

Supporting Information

Band Gap Engineering in Fluorescent Conjugated Microporous Polymers

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Experimental Section

Chemicals: Bis(1,5-cyclooctadine)nickel(0) (Ni(cod)₂) was purchased from Acros. Pyrene, 1,4-dibromobenzene, 4,4'-dibromobiphenyl, 2,2'-bipyridine, 1,5-cyclooctadiene, 1,4-benzene diboronic acid and solvents were purchased from Aldrich and used as received.

1,3,6,8-Tetrabromopyrene (TBrPy) was prepared according to published procedures.^{S1}

Synthesis of polymer networks: The YPy homopolymer and the two statistical copolymers, YDBPy and YDPPy, were synthesized by Ni-catalyzed Yamamoto polycondensation of 1,3,6,8-tetrabromopyrene optionally with 1,4-dibromobenzene or 4,4'-dibromobiphenyl as comonomers.

YPy: 1,5-Cyclooctadiene (cod, 0.67 mL, 5.3 mmol) was added to a solution of bis(1,5-cyclooctadine)nickel (0) (Ni(cod)₂, 1.43 g, 5.2 mmol) and 2,2'-bipyridyl (811 mg, 5.2 mmol) in DMF (100 mL). The mixture was heated to 80 °C and stirred for 1 hour under a nitrogen atmosphere to produce a purple solution. To the resulting solution was added 1,3,6,8-tetrabromopyrene (514 mg, 1.0 mmol) and the mixture was stirred for another 24 hours at 80 °C to form a deep purple suspension. After cooling to room temperature, concentrated HCl (30 mL) was added to the mixture. After filtration, the residue was washed with CHCl₃ (3×200 mL), THF (3×200 mL) and H₂O (3×200 mL), respectively. Further purification of the polymer was carried out by Soxhlet extraction with THF for 48 hours. The product was dried in vacuum for 24 hours at 70 °C as a fine brown powder (Yield: 155 mg, 78.3%). Elemental combustion analysis (%) Calcd for C₁₆H₆: C 96.95, H 3.05; Found: C 91.75, H 3.92, Br 0.2 (measured by

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Butterworth Laboratories Limited using in-house analysis method BLM 5).

YDBPy: 1,3,6,8-Tetrabromopyrene (257 mg, 0.5 mmol), 1,4-dibromobenzene (234 mg, 1.0 mmol), 1,5-cyclooctadiene (0.67 mL, 5.3 mmol), bis(1,5-cyclooctadiene)nickel (0) (1.43 g, 5.2 mmol) and 2,2'-bipyridyl (811 mg, 5.2 mmol) were used in this polymerization, details as above for **YPy**. Elemental combustion analysis (%) Calcd for C₂₈H₁₄: C 95.97, H 4.03; Found: C 91.67, H 4.06, Br 0.6.

YDPPy: 1,3,6,8-Tetrabromopyrene (257 mg, 0.5 mmol), 4,4'-dibromophenyl (310 mg, 1.0 mmol), 1,5-cyclooctadiene (0.67 mL, 5.3 mmol), bis(1,5-cyclooctadiene)nickel (0) (1.43 g, 5.2 mmol) and 2,2'-bipyridyl (811 mg, 5.2 mmol) were used in this polymerization, details as above for **YPy**. Elemental combustion analysis (%) Calcd for C₄₀H₂₂: C 95.59, H 4.41; Found: C 91.92, H 4.74, Br 1.6.

The alternating copolymer network, **SDBPy**, was prepared by Suzuki polymerization: To a mixture of TBrPy (513 mg, 1.0 mmol) and 1,4-benzene diboronic acid (332 mg, 2.0 mmol) in dimethylformamide (DMF, 15 mL), an aqueous solution of K₂CO₃ (2.0 M, 3 mL) and tetrakis(triphenylphosphine)palladium(0) (15 mg, 13 μmol) were added. The mixture was degassed under freeze-pump-thaw, purged with N₂, and stirred at 150 °C for 48 h. The mixture was cooled to room temperature and poured into water. The precipitate was collected by filtration, and washed with H₂O, CHCl₃, THF and methanol respectively. Further purification of the polymer was carried out by Soxhlet extraction with THF for 72 hours. The product was dried in vacuum for 24 hours at 70 °C as a fine green powder (Yield: 330 mg, 95.6%). Elemental combustion analysis (%) Calcd for C₂₈H₁₄: C 95.97, H 4.03; Found: C 91.12, H 4.15.

FT-IR Spectroscopy.

The polymer sample was ground with KBr and then pressed into transparent pellet. FT-IR spectra were collected in transmission on a Bruker Tensor 27 at room temperature.

Thermogravimetric Analysis

The thermal properties of the polymer networks were evaluated using a thermogravimetric analysis (TGA)–differential thermal analysis instrument (EXSTAR6000) over the temperature range 30 to 1000 °C under a nitrogen atmosphere with a heating rate of 10 °C/min.

Gas Sorption: Polymer surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using either a Micromeritics ASAP 2420 or ASAP 2020 volumetric adsorption analyzer. The surface areas were calculated in the relative pressure (P/P_0) range from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT). Samples were degassed at 120 °C for 15 hours under vacuum (10^{-5} bar) before analysis.

UV-Visible absorption and photoluminescence measurements

The UV-Visible absorption spectra of the 1,3,6,8-tetrabromopyrene monomer and the polymer networks were recorded on UV-Vis spectrometer (Perkin Elmer, Lambda 650 S) in solid state powder. The fluorescent spectra of solid state powder monomers and the polymer networks were measured with a fluorescence spectrometer (Perkin Elmer LS 55) by using excitation wavelength of 360 nm.

Scanning Electron Microscopy

High resolution imaging of the polymer morphology was achieved using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM). The dry polymers samples were prepared on 15 mm Hitachi M4 aluminium stubs using either silver dag or an adhesive high purity carbon spectro tab. The samples were then coated with a 2 nm layer of gold using an Emitech K550X automated sputter coater. The FE-SEM measurement scale bar was first calibrated using certified SIRA calibration standards and elemental quantification standards were also used to calibrate the Oxford Instruments EDX detector. Imaging was conducted at a working distance of 8 mm and a landing voltage of 3 kV using a mix of upper and lower secondary electron detectors. An Oxford Instruments 7200 EDX detector was used to conduct elemental analysis of polymer composition.

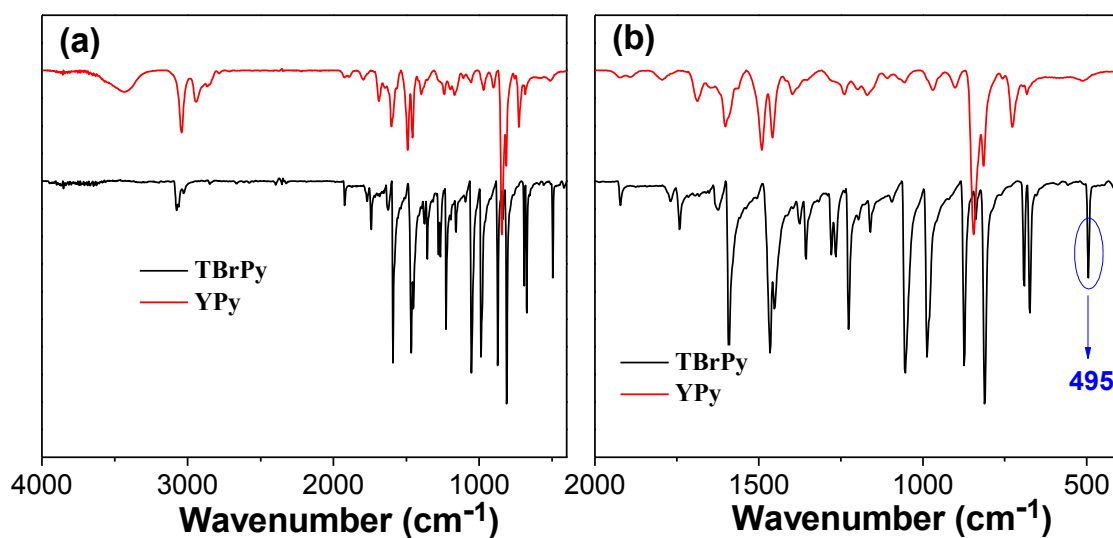


Figure S1. FT-IR spectra of the monomer **TBrPy** and polymer **YPy** from 400–4000 cm^{-1} (a) and 400–2000 cm^{-1} (b). The characteristic C-Br band can be observed at 495 cm^{-1} for the monomer; the absence of this band in the polymer is consistent with the lack of bromine in the product.

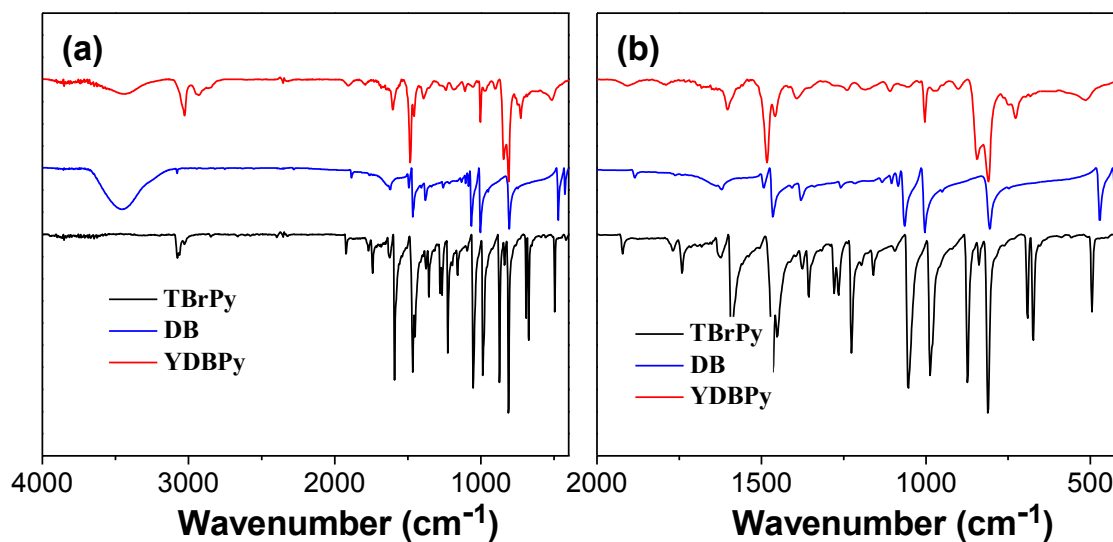


Figure S2. FT-IR spectra of the two monomers **TBrPy** and 1,4-dibromobenzene (**DB**), and the statistical copolymer **YDBPy** from 400–4000 cm^{-1} (a) and 400–2000 cm^{-1} (b).

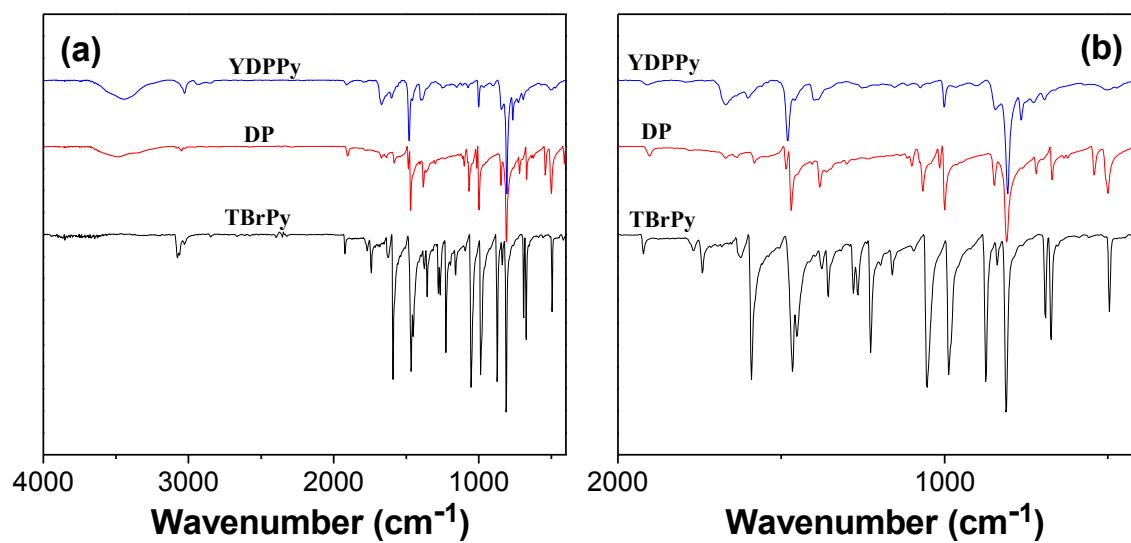


Figure S3. FT-IR spectra of the two monomers **TBrPy** and 4,4'-dibromophenyl (**DP**), and the statistical copolymer **YDPPy** from 400–4000 cm^{-1} (a) and 400–2000 cm^{-1} (b).

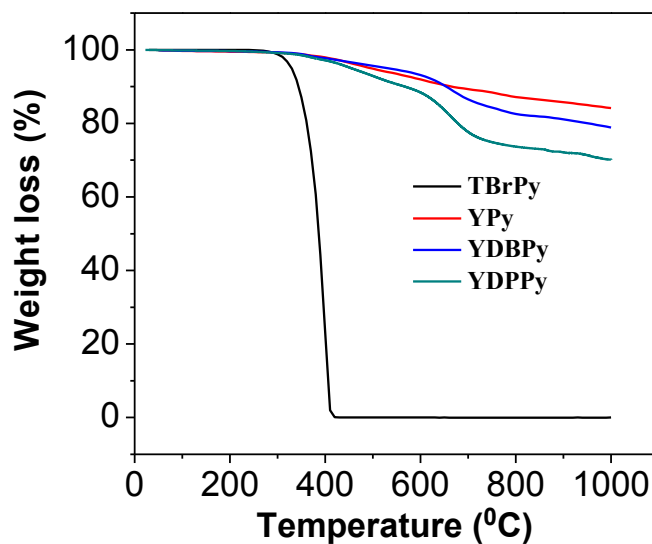


Figure S4. Thermogravimetric Analysis (TGA) curves for the three statistical, Yamamoto-coupled copolymers and the monomer **TBrPy**.

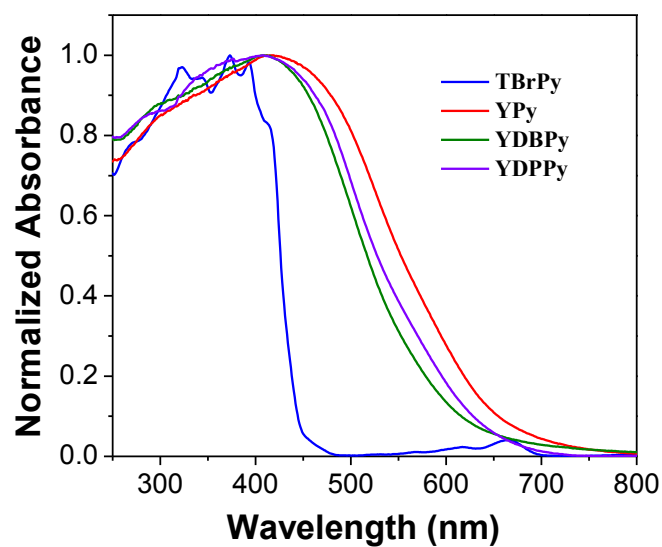


Figure S5. UV-Visible absorption spectra for the monomer of **TBrPy** and the three statistical copolymers.

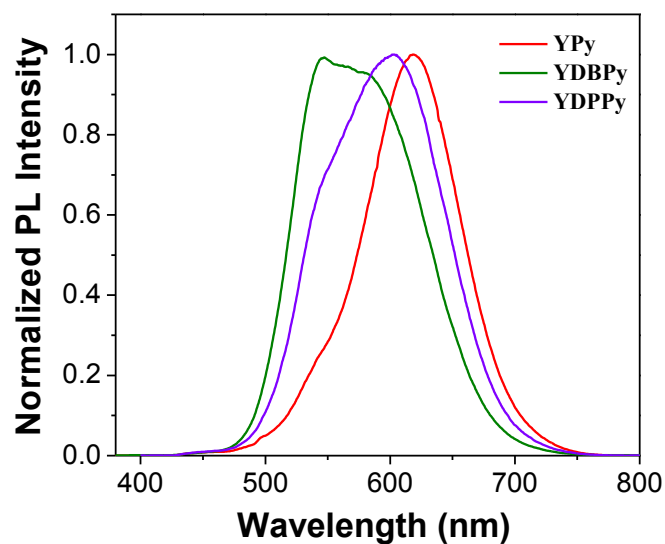


Figure S6. Photoluminescent spectra for the statistical copolymers measured as solid state powders ($\lambda_{\text{excit}} = 360$ nm).

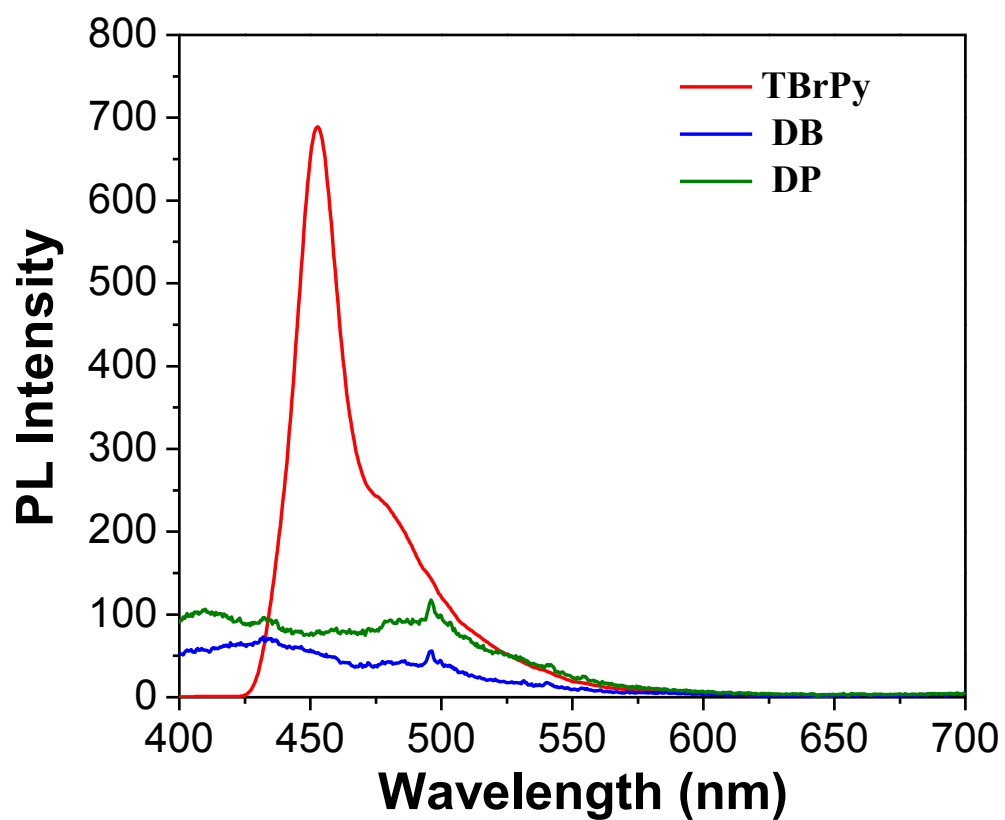


Figure S7. Photoluminescent spectra of the monomers of TBrPy, DB and DP measured as solid state powder ($\lambda_{\text{excit}} = 360$ nm).

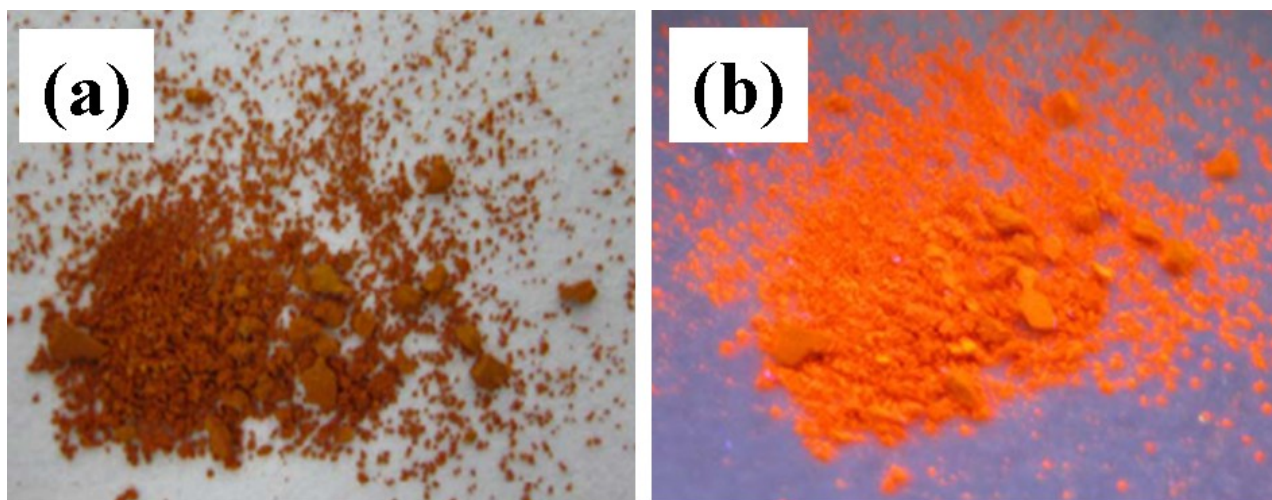


Figure S8. Photographs of the polymer YPy under ambient conditions, and (b) under irradiation with UV light ($\lambda_{\text{excit}} = 365$ nm using a portable UV lamp).

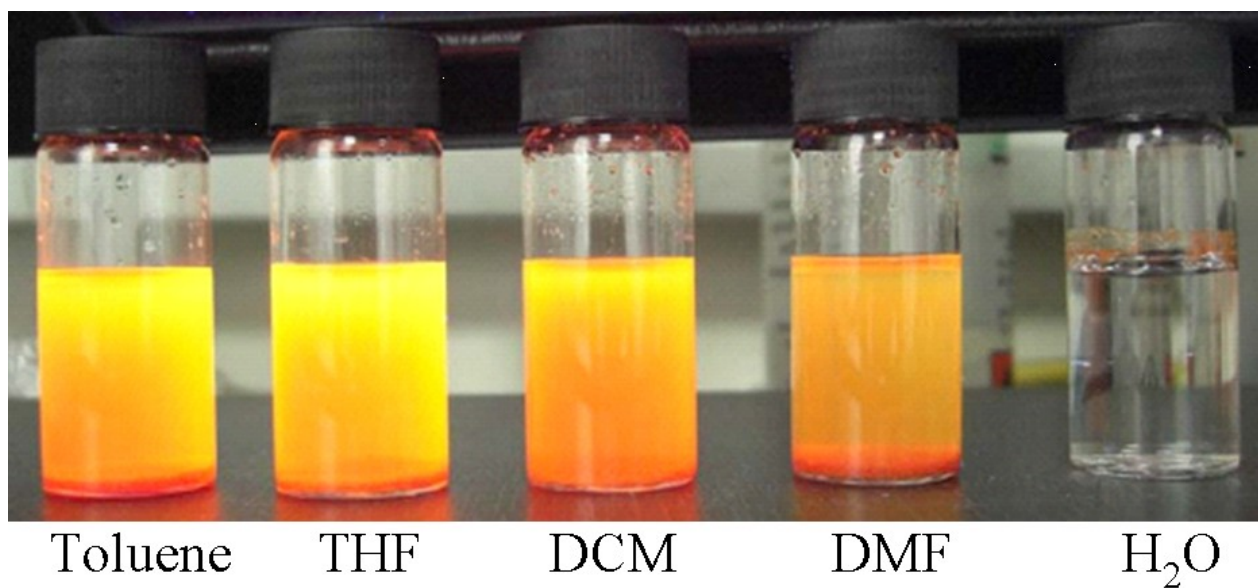


Figure S9. Photographs of YPy in different solvents (excited under $\lambda_{\text{excit}} = 365$ nm using a portable UV lamp).

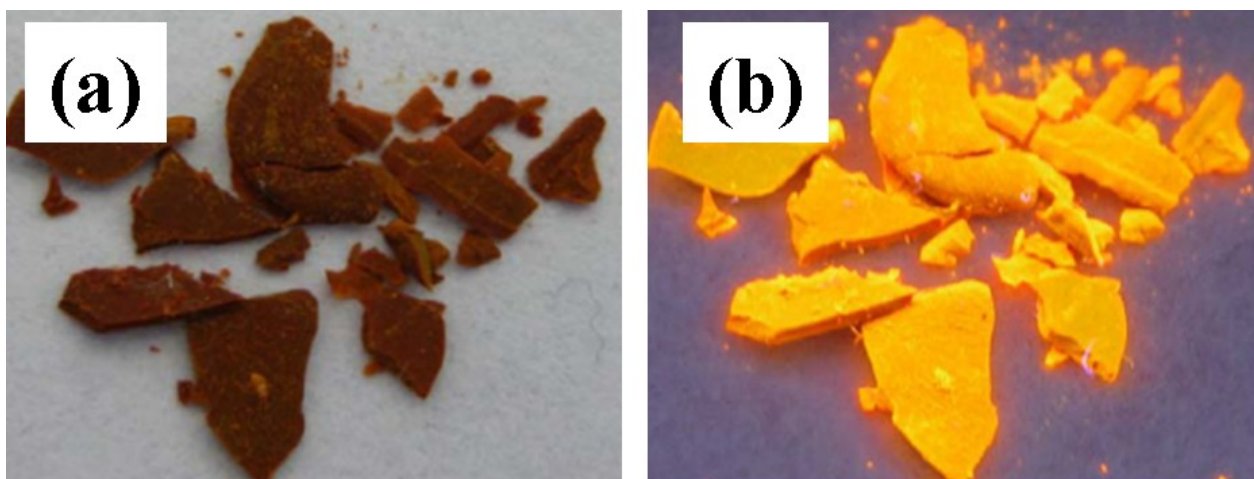


Figure S10. (a) Photographs of polymer YDPPy under ambient conditions, and (b) under irradiation with UV light ($\lambda_{\text{excit}} = 365$ nm using a portable UV lamp).

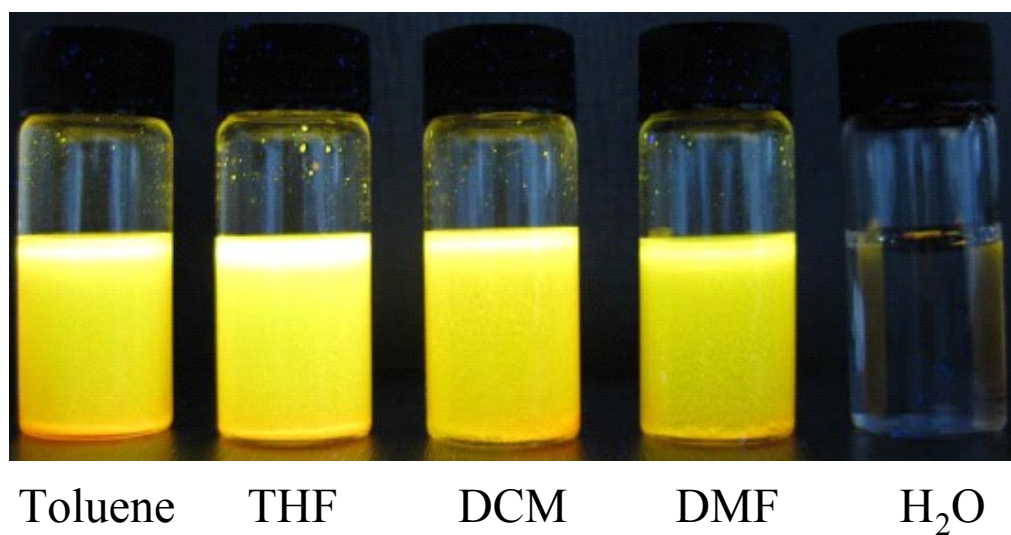


Figure S11. Photographs of YDPPy in different solvents (excited under $\lambda_{\text{excit}} = 365$ nm using a portable UV lamp). The material does not disperse effectively in water but floats on the meniscus.

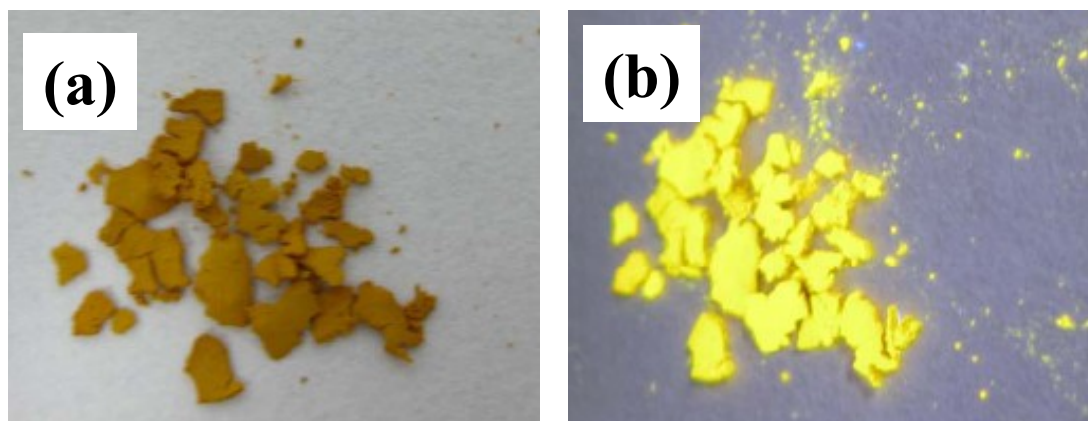


Figure S12. (a) Photographs of polymer **YDBPy** under ambient conditions, and (b) under irradiation with UV light ($\lambda_{\text{excit}} = 365$ nm using a portable UV lamp).

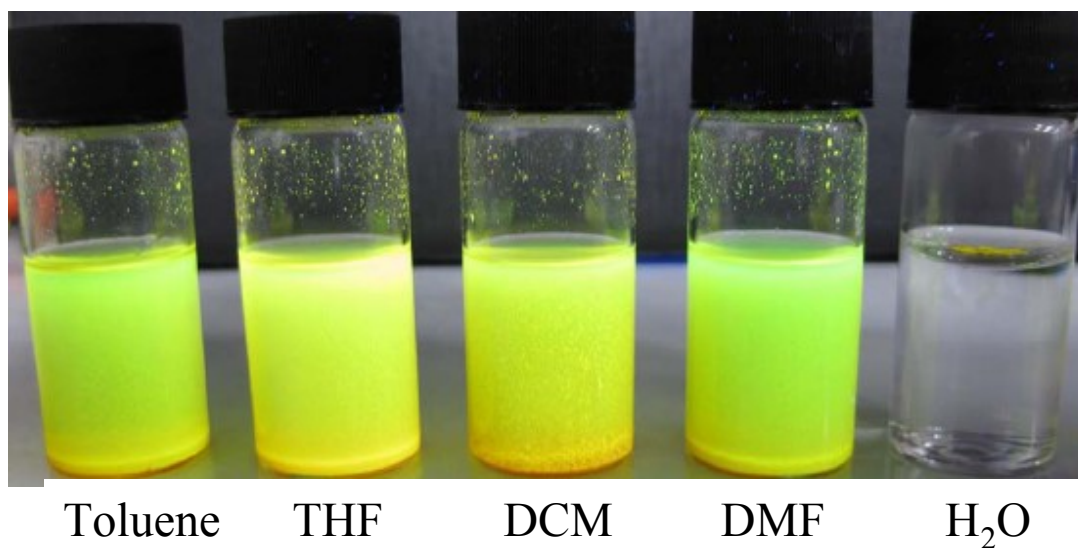


Figure S13. Photographs of **YDBPy** in different solvents (excited under $\lambda_{\text{excit}} = 365$ nm using a portable UV lamp). The material does not disperse effectively in water but floats on the meniscus.

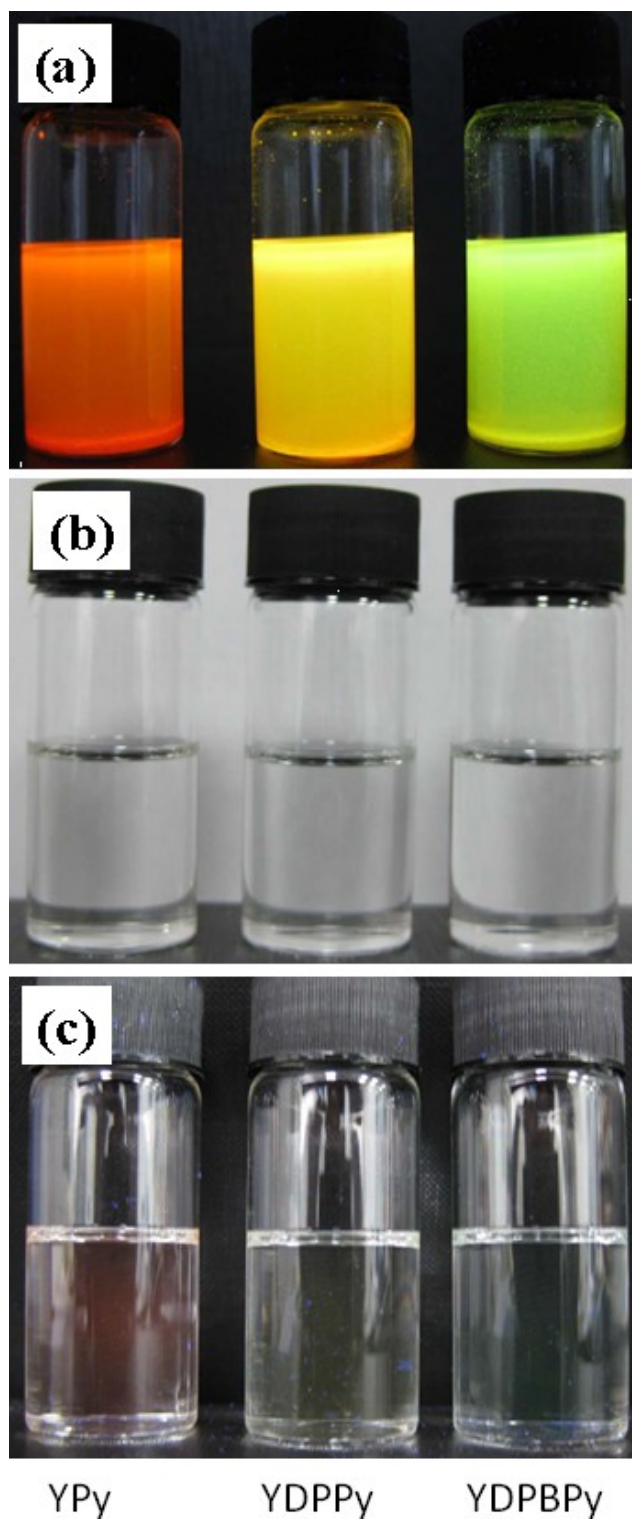


Figure S14. (a) Photographs of suspensions of polymers in THF (10 mg / 10 mL) under irradiation with UV light ($\lambda_{\text{excit}} = 365$ nm using a portable UV lamp), (b) Photographs of the filtrate of the polymer suspension after stirring for 24 hours were collected under ambient conditions, and (c) Photographs of the filtrate were collected under irradiation with UV light ($\lambda_{\text{excit}} = 365$ nm using a portable UV lamp). (b) and (c) show that the fluorescence is arising from the insoluble networks, not soluble molecular species. The trace of fluorescent for the **YPy** filtrate can be ascribed to very small particles of the sample which are not removed by standard filtration.

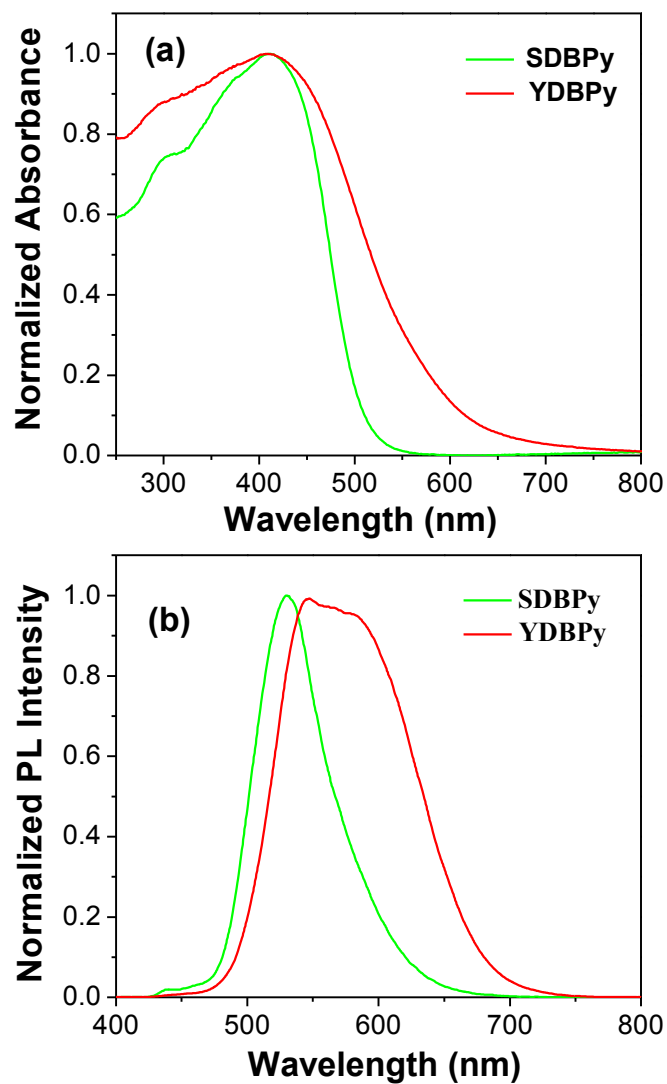


Figure S15. (a) UV-Visible absorption spectra and (b) photoluminescent spectra of the polymers **SDBPy** and **YDBPy** measured as solid state powder ($\lambda_{\text{excit}} = 360$ nm). The narrower emission peak for the alternating polymer **SDBPy** can be ascribed to its more regular monomer sequence distribution and, hence, narrower diversity of effective chromophores.

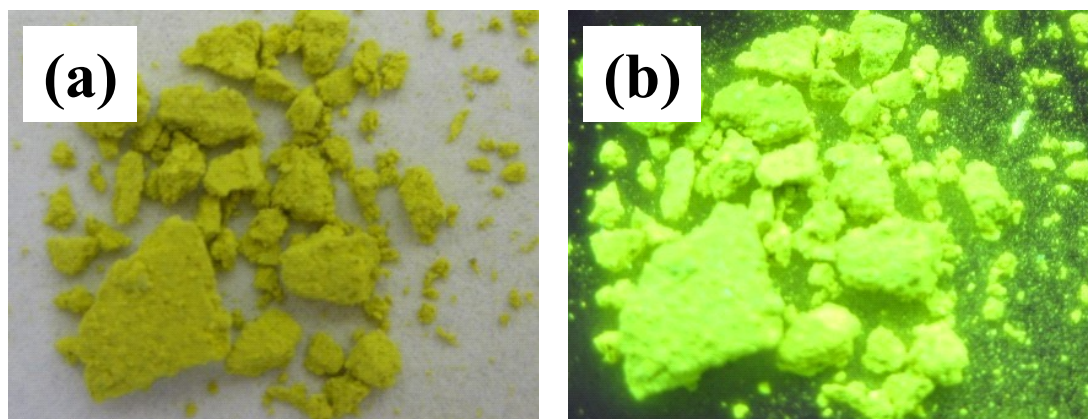


Figure S16. (a) Photographs of polymer **SDBPy** under ambient conditions, and (b) under irradiation with UV light ($\lambda_{\text{excit}} = 365$ nm using a portable UV lamp).

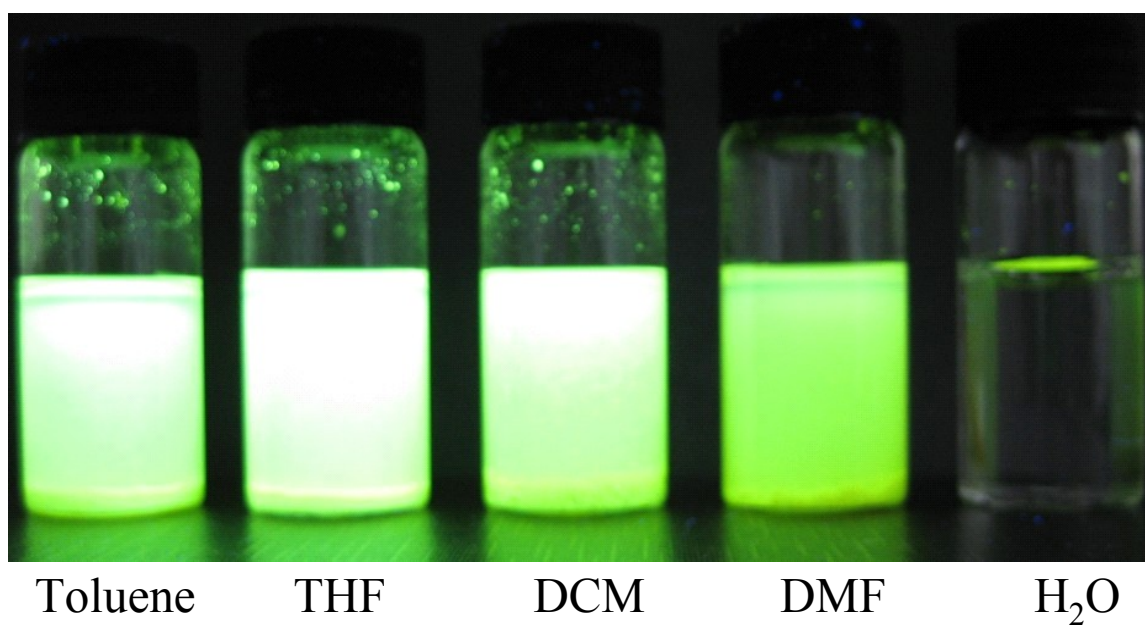


Figure S17. Photographs of **SDBPy** in different solvents (excited under $\lambda_{\text{excit}} = 365$ nm using a portable UV lamp).

The material does not disperse effectively in water but floats on the meniscus.

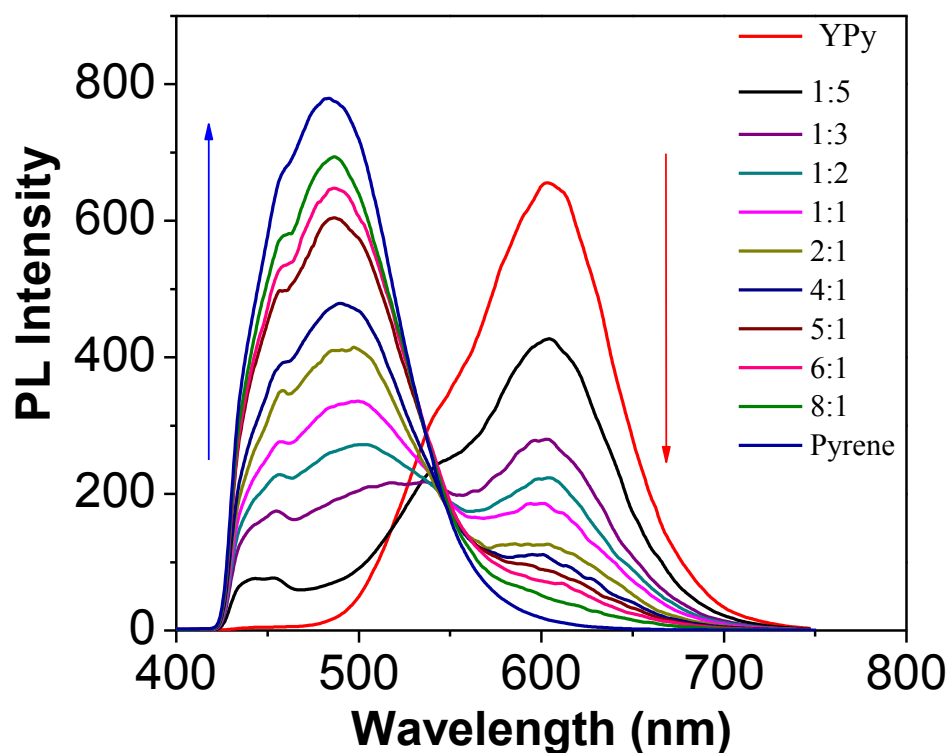


Figure S18. PL spectra for the pure polymer YPy in THF (1.0×10^{-3} mol/L), pure pyrene in THF (2.5×10^{-3} mol/L), and mixtures of the two solutions in different ratios of pyrene to YPy (v/v) ($\lambda_{\text{excit}} = 360$ nm). The fluorescence in the YPy network can be almost totally quenched, suggesting that most of the pyrene chromophores in the network are accessible as a result of its highly porous structure ($S_{\text{BET}} = 1508$ m²/g).

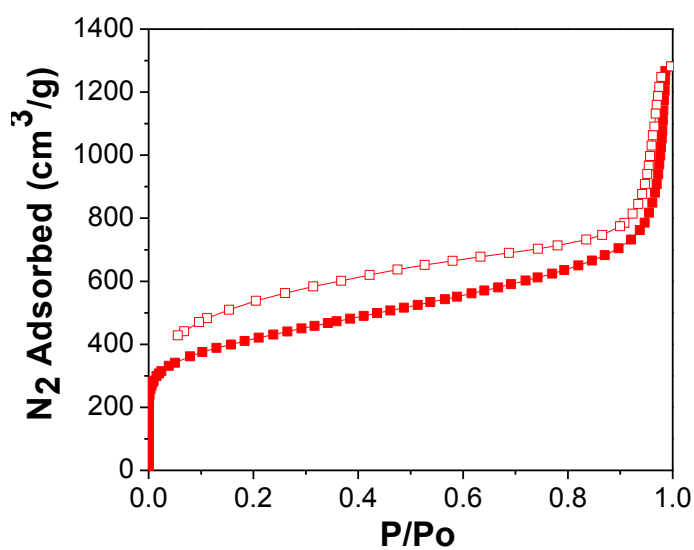


Figure S19. N₂ adsorption-desorption isotherms for **YPy** measured at 77.3 K (adsorption branch is labeled with filled symbols).

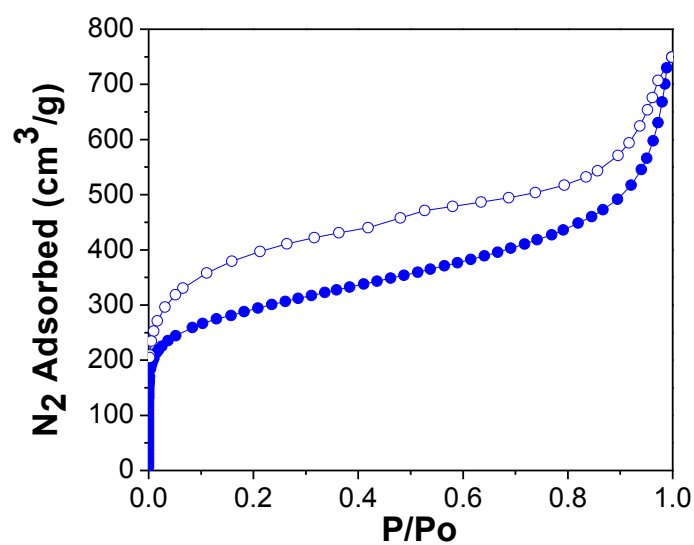


Figure S20. N₂ adsorption-desorption isotherms for **YDBPy** measured at 77.3 K (adsorption branch is labeled with filled symbols).

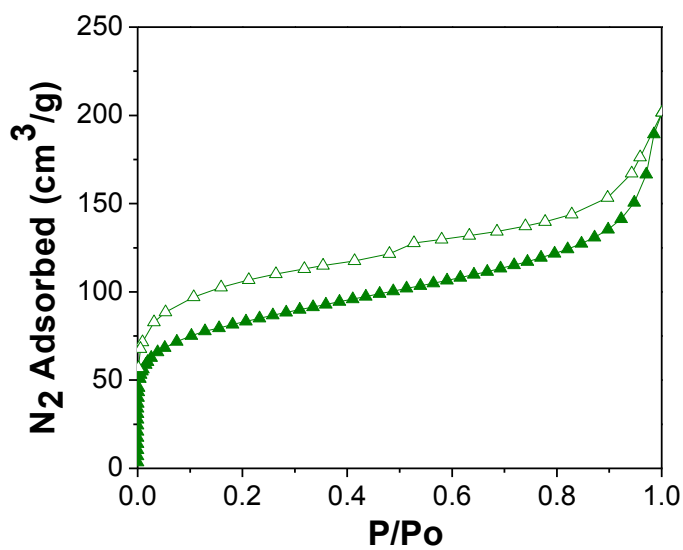


Figure S21. N₂ adsorption-desorption isotherms for YDPPy measured at 77.3 K (adsorption branch is labeled with filled symbols).

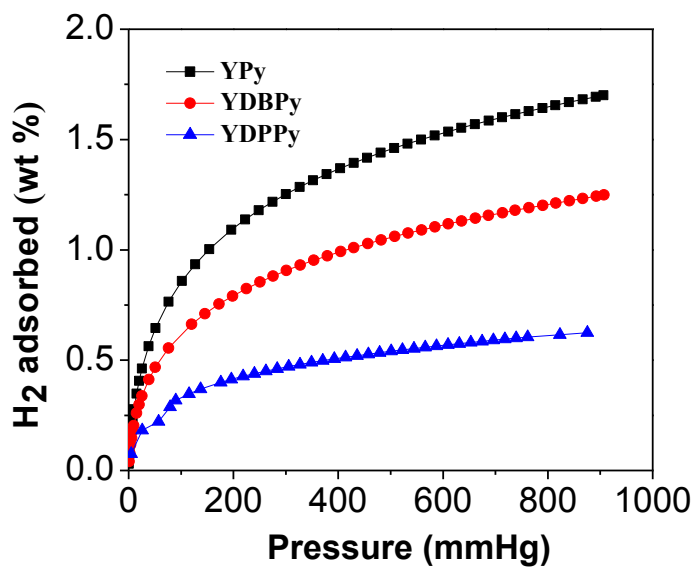


Figure S22. Hydrogen adsorption isotherms of the three statistical copolymers at 77.3 K.

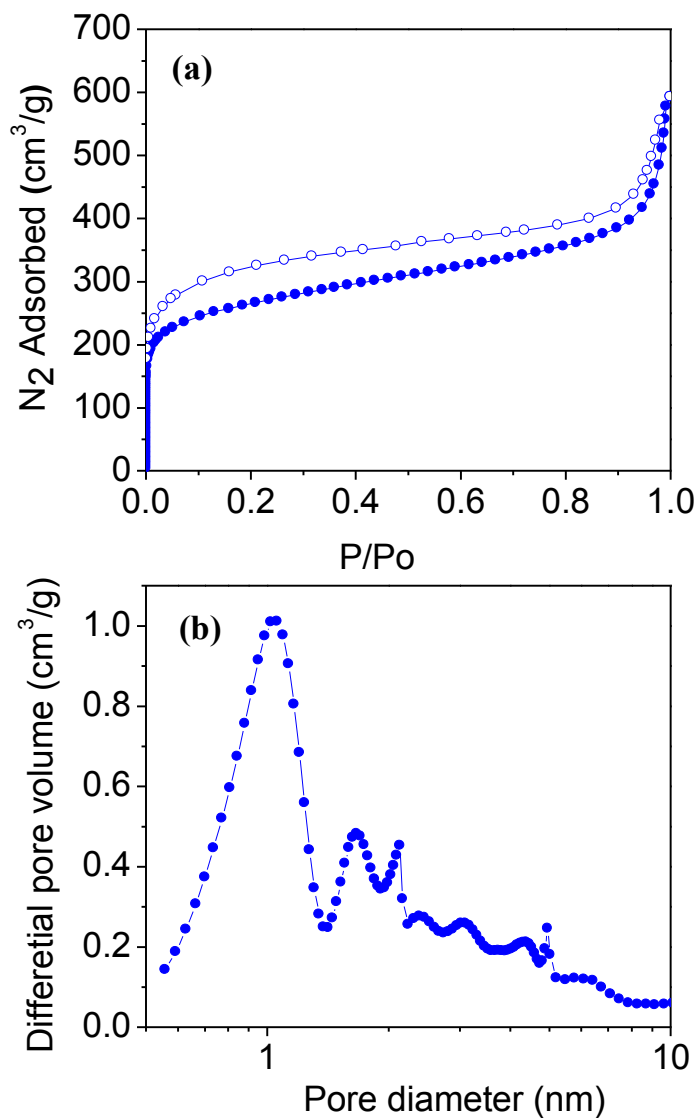


Figure S23. (a) N₂ adsorption-desorption isotherms for alternating copolymer **SDBPy** measured at 77.3 K (adsorption branch is labeled with filled symbols) and NL-DFT pore size distribution curves.

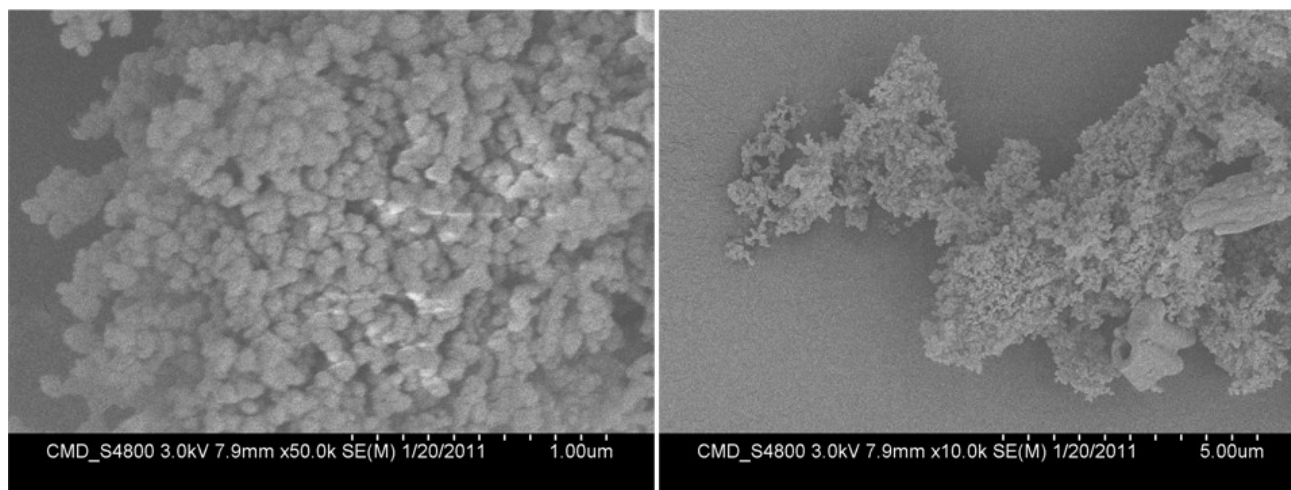


Figure S24. SEM images for **YPy**.

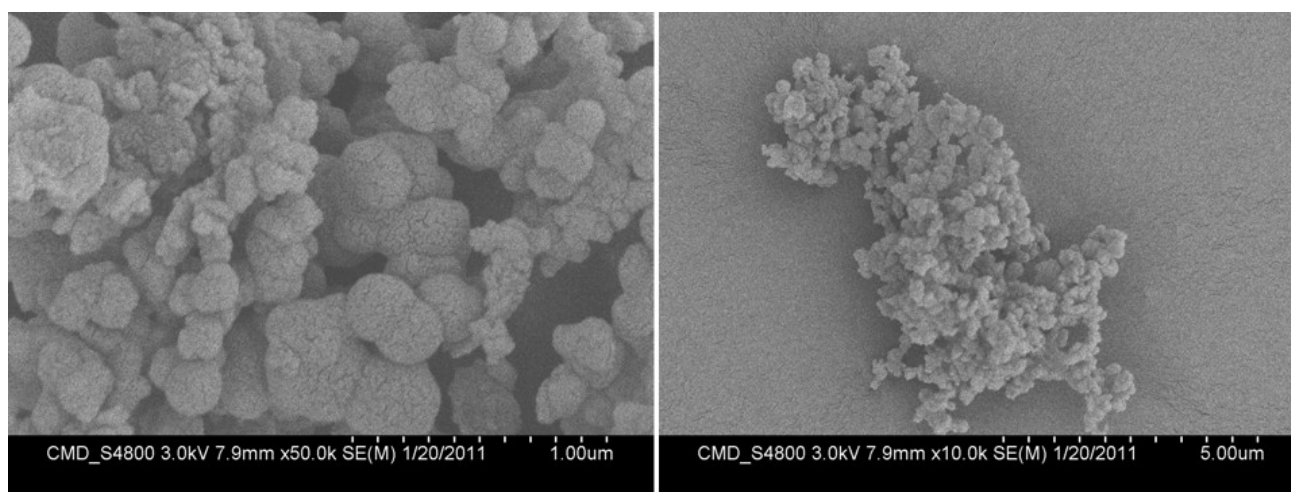


Figure S25. SEM images for **YDBPy**.

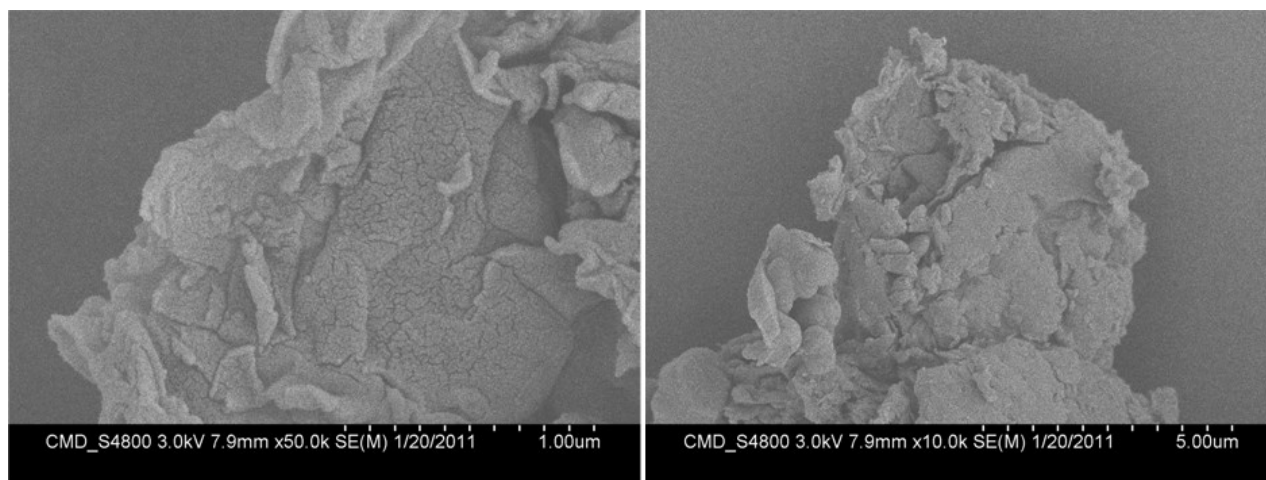


Figure S26. SEM images for **YDPPy**.

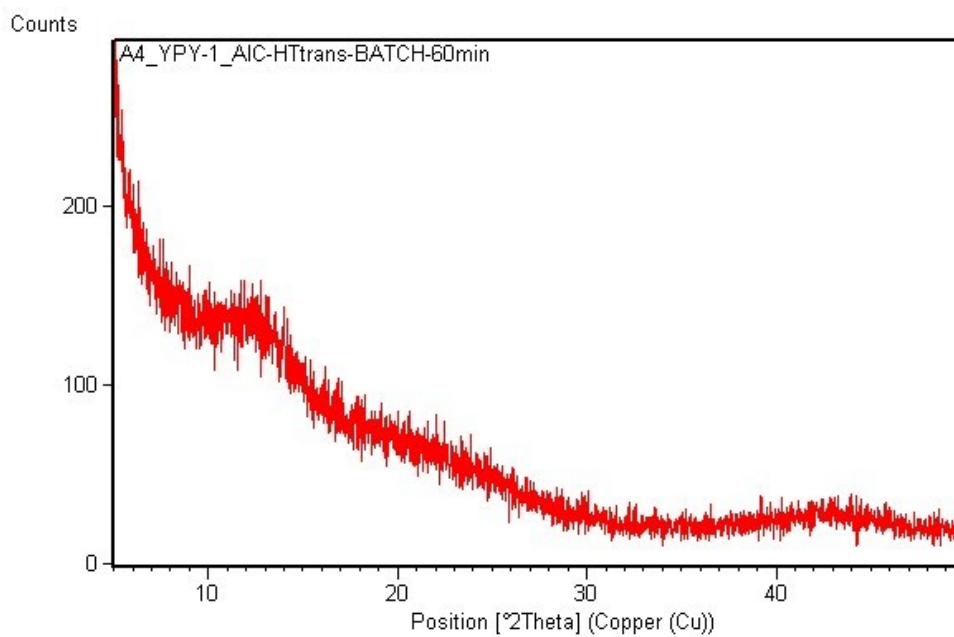


Figure S27. Example PXRD pattern for **YPy**

References

- S1. Bernhardt, S.; Kastler, M.; Enkelmann, V.; Baumgarten, M.; Mullen, K. In *1st European Chemistry Congress* Budapest, HUNGARY, 2006, p 6117.