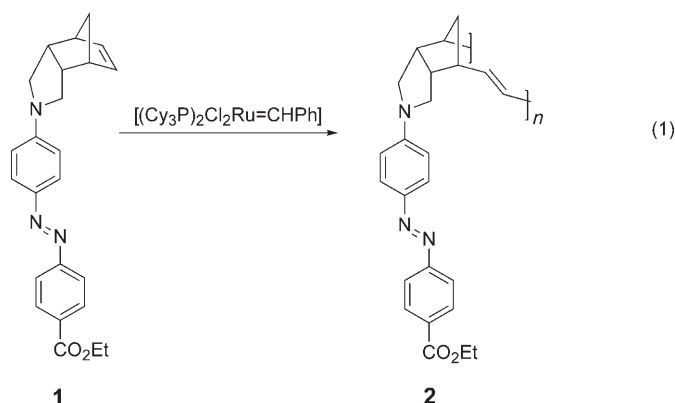
Absorption spectra: The λ_{max} and the extinction coefficients ε of monomers **1** and **3** and polymers **2** and **4** of different molecular weights (M_n) are compared in Table 1, and the absorption profiles were concentration independent. Interestingly, the λ_{max} values of polymers **2** and **4** consistently appeared at shorter wavelengths than those of the corresponding monomers **1** and **3**. Although aggregations between chromophores may lead to a hypsochromic shift in the absorption maxima,[15] a relief of strain by ring opening of norbornene moiety may also exhibit a similar effect.[16] The extinction coefficients of the polymers **2** and **4** also decreased with increasing M_n as compared with those of the corresponding monomers **1** and **3**. These results suggested that intrachain aggregation of the chromophores might occur in these polymers.[15]

The space occupied by a monomer unit in PNBs was found to be 5–6 Å as revealed by the X-ray structure of **9**.[17] By simply twisting the phenylene moiety in PNBs **2** and **4**, interactions between chromophores in pendant groups of these polymers might be feasible. The blue shifts in the absorption maxima in the polymers **2** and **4**, and a decrease in the extinction coefficients with increasing M_n in the polymers **2** and **4** are consistent with the fact that the pendant groups in these polymers might be oriented in a similar direction.

EFISH measurements: The electric field induced second harmonic generation (EFISH) method is used for the measurements of second-order nonlinearity of conjugated dipolar chromophores and recorded as μβₒ values, where μ is the permanent dipole moment and β is the vectorial part of the first hyperpolarizability of such dipolar units.[1,18] The dipolar moieties of the molecules can be aligned by employing an applied electric field. As such, when a series of dipolar chromophores are attached to a supramolecular framework, they will also align coherently in response to such an external electric field so that the μβₒ values might be enhanced.[19] It is envisaged that this methodology might be employed for the elucidation of the orientation of the pendant groups in the PNBs **2** and **4**. In other words, the μβₒ values of **2** and **4** might be expected to increase with increasing molecular weights. Table 1 also summarizes the EFISH results and the corresponding μβₒ values were corrected by using the two-level dispersion factor.[18] As shown in Figure 1, the μβₒ-(polymer)/μβₒ(monomer) ratios increase with M_n. This observation suggested that the dipolar chromophores in **2** and **4** might be aligned coherently along the respective polymeric backbones.

Table 1. Absorption and EFISH[a] results of monomers **1** and **3** and polymers **2** and **4** of different molecular weights.

Compd	M_n(PDI)	λ_{max} [nm] (ε [g^{-1} cm^2])[a]	$\mu\beta$ $\times 10^{46}$ esu[b]	$\mu\beta_o$ $\times 10^{46}$ esu	$\mu\beta_o$(polymer)/ $\mu\beta_o$(monomer)
1	388	458 (28.2)	3.6	2.6	1
2a	6700 (1.4)	443 (26.1)	98.5	73.0	28.1
2b	11 900 (1.3)	444 (23.3)	127.6	94.4	36.3
2c	15 100 (1.2)	445 (23.1)	145.0	107.7	41.4
2d	17 600 (1.3)	445 (22.9)	190.0	141.1	54.3
2e	25 800 (1.3)	445 (22.2)	199.0	147.8	56.8
2f	32 800 (1.3)	445 (22.1)	169.3	125.8	48.4
3	486	433 (68.7)	2.4	1.8	1
4a	7800 (1.6)	425 (59.4)	154.0	117.5	65.3
4b	13 100 (1.8)	425 (47.1)	232.9	177.7	98.7
4c	14 800 (2.2)	425 (45.7)	251.4	191.7	105.0
4d	21 100 (2.7)	425 (38.7)	293.0	223.5	124.2
4e	34 400 (1.8)	425 (34.4)	250.3	191.2	106.2

[a] Concentration: 10^{-5} gL^{-1} for **2** and **4**. [b] Measured in $CHCl_3$ using 1907 nm fundamental wavelength
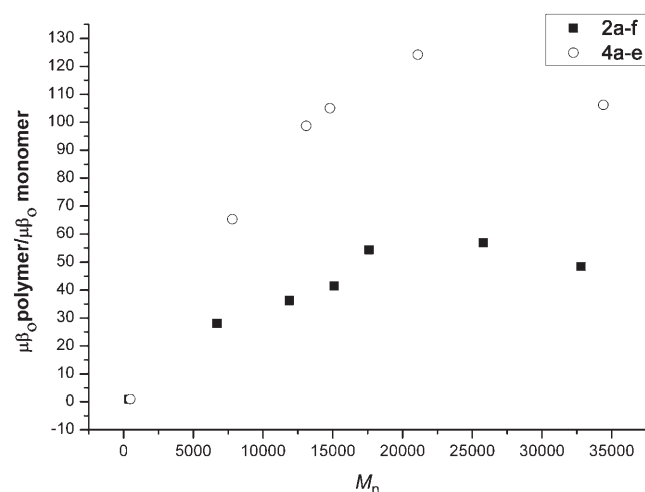
Atomic force microscopy image of 4: Atomic force microscopy (AFM) is known to provide a useful tool to directly observe the morphology of polymers.[20] Figure 2 shows the tapping mode AFM (TMAFM) images of polymer **4b** (repetitive unit: 28). The rod-like morphology of **4** was consistent with the results from EFISH and spectroscopic measurements. As shown in Figure 2, the nominal heights of the rod-like features were about 0.6–1.4 nm, and the domain size of the polymer appeared to be quite uniform.
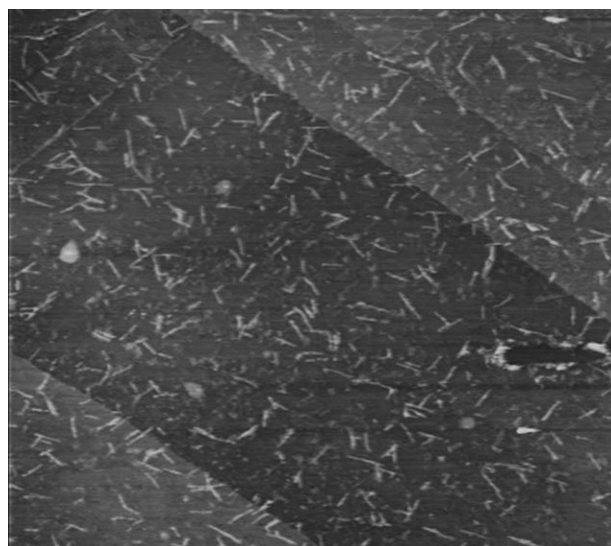

Figure 1. Relationship between $\mu\beta_o$ ratios of polymers versus monomers and M_n of polymers.

Figure 2. A 4×4-μm Tapping mode AFM image of **4b** on HOPG.

As shown in Figure 1, the degree of enhancement of the $\mu\beta_o$ values appeared to be dependent on the rigidity of the polymeric backbones. It is noteworthy that the $\mu\beta_o$ ratios of **4** versus **3** were larger than that of **2** versus **1**. As can be seen from the structural feature of these polymers, **3** contains a propellane skeleton. Accordingly, the structure of **3** would be more rigid than that of **1**, and the polymers **4** thus obtained might also be expected to be stiffer than **2**. Interestingly, the extinction coefficients of **4** having different molecular weights decrease more sharply than those of **2** (Table 1), which is consistent with the EFISH results.

As shown in Table 1 and Figure 1, the $\mu\beta_o$ ratios reached a maximum and then decreased as the molecular weight increased. The pendant chromophores may be oriented perpendicular to the polymeric backbone. When the number of repetitive units increases, the polymers **2** and **4** may be more twisted. Accordingly, certain dipolar vectors may be cancelled, resulting in a decrease in the $\mu\beta$ values for higher molecular weights.

Preliminary modeling of polymer **4** with ten repetitive units is shown in Figure 3. The pendant dipolar groups in this structure are probably fairly well aligned and consistent with the experimental results which indicate that polymer **4** might adopt a rod-like structure.

Importance of double bonds on the rigidity of PNBs: As discussed in the previous sections, PNBs **2** and **4** with pendant groups at C-5,6 positions appeared to be rigid-rod polymers. The nature of the rigidity apparently hinges on the *cis*-1,3-disubstituted cyclopentane ring, rigid pendant groups, and *trans* double bonds in the polymeric backbones. It is believed that the removal of double bond may lead to a more flexible conformation so that the above-mentioned physical properties may no longer exist. We have tested this viewpoint by reduction of the double bond with diazine [Eq. (2)]. Thus treatment of PNB **11**, prepared from ROMP
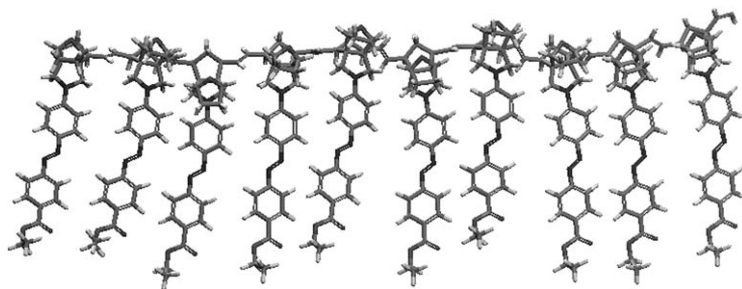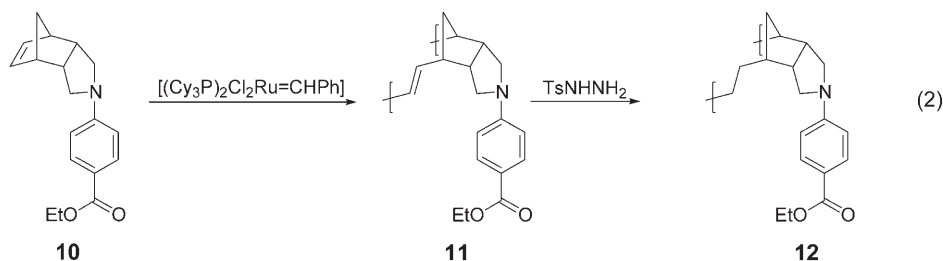
Figure 3. Structure of polymer **4**.

Table 2. EFISH measurements of monomer **10** and polymers **11** and **12** of different molecular weights in CHCl$_3$ using 1907 nm fundamental wavelength.

Compd	M_n (PDI)	λ_{max} [nm] (ε [g^{-1} cm^2])[a]	$\mu\beta$ $\times 10^{48}$ esu	$\mu\beta_o$ $\times 10^{48}$ esu	$\mu\beta_o$(polymer)/ $\mu\beta_o$(monomer)
10	283	317 (33.12)	4.4	3.8	1
11a	4200 (1.2)	314 (21.07)	38.1	33.0	8.7
11b	6500 (1.1)	314 (20.12)	72.2	662.6	16.5
11c	9100 (1.2)	314 (18.54)	98.1	85.1	22.4
11d	17000 (1.4)	314 (15.21)	154.3	131.1	35.3
12a	4200 (1.2)	313.5 (29.13)	8.9	7.7	2.0
12b	6500 (1.1)	313.5 (30.08)	13.4	11.6	3.0
12c	9100 (1.2)	313.5 (29.34)	13.1	11.4	3.0
12d	17200 (1.4)	313.5 (29.22)	14.5	112.6	3.3

[a] Concentration: 10^{-5} g L^{-1} for **11** and **12**.

of **10**, with tosylhydrazide in refluxing chlorobenzene afforded **12** in 45 % isolated yield. The structure of **12** was unambiguously determined by spectroscopic means—the double bonds were reduced completely. Interestingly, no T_g and T_m were observed for **11** and **12**, and these polymers started to decompose at about 250 °C. The photophysical properties together with the EFISH data of **11** and **12** of different molecular weights are tabulated in Table 2. Interestingly, the extinction coefficients for the hydrogenated polymers **12** are somewhat independent of M_n, whereas those of **11**, like **2** and **4**, showed extinction coefficients dependent on the molecular weight. This observation suggested that intrachain interactions between the pendant chromophores may not exist in **12**.

trast, the $\mu\beta$ values for **12** were independent of M_n, but still slightly higher than that of the corresponding monomer **10**. These results indicated that polymer **12** may no longer be a rigid-rod polymer. Because the double bond is reduced, the polymeric backbone in **12** may become more flexible, presumably leading to a random coil conformation. The orientation of the pendant chromophores may therefore be randomly distributed, resulting in canceling the dipoles. These results suggest that the presence of the double bond in PNBS with pendant groups is indispensable for the rigid-rod structures of these polymers.

Conclusion

In summary, we have demonstrated for the first time a direct investigation of the rigidity of a range of PNBs with fused dipolar pendant groups at C-5,6 positions. Based on the absorption properties, enhancement of second-order optical nonlinearities, and atomic force microscopic images, these polymers have been shown to adopt rigid rod-like structures. The presence of the double bonds in PNBs appeared to be indispensable for the rigidity of the polymers. Interaction between unsaturated pendant groups may result in coherent alignment, leading to the rod-like structure. Because pendant groups can easily be modified, further studies involving molecular architectures of double-stranded and related polymers based on the present work are in progress in our laboratory.

Experimental Section

As can be seen from Table 2, the EFISH data for **11** exhibited similar behavior to those for **2** or **4**, the $\mu\beta$ values for polymers **11a–d** increased with molecular weight. In con-

($20\,°C\,min^{-1}$) from 30 to 200 °C, then quenched with liquid nitrogen, and scanned for a second time from 30 to 300 °C ($10\,°C\,min^{-1}$). Thermogravimetric analysis (TGA) was carried out on a TA Instrument TGA-2950. The thermal stability of the samples was determined under nitrogen by measuring the weight loss while heating at a rate of $20\,°C\,min^{-1}$.

Ethyl 4-[[4-(1,3,3a,4,7,7a-hexahydro-4,7-methano-2H-isoindol-2-yl)phenyl]azo]benzoate (1): A solution of $NaNO_2$ (148 mg, 2.1 mmol) in minimum amount of water was added to a mixture of ethyl 4-aminobenzoate (330 mg, 2.0 mmol) and HCl (5 mL, 20 %) cooled to 5 °C. After 3 min, 2-phenyl-4,7-methano-1H-2,3,3a,4,7,7a-hexahydroisoindole (420 mg, 2.0 mmol) in THF (10 mL) was added slowly and stirring was continued for 2 h. The reaction mixture was warmed to room temperature and neutralized with NaOAc and then stirred at room temperature overnight. CH_2Cl_2 (50 mL) was added and the organic layer was washed with $NaHCO_3$ (5 %, 3×100 mL) and brine (100 mL), and dried ($MgSO_4$). Removal of the solvent in vacuo and purification on a column (silica gel, CH_2Cl_2/hexane, 1:1) afforded **1** as a red solid (550 mg, 71 %): m.p. 189–190 °C; IR (KBr): $\tilde{v}=3056, 2976, 2951, 2935, 2850, 1703, 1511, 1403, 1366, 1352, 1345, 1310, 1275, 1186, 1089, 1106, 1094, 970, 810\,cm^{-1}$; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.40$ (t, $J=6.9$ Hz, 3H), 1.49 (1H, d, $J=8.3$ Hz, 1H), 1.60 (d, $J=8.3$ Hz, 1H), 2.97–3,12 (m, 6H), 3.30–3.40 (m, 2H), 4.37 (q, $J=6.9$ Hz, 2H), 6.17 (t, $J=1.6$ Hz, 2H), 6.46 (d, $J=8.9$ Hz, 2H), 7.81–7.87 (m, 4H), 8.12 ppm (d, $J=8.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.3, 45.4, 46.6, 50.6, 52.0, 61.0, 111.7, 121.8, 125.6, 130.2, 130.4, 135.8, 143.4, 150.0, 156.0, 166.3$ ppm; MS (70 eV): m/z (%): 387 ([M]$^+$, 100), 345 (26), 319 (60), 291 (22), 210 (25), 143 (15); HRMS (EI) (C$_{24}$H$_{25}$N$_3$O$_2$): calcd: 387.1946; found: 387.1938; elemental analysis (%) calcd for C$_{24}$H$_{25}$N$_3$O$_2$: C 74.39, H 6.50, N 10.84; found: C 74.30, H 6.48, N 11.09.

***exo,endo*-4a,8a-Dimethyl-1,4-epoxy-1,8-methylene-1,2,3,4,4a,5,8,8a-octahydronaph-thalene-4a,8a-dicarboxylate (6)**: Freshly distilled cyclopentadiene (4 mL, 75 mmol) was added dropwise to a cold solution of **5**[21] (1.00 g, 4.70 mmol) in benzene (5 mL) at 0 °C. After the addition had been completed, the mixture was allowed to reflux for 12 h. The solvent was evaporated in vacuo and the residue was chromatographed (silica gel, hexane/EtOAc, 85:15) to give **6** (2 g, 77 %): m.p. 68–70 °C; IR (KBr): $\tilde{v}=2958, 1738, 1722, 1463, 1110, 1069, 735\,cm^{-1}$; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.26$ (d, $J=8.8$ Hz, 1H) 1.54–1.59 (m, 2H), 1.83–1.86 (m, 2H), 2.03 (d, $J=8.8$ Hz, 1H), 3.21–3.23 (m, 2H), 3.69 (s, 6H), 4.23 (dd, $J=2.0, 3.4$ Hz, 2H), 6.1 ppm (t, $J=2.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=28.3, 49.9, 52.0, 52.5, 66.4, 80.3, 136.0, 172.9$ ppm; MS (EI): m/z (%): 278 ([M]$^+$, 2), 246 (18), 184 (36), 153 (100), 123 (25), 66 (42); HRMS (EI) (C$_{15}$H$_{18}$O$_5$): calcd 278.1154; found 278.1159; elemental analysis (%) calcd for C$_{15}$H$_{18}$O$_5$: C 64.74, H 6.52; found: C 65.14, H 6.05.

Cyclic imide 7: Me$_3$Al (2.1 g, 29 mmol) was added dropwise at 0 °C to a solution of **6** (1.00 g, 3.59 mmol) and freshly distilled aniline (2.61 mL, 28.8 mmol) in benzene (25 mL). The solution was refluxed for 12 h after which water (20 mL) was added. The aqueous layer was extracted with EtOAc (3×20 mL). The combined organic layers were washed with HCl (10 %, 2×30 mL), saturated NaHCO$_3$ (2×30 mL) and brine (30 mL), and then dried (MgSO$_4$), filtered, and concentrated in vacuo. Chromatography of the residue (silica gel, hexane/EtOAc 90:10) afforded **7** (1.00 g, 90 %): m.p. 182–184 °C; IR (KBr): $\tilde{v}=1872, 1771, 1712, 1475, 844, 738, 687, 578\,cm^{-1}$; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.51$–1.56 (m, 2H), 1.71–1.83 (m, 4H), 3.41 (d, $J=2.0$ Hz, 2H), 4.54 (dd, $J=2.0, 4.0$ Hz, 2H), 6.25 (s, 2H), 7.21 (d, $J=7.6$ Hz, 2H), 7.39 (t, $J=7.6$ Hz, 1H), 7.47 ppm (t, $J=7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=28.2, 48.5, 48,6, 68.1, 78.4, 126.4, 129.1, 129.6, 131.9, 135.8, 177.3$ ppm; MS (EI): 307 ([M]$^+$, 8), 246 (25), 213 (45), 184 (36), 153 (100), 66 (52), 58 (65); HRMS (EI) (C$_{19}$H$_{17}$NO$_3$): calcd: 307.1208; found 307.1210; elemental analysis (%) calcd for C$_{19}$H$_{17}$NO$_3$: C 74.25, H 5.57, N 4.56; found: C 74.12, H 5.79, N 4.45.

Cyclic amine 8: Compound **7** (1.0 g, 3.2 mmol) in toluene (20 mL) was added slowly to a slurry of LiAlH$_4$ (1.2 g, 31.5 mmol) in toluene (30 mL), and the mixture was stirred at room temperature for 1 h and then refluxed overnight. After cooling to room temperature, a mixture of wet diethyl ether and ethyl acetate was carefully added. Water was then introduced and the resulting suspension was filtered, and the organic layer

was dried and evaporated in vacuo to give the residue which was triturated with diethyl ether repeatedly. The ethereal solution was dried (MgSO$_4$) and filtered. The solvent was removed in vacuo and the residue was chromatographed on silica gel (hexane/EtOAc, 85:15) to give the **8** as a colorless solid (460 mg, 50 %): m.p. 118–120 °C; IR (KBr): $\tilde{v}=2833, 1601, 1498, 1461, 1345, 1160, 1004, 804, 749, 60$ ppm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.37$ (d, $J=8.8$ Hz, 1H), 1.43–1.48 (m, 3H), 1.68–1.73 (m, 2H), 2.84 (d, $J=10.0$ Hz, 2H), 2.845 (s, 2H), 3.68 (d, $J=10.0$ Hz, 2H), 4.27 (dd, $J=2.4, 3.2$ Hz, 2H), 6.16 (d, $J=2.0$ Hz, 2H), 6.58 (d, $J=7.5$ Hz, 2H), 6.73 (t, $J=7.5$ Hz, 1H), 7.25 ppm (d, $J=7.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=26.2, 48.7, 50.8, 55.5, 64.5, 81.3, 112.6, 116.5, 129.2, 135.3, 147.8$ ppm; MS (EI): m/z (%): 279 ([M]$^+$, 100), 278 (33), 213 (28), 185 (36), 106 (28), 77 (9); HRMS (EI) (C$_{19}$H$_{21}$NO): calcd: 279.1263; found: 327.1265; elemental analysis (%) calcd for C$_{19}$H$_{21}$NO: C 81.68, H 7.58, N 5.01; found: C 81.46, H 7.48, N 4.95.

Azo-monomer 3: In a manner similar to that described for the preparation of **1**, the reaction of the diazonium ion, prepared from ethyl 4-aminobenzoate (890 mg, 5.4 mmol), and **8** (1.50 g, 5.4 mmol) afforded **4** as red crystals (1.67 g, 68 %): m.p. 166–168 °C; IR (KBr): $\tilde{v}=2839, 1602, 1515, 1492, 1273, 818, 692, 539\,cm^{-1}$; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.38$–1.51 (m, 7H, embodied a triplet at 1.40 $J=7.2$ Hz), 1.60–1.70 (m, 2H), 2.88 (m, 2H), 3.00 (d, $J=11.0$ Hz, 2H), 3.79 (d, $J=11.0$ Hz, 2H), 4.28 (m, 2H), 4.38 (q, $J=7.2$ Hz, 2H), 6.17 (s, 2H), 6.63 (d, $J=9.1$ Hz, 2H), 7.84 (d, $J=8.4$ Hz, 2H), 7.90 (d, $J=9.12$ Hz, 2H), 8.13 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.3, 26.1, 48.7, 51.0, 55.7, 61.0, 64.8, 81.3, 112.3, 121.9, 125.6, 130.5, 130.6, 135.2, 144.2, 150.1, 155.8, 166.3$ ppm; MS (EI): m/z (%): 455 ([M]$^+$, 44), 294 (73), 278 (29), 200 (48), 120 (100), 66 (34); HRMS (EI) (C$_{28}$H$_{29}$N$_3$O$_3$): calcd: 455.2209; found: 455.2204; elemental analysis (%) calcd: C$_{28}$H$_{29}$N$_3$O$_3$: C 73.82, H 6.42, N 9.22; found: C 73.47, H 6.33, N 9.09.

4-(4-Aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)benzaldehyde (13): 2,3-Dichloro-5,6-dicyanobenzoquinone (454 mg, 2.0 mmol) was added to a solution of 4-(4-aza-tricyclo[5.2.1.02,6]dec-8-en-4-yl)benzyl alcohol[22] (482 mg, 2.0 mmol) in dioxane (12 mL). The reaction was exothermic and the mixture immediately turned blue-green. The completion of reaction was monitored by TLC (approximately 24 h). After the completion of reaction, dioxane was removed in vacuo, benzene (50 mL) was added, and the residue was filtered. Removal of the solvent, followed by chromatographic purification (silica gel, CH$_2$Cl$_2$/hexane, 1:1) afforded **13** (309 mg, 64 %): m.p. 137–138 °C; IR (KBr): $\tilde{v}=3059, 2979, 2854, 1669, 1593, 1547, 1524, 1473, 1439, 1385, 1356, 1346, 1298, 1237, 1155, 1116, 1091, 819, 807, 788, 724, 662\,cm^{-1}$; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.49$ (d, $J=8.4$ Hz, 1H), 1.60 (d, $J=8.4$ Hz, 1H), 2.90–3.34 (m, 8H), 6.13 (m, 2H), 6.40 (d, $J=8.7$ Hz, 2H), 7.65 (d, $J=8.7$ Hz, 2H), 9.66 ppm (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=45.3, 46.6, 50.5, 52.0, 111.3, 124.8, 132.0, 135.8, 151.4, 190.2$ ppm; MS (70 eV): m/z (%): 239 ([M]$^+$, 95), 172 (100); elemental analysis (%) calcd for C$_{16}$H$_{17}$NO: C 80.30, H 7.16, N 5.85; found: C 80.25, H 7.33, N 5.85; HRMS calcd for C$_{16}$H$_{17}$NO: 239.1310; found: 239.1317; elemental analysis (%) calcd for C$_{16}$H$_{17}$NO: C 80.40, H 7.16, N 5.85; found: C 80.25, H 7.33, N 5.85.

4-(4-Aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)benzoic acid (14): NaOH (2 g, 50 mmol) and KOH (1.5 g, 26 mmol) in H$_2$O (7 mL) was placed in a stainless-steel beaker.[23] The mixture was heated to 170 °C, and **13** (2.4 g 10 mmol) was added to the reaction mixture. After stirring for another 5 min, the mixture was cooled and poured into ice water (1 L). The solution was acidified to pH 6 with HCl (6 N, 100 mL). The light-tan precipitate was filtered, washed with water, dried, and recrystallized from EtOAc/CHCl$_3$ to yield **14** (1.91 g ,75 %): m.p. 310 °C (decomp); IR (KBr): $\tilde{v}=3387, 2958, 2864, 2541, 1715, 1651, 1660 ,1600, 1383, 1279, 1180, 1019, 799\,cm^{-1}$; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.53$ (s, 2H), 1.65 (s, 2H), 3.00–3.31 (m, 8H), 6.18 (s, 2H), 6.41 (s, 2H), 7.91 ppm (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=45.4, 47.1, 50.5, 52.1, 60.0, 110.8, 117.6, 130.2, 135.9, 151.3, 171.3$ ppm; HRMS (FAB) ([M]$^+$, C$_{16}$H$_{17}$NO$_2$): calcd: 255.1259; found: 255.1264.

Ethyl 4-(4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)benzoate (10): Oxalyl chloride (1.8 mL, 20 mmol) and DMF (1 drop) were added to a solution of **14** (2.55 g, 10 mmol) in CH$_2$Cl$_2$ 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 THF (50 mL). To this solution, EtOH (10 mL) was added 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 (100 mL), and then dried (MgSO$_4$). The solvent was removed in vacuo to give **10** as a white solid (2.70 g, 95%): m.p. 145–146°C; IR (KBr): $\tilde{\nu}$ = 2967, 2939, 2856, 1693, 1608, 1525, 1479 1384, 1364, 1278 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.35 (t, J = 7.1 Hz, 3H), 1.51 (d, J = 7.1 Hz, 1H), 1.60 (d, J = 7.1 Hz, 1H), 2.91–3.29 (m, 8H), 4.30 (q, J = 7.1 Hz, 2H), 6.16 (s, 2H), 6.37 (d, J = 8.9 Hz, 2H), 7.86 ppm (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.5, 45.4, 46.6, 50.5, 52.1, 60.0, 110.8, 116.6, 131.2, 135.8, 150.3 ppm; HRMS (FAB) ([M]$^+$, C$_{18}$H$_{21}$NO$_2$): calcd: 283.1572. found 283.1573; elemental analysis (%) calcd for C$_{18}$H$_{21}$NO$_2$: C 73.82, H 6.42, N 9.22; found: C 73.47, H 6.33, N 9.09.

Polymer 2: Under argon, a solution of **1** (240 mg, 0.6 mmol) and [(Cy$_3$-P)$_2$Cl$_2$Ru=CHPh] (30 mg, 0.03 mmol) in CH$_2$Cl$_2$ (6 mL) was stirred at room temperature for 30 min, quenched with ethyl vinyl ether (2 mL), and poured into MeOH (20 mL). The solid was collected, redissolved in CHCl$_3$ (5 mL), and reprecipitated by adding MeOH (20 mL). This procedure was repeated two or three times and the solid was collected to afford **1** as a red solid (216 mg, 91%): IR (KBr): $\tilde{\nu}$ = 3318, 2960, 2891,1726, 1613, 1438, 1355, 1184, 1113, 1066, 1037, 964, 926 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.36 (br, 3H), 1.56 (br, 2H), 2.75- 3.22 (br, 8H), 4.36 (br, 2H), 5.29 (br, 2H), 67 (br, 2H), 7.80 (br, 4H), 8.34 ppm (br, 2H); ^{13}C NMR (125 MHz): δ = 14.3, 44.2, 46.3, 46.6, 49.6, 61.1, 112.1, 121.9, 125.6, 130.4, 131.6, 143.7, 150.3, 155.8, 166.2 ppm; GPC (THF): M_n: 15100; M_w: 18120; PDI: 1.2; elemental analysis (%) calcd for C$_{24}$H$_{25}$N$_3$O$_2$: C 74.39, H 6.50, N 10.84; found: C 72.60, H 6.38, N 10.32.

Polymer 4: Under argon, a solution of **3** (455 mg, 1 mmol) and [(Cy$_3$-P)$_2$Cl$_2$Ru=CHPh] (41 mg, 0.05 mmol) in 1,2-dichloroethane (10 mL) was stirred at room temperature for 60 min, quenched with ethyl vinyl ether (2 mL), and poured into MeOH (20 mL). The solid was collected, redissolved in CHCl$_3$ (10 mL), and reprecipitated by adding MeOH (20 mL). This procedure was repeated two or three times and the solid was collected to afford **4** as a red solid (377 mg, 83%): IR (KBr): $\tilde{\nu}$ = 2976, 2951, 2935, 2850, 1703, 1511, 1275, 1186, 1089, 1106, 1094, 970, 810 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ: 1.36 (br, 3H), 1.56 (br, 2H), 2.90–3.18 (br, 4H), 3.80 (br, 2H) 4.40 (br, 2H), 4.73–4.86 (br, 2H), 5.83 (br, 2H), 6.74 (br, 2H), 7.80 (br, 4H), 8.06 ppm (br, 2H); ^{13}C NMR (100 MHz): δ = 13.8, 25.2, 53.1, 53.7, 56.0, 67.1, 81.7, 112.3, 121.6, 125.1, 130.0, 130.3, 144.0, 149.7, 155.3, 165.8 ppm; GPC (THF): M_n: 14800, PDI: 2.2; elemental analysis (%) calcd for C$_{28}$H$_{29}$N$_3$O$_3$: C 73.82, H 6.42, N 9.22; found: C 72.66, H 6.51, N 8.78.

Polymer 11: In a manner similar to that described for the preparation of **2**, **11** was obtained as a white solid (269 mg, 95%): IR (KBr): $\tilde{\nu}$ = 2925, 2852, 1776, 1707, 1597, 1500, 1380, 1320, 1170, 1070, 972, 830 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.43 (br, 4H), 1.59 (br, 1H), 2.73–3.24 (br, 8H), 4.27 (br, 2H), 5.36 (br, 2H), 6.47 (br, 2H), 7.84 ppm (br, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.4, 35.71, 36.1, 44.5, 46.4, 49.4, 60.0, 111.4, 117.4, 131.2, 131.7, 150.8, 167.0 ppm (peaks at 126.0, 128.5 belong to the end groups of the polymer); GPC (THF): M_n: 9100; PDI: 1.2; elemental analysis (%) calcd for C$_{18}$H$_{21}$NO$_2$: C 76.29, H 7.47, N 4.94; found: C 76.65, H 7.73, N 4.62.

Polymer 12: Under argon, a solution of **11** (200 mg, 0.7 mmol) and p-tosylhydrazide (2 g, 10.9 mmol) in PhCl (10 mL) was stirred at 120°C for 2 h and then filtered. The hot 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 **12** (90 mg, 45%): IR (KBr): $\tilde{\nu}$ = 2924, 177, 1707, 1700, 1596, 1500, 1455, 1375, 1320,1177, 1020 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.91 (br, 1H), 1.32 (br, 8H), 1.95 (br, 3H), 2.84 (br, 2H), 3.20 (br, 4H), 4.27(br, 2H), 6.48 (br, 2H), 7.87 ppm (br, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.5, 31.0 (C$_{2,3}$), 37.0 (C$_7$), 41.6 (C$_{1,4}$), 45.1 (C$_{5,6}$), 48.6, 60.1, 111.1, 117.3, 131.1, 151.0, 167.0 ppm; GPC (THF): M_n: 9140; PDI: 1.2; elemental analysis (%) calcd for C$_{18}$H$_{21}$NO$_2$: C 75.76, H 8.12, N 4.91; found: C 75.45, H 7.42, N 5.32.

EFISH measurements: EFISH measurements were taken with a nonlinear optics spectrometer from SOPRA. The fundamental light at 1907 nm was 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 pps, 8 ns, pulse). That light was passed through a linear polarizer and focused on 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 light (954 nm), which was detected with a R642 photomultiplier from Hamamatsu. Static $\mu\beta_{(0)}$ values were deduced from the experimental values by using a two-level dispersion model. Each sample was measured by using chloroform (CHCl$_3$) as a solvent, and the concentration was about 10^{-3} M for monomers and 10^{-5} M for polymers.

AFM measurements: Tapping mode atomic force microscopy (TMAFM) measurements were carried out with a NanoScope IIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA, USA). Commercially available cantilevers (non-contact silicon, NSC15/Pt/50, Mikro-Masch, Spain) were employed. The microscope was housed in a chamber through which dry N$_2$ was purged throughout the experiments and the humidity was lower than 2%. Samples for TMAFM measurements were prepared by placing a drop of the CHCl$_3$ solution on freshly cleaved HOPG (highly oriented pyrolytic graphite, MikroMasch, Spain) with a Pasteur pipette. To remove trace amounts of solvent, the sample was dried under vacuum (ca. 30 min, 120 mTorr) prior to imaging.

Acknowledgements

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