# Preparation of Recyclable and Versatile Porous Poly-Arylthioethers by Reversible Pd-Catalyzed C–S/C–S Metathesis

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1. General information

Unless otherwise noted, all reactions were carried out under argon in oven-dried 4 mL screw-top glass vials using anhydrous solvents. The anhydrous solvents were prepared by distillation over appropriate drying agents or by using a solvent purification system (LC Technology Solutions, Inc.) under N₂ atmosphere (H₂O content: below 10 ppm, as determined by Karl Fischer titration) and stored over molecular sieves prior to use. All commercially available compounds were used as received from common suppliers (Sigma-Aldrich, Strem Chemicals, abcr, TCI, Fluorochem, Acros Organics, Alfa Aesar and Apollo Scientific).

1.1. Characterization techniques

**Thin layer chromatography (TLC):** Aluminum TLC plate, silica gel coated with fluorescent indicator F254 (TLC Silica gel 60 F254, Merck). Visualization was accomplished using UV light (254 nm) or KMnO₄ stain.

**Flash column chromatography:** SiliaFlash P60 silica gel (60 Å, 40–63 μm, SiliCycle Inc.) with reagent grade solvents.

**NMR:** Spectra were recorded on Bruker AVANCE III 400, Neo 400, Neo 500, or 600 spectrometers at room temperature, unless indicated otherwise; the chemical shifts are reported with respect to internal solvent: δH = 7.26 ppm, and δC = 77.16 (t) ppm (CDCl₃); δH = 7.16 ppm, and δC = 128.06 (t) ppm (C₆D₆); δH = 2.50 (p) ppm, and δC = 39.52 (hept) ppm (DMSO-d₆). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (sextet), hept (septet), m (multiplet), br (broad), or combinations thereof. 13C CP-MAS solid state NMR was recorded on a Bruker AV NEO 400 using a MADSVT 400WB probe.

**GC/FID and GC/MS:** Shimadzu GC-2025 (capillary column: Macherey-Nagel OPTIMA 5, 30.0 m×0.25 mm × 0.25 μm; carrier gas: H₂); To determine GC yields, calibration curves were generated using n-dodecane as an internal standard. Shimadzu GCMS-QP2020 (capillary column: Macherey-Nagel OPTIMA 5, 30.0 m×0.25 mm × 0.25 μm; carrier gas: He).

**High-resolution MS (HRMS):** Thermo scientific Q-Exactive GC Orbitrap for EI. Bruker Daltonics maXis ESI-QTOF or solariX ESI-FTICR-MS for ESI. HRMS data were obtained by the mass spectrometry service (MoBiAS, Molecular and Biomolecular Analysis Service) in the Laboratorium für Organische Chemie at ETH Zürich.

**X-ray powder diffraction patterns (PXRD):** were measured in a PANalytical X’Pert Pro diffractometer using Ni-filtered Cu Kα radiation (λ = 0.1541 nm). Data were recorded in the 2θ range of 2–30° with an angular step size of 0.05° and a counting time of 1.5 s per step.

**N₂ physisorption:** The specific surface area of the materials and the porosity were measured from a nitrogen physisorption isotherm recorded at -196 °C on a BEL JAPAN Belsorp-min apparatus. The surface area values were obtained by the BET method.¹ The porosity values were obtained by the BJH
method using the adsorption branch. The samples were dried at 60 °C under N₂ flow for 16 hours and then 2 hours under vacuum at 100 °C.

**Thermogravimetric Analysis (TGA)** was performed with a Mettler Toledo TGA/DSC 3+ STARRe system instrument (Mettler-Toledo, Schwerzenbach, Switzerland) heating the samples from 25 to 700 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

**Elemental Analysis (EA):** Was performed by the Molecular and Biomolecular Analysis Service (MoBiAS) in the Laboratorium für Organische Chemie at ETH Zürich. C, H, and N measurements were performed in a LECO TruSpec Micro instrument. The gaseous combustion products of C (CO₂) and H (H₂O) were quantified by means of infrared spectroscopy. Nitrogen was measured as N₂ with a thermal conductivity detector. Sulfur was measured in a HEKAtech EuroVector instrument by burning the sample at 1000 °C with an excess of O₂. The composition products were chromatographically separated and measured with a thermal conductivity detector.

**Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES):** Elemental analyses of Pd and Au for all materials were performed by the Mikroanalytisches Labor Pascher, Remagen.

**Transmission Electron Microscopy (TEM):** The morphology of the samples, as well as metal distribution and metal particle sizes were obtained by high resolution TEM using a FEI Talos F200X instrument. The samples were prepared by dropcasting a dispersion of the polymers on a copper grid coated with carbon film.

**Scanning Electron Microscopy (SEM):** The morphology and particle sizes of the polymers were analysed by field emission scanning electron microscopy (FE-SEM) using a JEOL JSM-7100F instrument. The samples were prepared by dropcasting a dispersion of the polymers on a copper tape film.

**Fourier Transformed Infrared spectroscopy (FT-IR):** FT-IR measurements were carried out using a Bruker INVENIO-R FT-IR Spectrometer equipped with a diamond ATR.

**X-ray Absorption Spectroscopy (XAS) experiments** were conducted at the SuperXAS beamline of the Swiss Light Source (proposal number 20200442). The X-ray beam from the 2.9 T superbend was collimated using a Pt-coated mirror, monochromatised using a Si(111) channel cut monochromator, and focused to a spot size of 500×100 μm (horizontal×vertical) using a Pt-coated toroidal mirror. Data were acquired in air from pressed pellets at the Pd K-edge in transmission and fluorescence modes simultaneously using Quick XAS data acquisition mode, using three 15 cm long Ar/N₂-filled ionization chambers for transmission detection and PIPS diode for fluorescence detection. The samples were placed between the first and the second ionisation chamber. For the absolute energy calibration, a Pd foil was measured simultaneously between the second and a third ionisation chambers. The resulting data were averaged and energy calibrated using ProXAS in house software and background corrected and normalized using the Athena program from the Demeter software suite. Fourier transformation of EXAFS data was performed using k³ weightings in the range of 3-12 Å⁻¹.

**Ultraviolet-visible spectroscopy (UV-vis):** UV-vis measurements of the polymers were carried out in a dispersion of dichloromethane using a quartz cuvette in a Cary 60 UV-Vis spectrophotometer.
**Fluorescence:** Fluorescence quenching experiments as well as fluorescence spectra of the polymers were performed in an aqueous dispersion (1% v/v NMP) using a Tecan Infinite 200 PRO plate reader.
2. Synthesis of starting materials

2.1. Hammett analysis.

Symmetrical diaryl thioethers used for the Hammett study (Figure 1 in the main text) have been prepared by copper catalyzed coupling of the corresponding aryl iodide with Na₂S₉H₂O. The general procedure is described as follows:

An oven-dried 250 ml round bottom flask containing a magnetic stirring bar was charged with CuI (2 mmol, 381 mg), K₂CO₃ (20 mmol, 2.80 g), Na₂S₉H₂O (12 mmol, 2.96 g) and the substituted iodobenzene (20 mmol). The mixture was evacuated and backfilled with N₂ (three cycles) before anhydrous DMF (40 mL) was added via cannula. The mixture was then heated at 120 °C for 18 h and allowed to cool to room temperature. The resulting mixture was diluted with water (200 ml) and extracted with ethyl acetate (3×200 mL). The combined organic layers were washed with LiCl (5% in water, 250 ml) and water (500 ml), dried with Na₂SO₄ and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent consisting of petroleum ether and ethyl acetate. The characterization of these compounds was in agreement with the data found in the literature.

Di-p-tolylsulfane (H2).

\[ \text{H NMR (400 MHz, CDCl}_3) \delta 7.24 (d, J = 8.2 \text{ Hz}, 4H), 7.11 (d, J = 7.9 \text{ Hz}, 4H), 2.33 (s, 6H). \]

Di-m-tolylsulfane (H3).

\[ \text{H NMR (400 MHz, CDCl}_3) \delta 7.26 - 7.21 (m, 4H), 7.20 - 7.16 (m, 2H), 7.12 - 7.07 (m, 2H), 2.36 (s, 6H). \]
Bis(4-(trifluoromethyl)phenyl)sulfane (H4).\textsuperscript{6}

\begin{center}
\includegraphics[width=0.2\textwidth]{molecule1.png}
\end{center}

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 8.1$ Hz, 4H), 7.46 (d, $J = 8.0$ Hz, 4H).

Bis(4-methoxyphenyl)sulfane (H5).\textsuperscript{5}

\begin{center}
\includegraphics[width=0.2\textwidth]{molecule2.png}
\end{center}

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 8.9$ Hz, 4H), 6.86 (d, $J = 8.9$ Hz, 4H), 3.81 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.97, 132.74, 127.42, 114.76, 55.36.
2.2. Monomers for the synthesis of frameworks.

Starting materials (1-Ph – 5-Ph) were synthesized following the reported procedures in the literature when available. Otherwise, we adapted well established synthetic methodologies in order to obtain the materials in high yields and purity.

1,3,5-Tris(4-phenylthiophenyl)benzene (1-Ph) (adapted from ref. 7)

To an oven dried round-bottom flask containing a magnetic stirring bar were added aryl halide (5 mmol, 2.80 g), i-Pr₂NEt (40 mmol, 7 ml) and dry 1,4-dioxane (20 ml). The mixture was evacuated and backfilled with nitrogen (3 cycles). Then, the catalyst Pd₂(dba)₃ (0.50 mmol, 458 mg), Xantphos (1.0 mmol, 579 mg) and thiophenol (30 mmol, 3.34 g) were added and then the mixture was degassed twice more. The mixture was heated to reflux for 24 h and TLC confirmed the completion of the reaction. The reaction mixture was then allowed to reach ambient temperature. The reaction mixture was then filtered through Celite® and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with n-hexane:DCM (9:1 to 7:3) to afford the desired thioether. The product was further purified by slow diffusion of n-hexane in DCM. The compound was obtained as a white solid (3.03 g, 96% yield).

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{5 mmol} & \quad \text{6 eq.} \\
\text{+} & \quad \text{Pd}_2(\text{dba})_3 (10 \text{ mol\%}) \\
& \quad \text{Xantphos (20 mol\%)} \\
& \quad \text{DIPEA (8 eq.)} \\
& \quad 1,4\text{-dioxane anh. (20 ml)} \\
& \quad \text{reflux, 24 h.} \\
\text{SPh} & \quad \text{PhS}^- \\
\text{1-Ph} & \quad \text{1-Ph}
\end{align*}
\]

\(^1\text{H NMR} (400 \text{ MHz, Chloroform-d}) \delta 7.75 (s, 3H), 7.67 – 7.58 (m, 6H), 7.49 – 7.40 (m, 12H), 7.40 – 7.34 (m, 6H), 7.34 – 7.29 (m, 3H).

\(^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 141.66, 139.54, 135.64, 135.40, 131.36, 131.19, 131.15, 129.32, 128.01, 127.32, 124.89.

\text{HRMS (ESI, m/z): [M]^+ calcd. for C}_{42}\text{H}_{30}\text{S}_{3} \text{630.1504; found 630.1503.}
1,1,2,2-tetrakis(4-(phenylthio)phenyl)ethene (2-Ph)

Synthesis of the precursor 1,1,2,2-tetrakis(4-fluorophenyl)ethene (2-F) (From ref. 8)

Zn dust (5.5 g, 84 mmol) and TiCl₄ (4.6 ml, 42 mmol) were refluxed for 3 h in 300 ml of dry THF under N₂ atmosphere. A solution of 4,4'-difluorobenzophenone (4.6 g, 21 mmol) in dry THF (100 ml) was added to the preceding suspension, and then the reaction was refluxed at 80 °C for 8 h. Then, an aqueous solution containing 10% K₂CO₃ (200 ml) was added after the reaction mixture was cooled down to room temperature. The resulting product was extracted with ethyl acetate (3 x 200 ml). The solvent was evaporated under reduced pressure and the crude product was purified by a silica gel column using pure petroleum ether as the eluent. 2-F was obtained as a yellow solid (2.37 g, 56% yield).

¹H NMR (400 MHz, Chloroform-d) δ 7.00 – 6.91 (m, 8H), 6.89 – 6.77 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 162.74, 160.28, 139.09, 139.06, 132.82, 132.74, 115.06, 114.84.

Synthesis of 2-Ph (Adapted from ref. 9)

An oven-dried 250 ml two-necked round-bottom flask equipped with a magnetic stirring bar and reflux condenser was charged with 2-F (5.0 mmol, 2.02 g) and potassium phosphate (10 eq., 11 g). The apparatus was evacuated and back-filled with nitrogen three times. Then, DMF (50 ml) was added under stirring. To the resulting suspension was added thiophenol (8 eq., 4.2 ml) dropwise via syringe and the resulting mixture was stirred at 140 °C for 24 hours. The reaction was quenched with H₂O (50 ml). The aqueous phase was extracted with DCM (3 x 50 ml). The combined organic phases were washed with aq. LiCl 5% aq. (2 x 100 ml) and H₂O (1 x 100 ml), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (Hexane:DCM 3:1) to yield 2-Ph as a yellow solid (3.21 g, 84% yield).

¹H NMR (400 MHz, Chloroform-d) δ 7.30 (m, 16H), 7.27 – 7.21 (m, 4H), 7.08 (d, J = 8.5 Hz, 8H), 6.94 (d, J = 8.0 Hz, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 135.27, 132.60, 131.12, 129.24, 127.17.

HRMS (ESI, m/z): [M]+ calcd. for C₅₀H₃₆S₄ 764.1694; found 764.1695.
1,3,6,8-Tetrakis(4-phenylthiophenyl)pyrene (3-Ph)

Synthesis of the precursor 1,3,6,8-Tetrakis(4-fluorophenyl)pyrene (3-F) (From ref. 10)

A mixture of 4-fluoro-benzeneboronic acid (5.77 g, 40 mmol), 1,3,6,8-tetrabromopyrene (2.67 g, 5 mmol), palladium tetrakistriphenylphosphine (0.292 g, 0.25 mmol), and potassium carbonate (9.8 g, 70 mmol) in dry 1,4-dioxane (50 mL) was stirred under nitrogen for 48 h at 85 °C. The reaction mixture was poured into a solution of ice and concentrated hydrochloric acid (3:1). The organic phase was extracted with dichloromethane (200 ml), dried over magnesium sulfate and the solvent was evaporated under reduced pressure. The crude product was recrystallized from toluene to give a yellow solid (2.1 g, 73% yield).

$^1$H NMR (400 MHz, Chloroform-d) δ 8.14 (s, 4H), 7.97 (s, 2H), 7.64 (dd, J = 8.7, 5.4 Hz, 8H), 7.27 (t, J = 8.7 Hz, 8H).

$^{13}$C NMR (100 MHz, CDCl₃) δ 163.63, 136.77 (d, $^4$J$_{C-F}$ = 3.4 Hz), 136.32, 132.16 (d, $^3$J$_{C-F}$ = 8.0 Hz), 129.59, 128.24, 125.84, 125.28, 115.51 (d, $^3$J$_{C-F}$ = 21.4 Hz).

$^{19}$F NMR (376 MHz, CDCl₃) δ -115.00.

Synthesis of 3-Ph (Adapted from ref. 9)

An oven-dried 250 ml two-necked round-bottom flask equipped with a magnetic stirring bar and reflux condenser was charged with 3-F (0.85 mmol, 0.5 g) and potassium phosphate (20 eq., 3.8 g). The apparatus was evacuated and back-filled with nitrogen three times. Then, DMF (50 ml) was added under stirring. To the resulting suspension was added thiophenol (16 eq., 1.45 ml) dropwise via syringe and the resulting mixture was stirred at 135°C for 48 hours. The reaction was quenched with H₂O (50 ml). The aqueous phase was extracted with DCM (3 x 50 ml). The combined organic phases were washed with aq. LiCl 5% aq. (2 x 100 ml) and H₂O (1 x 100 ml), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (Hexane:DCM 3:1 to 1:1) to yield 3-Ph as a yellow solid (0.55 g, 68% yield).

$^1$H NMR (400 MHz, Chloroform-d) δ 8.19 (s, 4H), 7.99 (s, 2H), 7.61 (d, J = 8.6 Hz, 8H), 7.53 – 7.48 (m, 16H), 7.43 – 7.36 (m, 8H), 7.36 – 7.30 (m, 4H).

$^{13}$C NMR (101 MHz, CDCl₃) δ 139.51, 136.57, 135.47, 135.28, 131.62, 131.56, 131.37, 130.54, 129.36, 128.13, 127.40, 125.94, 125.34.

HRMS (ESI, m/z): [M]$^+$ calcd. for C₆₄H₄₂S₄ 938.2164; found 938.2166.
Tetrakis((4-phenylthio)phenyl)methane (4-Ph)

Synthesis of the precursor tetrphenylmethane (4-H) (From ref. 11)

An oven dried 250 ml round bottom flask containing a magnetic stirring bar and a reflux condenser was charged with 15 g of trityl chloride (0.054 mol, 1 eq.) and 14.05 ml aniline (0.154 mol, 2.9 eq.) and heated up to 180 °C until the reaction mixture turned into a violet solid. The solid was cooled down, crushed and resuspended in 75 ml MeOH and 75 ml 2 M HCl. The suspension was refluxed for 30 min., filtered and washed with water. After resuspending in ethanol the reaction mixture was cooled down to -30 °C and 15.8 ml sulfuric acid and 9.44 g of isopentynitrite (0.081 mol, 1.5 eq.) were added under vigorous stirring. After stirring for 1 hour at -10 °C, 26.9 ml of phosphinic acid (0.609 mol, 11 eq.) were added slowly and the reaction mixture was refluxed for 1.5 h. After cooling down, the solid was filtered, washed with DMF, H₂O and hot ethanol and subsequently dried under vacuum to get a light brown powder. Further purification was done by recrystallisation in THF/methanol (1:1). Yield: 16.1 g (0.05 mol, 93 %).

Synthesis of the precursor tetrakis((4-bromo)phenyl)methane (4-Br) (From ref. 11)

In a three necked vessel with magnetic stirrer, thermometer and condenser 10 g tetraphenylmethane (31.2 mmol, 1 eq.) were cooled in an ice bath. Now 99.8 g Br₂ (624 mmol, 20 eq.) were added dropwise. After cooling to -78 °C, 140 ml ethanol (4.5 ml/mmol) were added and the mixture was allowed to reach room temperature overnight. Thereafter, sodium disulfide solution (sat.) was added until the end of precipitation. The resulting solid was filtered, washed with H₂O and dried in an oven at 110 °C. Further purification was carried out performing recrystallisation in a chloroform/ethanol mixture (1:1) to get a light brown solid. Yield: 12.9 g (20.3 mmol, 65 %).

¹H-NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.8 Hz, 8H), 7.03 (d, J = 8.8 Hz, 8H).

¹³C-NMR (101 MHz, CDCl₃) δ 144.43, 132.37, 131.09, 120.81, 63.64.

Synthesis of tetrakis((4-phenylthio)phenyl)methane (4-Ph) (adapted from ref. 7)

To an oven dried round-bottom-flask containing a magnetic stirring bar were added 4-Br (2.5 mmol, 1.59 g), i-Pr₂NEt (35 mmol, 6.10 ml) and dry 1,4-dioxane (15 ml). The mixture was evacuated and backfilled with nitrogen (3 cycles). Then, the catalyst Pd₂dba₃ (0.25 mmol, 236 mg), Xantphos (0.5 mmol, 298 mg) and thiophenol (30 mmol, 3.10 ml) were added and then the mixture was degassed twice more. The mixture was heated to reflux for 24 h and TLC confirmed the completion of the reaction. The reaction mixture was then allowed to reach ambient temperature. The reaction mixture was then filtered through Celite® and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with n-hexane:DCM (9:1 to 7:3) to afford the desired thioether. The product, was further purified by crystallization by slow diffusion of n-hexane in DCM. The compound was obtained as a white solid (1.56 g, 83% yield).

\[ \text{Cl} \rightarrow \text{Br} \rightarrow \text{PhSH} \]

\[ \text{Pd}_2\text{dba}_3 (10 \text{ mol}) \]

\[ \text{XantPhos} (20 \text{ mol}) \]

\[ \text{DIPEA} (14 \text{ eq}) \]

\[ 1,4\text{-dioxane, reflux} \]

\[ 48 \text{ h, } \text{N}_2 \]

\[ \text{4-Ph} \]
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (dd, J = 8.2, 1.5 Hz, 8H), 7.39 – 7.27 (m, 12H), 7.17 (d, J = 8.7 Hz, 8H), 7.10 (d, J = 8.8 Hz, 8H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.53, 134.49, 134.41, 132.05, 131.60, 129.30, 128.97, 127.56, 63.71.

HRMS (ESI, m/z): [M]$^+$ calcd. for C$_{49}$H$_{36}$S$_4$ 752.1694; found 752.1695.
Tetrakis(4-(phenylthio)phenyl)silane (5-Ph)

Synthesis of the precursor tetrakis([4-bromo]phenyl)silane (5-Br) (From ref. 12)

In a 250 ml round bottom flask containing a magnetic stirring bar under N\textsubscript{2} atmosphere, 1,4-dibromobenzene (30 mmol) was dissolved in dry diethyl ether. The solution was cooled down to -20°C using an ice/NaCl bath. \textit{n}-BuLi (2.4 M, 13.75 mL, 1.1 equivalents) was added dropwise to the solution through a syringe. The solution was stirred for 30 min and then the ice/NaCl bath was removed and the solution stirred for another 3 hours. Tetrachlorosilane (15 mmol) was added dropwise to the solution and the mixture was stirred overnight. Upon completion, the reaction mixture was poured onto ice/water. The reaction mixture was extracted with diethyl ether (3 x 100 ml), washed with water (2 x 200 ml) and the combined organic extracts were dried over anhydrous magnesium sulfate. The product was purified by crystallisation in a mixture of dichloromethane and ethanol (2.96 g, 61% yield).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.57 (d, J = 8.4 Hz, 8H), 7.37 (d, J = 8.5 Hz, 8H).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \delta 137.64, 131.50, 131.44, 125.47.

Synthesis of Tetrakis(4-(phenylthio)phenyl)silane (5-Ph) (adapted from ref. 7)

To an oven dried round-bottom-flask containing a magnetic stirring bar were added 5-Br (2.5 mmol, 1.68 g), \textit{i}-Pr\textsubscript{2}NEt (35 mmol, 6.10 ml) and dry 1,4-dioxane (15 ml). The mixture was evacuated and backfilled with nitrogen (3 cycles). Then, the catalyst Pd\textsubscript{2}(dba)\textsubscript{3} (0.25 mmol, 236 mg), Xantphos (0.5 mmol, 298 mg) and thiophenol (30 mmol, 3.10 ml) were added and then the mixture was degassed twice more. The mixture was heated to reflux for 24 h and TLC confirmed the completion of the reaction. The reaction mixture was then allowed to reach ambient temperature. The reaction mixture was then filtered through Celite® and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with \textit{n}-hexane:DCM (9:1 to 7:3) to afford the desired thioether. The product was further purified by slow diffusion of \textit{n}-hexane in DCM. The compound was obtained as a white solid (1.60 g, 83% yield).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.47 (dd, J = 8.1, 1.6 Hz, 8H), 7.43 – 7.30 (m, 20H), 7.22 (d, J = 8.4 Hz, 8H).

HRMS (ESI, m/z): [M]\textsuperscript{+} calcd. for C\textsubscript{48}H\textsubscript{38}S\textsubscript{4}Si 768.1464; found 768.1466.
1,3,5-Tris(4-phenylthiocyclohexyl)benzene (1-Cy)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (s, 3H), 7.63 (d, $J$ = 8.6 Hz, 6H), 7.51 (d, $J$ = 8.6 Hz, 6H), 3.20 (tt, $J$ = 10.5, 3.6 Hz, 3H), 2.16 – 1.99 (m, 6H), 1.83 (dt, $J$ = 12.2, 3.7 Hz, 6H), 1.71 – 1.61 (m, 3H), 1.50 – 1.25 (m, 15H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.73, 139.19, 134.83, 132.04, 127.60, 124.75, 77.35, 77.04, 76.72, 46.59, 33.36, 26.10, 25.79.

1,1,2,2-tetrakis(4-cyclohexylthio)phenyl)ethene (2-Cy)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 (d, $J$ = 8.6 Hz, 8H), 6.92 (d, $J$ = 8.3 Hz, 8H), 3.22 – 2.96 (m, 4H), 2.05 – 1.91 (m, 8H), 1.91 – 1.75 (m, 8H), 1.70 – 1.61 (m, 4H), 1.42 – 1.20 (m, 20H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.48, 140.03, 133.70, 131.72, 130.44, 77.35, 77.03, 76.71, 46.15, 33.28, 26.08, 25.80.

Tetrakis(4-cyclohexylthio)phenyl)methane (4-Cy)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 (d, $J$ = 8.6 Hz, 8H), 7.09 (d, $J$ = 8.6 Hz, 8H), 3.15 (tt, $J$ = 10.3, 3.5 Hz, 4H), 2.02 (d, $J$ = 10.2 Hz, 8H), 1.80 (d, $J$ = 9.6 Hz, 8H), 1.65 (d, $J$ = 9.5 Hz, 4H), 1.46 – 1.21 (m, 20H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.42, 133.31, 131.36, 129.93, 77.34, 77.02, 76.70, 46.05, 33.42, 26.06, 25.77.
3. Preliminary kinetic studies

**Scrambling kinetics of aryl thioethers with different substituents (Figures 1 and S1)**

In the glovebox, an oven dried 4 ml screw-cap vial containing a magnetic stirring bar was charged with the two aryldithioethers (H1-H5, 0.1 mmol), LiHMDS (0.05 mmol), thiophenol (0.005 mmol), dodecane (10 µl, internal standard) and o-xylene (0.95 ml). The vial was sealed with a cap containing a septum, taken outside the glovebox and placed in aluminum heating blocks preheated at 80 °C, where it was stirred for 15 minutes to reach the final temperature. Then, a solution containing Pd-SingaCycle A1 prepared in the glovebox (0.02 M in o-xylene) was added to the vial with a 50 µl Hamilton syringe (50 µl, 0.001 mmol) starting the reaction (t<sub>0</sub>). 20 µl aliquots were collected at different reaction times, diluted with ethyl acetate (1 ml) and measured by GC.

| Entry | σ<sub>1</sub> | σ<sub>2</sub> | rate (mMmin<sup>-1</sup>) |
|-------|---------------|---------------|----------------------------|
| 1     | 0             | -0.069        | 5.838                      |
| 2     | 0             | -0.17         | 11.904                     |
| 3     | 0             | -0.27         | 0.045                      |
| 4     | 0             | 0.54          | 0.407                      |
| 5     | -0.17         | -0.27         | 0.000                      |
| 6     | -0.17         | 0.54          | 0.078                      |
| 7     | -0.27         | 0.54          | 0.039                      |

*Figure S1.* Kinetic profiles for C-S/C-S metathesis reaction containing groups with different electronic properties (Hammett parameter).
Kinetic measurement of model imine condensation (Figure S2)

The reaction conditions for this experiment were taken from ref. 13 as a reference for standard imine-COFs synthesis. An oven dried 4 ml screw-cap vial containing a magnetic stirring bar was charged with aniline (0.100 mmol), acetic acid (0.05 ml of a 10.5 M aqueous solution), dodecane (25 µl, internal standard) and 1 ml of 1,4-dioxane:mesitylene mixture (4:1, v/v). The vial was sealed with a cap containing a septum, and placed in an aluminum heating block preheated at 70 °C, where it was stirred for 15 minutes to reach the final temperature. Then, benzaaldehyde (0.100 mmol) was added to the vial with a 50 µl Hamilton syringe starting the reaction (t₀). 20 µl aliquots were collected at different reaction times, diluted with ethyl acetate (1 ml) and measured by GC.

Figure S2. Comparison between reaction rate for (a) imine condensation and (b) C-S/C-S metathesis reactions at 70 °C and [Starting materials] = 0.1 M. Induction time appears as a result of the need to form toS⁻ anion in similar amounts as PhS anion.
Optimization of the reaction rate by changing reaction conditions (Figure S3 and Table S1)

To maximize reaction rate and minimize catalyst deactivation, we investigated the influence of reaction temperature and catalyst concentration. Reaction temperature seem to have a big influence on the deactivation of the catalyst. Indeed, while catalyst do not show significant deactivation up to 100 °C, at 120 °C the reaction stops during the first 10 minutes, before reaching the equilibrium. This effect is even more pronounced at 140 °C, pointing towards temperature-induced catalyst deactivation. Finally, we evaluated the effect of different parameters on the rate of the reaction in order to find the optimal range of conditions. In general, the reaction is favored by higher catalyst and base loading and apolar solvents (toluene, xylene, diphenyl ether, etc.). On the other hand, polar aprotic solvents or solvents containing aryl halides are not compatible with the reaction.

**Table S1. Effect of different reaction conditions on the rate**

| Entry | T (°C) | [cat] | [Reag] | [PhSH] | [LiHMDS] | Solvent     | Rate (Ms⁻¹) |
|-------|--------|-------|--------|--------|----------|-------------|-------------|
| 1     | 100    | 0.002 | 0.2    | 0.02   | 0.1      | o-xyl       | 0.0166      |
| 2     | 100    | 0.002 | 0.1    | 0.02   | 0.1      | o-xyl       | 0.0236      |
| 3     | 100    | 0.002 | 0.2    | 0.01   | 0.1      | o-xyl       | 0.0164      |
| 4     | 100    | 0.002 | 0.2    | 0.02   | 0.02     | o-xyl       | 0.0000      |
| 5     | 100    | 0.001 | 0.2    | 0.02   | 0.1      | o-xyl       | 0.0099      |
| 6     | 80     | 0.002 | 0.2    | 0.02   | 0.1      | o-xyl       | 0.0031      |
| 7     | 100    | 0.002 | 0.2    | 0.02   | 0.1      | o-xyl       | 0.0156      |
| 8     | 100    | 0.002 | 0.2    | 0.02   | 0.1      | 1,4-diox    | 0.0000      |
| 9     | 100    | 0.002 | 0.2    | 0.02   | 0.05     | o-xyl:1,4-diox(1:1) | 0.0000  |
| 10    | 100    | 0.002 | 0.2    | 0.02   | 0.05     | o-xyl       | 0.0074      |
| 11    | 100    | 0.002 | 0.2    | 0.02   | 0.1      | o-xyl       | 0.0008      |
| 12    | 100    | 0.002 | 0.2    | 0.02   | 0.02(CySH)| o-xyl       | 0.0262      |
| 13    | 100    | 0.002 | 0.2    | 0.02   | 0.02(BnSH)| o-xyl       | 0.0410      |
| 14    | 100    | 0.003 | 0.2    | 0.02   | 0.1      | o-xyl:1,4-diox(19:1) | 0.0007  |
| 15    | 100    | 0.002 | 0.2    | 0.02   | 0.1      | o-xyl:1,4-diox(19:1) | 0.0007  |

Figure S3. Summary of the reaction conditions screening.
4. Synthesis and chemical stability of the polymers P1-P5

Screening of conditions for the synthesis of P1-P5 (Tables S2-S6)

Synthesis conditions for each monomer were evaluated by maximizing the yield of Ph₂S measured by GC. In the case where yields were similar, low catalyst loading and temperatures were chosen. Tables S2-S6 show the results for the optimization for every monomer.

Table S2. Optimization of conditions for synthesis of P1. All yields are calculated after 20 hours. aIPr ligand added in 1 eq w.r.t. Pd catalyst.

| Entry | [1] | [Pd] | [LiHMDS] | [PhSH] | Solvent | V | T | Ph₂S (GC) |
|-------|-----|------|----------|--------|---------|---|---|-----------|
| 1     | 16.7 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 88.8 |
| 2     | 8.35 mM | 0.125 mM | 12.5 mM | 1.25 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 83.8 |
| 3     | 16.7 mM | 1.0 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 88.4 |
| 4a    | 16.7 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 90.5 |
| 5     | 16.7 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 100 °C | 94.9 |
| 6     | 16.7 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl | 1 ml | 80 °C | 85.9 |
| 7     | 16.7 mM | 0.25 mM | 50 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 86.8 |
| 8     | 8.35 mM | 0.50 mM | 12.5 mM | 1.25 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 86.6 |
| 9     | 33.4 mM | 0.50 mM | 50 mM | 5.0 mM | o-xyl:Ph₂O | 0.5 ml | 80 °C | 87.6 |

Table S3. Optimization of conditions for synthesis of P2. All yields are calculated after 20 hours. aIPr ligand added in 1 eq w.r.t. Pd catalyst.

| Entry | [2] | [Pd] | [LiHMDS] | [PhSH] | Solvent | V | T | Ph₂S (GC) |
|-------|-----|------|----------|--------|---------|---|---|-----------|
| 1     | 12.5 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 53.7 |
| 2     | 6.25 mM | 0.125 mM | 12.5 mM | 1.25 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 44.9 |
| 3     | 12.5 mM | 1.0 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 75.2 |
| 4a    | 12.5 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 66.5 |
| 5     | 12.5 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 100 °C | 52.5 |
| 6     | 12.5 mM | 0.25 mM | 25 mM | 2.5 mM | o-xyl | 1 ml | 80 °C | 52.4 |
| 7     | 12.5 mM | 0.25 mM | 50 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 53.6 |
| 8     | 6.25 mM | 0.50 mM | 12.5 mM | 1.25 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 49.0 |
| 9     | 25 mM | 0.50 mM | 50 mM | 5.0 mM | o-xyl:Ph₂O | 0.5 ml | 80 °C | 61.8 |

Table S4. Optimization of conditions for synthesis of P3. All yields are calculated after 20 hours. aStirring. bIPr ligand added in 1 eq w.r.t. Pd catalyst.

| Entry | [3] | [Pd] | [LiHMDS] | [PhSH] | Solvent | V | T | Ph₂S (GC) |
|-------|-----|------|----------|--------|---------|---|---|-----------|
| 1     | 6.25 mM | 0.125 mM | 12.5 mM | 0.625 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 59.2 |
| 2a    | 6.25 mM | 0.125 mM | 12.5 mM | 0.625 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 59.4 |
| 3     | 6.25 mM | 0.5 mM | 12.5 mM | 0.625 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 73.0 |
| 4b    | 6.25 mM | 0.125 mM | 12.5 mM | 0.625 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 63.6 |
| 5     | 6.25 mM | 0.125 mM | 12.5 mM | 0.625 mM | o-xyl:Ph₂O | 2 ml | 100 °C | 72.7 |
| 6     | 6.25 mM | 0.125 mM | 12.5 mM | 0.625 mM | o-xyl | 2 ml | 80 °C | 48.9 |
| 7     | 12.5 mM | 0.25 mM | 25 mM | 1.25 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 68.7 |
| 8     | 25 mM | 0.50 mM | 50 mM | 2.5 mM | o-xyl:Ph₂O | 1 ml | 80 °C | 64.6 |
| 9     | 12.5 mM | 0.50 mM | 50 mM | 1.25 mM | o-xyl:Ph₂O | 2 ml | 80 °C | 64.1 |
### Table S5. Optimization of conditions for synthesis of P4. All yields are calculated after 20 hours. a Stirring. b IPr ligand added in 1 eq w.r.t. Pd catalyst.

| Entry | [4] [Pd] | [LiHMDS] | [PhSH] | Solvent | V | T | Ph2S (GC) |
|-------|-----------|---------|--------|---------|---|---|-----------|
| 1     | 6.25 mM   | 0.125 mM| 12.5 mM| 0.625 mM| 2 ml | 80 °C | 15.7      |
| 2a    | 6.25 mM   | 0.125 mM| 12.5 mM| 0.625 mM| 2 ml | 80 °C | 12.8      |
| 3     | 6.25 mM   | 0.5 mM  | 12.5 mM| 0.625 mM| 2 ml | 80 °C | 56.1      |
| 4b    | 6.25 mM   | 0.125 mM| 12.5 mM| 0.625 mM| 2 ml | 80 °C | 19.3      |
| 5     | 6.25 mM   | 0.125 mM| 12.5 mM| 0.625 mM| 2 ml | 100 °C| 13.6      |
| 6     | 6.25 mM   | 0.125 mM| 12.5 mM| 0.625 mM| 2 ml | 80 °C | 16.9      |
| 7     | 12.5 mM   | 0.25 mM | 25 mM  | 1.25 mM | 2 ml | 80 °C | 60.2      |
| 8     | 25 mM     | 0.50 mM | 50 mM  | 2.5 mM  | 1 ml | 80 °C | 60.2      |
| 9     | 12.5 mM   | 0.50 mM | 50 mM  | 1.25 mM | 2 ml | 80 °C | 66.4      |

### Table S6. Optimization of conditions for synthesis of P5. All yields are calculated after 20 hours. a IPr ligand added in 1 eq w.r.t. Pd catalyst.

| Entry | [5] [Pd] | [LiHMDS] | [PhSH] | Solvent | V | T | Ph2S (GC) |
|-------|-----------|---------|--------|---------|---|---|-----------|
| 1     | 16.7 mM   | 0.25 mM | 25 mM  | 2.5 mM  | 1 ml | 80 °C | 77.6      |
| 2     | 8.35 mM   | 0.125 mM| 12.5 mM| 1.25 mM | 2 ml | 80 °C | 68.2      |
| 3     | 16.7 mM   | 1.0 mM  | 25 mM  | 2.5 mM  | 1 ml | 80 °C | 87.8      |
| 4a    | 16.7 mM   | 0.25 mM | 25 mM  | 2.5 mM  | 1 ml | 80 °C | 63.0      |
| 5     | 16.7 mM   | 0.25 mM | 25 mM  | 2.5 mM  | 1 ml | 100 °C| 72.1      |
| 6     | 16.7 mM   | 0.25 mM | 25 mM  | 2.5 mM  | 1 ml | 80 °C | 84.7      |
| 7     | 16.7 mM   | 0.25 mM | 50 mM  | 2.5 mM  | 1 ml | 80 °C | 83.1      |
| 8     | 8.35 mM   | 0.50 mM | 12.5 mM| 1.25 mM | 2 ml | 80 °C | 62.8      |
| 9     | 33.4 mM   | 0.50 mM | 50 mM  | 5.0 mM  | 0.5 ml| 80 °C | 84.9      |
Screening of co-solvents (Figure S4)

The solvent system is one of the key factors for materials synthesis, especially under DCC conditions. The solvent system has to ensure good solubility of the monomers and also stabilize the oligomers favoring nucleation and growth. In our case we need also to make sure that the solvent system is compatible with the reaction conditions. We selected 10 promising co-solvent candidates because of their known ability to partially solubilize PPS.\textsuperscript{14} Formation of P1 was used as a model reaction to test the compatibility of the co-solvents with the reaction. For that, 10% v/v of the co-solvent was added to the o-xylene and the reaction was performed under standard conditions. Among all the additives tested, only 3 showed compatibility with the reaction (>60% yield), while the rest were detrimental (Figure S4). At the end, Ph\textsubscript{2}O was chosen as the preferred additive due to its low price and the fact that the reaction rate was not affected by it even when employing 80% volume.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig_s4}
\caption{Additives used as co-solvents for the reaction in 10% v/v. Percentages indicate yield.}
\end{figure}
**Synthesis of P1-P5 (Table S7) and elemental analysis (Table S8)**

General procedure. In the glovebox, LiHMDS and the monomer were added to an oven-dried Schlenk tube. Anhydrous o-xylene and Ph₂O (1:1) were added. After the solids were dissolved, thiophenol and Pd-Singacycle A1 were added to the solution. The Schlenk tube was sealed, taken out of the glovebox and placed in a preheated oil bath (80-100 °C) for 20 hours without stirring. After this time the solution was cooled down and the solids were separated from the solution by centrifugation. Then, the polymers were washed with several solvents (2 x toluene, 2 x N,N-dimethylformamide, 2 x water, 2 x ethanol, 2 x dichloromethane and 2 x hexane), using 100-400 ml of solvent for every 1 gram of material, and were separated by centrifugation. Finally, the solid was dried at 50 °C under a N₂ flow for 16 hours to obtain the materials as powders. Table S7 shows the specific reaction conditions for each framework.

**Table S7.** Reaction conditions for the synthesis of frameworks P1-P5. All reactions were carried out for 20 hours.

| Framework | [monomer]  | [Pd]    | [LiHMDS] | [PhSH] | V  | T     | Yield | Ph₂S (GC) |
|-----------|-----------|---------|----------|--------|----|-------|-------|-----------|
| P1        | 5.0 mM    | 0.1 mM  | 30 mM    | 0.5 mM | 200 ml | 80 °C | 88% | 91%       |
| P2        | 12.5 mM   | 1.0 mM  | 25 mM    | 2.5 mM | 100 ml | 80 °C | 95% | 92%       |
| P3        | 6.25 mM   | 0.5 mM  | 25 mM    | 1.25 mM | 80 ml | 90 °C | 82% | 78%       |
| P4        | 12.5 mM   | 1.0 mM  | 50 mM    | 2.5 mM | 100 ml | 80 °C | 88% | 79%       |
| P5        | 12.5 mM   | 1.0 mM  | 50 mM    | 2.5 mM | 100 ml | 80 °C | 86% | 82%       |

**Table S8.** Elemental analysis values for the frameworks P1-P5.

| Polymer | Calculated | Measured | Deviation (%) |
|---------|------------|----------|---------------|
|         | C% | H% | N% | S% | C% | H% | N% | S% | C% | H% | N% | S% |
| P1      | 82.0 | 4.3 | 0.0 | 13.7 | 80.4 | 4.5 | 0.6 | 12.3 | -1.6 | 0.2 | - | -1.4 |
| P2      | 79.6 | 4.1 | 0.0 | 16.3 | 78.3 | 4.8 | 1.3 | 14.2 | -1.3 | 0.7 | - | -2.1 |
| P3      | 84.8 | 3.9 | 0.0 | 11.3 | 81.8 | 4.1 | 1.0 | 10.8 | -3.0 | 0.2 | - | -0.5 |
| P4      | 78.9 | 4.2 | 0.0 | 16.9 | 77.5 | 4.4 | 0.7 | 15.2 | -1.4 | 0.2 | - | -1.7 |
| P5      | 72.7 | 4.1 | 0.0 | 16.2 | 70.8 | 4.3 | 1.3 | 14.6 | -1.9 | 0.2 | - | -1.6 |
Synthesis of Pd$^{2+}$@P1-P5 (1 wt%)

General procedure. 100 mg of the as-synthesized polymers were added into a 100 ml round bottom flask containing a stirring bar. 20 ml of NMP and 4 ml of 1,3-diaminopropane were added and the dispersion was stirred at 50 °C for one hour. This process was repeated once more. Then, the solid was separated by centrifugation and washed 3 times with 60 ml of deionized water. Then, the solid was put into a 50 ml round bottom flask equipped with a stirring bar. 10 ml of deionized water were added and the dispersion was sonicated for 1 hour, after which time 0.95 ml of a solution containing 0.01 M of PdCl$_2$ and 0.04 M of NaCl were added dropwise while stirring. The mixture was sonicated for 1 hour and allowed to stir overnight. Then, the solid was separated by centrifugation and washed with 60 ml of deionized water (x 3). Finally, the solid was dried at 50 °C under a N$_2$ stream.

Table S9. ICP-OES analysis for the frameworks P1-P5.

| Entry | Sample                  | Pd% | Au% |
|-------|-------------------------|-----|-----|
| 1     | P1 as synthesized       | 0.30| -   |
| 2     | P2 as synthesized       | 1.06| -   |
| 3     | P3 as synthesized       | 1.06| -   |
| 4     | P4 as synthesized       | 0.54| -   |
| 5     | P5 as synthesized       | 1.65| -   |
| 6     | P1 washed               | 0.27| -   |
| 7     | P2 washed               | 0.51| -   |
| 8     | P3 washed               | 0.66| -   |
| 9     | P4 washed               | 0.38| -   |
| 10    | P5 washed               | 0.60| -   |
| 11    | Pd$^{2+}$@P1 1 wt%      | 1.00| -   |
| 12    | Pd$^{2+}$@P4 1 wt%      | 0.60| -   |
| 13    | Pd$^{2+}$@P5 1 wt%      | 1.11| -   |
| 14    | Pd@P1 after suzuki      | 0.78| -   |
| 15    | P1 sat. PdCl$_2$ 500 ppm| 7.21| -   |
| 16    | P2 sat. PdCl$_2$ 500 ppm| 9.35| -   |
| 17    | P1 sat. AuCl$_3$ 500 ppm| -   |12.10|
| 18    | P2 sat. AuCl$_3$ 500 ppm| -   |17.30|
Synthesis of P1'

Was carried out following a reported procedure for synthesis of PPS (Patent number JP2008144002A): 1,3,5-Tris(4-bromophenyl)benzene (0.5 mmol, 280 mg), Na₂S (0.75 mmol, 59.6 mg) and NMP (2 ml) were added into an oven-dried 8 ml scintillation vial equipped with a magnetic stirring bar under N₂. The mixture was stirred and taken during 2 hours from room temperature to 220 °C where stayed for 2 hours. Then it was further heated to 250 °C during 30 minutes where stayed for 3 hours, after which it was allowed to slowly cool down to room temperature. The solid was separated from the solution by centrifugation. Then, it was washed with several solvents (2 x toluene, 2 x N,N-dimethylformamide, 2 x water, 2 x ethanol, 2 x dichloromethane and 2 x hexane), using 30 ml of solvent each time, and was separated by centrifugation. Finally, the solid was dried at 50 °C under a N₂ flow for 16 hours to obtain the material P1' as a powder in 35% yield.

Synthesis of P1 with different amounts of pendant thiolate groups

Same procedure as for P1 synthesis was used changing the amount of PhSH (0.5, 1.25 and 2.5 mM, respectively).

Stability of P1 in different solutions (Figure 2d)

5 mg of P1 was added to a 4 ml scintillation vial equipped with a magnetic stirring bar. 1 ml of the solutions (deionized water, HCl 12 M, H₂SO₄ 18 M, NaOH 10 M, NMP, MeONa 5.4 M in methanol, LiAlH₄ 2.4 M in THF and H₂O₂ 35%) were added to the vial and was stirred for 24 hours at the required temperature (100 °C for water, 200 °C for NMP and r.t. for the rest). After this time the solids were washed with deionized water (x 2) and ethanol (x 2). Then they were dried and the FT-IR spectra was measured using the ATR detector. Additionally, the surface area of some samples was measured (H₂SO₄ 18 M and H₂O₂ 35%) starting from 20 mg of P1.
5. Applications of the frameworks

5.1. Metal capture

Metal capture experiments (Figures 3a, S5 and S6 and Table S10)

Pd$^{2+}$: 5 mg of the polymer was added into an 8 ml scintillation vial containing a stirring bar. 1 ml of NMP and 0.1 ml of 1,3-diaminopropane were added and the dispersion was stirred at 50 °C for one hour. This process was repeated once more. Then, the solid was separated by centrifugation and washed 3 times with 6 ml of deionized water. 6 ml of an aqueous solution containing 100 ppm of PdCl$_2$ was added and the mixture was stirred for 1 hour at room temperature. After that time, an aliquot of the solution was taken, filtered and analysed by UV-vis to calculate the amount of PdCl$_2$ left. Figure S5 show the calibration curves for Pd$^{2+}$.

![Graph showing calibration curves for Pd$^{2+}$](image)

\[
A_{446} = (1.546 \pm 0.005) \times 10^{-3} [\text{Pd}^{2+}]; R^2 = 0.9999 \\
A_{279} = (60.9 \pm 0.5) \times 10^{-3} [\text{Pd}^{2+}]; R^2 = 0.9998 \\
A_{222} = (182 \pm 3) \times 10^{-3} [\text{Pd}^{2+}]; R^2 = 0.9997
\]

Figure S5. Calibration for UV-vis absorbance of Pd$^{2+}$ using absorption maxima at $\lambda = 446, 279$ and 222 nm.

Au$^{3+}$: 5 mg of the polymer was added into an 8 ml scintillation vial containing a stirring bar. 1 ml of NMP and 0.1 ml of 1,3-diaminopropane were added and the dispersion was stirred at 50 °C for one hour. This process was repeated once more. Then, the solid was separated by centrifugation and washed 3 times with 6 ml of deionised water. 5 ml of an aqueous solution containing 500 ppm of AuCl$_3$ was added and the mixture was stirred for 1 hour at room temperature. After that time, an aliquot of the solution was taken, filtered and 0.020 ml were mixed with 0.88 ml of deionised water. Then, 0.100 ml of a solution promazine hydrochloride ($10^{-3}$ M) was added and after 3 minutes, the mixture was analysed by UV-vis to calculate the amount of AuCl$_3$ left. Figure S6 show the calibration curve for Au$^{3+}$.
**Figure S6.** Calibration for UV-vis absorbance of Au$^{3+}$ using the absorption maxima at 513 nm.

\[
A_{513} = (1.18 \pm 0.01) \times 10^{-3} \text{[Au}^{3+}\text{]; } R^2 = 0.9995
\]

**Table S10.** Metal sorption capacity of the different frameworks. *n.m.* stands for not measured.

| Framework | Pd$^{2+}$ (PdCl$_2$ 100 ppm) | Pd$^{2+}$ (PdCl$_2$ 500 ppm) | Au$^{3+}$ (AuCl$_3$ 500 ppm) |
|-----------|-----------------------------|-----------------------------|-------------------------------|
| P1        | 69 mg·g$^{-1}$              | 94 mg·g$^{-1}$              | 147 mg·g$^{-1}$               |
| P1'       | 13 mg·g$^{-1}$              | n.m.                       | 53 mg·g$^{-1}$               |
| PPS       | < 1 mg·g$^{-1}$             | n.m.                       | < 5 mg·g$^{-1}$              |
| P2        | 69 mg·g$^{-1}$              | 115 mg·g$^{-1}$            | 192 mg·g$^{-1}$              |
| P3        | 66 mg·g$^{-1}$              | n.m.                       | 295 mg·g$^{-1}$              |
| P4        | 57 mg·g$^{-1}$              | n.m.                       | 182 mg·g$^{-1}$              |
| P5        | 63 mg·g$^{-1}$              | n.m.                       | 157 mg·g$^{-1}$              |
Metal capture recycling experiments (Figure S7)

Pd$^{2+}$: 10 mg of the polymer P1 was added into a 15 ml scintillation vial containing a stirring bar. 2 ml of NMP and 0.2 ml of 1,3-diaminopropane were added and the dispersion was stirred at 50 °C for one hour. Then, the solid was separated by centrifugation and washed 3 times with 10 ml of deionised water. 10 ml of an aqueous solution containing 100 ppm of PdCl$_2$ was added and the mixture was stirred for 1 hour at room temperature. After that time, the solid was separated by centrifugation, washed 3 times with 10 ml deionised water and the process was repeated. The solution was filtered and analysed by UV-vis to calculate the amount of PdCl$_2$ left.

Au$^{3+}$: 10 mg of the polymer P1 was added into a 15 ml scintillation vial containing a stirring bar. 2 ml of NMP and 0.2 ml of 1,3-diaminopropane were added and the dispersion was stirred at 50 °C for one hour. Then, the solid was separated by centrifugation and washed 3 times with 10 ml of deionised water. 10 ml of an aqueous solution containing 500 ppm of AuCl$_3$ was added and the mixture was stirred for 1 hour at room temperature. After that time, the solid was separated by centrifugation, washed 3 times with 10 ml deionised water and the process was repeated. The solution was filtered and analysed by UV-vis to calculate the amount of AuCl$_3$ left.

Figure S7. Reuses of P1 for metal capture.
5.2. Metal sensing

**Sensing of Pd^{2+} by fluorescence quenching (Figure 3d)**

A dispersion of P2 (2 ppm) in water (with 1% v/v NMP to stabilize the particles) was prepared and different amounts of PdCl\(_2\) (0, 2, 4, 8, 10, 15, 20, 30, 50, 75 and 100 ppb) were added. Each solution was prepared as duplicates to calculate the standard deviation. Fluorescence intensity was recorded exciting at \(\lambda_{ex} = 370\) nm and the intensity was measured at the maximum emission \(\lambda_{em} = 540\) nm.

**Sensing of different metal cations by fluorescence quenching (Figures 3e, S8-S13)**

A dispersion of the polymers P2 and P3 (10 ppm) in water (with 1% v/v NMP to stabilize the particles) was prepared and different metals (PdCl\(_2\), K\(_2\)PtCl\(_6\), NiCl\(_2\), AuCl\(_3\), AgCl, CuCl\(_2\) and HgCl\(_2\)) were added (0.1, 1.0 and 10 ppm). Each solution was prepared as duplicates to calculate the standard deviation. Fluorescence intensity was recorded exciting at \(\lambda_{ex} = 370\) and 400 nm for P2 and P3 respectively, and the intensity was measured at the maximum emission \(\lambda_{em} = 550\) and 525 nm for P2 and P3, respectively. Relative intensity was calculated by dividing the intensity with the metal by the intensity without metal. Figures S8-S13 show the spectra for each combination of polymer and metal.

**Figure S8.** Fluorescence emission spectra of P2 (10 ppm) in contact with different metals (0.1 ppm). \(\lambda_{ex} = 370\) nm.
**Figure S9.** Fluorescence emission spectra of P2 (10 ppm) in contact with different metals (1.0 ppm). $\lambda_{\text{ex}} = 370$ nm.

**Figure S10.** Fluorescence emission spectra of P2 (10 ppm) in contact with different metals (10 ppm). $\lambda_{\text{ex}} = 370$ nm.
Figure S1. Fluorescence emission spectra of P3 (10 ppm) in contact with different metals (0.1 ppm). $\lambda_{ex} = 400$ nm.

Figure S12. Fluorescence emission spectra of P3 (10 ppm) in contact with different metals (1.0 ppm). $\lambda_{ex} = 400$ nm.
Figure S13. Fluorescence emission spectra of P3 (10 ppm) in contact with different metals (10 ppm). $\lambda_{ex} = 400$ nm.
5.3. Heterogeneous catalysis

Procedure for the Suzuki coupling (Figure 4a)

- without added ligand (GP1):
  An oven dried 4 mL vial equipped with a Teflon coated magnetic stir bar was charged with 1-iodo-4-methylbenzene (10.9 mg, 0.05 mmol, 1.0 eq.), anhydrous K$_2$CO$_3$ (20.7 mg, 0.15 mmol, 3.0 eq.) and phenylboronic acid (9.14 mg, 0.075 mmol, 1.5 eq.). Thereafter the vial was introduced to an Ar filled glovebox and the corresponding polymeric Pd-catalyst Pd$^{2+}@$P1 (1 wt% Pd, 2.5 mg, 0.5 mol%) was added followed by PhMe (0.5 mL). The vial was sealed with a rubber septum cap and taken out of the glovebox. Water (0.1 mL) was added via the septum and the reaction mixture was stirred at 100 °C for 18 h. After that, the reaction was cooled down and n-dodecane (11.4 μL, 0.05 mmol) was added as an internal standard. An aliquot was taken, filtered through a short plug of silica and analysed via GC-FID.

- with PPh$_3$ as a ligand (GP2):
  An oven dried 4 mL vial equipped with a Teflon coated magnetic stir bar was charged with 1-iodo-4-methylbenzene (10.9 mg, 0.05 mmol, 1.0 eq.), anhydrous K$_2$CO$_3$ (20.7 mg, 0.15 mmol, 3.0 eq.) and phenylboronic acid (9.14 mg, 0.075 mmol, 1.5 eq.). Thereafter the vial was introduced to an Ar filled glovebox and the corresponding polymeric Pd-catalyst Pd$^{2+}@$P1 (1 wt% Pd, 2.5 mg, 0.5 mol%) was added followed by a stock solution of PPh$_3$ in PhMe (0.5 mL; 1 μM). The vial was sealed with a rubber septum cap and taken out of the glovebox. Water (0.1 mL) was added via the septum and the reaction mixture was stirred at 100 °C for 18 h. After that, the reaction was cooled down and n-dodecane (11.4 μL, 0.05 mmol) was added as an internal standard. An aliquot was taken, filtered through a short plug of silica and analysed via GC-FID.

Results for the Suzuki-Miyaura type coupling using polymeric Pd-catalysts Pd$^{2+}@$P1:

| Pd-catalyst | Procedure | GC-Yield / % |
|-------------|-----------|--------------|
| Pd$^{2+}@$P1 | GP1       | 99           |
| Pd$^{2+}@$P1 | GP2       | quant.       |
| PdCl$_2$     | GP1       | 28           |
| PdCl$_2$     | GP2       | quant.       |

Procedure for the hot filtration experiment for Suzuki coupling (Figure S14)

In an N$_2$ filled glovebox, an oven dried 4 mL vial equipped with a Teflon coated magnetic stir bar was charged with 1-iodo-4-methylbenzene (21.8 mg, 0.10 mmol, 1.0 eq.), anhydrous K$_2$CO$_3$ (41.4 mg, 0.30 mmol, 3.0 eq.), phenylboronic acid (18.3 mg, 0.15 mmol, 1.5 eq.), n-dodecane (IS, 22.8 μL, 0.10 mmol) and the corresponding polymeric Pd-catalyst Pd$^{2+}@$P1 (1 wt% Pd, 5.0 mg, 0.5 mol%) followed by PhMe (1.0 mL) and water (0.2 mL). The reaction mixture was stirred at 100 °C and aliquots were taken at 0’ – 15’ – 30’ – 60’ – 120’ – 180’ – 240’ – 360’ – 480’. After 30 minutes of reaction time, 0.5 mL of the solution were taken with a syringe and filtered through a PTFE filter (0.2 microns) to remove the solid from the solution. This solution was directly put in an oven dried 4 mL vial equipped with a Teflon
coated magnetic stir bar and anhydrous K$_2$CO$_3$ (20.7 mg, 0.15 mmol, 1.5 eq.) preheated at 100 °C. Aliquots from this solution were taken at the same times as for the original reaction (60’, 120’, 180’, 240’, 360’ and 480’). Aliquots were analysed by GC-FID.

Figure S14. Hot filtration test for Suzuki coupling.

Procedure for the Heck reaction

- **without added ligand (GP3):**

  In an Ar filled glovebox, an oven dried 2 mL vial equipped with a Teflon coated magnetic stir bar was charged with the corresponding polymeric Pd-catalyst Pd$^{2+}$@P1 (1 wt% Pd, 2.5 mg, 0.5 mol%) followed by the addition of PhMe (0.5 mL). Thereafter iodobenzene (5.6 μL, 0.05 mmol, 1.0 eq.), ethyl acrylate (32 μL, 0.30 mmol, 6 eq.) and DIPEA (26 μL, 0.15 mmol, 3.0 eq.) were added sequentially. The vial was sealed with a cap, taken out of the glovebox and the reaction mixture was stirred at 100 °C for 18 h. After that, the reaction was cooled down and n-dodecane (11.4 μL, 0.05 mmol) was added as an internal standard. An aliquot was taken, filtered through a short plug of silica and analysed via GC-FID.

- **with PPh$_3$ as a ligand (GP4):**

  In an Ar filled glovebox, an oven dried 2 mL vial equipped with a Teflon coated magnetic stir bar was charged with the corresponding polymeric Pd-catalyst Pd$^{2+}$@P1 (1 wt% Pd, 2.5 mg, 0.5 mol%) added followed by the addition of a stock solution of PPh$_3$ in PhMe (0.5 mL; 4 μM). Thereafter iodobenzene (5.6 μL, 0.05 mmol, 1.0 eq.), ethyl acrylate (32 μL, 0.30 mmol, 6 eq.) and DIPEA (26 μL, 0.15 mmol, 3.0 eq.) were added sequentially. The vial was sealed with a cap, taken out of the glovebox and the reaction mixture was stirred at 100 °C for 18 h. After that, the reaction was cooled down and n-dodecane (11.4 μL, 0.05 mmol) was added as an internal standard. An aliquot was taken, filtered through a short plug of silica and analysed via GC-FID.
Results for the Heck type reaction using polymeric Pd-catalysts catalysts Pd^{2+}@P1:

| Pd-catalyst | Procedure | GC-Yield / % |
|-------------|-----------|--------------|
| Pd^{2+}@P1  | GP3       | 22           |
| Pd^{2+}@P1  | GP4       | quant.       |

Procedure for the hot filtration experiment for Heck reaction (Figure S15)

In a N₂ filled glovebox, an oven dried 2 mL vial equipped with a Teflon coated magnetic stir bar was charged with the corresponding polymeric Pd-catalyst Pd^{2+}@P1 (1 wt% Pd, 5.0 mg, 0.5 mol%) added followed by the addition of a stock solution of PPh₃ in PhMe (1.0 mL; 4 μM). Thereafter iodobenzene (11.2 μL, 0.10 mmol, 1.0 eq.), ethyl acrylate (64 μL, 0.60 mmol, 6 eq.), DIPEA (52 μL, 0.30 mmol, 3.0 eq.) and n-dodecane (15, 22.8 μL, 0.10 mmol) were added sequentially. The vial was sealed with a cap, the reaction mixture was stirred at 100 °C and aliquots were taken at 1h – 2h – 3h – 4h – 6h – 8h. After 3 hours of reaction time, 0.5 ml of the solution were taken with a syringe and filtered through a PTFE filter (0.2 microns) to remove the solid from the solution. This solution was directly put in an oven dried 2 mL vial equipped with a Teflon coated magnetic stir bar preheated at 100 °C. Aliquots from this solution were taken at the same times as for the original reaction (4h, 6h and 8h). Aliquots were analysed by GC-FID.

![Hot filtration test for the Heck reaction](image)

**Figure S15.** Hot filtration test for the Heck reaction. The results indicate leaching of Pd to the solution favored by the addition of ligand (PPh₃).

Procedure for the semi-hydrogenation of phenylacetylene (Figure 4a)

An oven dried 4 mL vial equipped with a Teflon coated magnetic stir bar was charged with Pd^{2+}@P1 catalyst (1 wt% Pd, 2.1 mg, 0.1 mol%), phenylacetylene (23 μL, 0.2 mmol), n-dodecane (20 μL, internal standard) and toluene (1.0 ml). The vial was sealed and purged by bubbling with N₂ followed by H₂ for 10 seconds each. Then, a balloon full with H₂ was attached to the vial and the vial was placed in a heating plate at 60 °C for 2.5 hours under stirring (700 rpm). After this time, the solution was cooled down to room temperature and an aliquot was taken and analysed via GC-FID.
Procedure for the alkene/alkyne competition experiments (Figure 4a)

An oven dried 4 mL vial equipped with a Teflon coated magnetic stir bar was charged with Pd^{2+}@P1 catalyst (1 wt% Pd, 2.1 mg, 0.1 mol%), alkyne (0.2 mmol), alkane (0.2 mmol), n-dodecane (20 μL, internal standard) and toluene (1.0 ml). The vial was sealed and purged by bubbling with N\textsubscript{2} followed by H\textsubscript{2} for 30 seconds each. Then, a balloon full with H\textsubscript{2} was attached to the vial and the vial was placed in a heating plate at 60 °C for 2.5 hours under stirring (700 rpm). After this time, the solution was cooled down to room temperature and an aliquot was taken and analysed via GC-FID.

Procedure for the catalyst reusability in semi-hydrogenation of phenylacetylene (Figure 4b)

An oven dried 4 mL vial equipped with a Teflon coated magnetic stir bar was charged with Pd^{2+}@P1 catalyst (1 wt% Pd, 4.2 mg, 0.1 mol%), phenylacetylene (46 μL, 0.4 mmol), n-dodecane (40 μL, internal standard) and toluene (2.0 ml). The vial was sealed and purged by bubbling with N\textsubscript{2} followed by H\textsubscript{2} for 10 seconds each. Then, a balloon full with H\textsubscript{2} was attached to the vial and the vial was placed in a heating plate at 60 °C for 2.5 hours under stirring (700 rpm). After this time, the solution was cooled down to room temperature and an aliquot was taken and analysed via GC-FID. The solid was washed with toluene (2 x 10 ml), separated by centrifugation and placed in a vial for a subsequent reaction without any further treatment.

Procedure for the hot filtration experiment for semi-hydrogenation of phenylacetylene (Figure S16)

An oven dried 4 mL vial equipped with a Teflon coated magnetic stir bar was charged with Pd^{2+}@P1 catalyst (1 wt% Pd, 4.2 mg, 0.1 mol%), phenylacetylene (46 μL, 0.4 mmol), n-dodecane (40 μL, internal standard) and toluene (2.0 ml). The vial was sealed and purged by bubbling with N\textsubscript{2} followed by H\textsubscript{2} for 10 seconds each. Then, a balloon full with H\textsubscript{2} was attached to the vial and the vial was placed in a heating plate at 60 °C under stirring (700 rpm). Aliquots were taken at 0', 20', 40', 60', 90' and 150'. After 40', 1 ml of the solution was taken with a syringe and filtered through a PTFE filter (0.2 microns) to remove the solid from the solution. This solution was directly put in an oven dried 4 mL vial equipped with a teflon coated magnetic stir bar preheated at 60 °C and attached to a H\textsubscript{2} balloon. Aliquots from this solution were taken at the same times as for the original reaction (60', 90' and 150'). Aliquots were analysed by GC-FID. Remaining catalytic activity can be explained by some of the polymer particles (50 nm particle size) going through the filter (200 nm).
Figure S16. Hot filtration test for semi-hydrogenation of phenylacetylene. Top) Phenylacetylene conversion. Bottom) Styrene production.

In-situ EXAFS study of Pd$^{2+}@P1$ and Pd$^{2+}@P4$ under H$_2$ and temperature (Figure 4e)

A 3 mm quartz capillary tube was charged with 30 mg of Pd$^{2+}@P1$ or Pd$^{2+}@P4$ (1 wt% Pd) with a particle size of 0.1-0.3 mm between two pieces of glass wool. The tube was connected to a H$_2$ in He (5% v/v) bottle and the gas with 5 bars of pressure was passed through the sample at 50 ml/min. The capillary was heated from room temperature to 300 °C with a rate of 2 °C/min and stayed at this temperature for 1 hour before cooling down to room temperature. EXAFS spectra were constantly recorded during all the experiment.
5.4. Recyclability

**Optimization of recyclability of P1 (Table S11)**

In a glovebox, P1 (11.8 mg, 0.1 mmol of ArSAr groups) and LiHMDS (138 mg, 0.8 mmol) were added to an oven-dried scintillation vial equipped with a magnetic stirring bar. A one-to-one mixture of o-xylene and Ph$_2$O was added to the vial. When the LiHMDS was dissolved, cyclohexanethiol (52 μl, 0.4 mmol) and Pd Singacycle-A1 (2.7 mg, 0.004 mmol) were added to the solution, the vial was sealed, taken out of the glovebox and placed in a preheated aluminium block at 140 or 160 °C where it was left for 24h under vigorous stirring. After cooling down, 5 ml of aqueous NaOH (1 M) was added the reaction mixture which was extracted with DCM (3 x 5 ml). The combined organic phase was washed with 15 ml of NaOH (1 M, x 3), dried with Na$_2$SO$_4$, the solvent was evaporated and the product was purified by column chromatography (hexane:DCM, 7:3). The yield was calculated by $^1$H NMR using trimethoxybenzene as internal standard.

**Table S11.** Recyclability of the framework P1.

| Entry | R-SH   | Solvent             | T (°C) | [Pd] | Stirring (rpm) | Yield |
|-------|--------|---------------------|--------|------|----------------|-------|
| 1     | Cy-SH  | o-xyl               | 160    | 2 mol% | 600            | 50%   |
| 2     | Cy-SH  | o-xyl:Ph$_2$O (1:1)| 160    | 2 mol% | 600            | 56%   |
| 3     | Cy-SH  | o-xyl:Ph$_2$O (1:1)| 140    | 2 mol% | 600            | 60%   |
| 4     | Ph-SH  | o-xyl:Ph$_2$O (1:1)| 160    | 2 mol% | 600            | < 5%  |
| 5     | Cy-SH  | o-xyl:Ph$_2$O (1:1)| 140    | 2 mol% | 1400           | 73%   |
| 6     | Cy-SH  | o-xyl:Ph$_2$O (1:1)| 140    | -     | 1400           | 55%   |
| 7     | Ph$_2$S (20 eq.) | o-xyl:Ph$_2$O (1:1)| 120    | 2 mol% | 800            | 11%   |
Two-step recyclability of P1, P2 and P4 to the original monomers (Figure 5)

In a glovebox, P1, P2 or P4 (0.25 mmol of ArSAr groups: 29.5, 24.5 and 25.0 mg, respectively) and LiHMDS (345 mg, 2.0 mmol) were added to an oven-dried scintillation vial equipped with a magnetic stirring bar. Then, 5 ml of o-xylene was added to the vial followed by cyclohexanethiol (130 µl, 1.0 mmol) and Pd Singacycle-A1 (7.0 mg, 0.01 mmol) were added to the solution, the vial was sealed, taken out of the glovebox and placed in a preheated aluminium block at 140 °C where was left for 24h under vigorous stirring (1000 rpm). After cooling down to r.t., 5 ml of aqueous NaOH (1 M) was added the reaction mixture which was extracted with DCM (3 x 5 ml). The combined organic phase was washed with 15 ml of NaOH (1 M, x 3), dried with Na₂SO₄, the solvent was evaporated and the product was purified by column chromatography (hexane:DCM, 95:5 to 60:40) to obtain the pure products 1-Cy, 2-Cy and 4-Cy, respectively.

S-Arylation: In a 20 ml scintillation vial equipped with a magnetic stirring bar 1-Cy, 2-Cy or 4-Cy (0.25 mmol ArSCy: 56.0, 50.9 and 50.1 mg, respectively), [Ph₂I][PF₆] (163 mg, 1.5 eq.) and Cul (5.0 mg, 5 mol%) were added. Then, 5 ml of PhCl was added, the vial was sealed with a cap with septum and the solution was bubbled with N₂ for 5 minutes and then placed in a preheated in an aluminium block at 125 °C under stirring where was left for 18 h to react. Nucleophilic substitution: Then, the reaction mixture was left to cool down at r.t., the vial was opened and K₃PO₄ (110 mg, 0.5 mmol, 2 eq.), PhSH (45 µl, 1.5 eq) and 5 ml DMF were added. The vial was closed again and placed in a preheated in an aluminium block at 125 °C under stirring where was left for 18 h to react. After this time, the reaction mixture was left to cool down at r.t., and then it was poured over 20 ml NaOH (1 M) and extracted with DCM (3 x 20 ml). The combined organic fractions were washed with NaOH (1 M), brine and LiCl (5%), then washed over Na₂SO₄, the solvent was evaporated and the crude was purified by column chromatography (hexane:DCM, 95:5 to 60:40) to obtain the original monomers. 1-Ph, 2-Ph or 4-Ph, respectively.
6. Characterization of the frameworks

6.1. FT-IR spectra

FT-IR was used to characterize the monomers and the polymers. In particular, we used it as a powerful tool to study semi-quantitatively the extent of the polymerization. We could tentatively assign the most representative bands of the spectra of the monomer 1 (Figure S17) $\nu_a = 690 \text{ cm}^{-1}$, $\nu_b = 740 \text{ cm}^{-1}$ and $\nu_c = 810 \text{ cm}^{-1}$ with help of preliminary DFT calculations. In fact, $\nu_a$ and $\nu_b$ are associated with out-of-plane C–H vibrations (symmetric and asymmetric, respectively) corresponding mainly to the pendant –SPh groups, whereas $\nu_c$ is associated with the out-of-plane C–H vibrations of the aromatic 1,3,5-triphenylbenzene core. That explains why after the polymerization $\nu_a$ and $\nu_b$ decrease their intensity and $\nu_c$ remains as the most intense vibration. This observation is further confirmed by the absence of $\nu_a$ and $\nu_b$ vibrations for the analogous 1-Cy, sharing the same core as the monomer 1 but with pendant –SCy instead of –SPh. In general, we can conclude that the disappearance of the $\nu_a$ and $\nu_b$ bands is a general feature common to all the polymers shown in the paper.

Figure S17. FT-IR spectra of the monomer 1-Ph and polymer P1 after different treatments.
Figure S18. FT-IR spectra of the monomer 2-Ph and polymer P2 after different treatments.

Figure S19. FT-IR spectra of the monomer 3-Ph and polymer P3 after different treatments.
Figure S20. FT-IR spectra of the monomer 4-Ph and polymer P4 after different treatments.

Figure S21. FT-IR spectra of the monomer 5-Ph and polymer P5 after different treatments.
Figure S22. FT-IR spectra of the monomer 1-Ph and polymers P1 and P1′.
Figure S23. Top) FT-IR spectra of P1 after immersion in different solvents for 24 hours (Figure 2d). Bottom) FT-IR subtracted spectra of P1 after immersion in different solvents with respect P1.
6.2. UV-vis and fluorescence spectra

Figure S24. UV-vis spectra of the monomers 1Ph-4-Ph.

Figure S25. UV-vis spectra of the polymers P1-P5.
Figure S26. Fluorescence emission spectra of the monomers 1Ph-4-Ph.

Figure S27. Fluorescence emission spectra of the polymers P1-P4.
6.3. Powder XRD

Figure S28. a) Powder X-ray diffractograms (PXRD) of the polymers P1-P5. b) Time-dependent study of the crystallinity of P1.
6.4. N$_2$ physisorption

**Figure S29.** Right) N$_2$ adsorption and desorption isotherms for P1. Left) Pore distribution by BJH method.

**Figure S30.** Right) N$_2$ adsorption and desorption isotherms for P1 in pure o-xylene as solvent. Left) Pore distribution by BJH method.

**Figure S31.** Right) N$_2$ adsorption and desorption isotherms for P1 synthesized at 120 °C. Left) Pore distribution by BJH method.
**Figure S32.** Right) N$_2$ adsorption and desorption isotherms for P1 after 24 hours contact with H$_2$SO$_4$ (18 M). Left) Pore distribution by BJH method.

**Figure S33.** Right) N$_2$ adsorption and desorption isotherms for P1 after 24 hours contact with H$_2$O$_2$ (35% v/v). Left) Pore distribution by BJH method.

**Figure S34.** Right) N$_2$ adsorption and desorption isotherms for P2. Left) Pore distribution by BJH method.

**Figure S35.** Right) N$_2$ adsorption and desorption isotherms for P3. Left) Pore distribution by BJH method.
Figure S36. Right) N₂ adsorption and desorption isotherms for P4. Left) Pore distribution by BJH method.

Figure S37. Right) N₂ adsorption and desorption isotherms for P5. Left) Pore distribution by BJH method.

Table S12. Surface area (S_{BET}), pore volume (V_p) and pore size at the peak for the different polymers synthesized in the manuscript.

| Sample | Deviation from std. cond. | S_{BET} (m²g⁻¹) | V_p (cm³g⁻¹) | Pore size (nm) |
|--------|---------------------------|-----------------|--------------|----------------|
| P1     | none                      | 192             | 0.719        | 1.3            |
| P1     | o-xyl as solvent          | 29              | 0.139        | 1.5            |
| P1     | 120 °C                    | 36              | 0.145        | 1.4            |
| P1     | H₂SO₄ (18 M) 24 h          | 101             | 0.467        | 1.1            |
| P1     | H₂O₂ (30% v/v) 24 h       | 159             | 0.609        | 1.1            |
| P1'    | none                      | <5              | -            | -              |
| P2     | none                      | 18              | 0.0273       | 1.8            |
| P3     | none                      | 410             | 0.719        | 1.0            |
| P4     | none                      | 526             | 0.744        | 1.2            |
| P5     | none                      | 421             | 0.518        | 1.0            |
6.5 Thermogravimetric analysis (TGA)

**Figure S38.** Thermogravimetric analysis of all the polymers synthesized in the work and commercial PPS under a) N₂ atmosphere and b) air.
6.6. SEM images

Figure S39. FESEM images of P1.
Figure S40. FESEM images of P2.
Figure S41. FESEM images of P3.
Figure S42. FESEM images of P4.
Figure S43. FESEM images of P5.
Figure S44. FESEM images of P1 synthesized in pure o-xylene.
Figure S45. FESEM images of P1 synthesized at 120 °C in o-xylene:Ph₂O (1:1 mixture).
Figure S46. FESEM images of P1' synthesized by polycondensation reactions.
Figure S47. FESEM images of P1 after immersion in boiling water for 24h.
**Figure S48.** FESEM images of P1 after immersion in HCl (12M) for 24h.
Figure S49. FESEM images of P1 after immersion in H₂SO₄ (18 M) for 24h.
Figure S50. FESEM images of P1 after immersion in NaOH (10 M) for 24h.
Figure S51. FESEM images of P1 after immersion in NMP at 200 °C for 24h.
Figure S52. FESEM images of P1 after immersion in MeONa (5.4 M in MeOH) for 24h.
Figure S53. FESEM images of P1 after immersion in LiAlH$_4$ (2.4 M in THF) for 24h.
Figure S54. FESEM images of P1 after immersion in H₂O₂ (35% in water) for 24h.
Figure S55. HR-TEM images of Pd\textsuperscript{2+}@P1 (1 wt%).
Figure S56. HAADF images of Pd^{2+}@P1 (1 wt%).

Figure S57. HR-TEM images of Pd^{2+}@P1 (1 wt%) after Suzuki reaction.
Figure S58. HAADF images of Pd^{2+}@[P1] (1 wt%) after Suzuki reaction.
Figure S59. HR-TEM images of Pd^{2+}@P1 (1 wt%) after phenylacetylene semi-hydrogenation reaction.
Figure S60. HAADF images of Pd\textsuperscript{2+}@P1 (1 wt\%) after phenylacetylene semi-hydrogenation reaction.
Figure S61. HR-TEM images of Pd$^{2+}@P1$ (1 wt%) after 6 cycles of phenylacetylene semi-hydrogenation reaction.
Figure S62. HAADF images of Pd\textsuperscript{2+}@P1 (1 wt%) after 6 cycles of phenylacetylene semi-hydrogenation reaction.
Figure S63. HR-TEM images of Pd^{2+}@P4 (1 wt%).
Figure S64. HAADF images of Pd^{2+}@P4 (1 wt%).
Figure S65. HR-TEM images of P5.
6.8. XAS spectra

**Figure S66.** Pd-K edge EXAFS experiments for as synthesized samples P1-P5. Top) Normalized spectra. Middle) $k^2$-weighted phase-uncorrected $\chi(k)$ functions. Down) $k^2$-weighted |FT| of the EXAFS function.
Figure S6. Pd-K edge EXAFS experiments for P1 under different synthesis conditions. Top) Normalized spectra. Middle) $k^2$-weighted phase-uncorrected $\chi(k)$ functions. Down) $k^2$-weighted $|FT|$ of the EXAFS function. Table shows the synthesis conditions.
Figure S68. Pd-K edge EXAFS experiments for Pd^{2+}@P1-P5 (1 wt%). Top) Normalized spectra. Middle) $k^2$-weighted phase-uncorrected $\chi(k)$ functions. Down) $k^2$-weighted $|\text{FT}|$ of the EXAFS function.
Figure S6. Pd-K edge EXAFS in-situ experiments for Pd$^{2+}$@P1 (1 wt%) heating under H$_2$ atmosphere (5 bar H$_2$ 5% in He, 3 °C/min from 20 to 400 °C). Top) Normalized spectra. Middle) XANES region. Down) $k^2$-weighted |FT| of the EXAFS function.
Figure S70. Pd-K edge EXAFS in-situ experiments for Pd$^{2+}$$\oplus$$\text{Pd}4$ (0.6 wt%) heating under $\text{H}_2$ atmosphere (5 bar $\text{H}_2$ 5% in He, 3 °C/min from 20 to 300 °C and 1 hour at 300 °C). Top) Normalized spectra. Middle) XANES region. Down) $k^2$-weighted $|\text{FT}|$ of the EXAFS function.
7. NMR spectra
*Di-p-tolylsulfane (H2).*
Di-m-tolylsulfane (H3).
Bis(4-(trifluoromethyl)phenyl)sulfane (H4).
Bis(4-methoxyphenyl)sulfane (H5).
1,3,5-Tris(4-phenylthiophenyl)benzene (1-Ph)
1,1,2,2-tetrakis(4-fluorophenyl)ethene (2-F)
1,1,2,2-tetrakis(4-phenylthio)phenyl]ethene (2-Ph)
1,3,6,8-Tetrakis(4-fluorophenyl)pyrene (3-F)
1,3,6,8-Tetrakis(4-phenylthiophenyl)pyrene (3-Ph)
Tetrakis(4-bromophenyl)silane (4-Br)
Tetrakis(4-phenylthio)phenyl)methane (4-Ph)
Tetrakis(4-bromophenyl)silane (5-Br)
Tetrakis(4-(phenylthio)phenyl)silane (5-Ph)
1,3,5-Tris(4-phenylthiocylohexyl)benzene (1-Cy)
1,1,2,2-tetrakis([4-cyclohexylthio]phenyl)ethene (2-Cy)
Tetrakis(4-cyclohexylthio)phenyl)methane (4-Cy)
8. References

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