Supporting Information

π-Conjugated PolyHIPEs as Highly Efficient and Reusable Heterogeneous Photosensitizers

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Introduction

Synthetic routes, elemental analysis, FTIR spectra, CD MAS ^{13}C NMR in solid state, TGA analysis and surface area analysis of **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL** are shown. Experimental details of singlet oxygen generation set-up are provided. Synthetic procedure, ^{1}H NMR spectrum and UV absorption of **BT-FL** is shown.

Experimental Section

All chemicals and solvents were purchased from commercial sources and used without further purification. Air- and/or water-sensitive reactions were conducted under nitrogen using anhydrous solvents.

General

^{1}H-NMR was performed on a Brucker 400-MHz spectrometer, operating at 400 MHz.

Solid State NMR. ^{13}C CP MAS measurements were carried out using Bruker Avance II solid-state NMR spectrometer operating at 300 MHz Larmor frequency equipped with a standard 4 mm magic angle spinning (MAS) double resonance probe head.

Infrared Spectroscopy. FT-IR spectra for the characterization of the compounds were recorded on a Varian1000 FT-IR spectrometer.

Elemental Analysis. EA were obtained on a Perkin-Elmer 2400 elemental analyzer.

UV/Vis. UV/Vis absorption spectra in solution (**BT-FL**) were measured on a Perkin-Elmer spectrophotometer. The insoluble networks (**CP-HIPEs**) were first grounded and measured in solid state using Perkin Elmer lambda 900 spectrometer.

Fluorescence. Fluorescence measurements were performed on a Perkin-Elmer Luminescence Spectrometer LS 50B, the solid samples of the polymers were measured in a quartz sample chamber. The excitation wavelength was 300, 323 and 400 nm for **B-FL$_3$**, **B-BT-FL$_2$**, and **B-BT$_2$-FL**, respectively.

Thermogravimetric Analysis (TGA). TGA analysis was performed using a NETZSCH TG209 F1 instrument. Samples scans were carried out using a heating rate of 10 °C/min under nitrogen atmosphere.

Scanning electron microscopy (SEM) was performed on a LEO 1550-Gemini instrument.

Gas sorption analysis. Polymer surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using Quadrasorb SI (Quantachrome Instruments). Data evaluation was performed using the QuadraWin Software from Quantachrome Instruments. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the Quenched Solid Density Functional Theory (QSDFT, N2, assuming carbon adsorbent with slit pores). Samples were degassed at 80 °C for 24 h under high vacuum before analysis.

General synthetic procedure for the CMP-HIPEs.

The monomers (ratio described in **Table S1**), tetrakis(triphenylphosphine)palladium(0) (22mg, 0.015 mmol) and Span 80 (200 mg) were dissolved in 2 ml toluene. Then an aqueous solution of K_2CO_3 (250 mg, 1.8 mmol) in 18 ml water was added slowly into the organic solution, which vigorously stirred using a XENOX stirrer. After stirring for 10 min a stable emulsion was formed and heated at 80°C overnight without stirring. After cooling, the formed monolith was washed in a Soxhlet extractor with water, methanol and chloroform and dried using a Bal-Tec CPD 030 Critical Point Dryer.

Scheme S1. Synthesis and idealized structures of **B-FL$_3$** (x:y = 3:1, z = 0), **B-BT-FL$_2$** (x:y:z = 2:1:1), and **B-BT$_2$-FL** (x:y:z = 1:2:1).

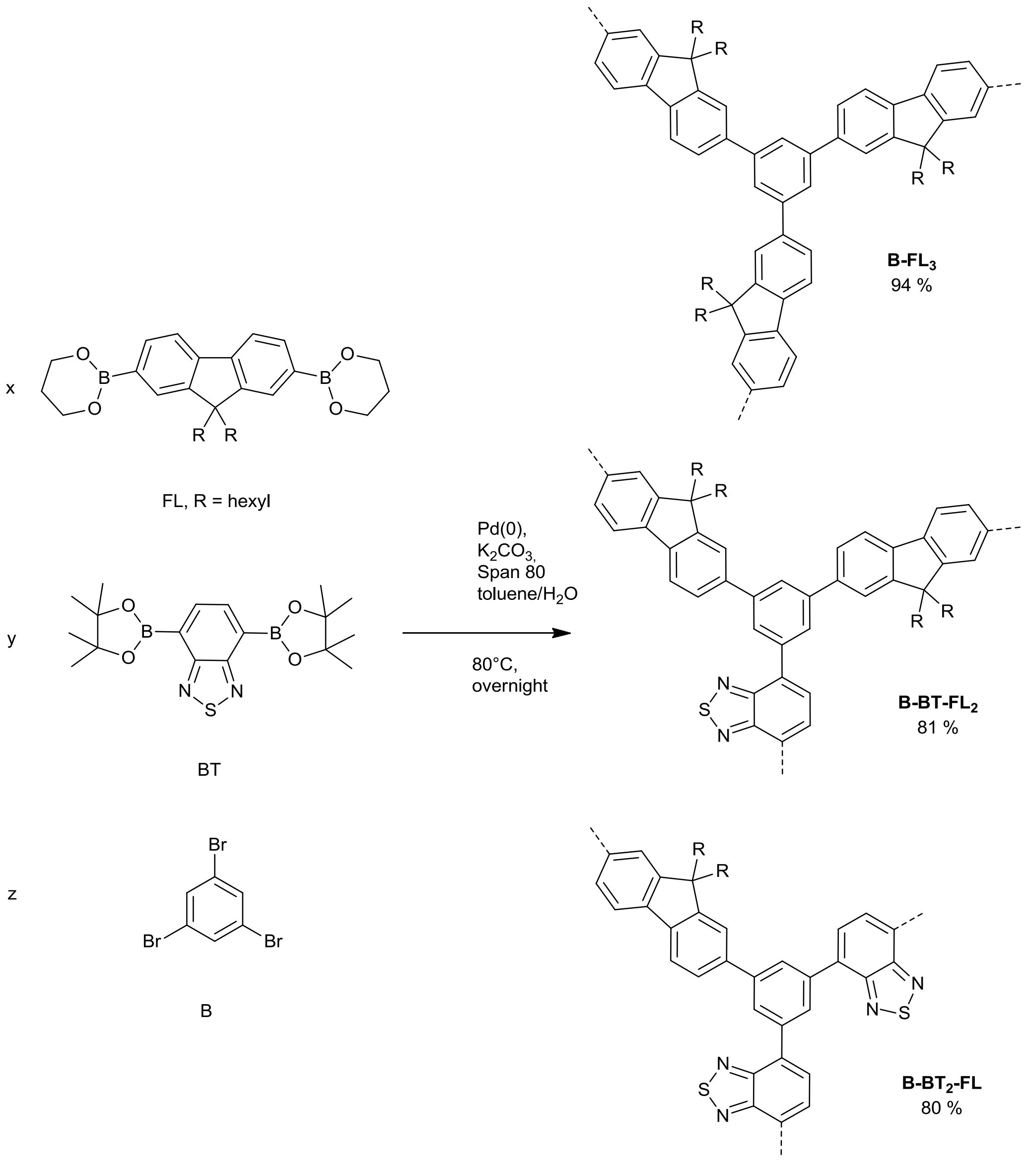


Table S1. Reaction conditions for **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL**.

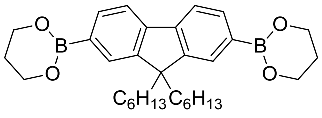
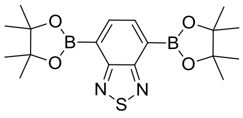
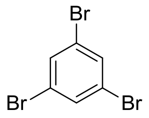
CP-HIPEs				Yield of CMP-HIPE (%)
B-FL$_3$,	225 mg (0,45 mmol)	-	93 mg (0,30 mmol)	160 mg (94 %)
B-BT-FL	150 mg (0,30 mmol)	60 mg (0,15 mmol)	93 mg (0,30 mmol)	115 mg (81 %)
B-BT$_2$-FL	75 mg (0,15 mmol)	116 mg (0,30 mmol)	93 mg (0,30 mmol)	90 mg (80 %)

Table S2: Elemental Analysis Data of **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL**.

CP-HIPEs		**N [%]**	**C [%]**	**H [%]**	**S [%]**
B-FL$_3$,	Expected	-	90.63	9.37	-
	Found	0.21	86.90	8.63	0.59
B-BT-FL$_2$	Expected	3.20	85.17	7.95	3.67
	Found	2.35	75.87	6.70	3.39
B-BT$_2$-FL	Expected	8,29	76.41	5.82	9.49
	Found	6.03	72.22	5.33	7.35

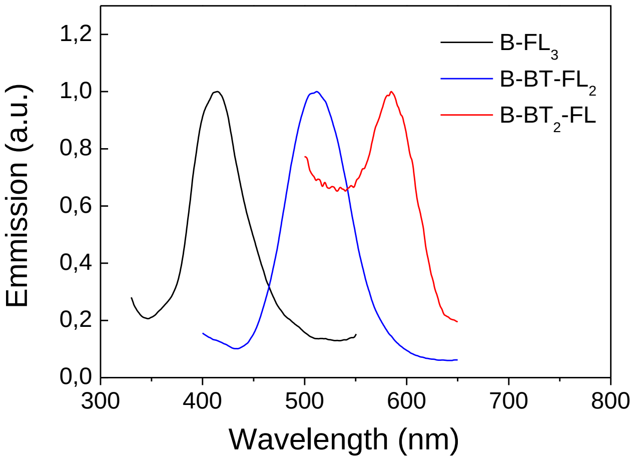


Figure S1. Normalized fluorescence spectra of the CMP-HIPEs.

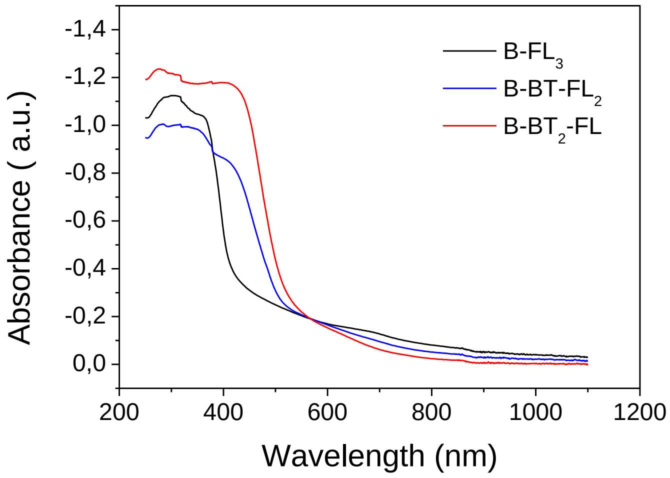


Figure S2. UV spectra of the CMP-HIPEs.

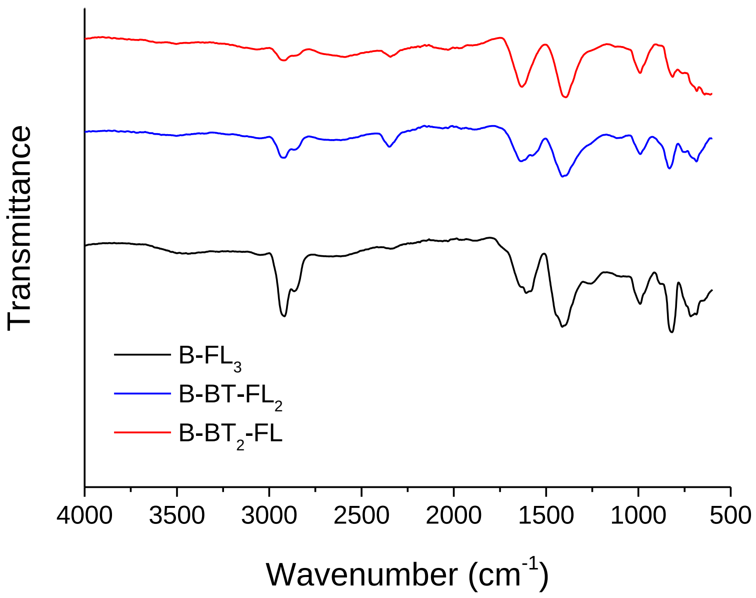


Figure S3: FTIR spectra of the polymers **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL**.

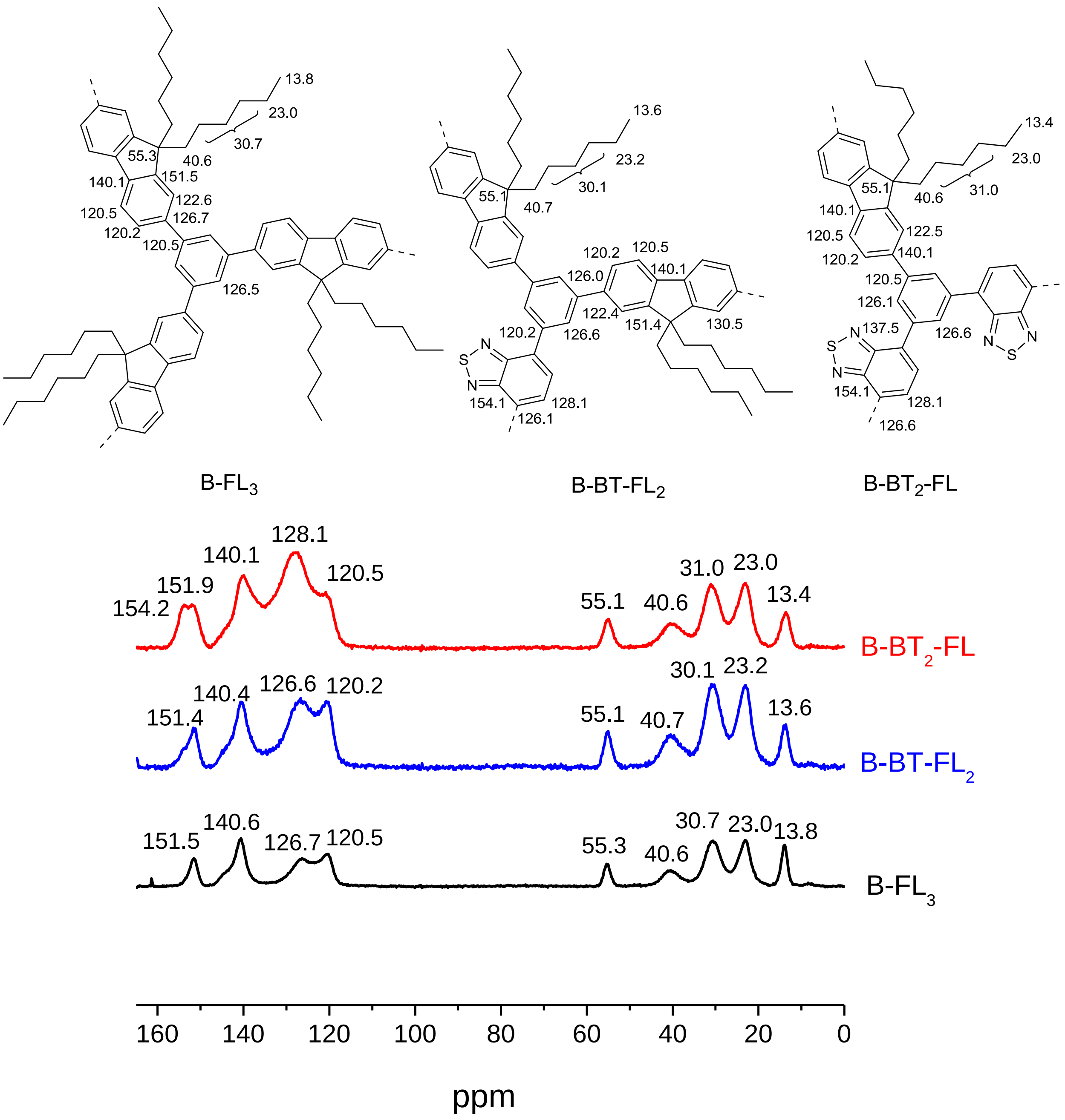
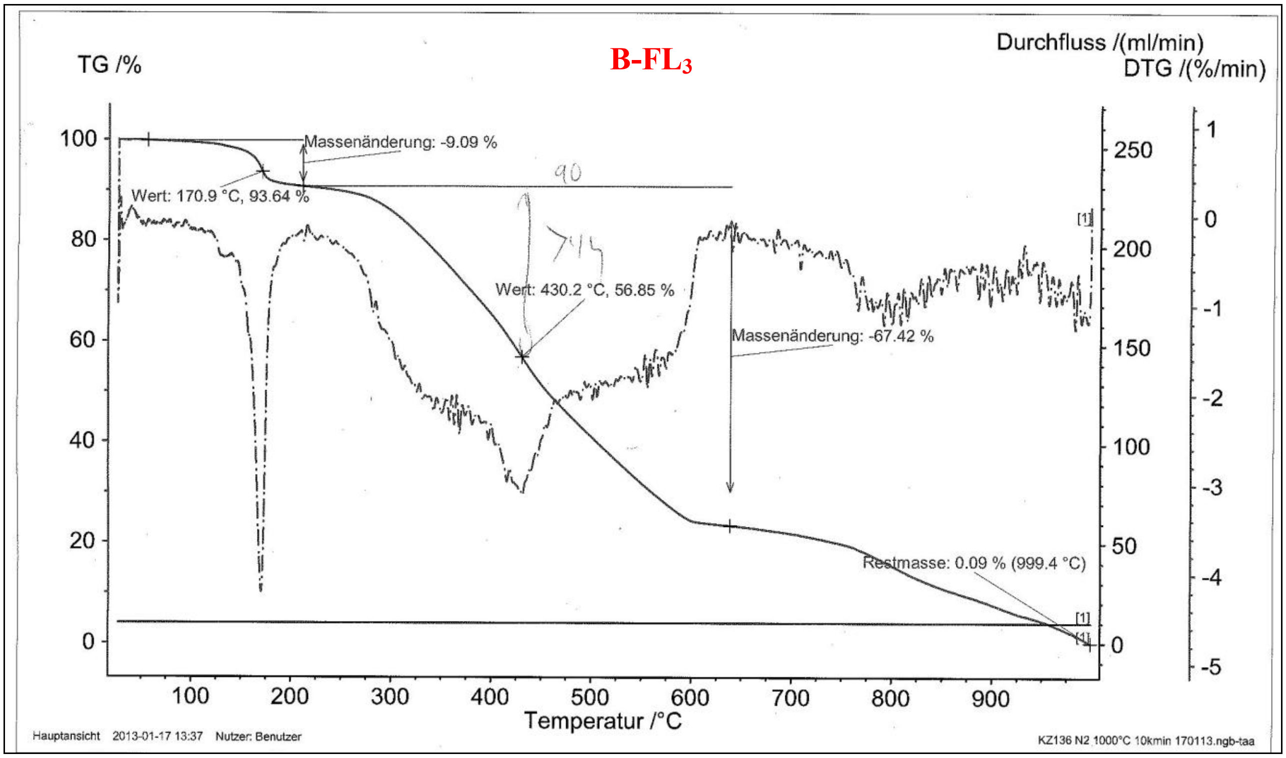


Figure S4: ^{13}C CP MAS spectra of **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL**.



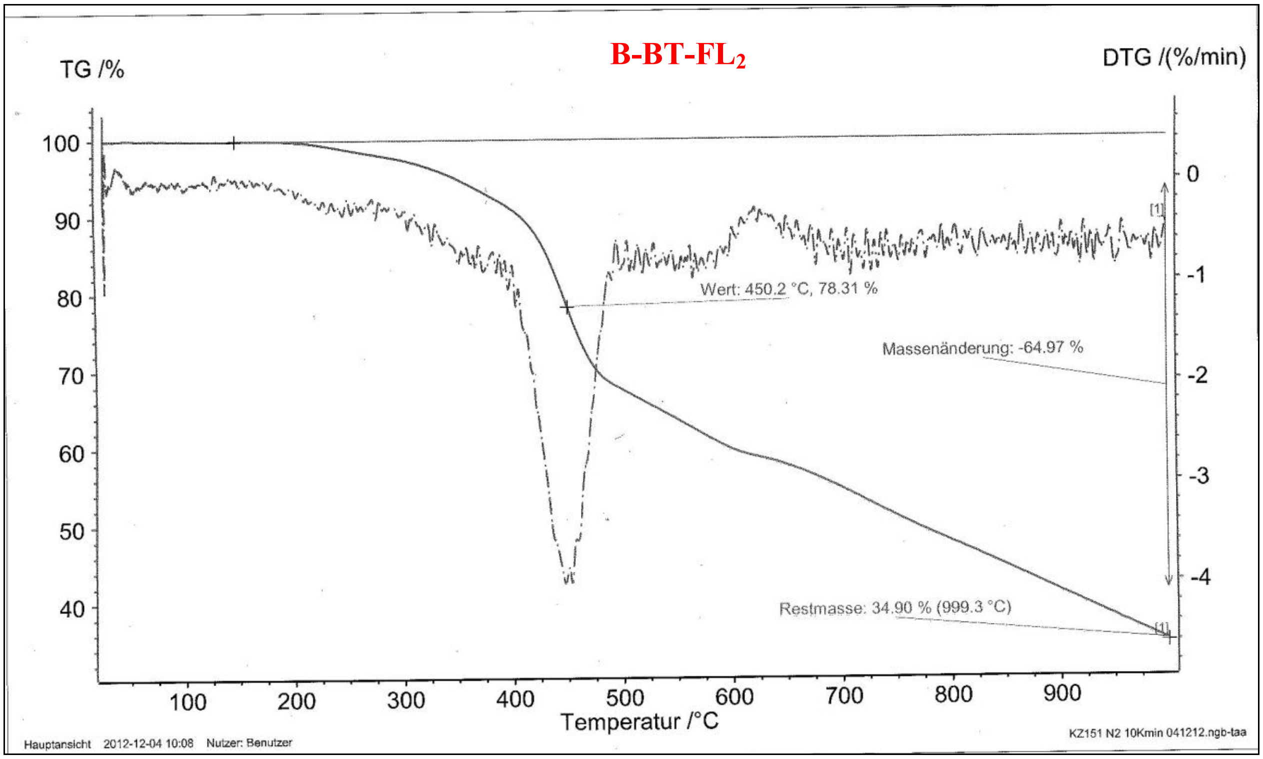


Figure S5: TGA of **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL**.

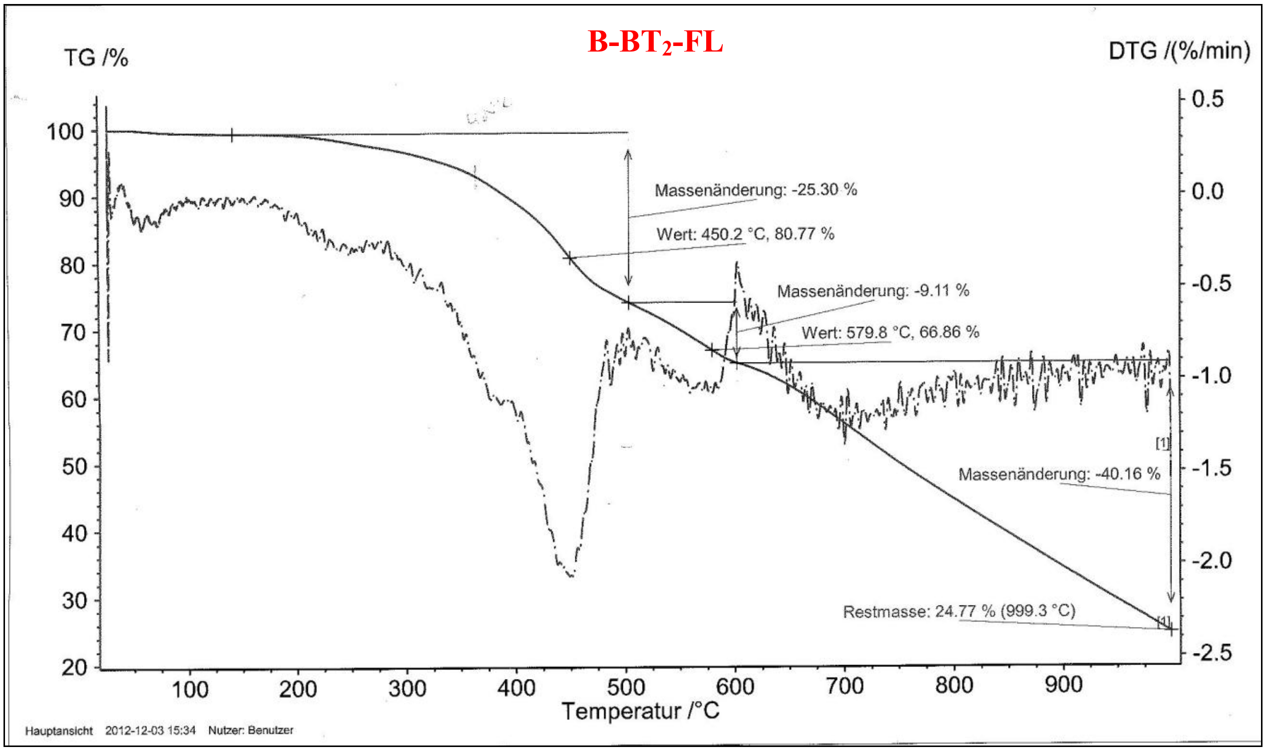


Figure S5 – continued: TGA of **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL**.

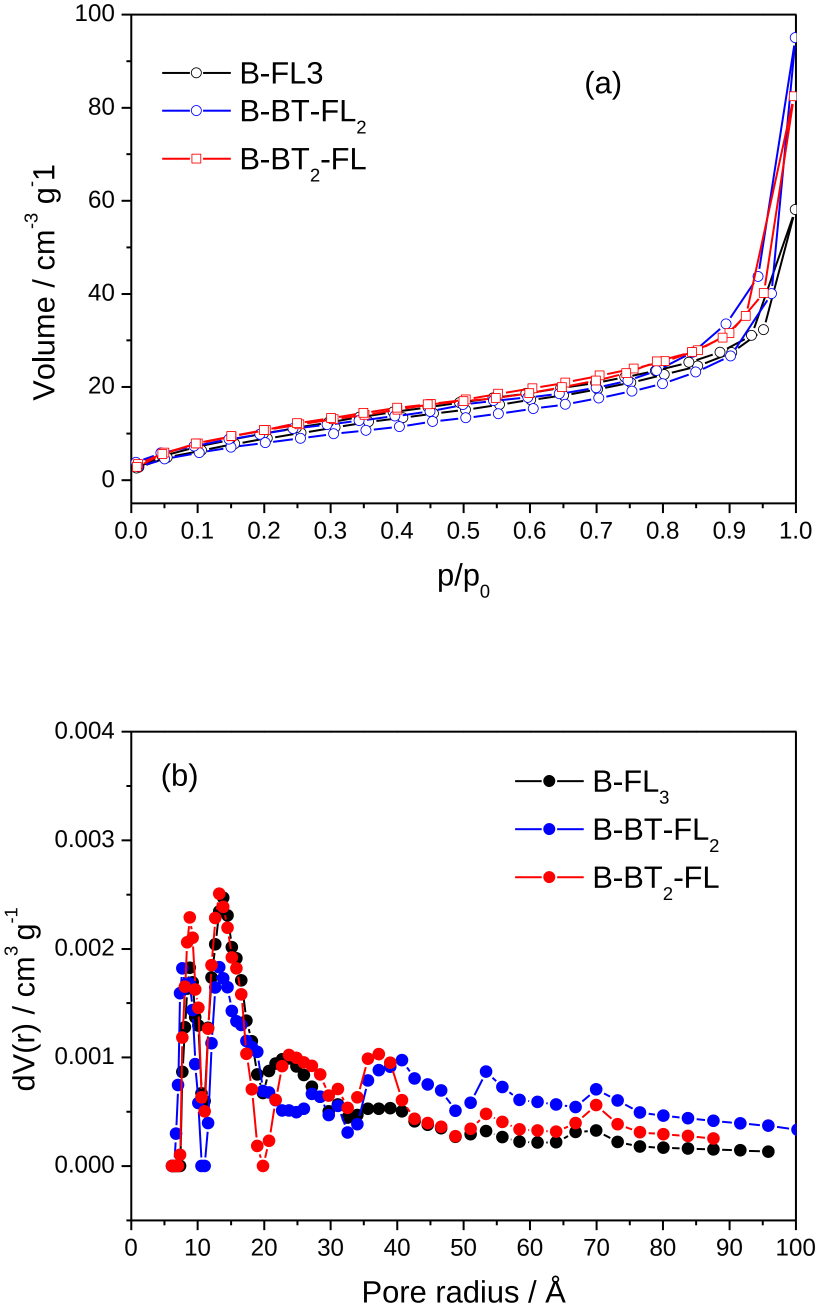


Figure S6: (a) BET isotherms and (b) The pore size distribution of **B-FL$_3$, B-BT-FL$_2$** and **B-BT$_2$-FL**.

Table S3. BET measurements data for **B-FL$_3$**, **B-BT-FL$_2$** and **B-BT$_2$-FL**.

Polymer	**Surface area (m^2g^{-1})**	**Pore Diameter (nm)**	**Pore Volume (cm^3 g^{-1})**
B-FL$_3$,	38	2.8	0.045
B-BT-FL$_2$	31	2.6	0.063
B-BT$_2$-FL	44	2.6	0.051

Photooxidation of α-terpinene into ascaridole.

Classical reaction set-up. Oxygen was bubbled (flow rate = 10 ml min^{-1}) through a glass vial containing 5 mg of small pieces of CMP-HIPEs and 20 ml of α-terpinene (0.1 M in chloroform). The light source - a LED module emitting at 420 nm with 12 W light output (OSA Opto Lights) – was mounted in a 2 cm distance from the vial. The reaction mixture was sampled in several different time intervals and the conversion was determined by ^{1}H-NMR.

Continuous flow system. The system consists of a transparent glass column (Omnifit, r = 0.35 cm, L = 7 cm) end-capped with two frits, equipped with FEP-tubing and charged with 10 mg of CMP-HIPE. T-part fitting was used to mix the solution of α-terpinene (0.1 M in 10 mL chloroform), which was delivered by a syringe pump, with oxygen gas (5 mL min^{-1}). The transparent glass column was irradiated with the blue light LED lamp at 420 cm (OSA Opto Lights). Samples were taken directly from the output and the conversion was determined by ^{1}H-NMR.

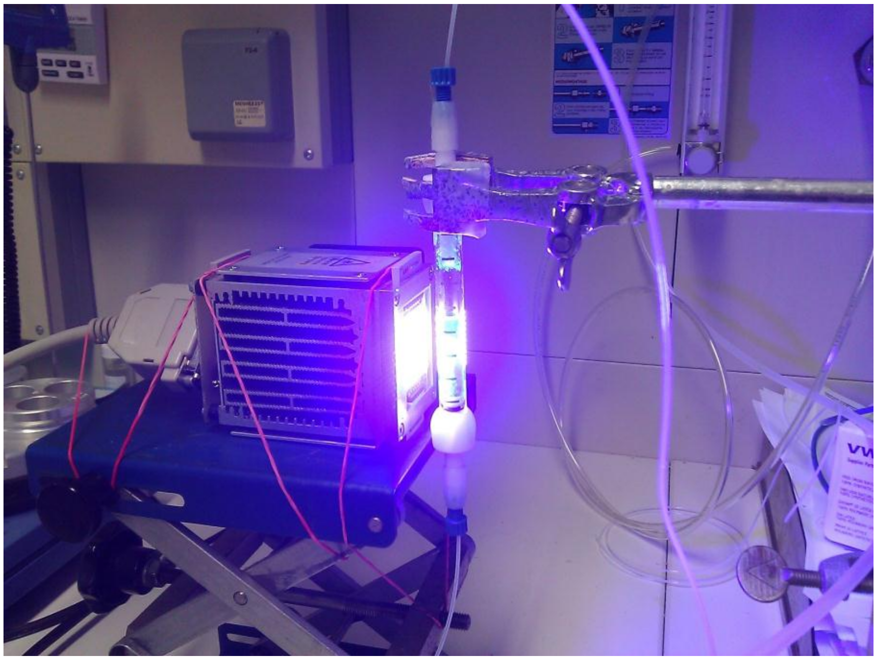


Figure S7: Photograph of the glass column photoreactor.

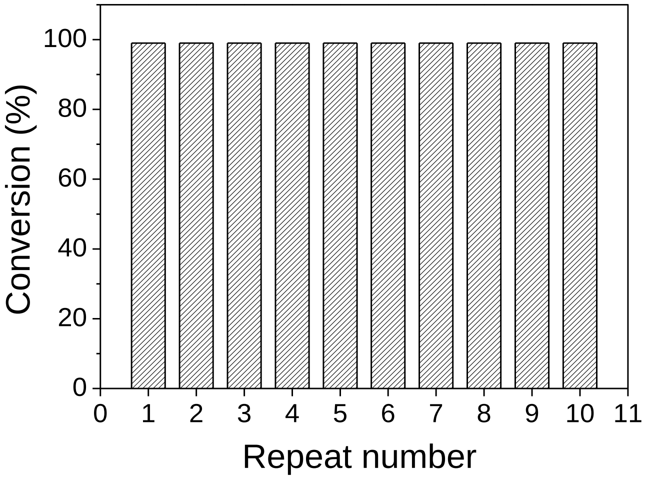


Figure S8: Repeatability test using the same batch **of B-BT$_2$-FL**.

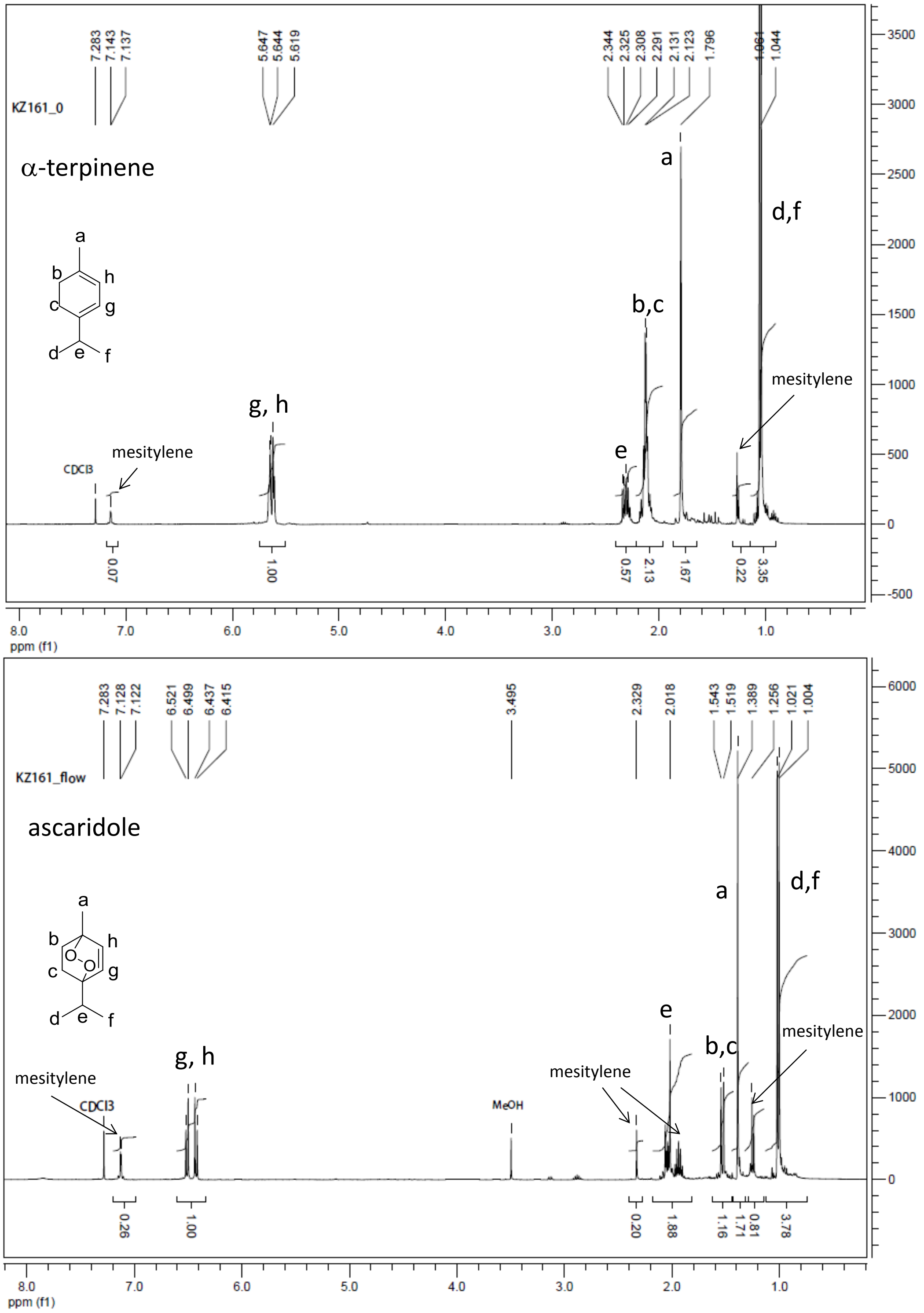


Figure S9: ^{1}H-NMR spectra of α-terpinene and ascaridole produced in the 10th run during the repeating experiment using **B-BT$_2$-FL** in the glass column reactor (taken in $CDCl_3$).

Procedure of the linear polymer (BT-FL).

2,7-dibromo-9,9-dihexyl-9H-fluorene (100 mg, 0.2 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (79 mg, 0.2 mmol), tetrakis(triphenylphosphine)-palladium(0) (12 mg, 0.01 mmol) were dissolved in 10 ml toluene, an aqueous solution of potassium carbonate (110 mg, 0.8 mmol) in 5 ml water was added. The reaction mixture was stirred at 80 °C for 10 h. After cooling, the reaction mixture was diluted with 50 ml dichloromethane, washed with brine and water. The organic phase was dried over dry magnesium sulphate, the solvent evaporated and the polymer was precipitated in cold methanol. Yield: 90 mg (67%). Molecular weight was measured on a gel permeation chromatography (GPC) equipment by TSP (Thermo Separation Products), $M_w = 9100$ $M_n = 4500$ PD = 2.0.

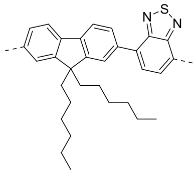


Figure S10: Chemical Structure of linear **BT-FL** polymer.

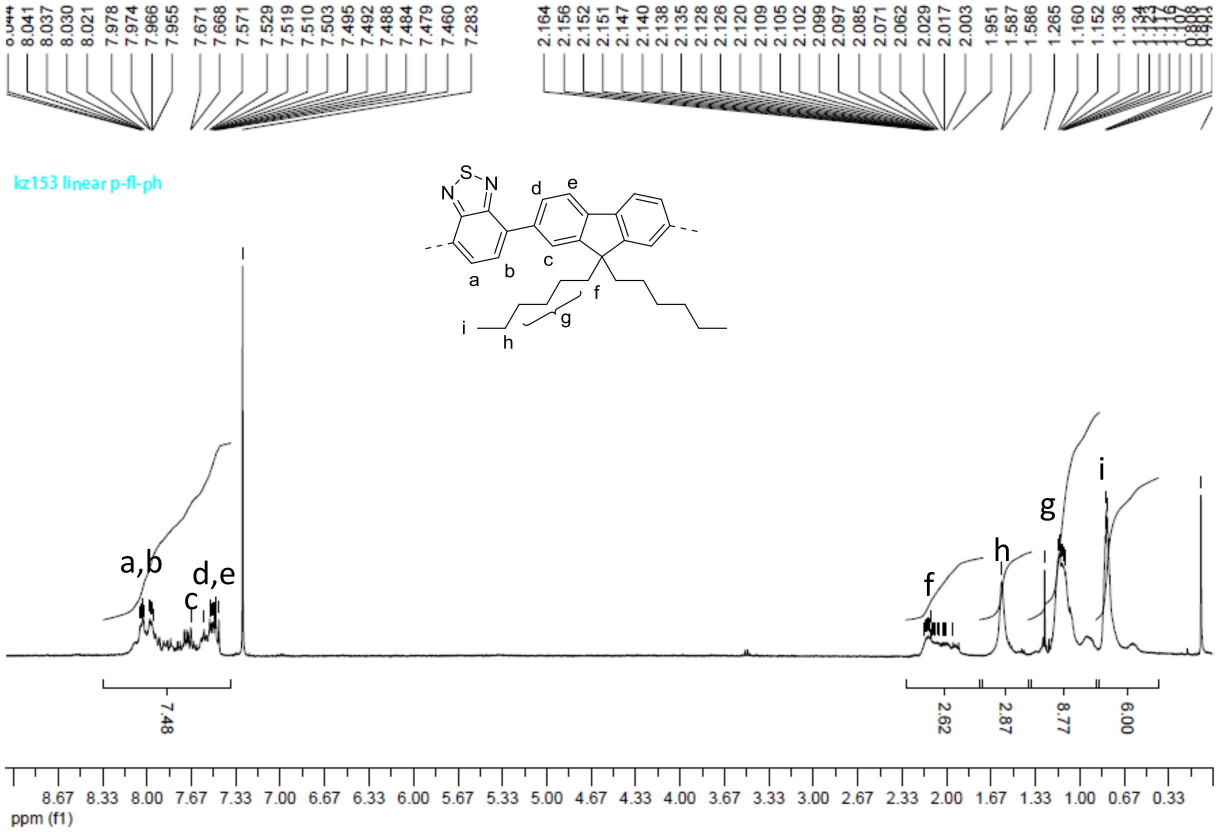


Figure S11: ^{1}H-NMR spectrum of the linear polymer **BT-FL** taken in $CDCl_3$.

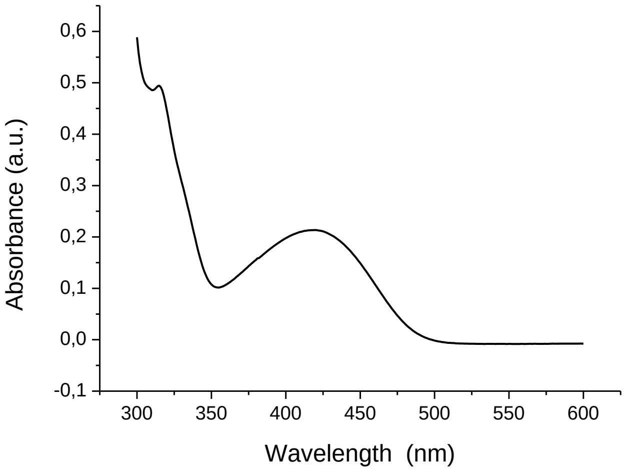


Figure S12: UV-vis absorption spectrum of the linear polymer **BT-FL**.