

Electronic Supporting Information

for the manuscript

Tunable Absorption and Emission Wavelength in Conjugated Microporous Polymers by Copolymerization

by

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Materials and Methods.

Materials: 2,2',7,7' – tetrabromospirobifluorene was prepared according to reported protocols.¹ 1,4-benzene diboronic acid (Aldrich 417130) was purchased from Sigma-Aldrich. 2,5 thiophene diboronic acid (98%) was purchased from Alfa-Aesar and used as received. Pd(PPh₃)₄ was obtained from Aldrich (216666) and used as received. DMF (dry, over mole sieve) was purchased from Fluka.

Methods:

Elemental analysis was obtained on a Vario EL micro and macro CHNOS elemental analyzer. Fourier transform infrared spectra (FTIR) were collected using a BIORAD FTS 6000 FTIR spectrometer under attenuated total reflection (ATR) conditions.

Prior to gas sorption measurements the samples were degassed at 150 °C in vacuo. The nitrogen and carbon dioxide sorption analyses were conducted on a Quantachrome Quadrasorb apparatus (N₂) at 77 K and on a Quantachrome Autosorb apparatus at 273 K (CO₂) respectively. BET surface areas were determined in a p/p₀ range from 0.05 to 0.1. Data evaluation was undertaken using the AS1Win software from Quantachrome Instruments.

Photoluminescence spectra were recorded using a Perkin-Elmer luminescence spectrometer (LS 50 D). Samples were sandwiched between two quartz slides for measurement.

UV-VIS spectra were measured on Varian Cary 300 spectrophotometer. The solid-state NMR ¹³C{¹H} CP/MAS measurements were carried out using a Bruker Avance 400 spectrometer operating at 100.6MHz for ¹³C with a Bruker 4mm double resonance probe-head operating at a spinning rate of 6 kHz.

Synthetic Protocol.

Tetrabromospirobifluorene (e.g. 246.4 mg, 0.39 mmol) and the corresponding amount of boronic acid (e.g. phenyl diboronic acid, 129 mg, 0.78 mmol, 2 eq.) were weighed into a 100 mL 3-necked round flask equipped with a condenser and magnetic stirring bar. The materials were degassed by evacuation followed by Ar purge (3 times). DMF (dry, 12

mL) was added under Ar flow. The monomer solution was degassed by 3 freeze-thaw cycles. Afterwards 1.5 mL of a 2M aqueous K_2CO_3 solution was added under Ar flow and the mixture was again degassed by 2 freeze-thaw cycles. Finally, $Pd(PPh_3)_4$ (45 mg, 0.1 mmol) was added under Ar flow. After a final degassing by freeze-thaw cycles (3 times), the mixture was heated to 150°C for 24 h under Ar atmosphere. After cooling to room temperature, water was added and the solid polymer precipitate was collected by filtration. The gel was washed with 1N HCl, water, and THF followed by extraction with THF (24 h) and DCM (24h) and drying under high vacuum.

The obtained yield was quantitative. In some cases yields higher than 100% (calculated based on the ideal repeating unit) were obtained, which points to the presence of unreacted end groups (bromine)

Loading protocol: Rhodamine 6G @ SpTh₂:

For loading experiments 10 mg of SpTh₂ were placed in a schlenk flask and degassed by repeated evacuation/Ar purge (3x). 10 mL of a Rhodamine 6G solution in methanol (1 mg/mL for high loading and 0.01 mg/mL for low loading) were added under Ar flow. The mixture was refluxed for 24 h and the solid was separated by centrifugation after cooling. The solid was washed with methanol in order to remove Rhodamine 6G which was only adhering on the outer surface. Finally, the materials were dried under high vacuum.

Spectral analysis.

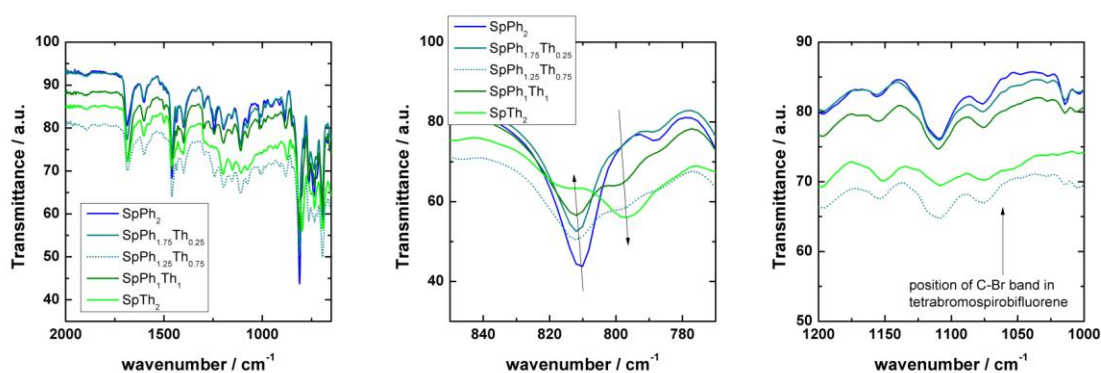


Figure S1. FTIR (ATR) spectra of the polymer networks: *left-hand side*: overview; *middle*: CH bending band region; *right-hand side*: C-Br region, C-Br band of tetrabromospirobifluorene was reported to show up at 1060 cm^{-1} [2]

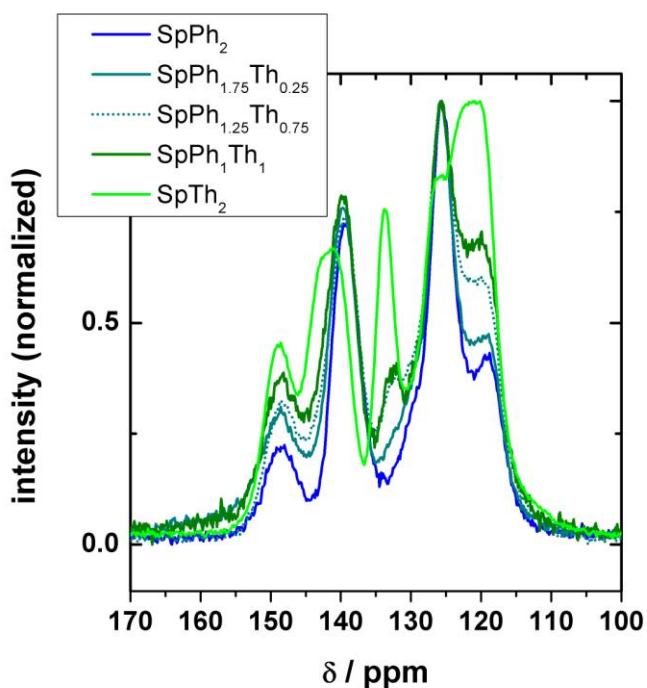


Figure S2. ^{13}C -solid state NMR spectra of the polymer networks (Note: SpTh₂ was recorded at different conditions, resulting in better signal to-noise ratio and slight differences); the peak due to the tetrahedral $\text{sp}^3\text{-C}$ atom of spirobifluorene could be observed but is overlaid by spinning side bands.

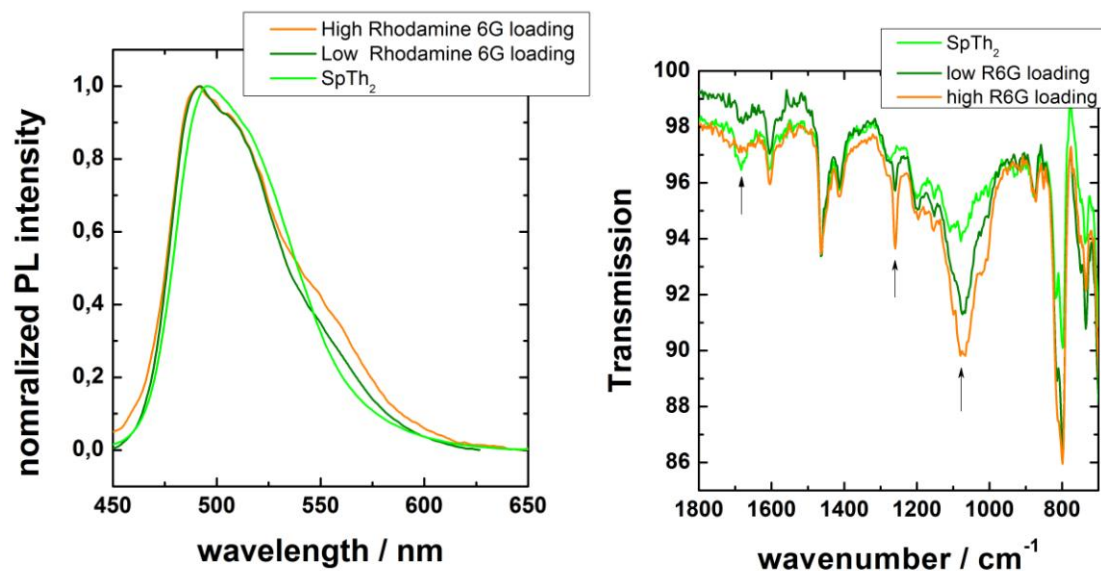


Figure S3a. PL spectra (excitation: 350 nm) of SpTh₂ (green) and of R6G loaded SpTh₂ (olive: low loading, orange: high loading, see experimental for details), compare also to Fig S4

Figure S3b. FTIR spectra of SpTh₂ (green) and of R6G loaded SpTh₂ (olive: low loading, orange: high loading,), arrows indicate significant differences

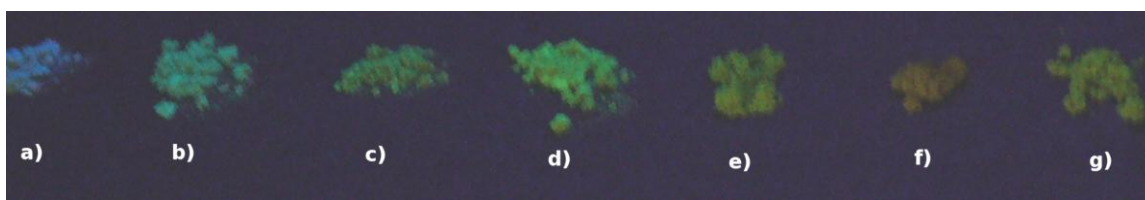


Figure S4. Photograph of the powders under 360 nm illumination; a) SpPh₂, b) SpPh_{1.75}Th_{0.25}, c) SpPh_{1.25}Th_{0.75}, d) SpPh₁Th₁, e) SpTh₂, f) SpTh₂, high Rhodamine 6G loading, g) SpTh₂, low Rhodamine 6G loading

Elemental Analysis

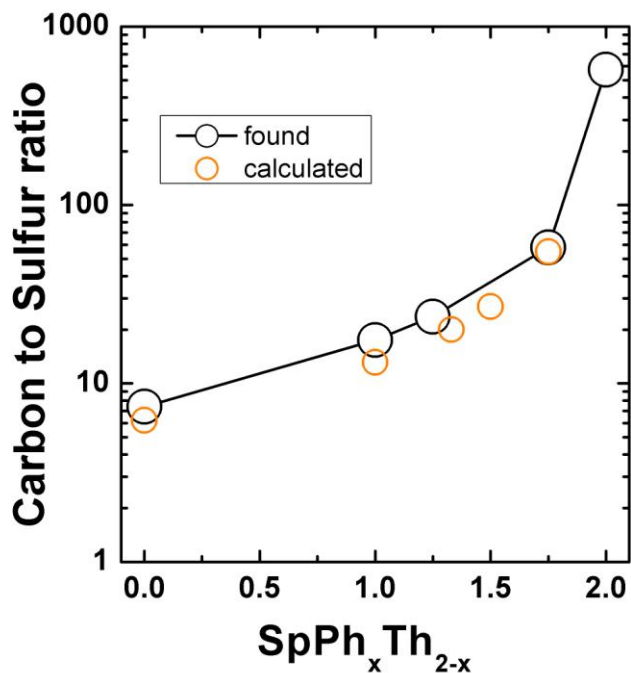


Figure S5. Carbon to Sulfur ratio (C/S; by weight) obtained from elemental analysis of the polymer networks (black circles) and the calculated values (orange circles). Please note that the calculated C/S value for SpPh₂ would be infinitely high. The found ratio of ~570 is due to the experimental error in the determination of sulfur (measured sulfur content ~0.2)

Gas sorption:

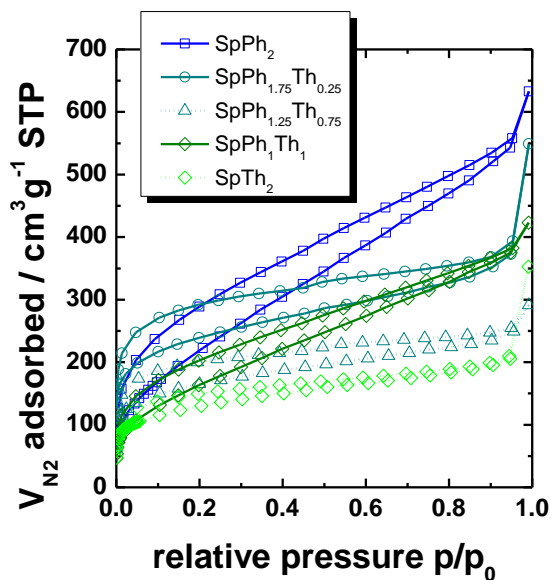


Figure S6. Nitrogen sorption isotherms (77.3 K) of the polymer networks. Strong swelling effects were observed in some cases, hindering a detailed analysis

References:

- (S1) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *The Journal of Organic Chemistry* **1996**, *61*, 6906-6921.
(S2) Schmidt, J.; Werner, M.; Thomas, A. *Macromolecules* **2009**, *42*, 4426-4429.