

Photoreactive Polynorbornene Bearing 4-(Diphenylamino)benzoate Groups: Synthesis and Application in Electroluminescent Devices

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Summary. A new fluorescent and photoreactive polymer, poly-(*endo,exo*-bis(4-(4-(diphenylamino)benzoyloxy)benzyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate), was prepared by ring opening metathesis polymerization. This polymer combines the photoreactivity of aryl esters with the fluorescence properties of derivatives of 4-(diphenylamino)benzoic acid. The polymer exhibits blue photo- and electroluminescence and can be used as active layer in organic light emitting devices (OLED). Upon irradiation with UV light (254 nm) the aromatic ester groups undergo decarboxylation, which is accompanied by the loss of photoluminescence. Photolithographic patterning of the polymer surface was used to obtain structured fluorescent surfaces and patterned OLEDs.

Keywords. Polymerisation; Photochemistry; Metathesis; Light emitting devices; Decarboxylation.

Introduction

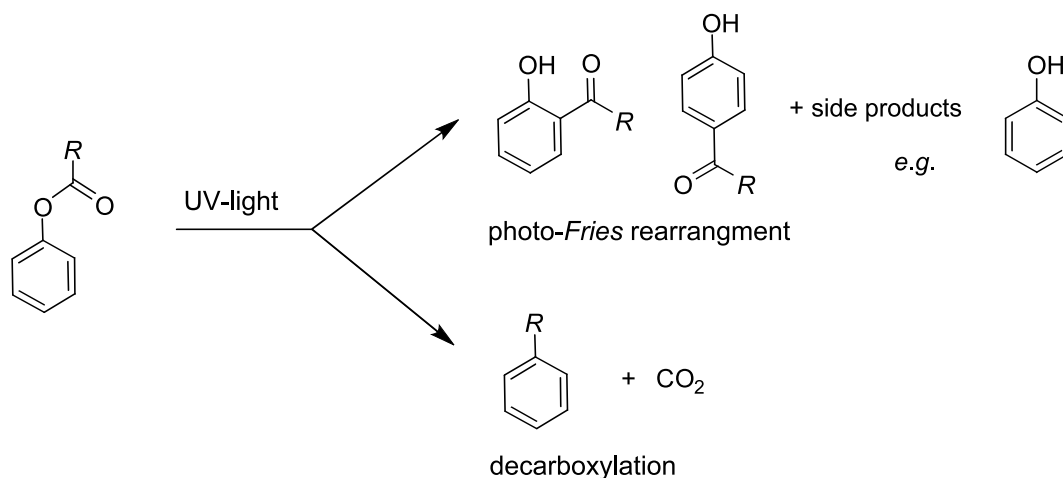
Photoreactive polymers offer the possibility of structuring polymer materials and surfaces by lithographic patterning. During the past years we have demonstrated that polymers bearing the benzyl thiocyanate group (*R*-SCN) can be used for a broad variety of applications, among them the preparation of refractive index gratings for data storage, gratings for thin film DFB lasers [1–3] as well as the immobilization of amines [4, 5] and amino-functionalized biomolecules [6] on the illuminated areas. It has also been shown that the photoreactive group can be

introduced to electroactive polymers [7]. By irradiation of the benzyl thiocyanate a photoisomerisation (SCN → NCS) takes place that leads to a refractive index patterning in the material.

Recently we have exploited the so-called photo-*Fries* reaction in poly(norbornene carboxylic acid phenyl esters) [8]. In the photo-*Fries* reaction, aromatic esters undergo an acyl shift to the corresponding *ortho*- and *para*-hydroxyketones [9–12] as depicted in Scheme 1. By this reaction, the refractive index and the surface properties are changing dramatically due to the generation of aromatic hydroxyl groups. As a competing reaction, decarboxylation is observed as reported in Refs. [13–15].

In this contribution, we combined the photo-reactivity of aryl esters with the fluorescent properties of derivatives of 4-(diphenylamino) benzoic acid. This chromophore bears the diphenylamino group as a donor component and the ester group as acceptor component [16]. The model compound hexyl 4-(diphenylamino)benzoate absorbs in the UV range with a maximum at 335 nm and shows a bright blue emission peaking in the range between 380 nm and 480 nm depending on the solvent. The photochemistry of aryl esters (Scheme 1) provides a convenient route to modify the emission characteristics of this chromophore in polymeric media. Moreover, triphenylamine and 4-(diphenylamino)benzoic acid derivatives are interesting materials for conductive layers in organic light emitting devices [17, 18].

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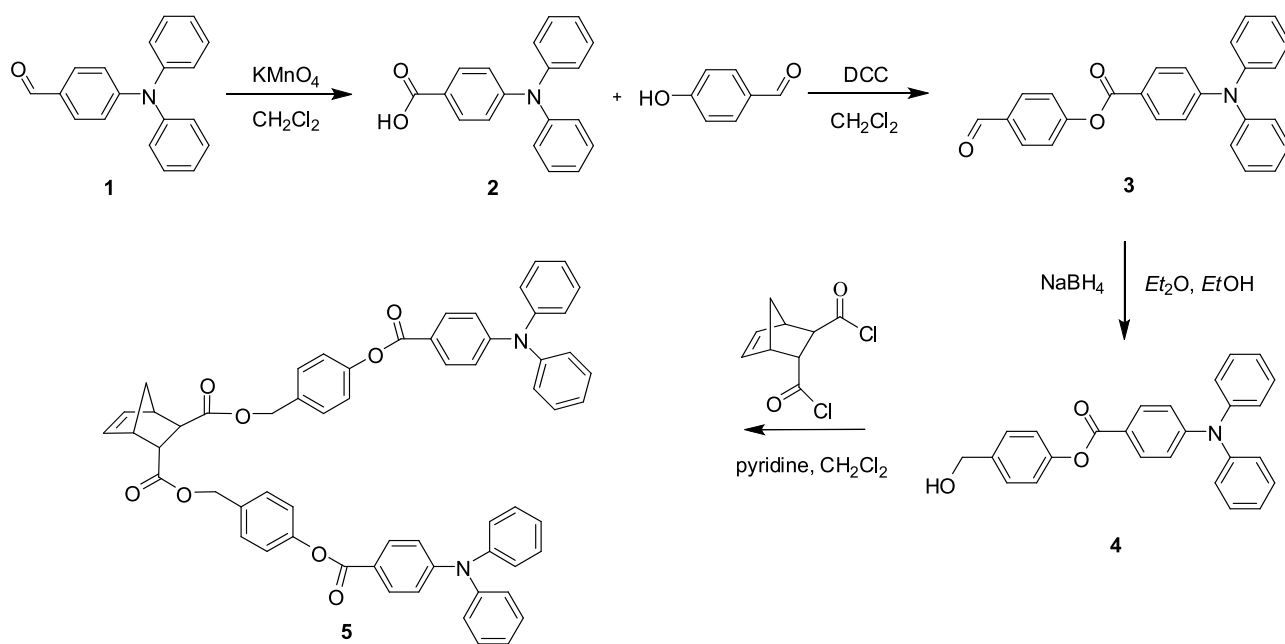


Scheme 1

Results and Discussion

The synthesis route towards the new fluorescent norbornene derivative (\pm)-*endo,exo*-bis(4-(4-(diphenylamino)benzoyloxy)benzyl)bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylate (**5**) is shown in Scheme 2. The design of this monomer was chosen such that the interposed phenyl ester moiety represents the photo-reactive group which is expected to undergo the photo-Fries reaction. In contrast to this, norbornene dicarboxylic ester units are aliphatic and remain inactive under UV light.

In a first step, 4-(diphenylamino)benzaldehyde (**1**) was oxidized with KMnO_4 using a modified literature protocol [18] giving 4-(diphenylamino) benzoic acid (**2**) in a rather low yield (29%). In the next step, compound **2** was coupled with 4-hydroxybenzaldehyde using dicyclohexyl carbodiimide (*DCC*) as catalyst to give (4-formylphenyl) 4-(diphenylamino)benzoate (**3**). The aldehyde functionality in **3** was then reduced with NaBH_4 to obtain the corresponding alcohol, (4-(hydroxymethyl)phenyl) 4-(diphenylamino)benzoate (**4**). The reaction of (\pm)-*endo,exo*-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid chloride

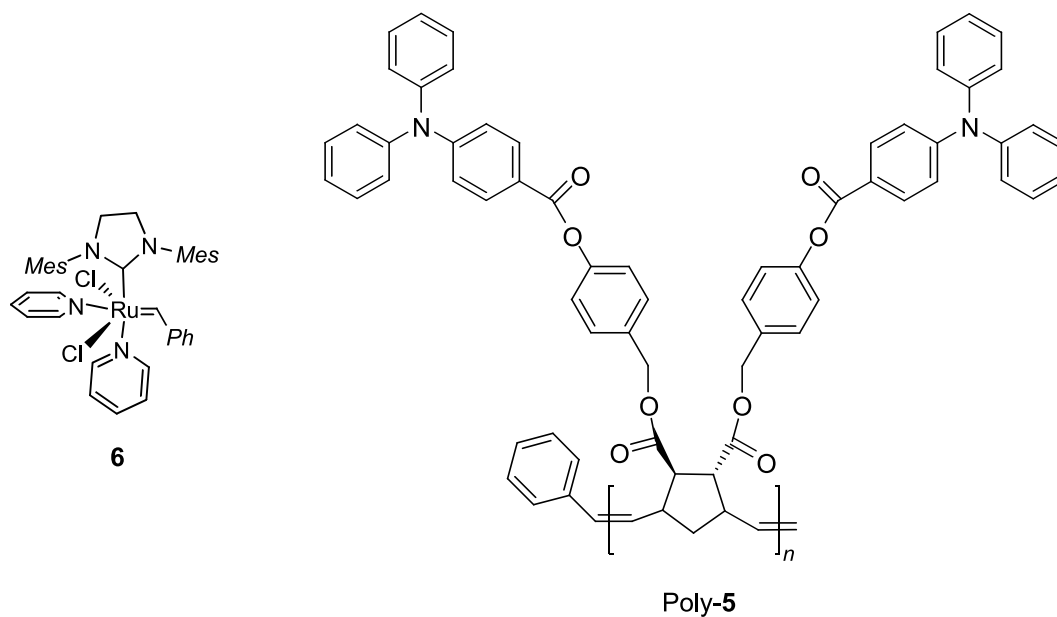


Scheme 2

with **4** then leads to the new fluorescent norbornene derivative (\pm)-*endo,exo*-bis(4-(4-(diphenylamino)benzoyloxy)benzyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**5**). The yield of this last step was rather low (7%), which may be explained by the sensitivity of this molecule towards light and hydrolysis. The spectroscopic data of this new photoreactive and fluorescent monomer are in good agreement with its constitution, see the Experimental section.

Monomer **5** was polymerized by ring opening metathesis polymerization (ROMP) using the ‘Grubbs-pyridine initiator’ $\text{RuCl}_2(\text{pyridine})_2(\text{H}_2\text{IMes})(\text{CHPh})$ (**6**, H_2IMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) at ambient temperature in

a 200:1 monomer to initiator ratio, see Scheme 3. Poly(*endo,exo*-bis(4-(4-(diphenylamino)benzoyloxy)benzyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (poly-**5**) was obtained as a white powder. The amine functionality in the monomer makes it necessary to use a highly reactive initiator, *e.g.* catalyst **6**, which represents one of the most reactive and suitable initiators for the preparation of well defined polymers [19, 20]. Even though, complete conversion of monomer **5** was not achieved (about 15% monomer did not react) and a comparable high polydispersity (PDI) of the molar mass distribution was obtained ($\text{PDI} = M_w/M_n = 1.58$). The polymer had a number average molar mass $M_n = 26300 \text{ g mol}^{-1}$ and a glass



Scheme 3

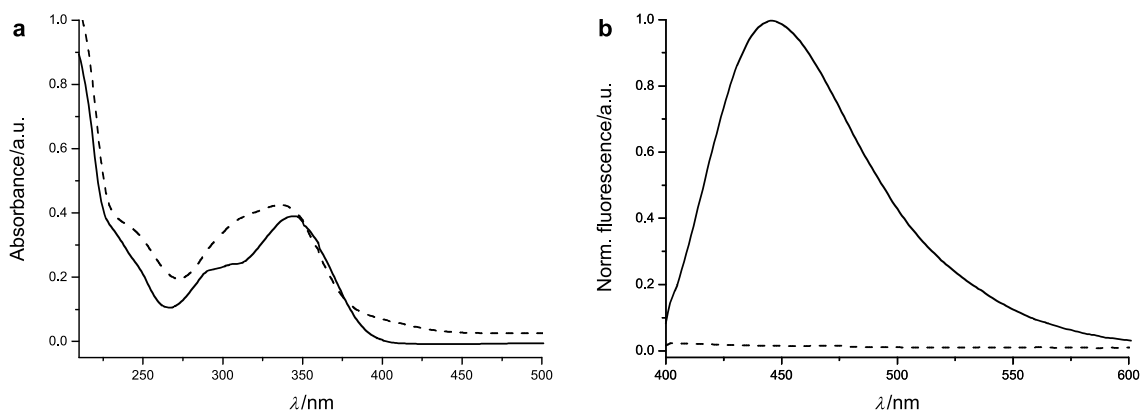


Fig. 1. UV-VIS (a) and PL-spectra (b) of poly-**5** before (solid line) and after illumination with 254 nm (irradiation dose 1.35 J/cm^2) for 120 min (dashed line)

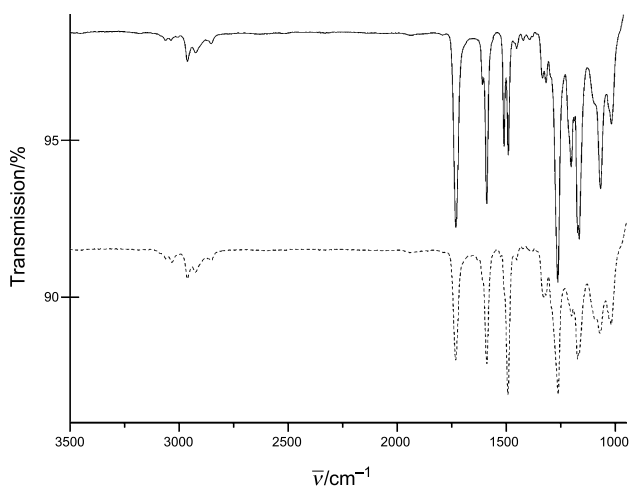


Fig. 2. FT-IR spectra of poly-5 before (solid line) and after illumination for 120 min (1.35 J/cm^2 – dashed line – spectrum shifted (-7 units) for better visibility)

transition temperature $T_g = 104.2^\circ\text{C}$. Poly-5 exhibits excellent film forming properties when spin-coated onto crystal plates from dichloromethane solution.

The UV-VIS absorbance spectrum of a solid film of poly-5 is shown in Fig. 1a and exhibits a peak at 347 nm and a shoulder at about 310 nm. In the photoluminescence spectra in Fig. 1b, a broad blue fluorescence emission with a maximum at 446 nm can be observed when the polymer film is excited at a wavelength of 346 nm.

FT-IR spectroscopy was used to investigate the photo-reactivity of poly-5. Figure 2 displays the FT-IR spectrum of a thin film of poly-5 on CaF_2 . In this spectrum several bands are attributable to ester groups: 1730 cm^{-1} (C=O valence vib.), 1263 cm^{-1} (C–O–C asym. stretch) and 1170 cm^{-1} (split band, sym. C–O–C). It is difficult to distinguish between the (aliphatic) ester groups attached to the cyclopentane ring and the fully aromatic ester bearing the triphenylamine chromophore. The split peak at 1170 cm^{-1} is typical for ROMP polymers of norbornene di-esters because both the *endo* and the *exo* isomer are present in the polymer. The strong bands at 1203 and 1060 cm^{-1} in the FT-IR spectrum are attributable to the aromatic ester units (C–O–C sym. stretch), which is indicated by reference spectra of phenyl benzoate with strong bands at 1266 , 1200 and 1060 cm^{-1} [21].

When a film of poly-5 was irradiated with 313 nm UV-light near the absorption maximum (under inert gas conditions), no photo-reaction was observed

even after prolonged irradiation time. The bright blue fluorescence of the polymer remained unchanged under these conditions. However, when UV illumination was carried out with higher-energetic light (254 nm; under inert gas), the blue fluorescence bleached slowly and vanished to a large extent after 30 minutes. After 120 min of 254 nm illumination the fluorescence disappeared completely.

In Fig. 1a and b, also the UV-VIS absorbance and the fluorescence spectra of poly-5 are shown, which were recorded after 120 min of illumination with 254 nm UV light (under inert gas atmosphere). While the UV-VIS absorbance changed only slightly the fluorescence disappeared entirely.

Having a closer look at the FT-IR spectrum of an irradiated film of poly-5, significant changes are discernible. The ester signals at 1730 , 1263 , and 1170 cm^{-1} are reduced to approximately half of their intensity, whereas the signals at 1203 and 1060 cm^{-1} disappear to a large extent. In comparison, the aliphatic C–H stretching vibrations in the range 2960 – 2850 cm^{-1} and also the aromatic C–H vibrations in the range 3100 – 3000 cm^{-1} are of equal intensity prior to and after UV illumination.

The results from UV-VIS and FTIR spectroscopy indicate that, first, the overall thickness of the film does not change significantly, which rules out oxidative photo-degradation. The reduction of the intensity of the ester bands 1730 , 1263 , and 1170 cm^{-1} to approx. 50% shows that a significant fraction of the ester units is transformed during the irradiation. From the fact that the FTIR signals typical of the aromatic ester units (1203 and 1060 cm^{-1}) are decreased to a far larger extent while the remaining signals are attributable to aliphatic ester units, we conclude that the photosensitive group (*i.e.* the phenylester of 4-(diphenylamino)benzoic acid) reacted selectively and almost completely. This is also the reason for the loss of fluorescence of the material. However, the expected photo-Fries reaction should lead to the formation of aromatic hydroxyketones, and therefore new bands around 1630 cm^{-1} should appear. However, in the FTIR spectrum recorded after illumination for 120 min only negligible absorbance at 1630 cm^{-1} was detected. Thus, the main photolysis reaction must be a different one. In addition, no other carbonyl vibrations evolve in the FTIR-spectrum. From literature [13, 14] it is known that the loss of carbon dioxide in aromatic esters occurs as a competing reaction in this type of pho-

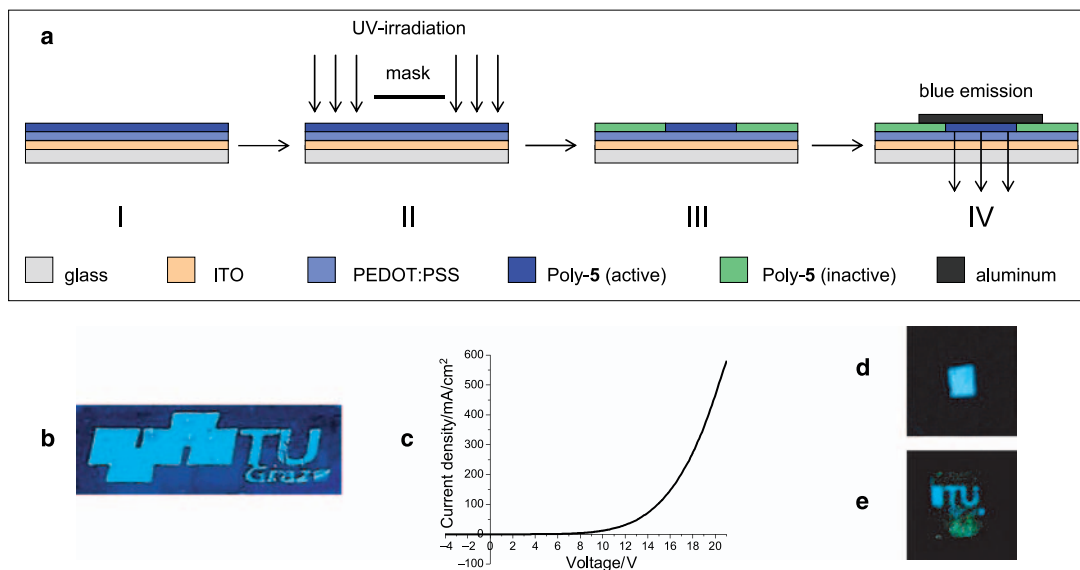


Fig. 3. a) Scheme of the preparation of a (structured) OLED using a simple lithographic mask for patterning; b) a photograph of a structured film taken under UV-light of 302 nm shows the bright fluorescence of the material; c) shows the current density-voltage characteristics of a non structured OLED. Pictures of such an OLED and a structured OLED are shown in d and e

tochemistry. It has been proposed that the photodecarboxylation of $R-(CO_2)-R'$ to give $R-R'$ (R = aromatic, R' = benzyl or alkyl) proceeds *via* a concerted, non-radical mechanism from the excited S_1 state [15]. Steric hindrance due to substituents on the aromatic rings and limited mobility in the polymer matrix enhance the yield of the photoextrusion product $R-R'$. Generally, photodecarboxylation is enhanced in constrained media and at lower temperatures.

In poly-5 the loss of carbon dioxide would destroy the push-pull chromophore, which explains the loss of blue fluorescence. This process was applied for photolithographic patterning of fluorescent films. For this purpose, a thin film of poly-5 was UV illuminated through a contact mask (254 nm, inert atmosphere), see Fig. 3a. Figure 3b shows the fluorescent image of a structured film which was taken while the sample was excited with 302 nm UV-light.

In an additional experiment we tested this new material as light emitter in organic light emitting devices (OLED). For this purpose a simple OLED was assembled on an indium-tin oxide (ITO) coated glass substrate. The build-up is schematically depicted in Fig. 3a. The transparent ITO electrode was covered with a film of poly(3,4-ethylene-dioxythiophene)/poly(styrene-4-sulfonate) (PEDOT-PSS) which acts as electron injection layer, followed by a layer of

poly-5 as emissive material. Finally, on top of this device a layer of aluminum was evaporated (contact electrode). Figure 3c shows the current density/voltage characteristics of this device, Fig. 3d shows the blue electroluminescence of this device when operated at 18 V.

The combination of the above-mentioned photo-reaction with the electroluminescence of this polymer was employed for patterning the OLED. In Fig. 3a the schematic preparation of a structured device is depicted. After deposition of poly-5 a contact mask is placed on the surface and the sample is irradiated with 254 nm UV light. The photo-reaction leads to the destruction of electroluminescence in the illuminated areas. In Fig. 3e a photograph of a structured OLED based on this process is shown. A more detailed characterization of the electroluminescence of poly-5 and the fabrication of color-patterned devices are subjects of current research.

Conclusion

The functional polymer poly-5 is a photoreactive material that additionally shows bright fluorescence in the blue region. Irradiation with UV light (254 nm) under inert atmosphere causes decarboxylation of the aromatic ester groups, which leads to a complete loss of photoluminescence and electrolumi-

nescence. It has been shown that thin films of this polymer can be easily patterned by photolithography. This provides a convenient route to produce structured OLEDs.

Experimental

All chemicals were purchased from commercial sources and used without further purification. $\text{RuCl}_2(\text{pyridine})_2(\text{H}_2\text{Mes})$ (CHPh) (**6**) was prepared according to Ref. [22]. CH_2Cl_2 was distilled over CaH_2 and degassed with Ar. All experiments were carried out under inert atmosphere using *Schlenk*-technique or a glove box.

Size exclusion chromatography (SEC): The weight and number average molecular weights (M_w and M_n) as well as the polydispersity index (PDI) were determined by size exclusion chromatography with *THF* as solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8×300 mm STV $5 \mu\text{m}$ grade size (106, 104, and 103 \AA), combined refractive index – viscosity detector from Viscotec, Viscotec 200. Polystyrene standards purchased from Polymer Standard Service were used for calibration.

^1H -NMR and ^{13}C -NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 499.803 and 125.687 MHz, and were referenced to *TMS*. A relaxation delay of 5 s and 45° pulse were used for acquisition of the ^1H -NMR spectra to guarantee accurate integration of the corresponding signals. Peak shapes are indicated as follows: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet), b (broad), v (virtual splitting). Solvent residual peaks were used for referencing the NMR-spectra to the corresponding values given in Ref. [23]. MALDI-TOF mass spectra were performed on a Micromass ToFSpec2E time-of-flight mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm, operated at 5 Hz) and a time-lag focussing unit. Ions were generated by irradiation just above the threshold laser power. The spectra were recorded in the reflectron mode with an acceleration voltage of 20 kV and externally calibrated with a suitable mixture of poly(ethylene glycol)s (PEG). Sample solutions were prepared by mixing solutions of the matrix (dithranol in *THF*, $c = 10 \text{ mg/cm}^3$), sodium trifluoroacetate (in *THF*, 1 mg/cm^3), and the analyte ($c = 1 \text{ mg/cm}^3$) in a ratio of 20:1:1 (v/v). 0.5 mm^3 of the mixture were deposited on the sample plate (stainless steel) and allowed to dry under air. The spectra of 100–150 shots were averaged. In this work m/z values of the monoisotopic peaks of any isotope distributions are reported. DSC measurements were made with a Perkin Elmer Pyris Diamond DSC Differential Scanning Calorimeter equipped with a Perkin Elmer CCA7 cooling system using liquid nitrogen. A nitrogen flow of $20 \text{ cm}^3/\text{min}$ and a heating rate of $10^\circ\text{C}/\text{min}$ were used. Glass transition temperatures (T_g) from the second heating run were read as the midpoint of change in heat capacity. FT-IR spectra were recorded with a Perkin Elmer Spectrum One instrument (spectral range between 4000 and 450 cm^{-1}). All FT-IR spectra of the samples were recorded in transmission mode (films on CaF_2

discs). UV/VIS spectra were measured with a Jasco V-530 UV/VIS spectrophotometer. All UV/VIS spectra were taken in the absorbance mode. Photoluminescence spectra were measured on a Shimadzu RF-5301PC Spectrofluorimeter (detector corrected).

4-(Diphenylamino)benzoic acid (**2**)

A mixture of 2.70 g 4-(diphenylamino)benzaldehyde (9.88 mmol) and 0.80 g KMnO_4 (5.06 mmol) in 20 cm^3 CH_2Cl_2 and 10 cm^3 H_2O was heated under reflux in presence of a catalytic amount of hexadecyl-trimethylammonium chloride as a phase transfer catalyst. After 20 h another portion of 0.80 g KMnO_4 (5.06 mmol) was added and the mixture was heated under reflux for 24 h. The mixture was cooled down and centrifuged (5 min, 4000 rpm). The supernatant was separated and the residue was extracted with *THF* and water and centrifuged again. The combined supernatants were acidified with diluted aqueous acetic acid (10% , $2 \times 50 \text{ cm}^3$) and then washed with saturated sodium chloride solution (50 cm^3) and NaHCO_3 solution ($2 \times 50 \text{ cm}^3$). The organic layer was dried over anhydrous sodium sulphate. Evaporation of the solvent yielded the crude 4-(diphenylamino)benzoic acid as brown oil. Purification by column chromatography (side products were removed by using ethyl acetate:cyclohexane 1:5 with a few drops of triethylamine, the product was eluted with ethyl acetate to which a few drops of acetic acid was added) gave 0.84 g (29%) orange crystals of **2**. The ^1H -NMR data are in good accordance to Ref. [24]. Mp $203\text{--}204^\circ\text{C}$; $^{13}\text{C}\{^1\text{H}\}$ NMR: 171.7 (COOH), 152.7 (C4), 146.4 (C1'), 131.6 (C2, C6), 129.6 (C3', C5'), 126.0 (C2', C6'), 124.7 (C4'), 119.5 (C3, C5), 120.8 (C1) ppm.

(4-Formylphenyl)-4-(diphenylamino)benzoate

(**3**, $\text{C}_{26}\text{H}_{19}\text{NO}_3$)

To an icecooled solution of 0.70 g of **2** (2.42 mmol) in anhydrous CH_2Cl_2 (20 cm^3), 1.22 g 4-hydroxybenzaldehyde (10 mmol) were added. After 20 min 2.06 g *DCC* (10 mmol) were added. The mixture was allowed to warm to room temperature and was stirred for 20 h. The reaction was quenched with aqueous HCl (5% , 20 cm^3) and stirred for 5 min. Then the reaction mixture was filtered over Celite. The filtrate was washed with saturated NaHCO_3 solution (50 cm^3) and H_2O ($50 \text{ cm}^3 \times 3$) and dried over anhydrous Na_2SO_4 . After evaporation of the solvent the crude product was purified by column chromatography (acetate:cyclohexane 1:5) to give 0.71 g (60%) of **3**. Mp $91\text{--}92.5^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3): $\delta = 10.02$ (s, H-CHO), 7.99 (d, $J = 8.83$ Hz, H-2,6), 7.95 (d, $J = 8.50$ Hz, H-2'',6''), 7.39 (d, $J = 8.50$ Hz, H-3'',5''), 7.35 (vt, H-3',5'), 7.20–7.15 (m, H-2',4',6'), 7.03 (d, $J = 8.83$ Hz, H-3,5) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 191.0$ (CHO), 164.2 (–COO–), 156.0 (C4), 152.9 (C4''), 146.3 (C1'), 133.8 (C1''), 131.7 (C2, C6), 131.20 (C2'', C6''), 129.7 (C3', C5'), 126.1 (C2', C6'), 124.9 (C4'), 122.6 (C3'', C5''), 120.0 (C1), 119.4 (C3, C5) ppm; IR (thin film on CaF_2): $\bar{\nu} = 2956, 2920, 2851, 1733, 1700, 1588, 1508, 1491, 1465, 1333, 1315, 1296, 1264, 1209, 1173, 1156, 1060 \text{ cm}^{-1}$; MALDI MS (m/z): $[\text{M} \cdot \text{Na}^+]$ 416.1273 (calcd. 416.1263).

4-(Hydroxymethyl)phenyl-4-(diphenylamino)benzoate
(**4**, C₂₆H₂₁NO₃)

A solution of 17 mg NaBH₄ (0.45 mmol) in 50 cm³ ethanol was dropped into a solution of 0.7 g **3** (1.78 mmol) in a 1:1 mixture of diethyl ether:ethanol (100 cm³) and the reaction mixture was stirred overnight at room temperature. Diluted HCl (100 mm³) was added to the reaction mixture. After evaporation of the solvent the crude product was purified by column chromatography (ethyl acetate/cyclohexane = 1/5) to give 0.51 g (72%) of **4**. ¹H NMR (500 MHz, CDCl₃): δ = 7.99 (d, *J* = 8.79 Hz, H-2,6), 7.41 (d, *J* = 8.27 Hz, H-2'', H6''), 7.34 (vt, H-3',5'), 7.19–7.13 (m, H-3'',5'',2',4',6'), 7.03 (d, *J* = 8.79 Hz, H-3,5), 4.71 (s, PH-CH₂-), 3.48 (s, OH) ppm; ¹³C{¹H}NMR (125 MHz, CDCl₃): δ = 165.0 (COOR), 152.6 (C4), 150.5 (C4''), 146.4 (C1'), 138.2 (C1''), 131.5 (C2, C6), 129.6 (C3', C5'), 128.1 (C2'', C6''), 126.0 (C2', C6'), 124.7 (C4'), 121.9 (C3'', C5''), 120.9 (C1), 119.6 (C3, C5) ppm; FT-IR (thin film on CaF₂): $\bar{\nu}$ = 3382, 3063, 3038, 2930, 2854, 1729, 1608, 1589, 1562, 1509, 1490, 1451, 1335, 1318, 1271, 1202, 1174, 1072, 1015 cm⁻¹; MALDI MS (*m/z*): [M · Na⁺] 418.1434 (calcd. 418.1419).

(±)-*Endo,exo-bis(4-(4-(diphenylamino)benzoyloxy)benzyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate*
(**5**, C₆₁H₄₈N₂O₈)

A solution of 0.50 g **4** (1.26 mmol) and 350 mm³ pyridine (4.3 mmol) in 20 cm³ of CH₂Cl₂ was cooled with an ice/H₂O bath. *Endo,exo*-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid chloride (132 mg, 0.60 mmol) was slowly dropped into the reaction mixture, afterwards, the cooling bath was removed, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was extracted with 5% HCl solution and saturated NaHCO₃ solution and dried with Na₂SO₄. After evaporation of the solvent the crude product was purified by column chromatography (ethylacetate/cyclohexane = 1/5) to give 80 mg (7%) white amorphous powder of **5**. mp amorphous, *T*_g not observed; ¹H NMR (500 MHz, CDCl₃): δ = 7.99 (d, *J* = 8.79 Hz, H-2,6), 7.40 (d, *J* = 8.33 Hz, H-2'',6''), 7.37 (d, *J* = 8.48 Hz, H-2'',6''), 7.33 (vt, H-3',5'), 7.20–7.13 (m, H-3'',5'',2',4',6'), 7.02 (d, *J* = 8.79 Hz, H-3,5), 6.27 (m, nb6), 6.01 (m, nb5), 5.19–5.05 (m, O-CH₂-Ph), 3.46 (m, nb3), 3.29 (m, nb4), 3.15 (m, nb1), 2.78 (m, nb2), 1.62 (m, nb7b), 1.46 (m, nb7a) ppm; ¹³C{¹H}NMR (125 MHz, CDCl₃): 174.1, 172.9 (nb-COO-), 164.8 (-COO-), 152.6 (C4), 151.0, 150.5 (C4''), 144.4 (C1'), 137.6 (nb6), 135.1 (nb5), 133.2, 133.3 (C1''), 131.5 (C2, C6), 129.6 (C3', C5'), 129.3, 129.3 (C2'', C6''), 126.0 (C2', C6'), 124.7 (C4'), 122.0, 121.9 (C3'', C5''), 120.8 (C1), 119.7 (C3, C5), 66.1, 65.8 (Ph-CH₂-O), 48.0 (nb3), 47.7 (nb1), 47.3 (nb7), 47.2 (nb2), 45.8 (nb4) ppm (nb = norbornene); FT-IR (thin film on CaF₂): $\bar{\nu}$ = 3063, 3041, 2960, 1729, 1607, 1588, 1510, 1490, 1333, 1317, 1262, 1202, 1173, 1164, 1067 cm⁻¹; MALDI MS (*m/z*): [M · Na⁺] 959.3360 (calcd. 959.3308).

Poly-(endo,exo-bis(4-(4-(diphenylamino)benzoyloxy)benzyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (poly-**5**)

To a solution of 80 mg **5** (85 μmol) in 4 cm³ CH₂Cl₂ 0.31 mg of initiator **6** (0.427 μmol) dissolved in 2 cm³ of CH₂Cl₂ were

added. The reaction mixture was stirred at room temperature for 12 h and then the reaction was stopped by adding five drops of ethyl-vinylether. The polymer was precipitated by dropping the solution into cold methanol. The precipitate were dried in vacuum and 55 mg of a white powder of poly-**5** were obtained (69%). SEC (*THF*): *M*_n = 26320 g/mol; *M*_w = 41700 g/mol; *T*_g = 104.2°C; ¹H NMR (500 MHz, CDCl₃): δ = 7.96–7.80 (H-2,6), 7.41 (H-2'',6''), 7.37 (H-2'',6''), 3',5',3'',5'',2',4',6',3,5), 5.55–4.69 (=CH, O-CH₂-Ph), 3.42–2.57 (nb1,2,3,5), 2.16–1.74 (nb4) ppm; ¹³C{¹H}NMR (125 MHz, CDCl₃): 174.6–172.5 (nb-COO-), 165.0–164.3 (-COO-), 152.5–152.3, 151.1–150.6 (C4''), 146.8–146.4 (C1'), 133.5–132.9 (C1''), 131.9–131.4 (C2, C6), 130.2–128.9 (C3', C5', C2'', C6'',=CH), 126.3–125.7 (C2', C6'), 124.7–124.3 (C4'), 122.4–121.6 (C3'', C5''), 121.3–120.7 (C1), 120.2–119.6 (C3, C5), 66.0–65.5 (Ph-CH₂-O), 53.6–38.7 (nb-CH,CH₂) ppm (nb = norbornene); IR (thin film on CaF₂): $\bar{\nu}$ = 3062, 3034, 2962, 2926, 2851, 1731, 1609, 1589, 1510, 1490, 1451, 1334, 1317, 1263, 1202, 1173, 1165, 1067 cm⁻¹.

UV-Irradiation Experiments

Irradiation experiments were carried out in inert atmosphere (nitrogen) using a UV lamp 8W-model UVLMS-38 3 UV assembly (UVP, Upland, CA) at a wavelength of 254 nm. For these experiments, the light intensity at the sample surface was measured with a spectroradiometer (Solatell, Sola Scope 2000TM, spectral range from 230 to 470 nm) to be 188 μW/cm². Patterned structures were obtained by placing a contact mask (Cr pattern on quartz) directly onto the polymer film prior to illumination.

Acknowledgments

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