

Supplementary information

Photochemical tuning of light emission in a conjugated polymer containing norbornadiene units in the main chain

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1) Synthesis and characterization of polymer **3**

A mixture of 2,3-dichloronorbornadiene **1** (0.26 g, 1.59 mmol), 1,4-bis(ethynyl)benzene **2** (0.20g, 1.59 mmol), Pd(PPh₃)₄ (0.093 g, 0.08 mmol), CuI (0.031 g, 0.16 mmol) and butylamine (9 ml) in 30 ml of benzene was stirred under a nitrogen atmosphere. After six days, the solvent was evaporated under reduced pressure. The crude polymer obtained was extracted in a soxhlet apparatus with hexane (6 h) and methanol (6 h), to eliminate residual phosphine. A final soxhlet extraction with chloroform afforded, after evaporation of the solvent, a red powder (0.33 g, 98%).

¹HNMR (500 MHz, CDCl₃): δ 2.15 (br.s 1H), 2.28 (br.s 1H), 3.75 (br.s 2H), 6.81 (br.s 2H), 7.45 (br.s 4H) ppm

¹³CNMR (125MHz, CDCl₃): δ 56.16, 71.34, 88.08, 103.46, 123.23, 131.30, 132.42, 141.91 ppm.

IR (KBr): ν 2938, 2190, 1600, 1300, 1017, 909, 835, 732, 702 cm⁻¹.

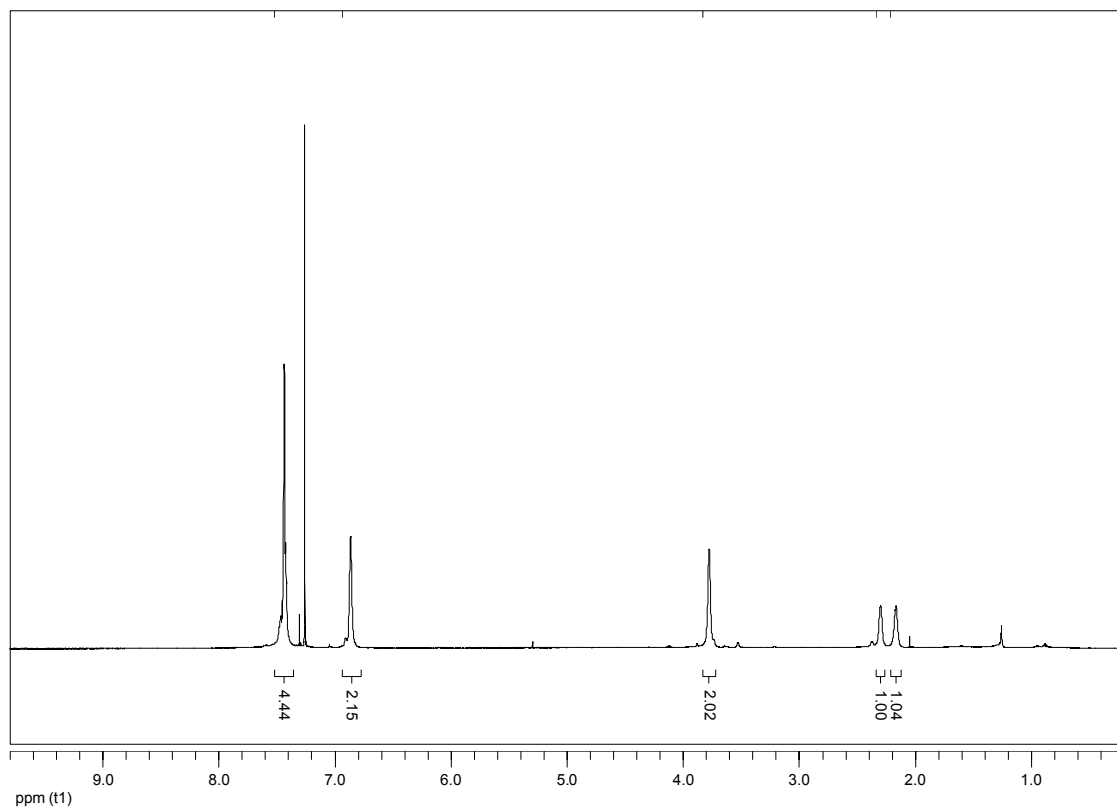


Figure 1. ¹H NMR spectrum of the polymer 3

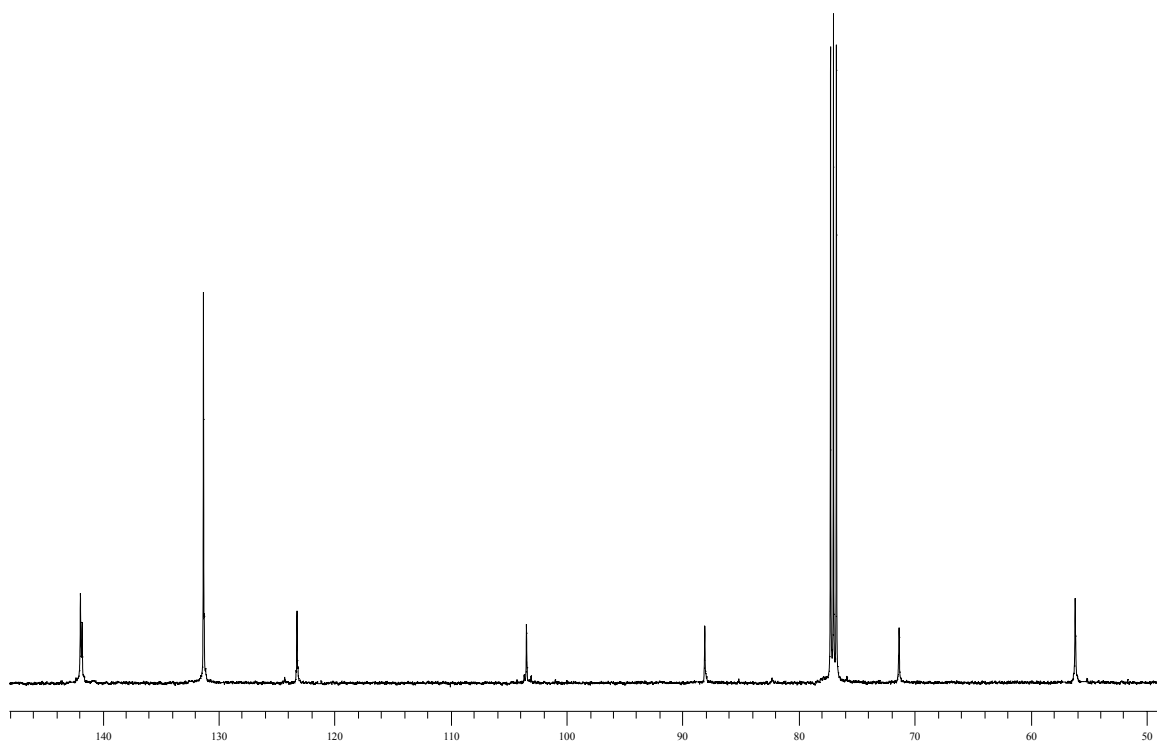


Figure 2. ¹³C NMR spectrum of the polymer 3

Thermal analysis of polymer **3**, performed via a Perkin Elmer Pyris DSC setup did not reveal the presence of any transition. No melting point was detected up to 260 °C. The possibility of a thermal isomerization to the quadricyclane isomer was therefore excluded (it is reported to involve ca. 24 Kcal/mol).¹

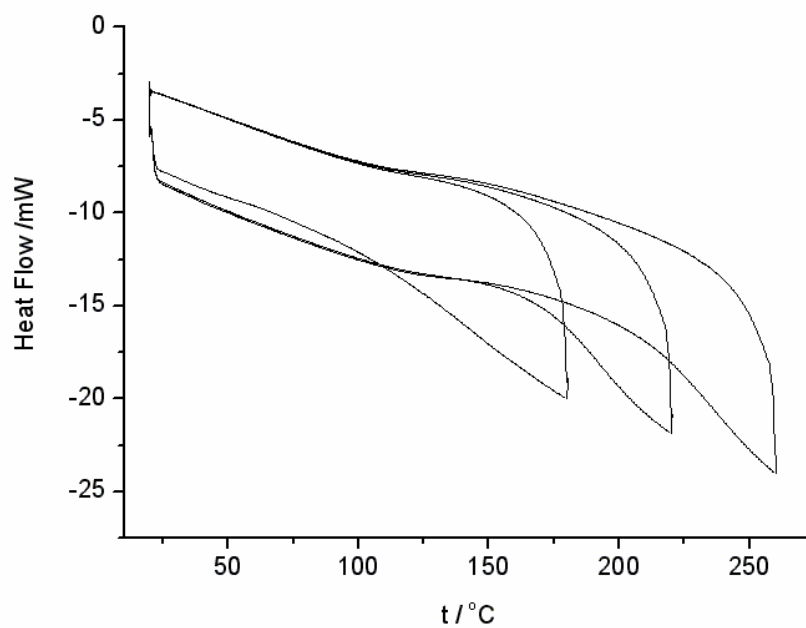


Figure 3. DSC traces of polymer **3** heated at 180, 220 and 260 °C.

2) Spectroscopic data for the model compound 4

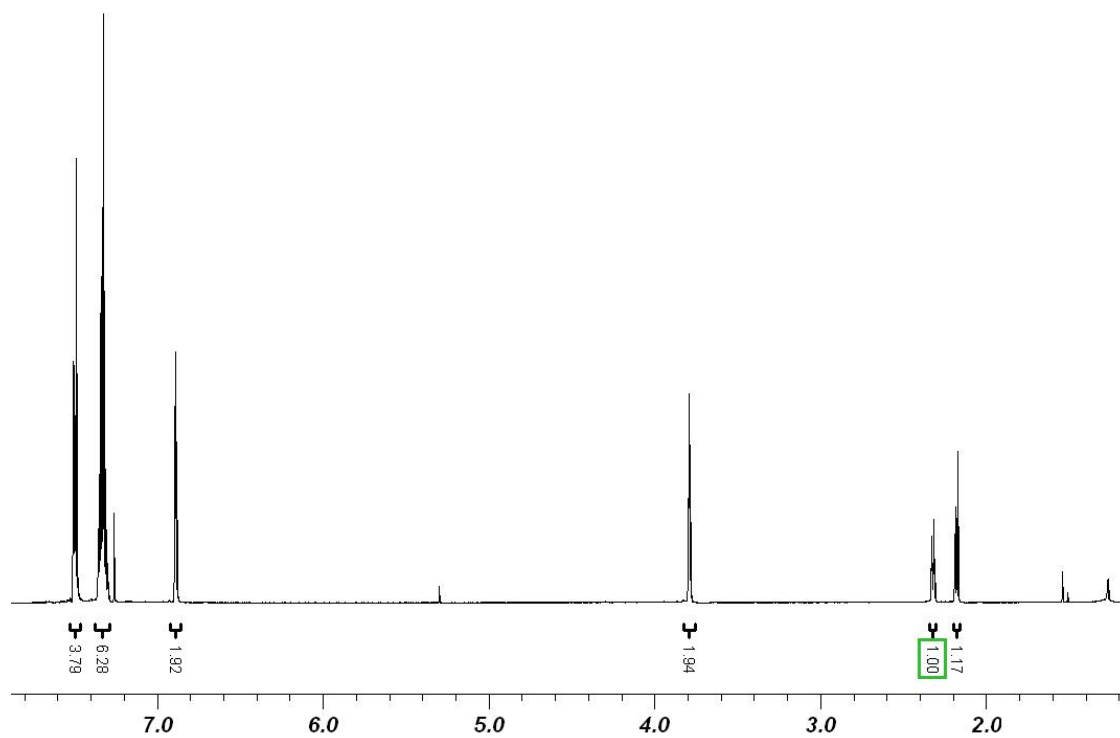


Figure 4. ^1H NMR spectrum of compound 4

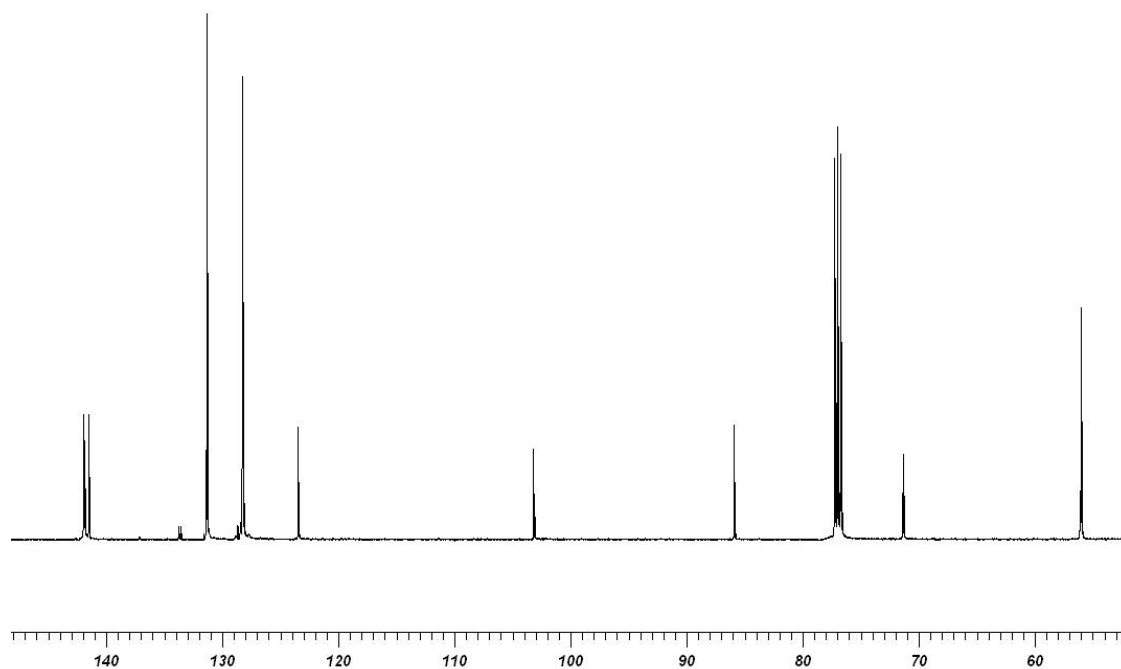


Figure 5. ^{13}C NMR spectrum of the model compound **4**

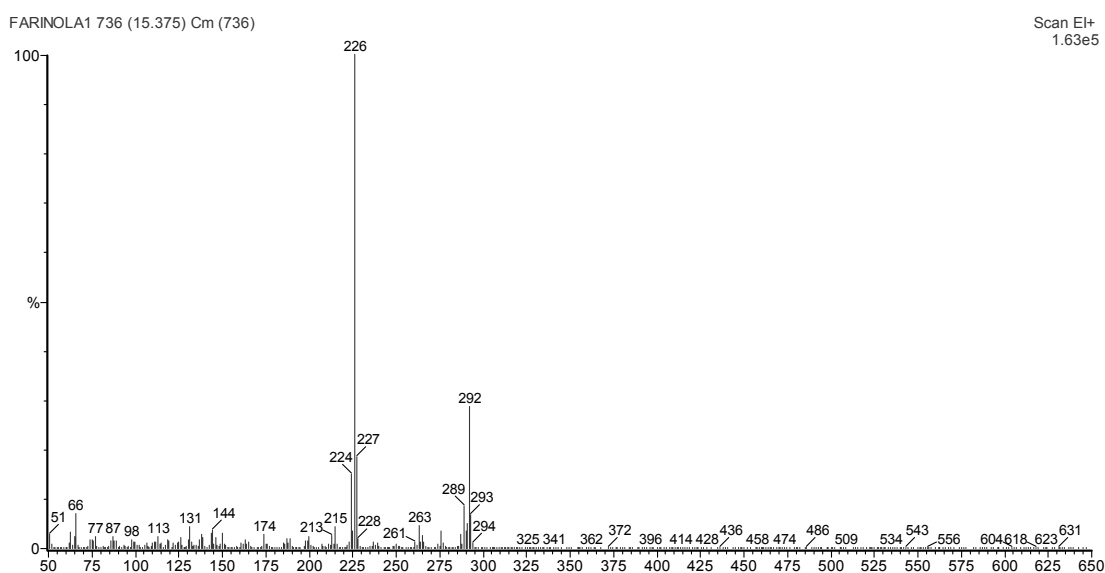


Figure 6. Low resolution mass spectrum of the model compound **4**

3) Photo-induced isomerization of the model compound **4**

Photo-induced isomerization of compound **4** was performed by irradiating a 3.5×10^{-5} M solution of **4** in spectroscopic grade THF, in quartz cells of 1 cm optical path, using a 30 W low pressure lamp, with emission centered at 302 nm (UVB). The lamp is just a normal UV lamp used for chromatography experiments due to the low photon emission. Absorption spectra were recorded with a Varian Cary 5000 UV-Vis-NIR spectrophotometer, subtracting the absorption spectrum of neat THF. The photo-conversion was calculated by the disappearance of the conjugated system $\pi-\pi^*$ transition centered at 355 nm for model compound **4**, according to the Lambert-Beer law.

Preparative photo-isomerization of compound **4** (50 mg) was performed in nitrogen flushed freshly distilled THF (over Na/Benzophenone) (80 ml), under nitrogen, using a 125 W high pressure Hg immersion lamp. After 3 minutes irradiation, the solvent was evaporated and the crude product was dissolved in CDCl_3 . By comparing, in the ^1H NMR spectrum, the integral value of the signal at $\delta = 2.10$ ppm, which is attributed to one of the two apical protons of **4** with that of the signals at $\delta = 2.05$ ppm, attributed to a proton in the same position of the quadricyclane **5**, it is possible to calculate the ratio between these two products in the photo-isomerized mixture. On this basis, the conversion of **4** into **5** via the photoisomerization process was estimated to be 73%. Attempts to purify product **5** by chromatography on silica gel resulted in quantitative back-conversion to **4**. Also chromatography on alumina failed to separate product **5** from compound **4**. The ^1H NMR signals were therefore assigned from the spectrum of the crude mixture, as the signals of compound **4** in chloroform were known.

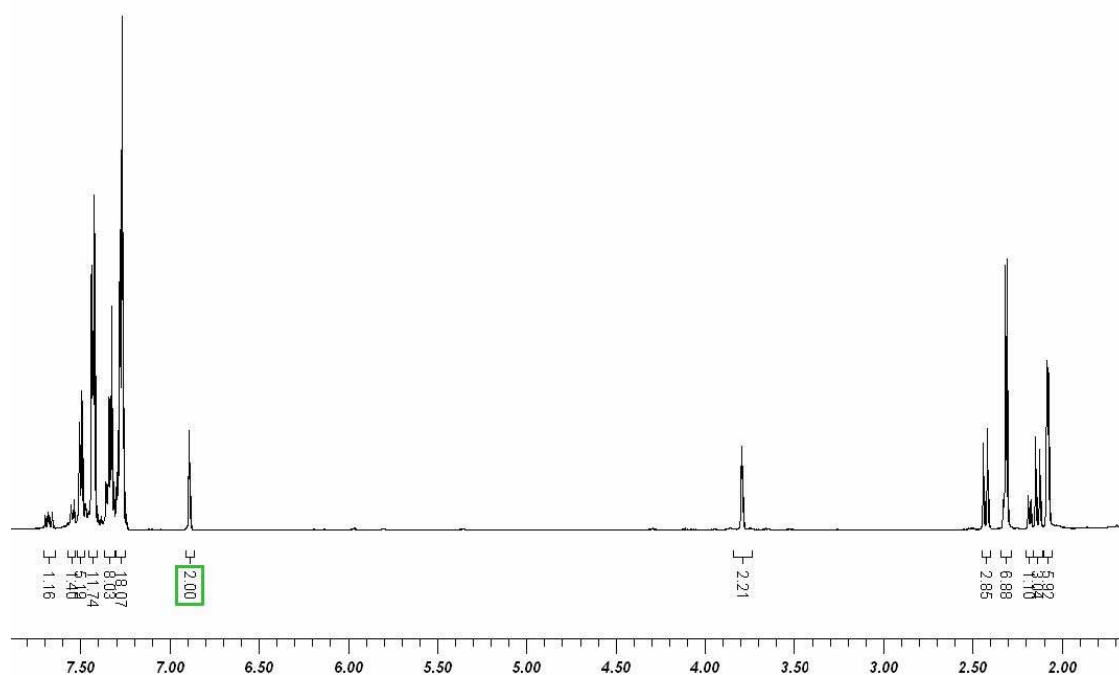


Figure 7. ^1H NMR spectrum of the photo-isomerization crude mixture

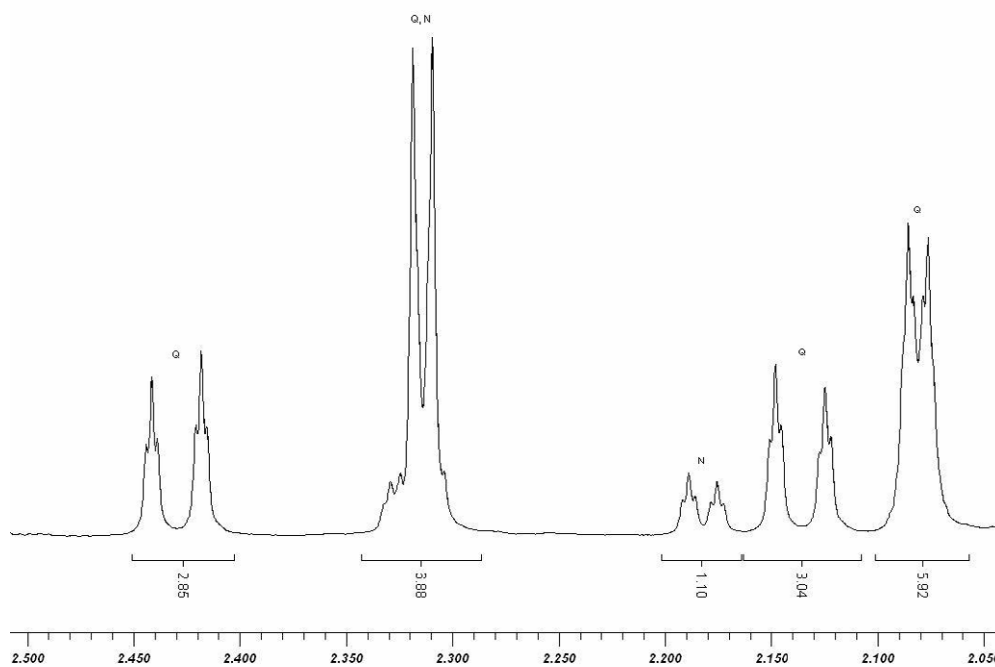


Figure 8. ^1H NMR spectrum of the photo-isomerization crude mixture: expanded region
Q signals are attributed to quadricyclane **5** unit; N signals are attributed to norbornadiene **4**

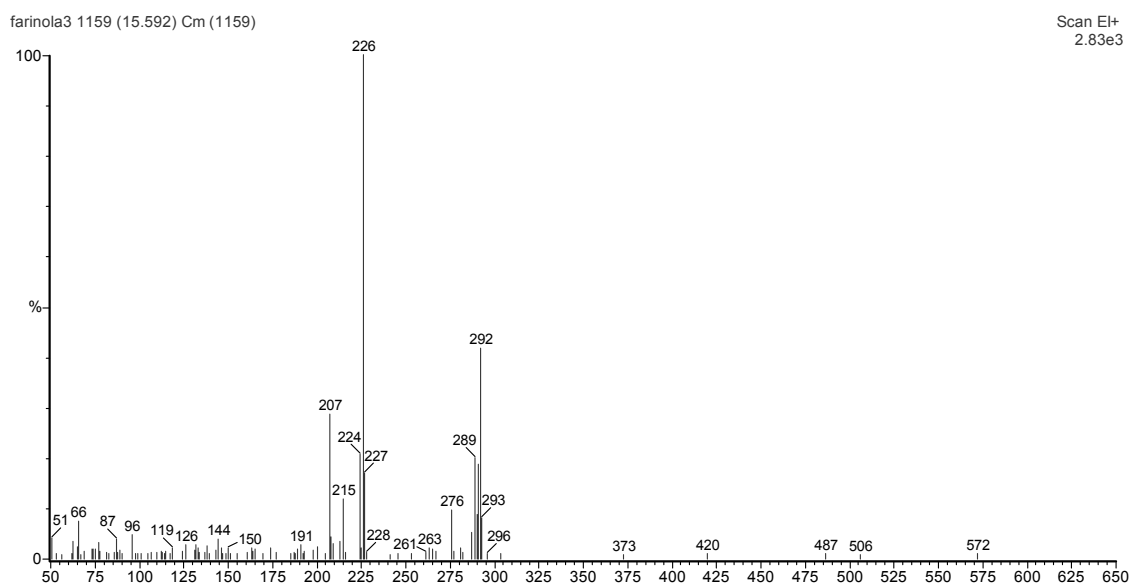


Figure 9. Low resolution mass spectrum of quadricyclane **5**.

4) Irradiation experiment of polymer **3** in solution

An argon flushed 3.5×10^{-5} M solution of polymer **3** (based on monomer molecular weight) in spectroscopic grade THF, in quartz cells of 1 cm optical path, was irradiated using a 30 W low pressure lamp, with emission centered at 302 nm (UVB). Absorption spectra were recorded with a Varian Cary 5000 UV-Vis-NIR spectrophotometer, subtracting the absorption spectrum of neat THF (fig.10). The photo-conversion was calculated by the disappearance of the conjugated system $\pi-\pi^*$ transition centered at 388 nm for polymer **3**, according to the Lambert-Beer law.

Emission spectra were recorded on the same solutions used for the absorption spectroscopy, by using a Varian Eclipse fluorimeter, with excitation wavelength centered at 309 nm for polymer **3**. An excitation filter was used to reduce the intensity of the 618 nm harmonic from the emission spectra. Excitation spectra were run on each sample and compared to the absorption spectra. Photoluminescence quantum yield of polymer **3** was measured using quinine sulfate in 0.5 M H_2SO_4 as reference ($\Phi = 0.546$), using a correction curve to equalize the response of the detector. The photoluminescence of polymer **3** at different irradiation times was measured against unconverted polymer **3**, as the excitation wavelength was selected as it is an isosbestic point in the UV-visible absorption spectrum.

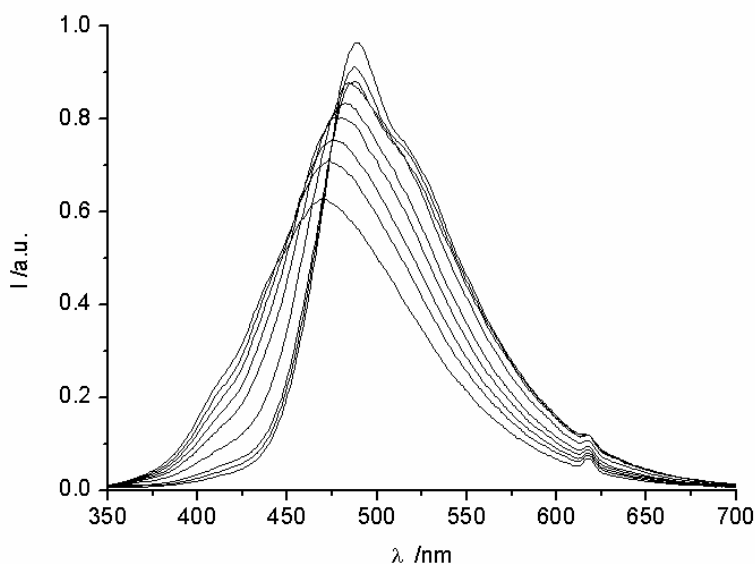


Figure 10. Emission spectra of polymer **3** in THF solution at different exposure times to UV light ($t = 0$ to one hour).

5) Irradiation experiments of polymer **3** in thin film

Thin films were obtained by spin coating a 4 g/L solution of polymer **3** in HPLC grade THF, filtered through a 0.45 μm PTFE membrane. To the solution, 0.4 g/L of PVC were added, to improve the film forming properties of the low molecular weight polymer **3** and to avoid the reorganization of the film in a polycrystalline configuration. As expected, bathochromic shifts either in absorption or in emission were observed for polymer **3** when passing from solution to solid state.

Thin film thickness was homogeneous along the 2 cm wide surfaces, with an average thickness of 95 nm, measured by means of a Veeco Dek-Tak 8 stylus profilometer.

Irradiation of thin films of polymer **3** on 2 cm wide glass slides was performed using a 30W UV lamp, with emission centered at 302 nm. The film was protected by oxygen with a quartz slide on top. Absorption spectrum after irradiation resulted in loss of conjugation, similarly to the solution behavior.

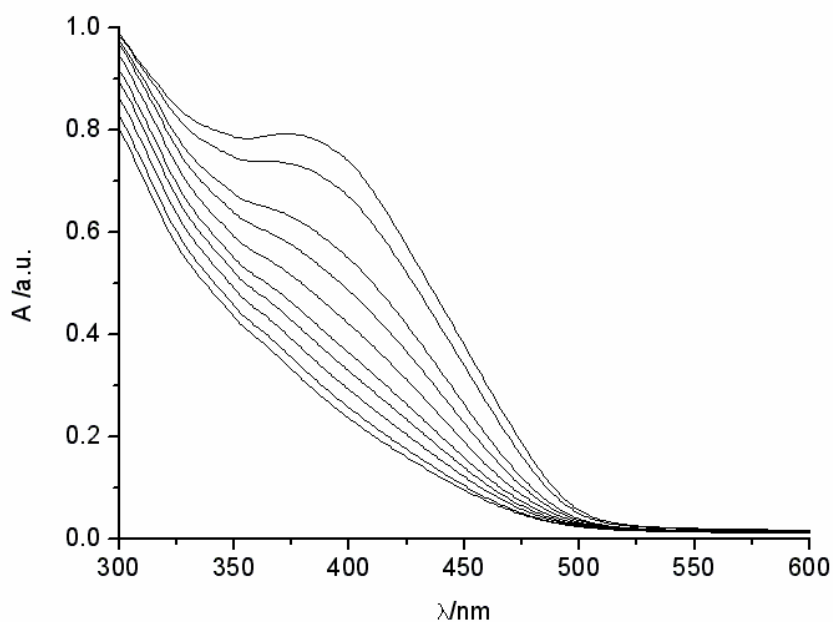


Figure 11. Decay of π - π^* absorption band in a film of polymer **3**, upon exposure to UV light. (t = 0 to one hour)

Supplementary Material (ESI) for Photochemical & Photobiological Sciences
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References.

1. Rogers D. W.; McLafferty F. J., *J. Phys. Chem. A*, **1999**, 8733.