

# Preparation of Recyclable and Versatile Porous Poly(aryl thioether)s by Reversible Pd-Catalyzed C–S/C–S Metathesis

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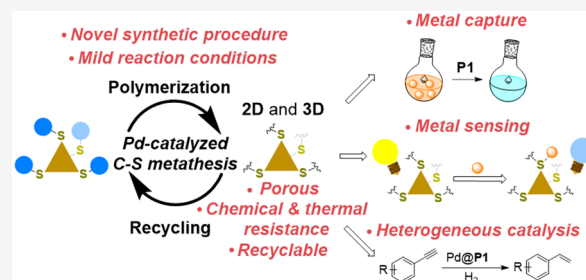
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**ABSTRACT:** Porous organic materials (polymers and COFs) have shown a number of promising properties; however, the lability of their linkages often limits their robustness and can hamper downstream industrial application. Inspired by the outstanding chemical, mechanical, and thermal resistance of the 1D polymer poly(phenylene sulfide) (PPS), we have designed a new family of porous poly(aryl thioether)s, synthesized via a mild Pd-catalyzed C–S/C–S metathesis-based method, that merges the attractive features common to porous polymers and PPS in a single material. In addition, the method is highly modular, allowing to easily introduce application-oriented functionalities in the materials for a series of environmentally relevant applications including metal capture, metal sensing, and heterogeneous catalysis. Moreover, despite their extreme chemical resistance, the polymers can be easily recycled to recover the original monomers, offering an attractive perspective for their sustainable use. In a broader context, these results clearly demonstrate the untapped potential of emerging single-bond metathesis reactions in the preparation of new, recyclable materials.



the harsh conditions required for the synthesis of PPS (Scheme 1a, polycondensation >250 °C, Na<sub>2</sub>S, autogenous pressure)<sup>4a,5</sup> and the extreme stability of the aryl thioether bonds make it difficult to fine-tune PPS's properties (e.g., *M<sub>w</sub>*, cross-linking, and polydispersity), although branched analogues of PPS have been occasionally reported following the polycondensation approach.<sup>6</sup> This dramatically limits the possibility to access more complex poly(aryl thioether)-based structures with 2D or 3D cores, despite their potential to exhibit advanced features such as porosity, metal-binding ability, or optoelectronic properties, among others. The synthesis of such advanced materials, which should be analogous to PPS in terms of chemical, thermal, and mechanical stability, would provide nearly unlimited opportunities for the design of robust functional porous polymers for key applications in academia and industry. Recently, significant efforts by the Swager group have been directed toward the synthesis of functional PPS analogues. By using disilyl thioethers as monomers, they have been able to prepare new poly(arylene sulfide)s under mild conditions that incorporate advanced functions such as photoluminescence and redox responsiveness and, moreover,

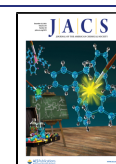
## INTRODUCTION

Porous organic materials, including amorphous polymers and covalent organic frameworks (COFs), are a privileged class of materials with high surface area, low mass density, and modular topology that have gathered a lot of attention among the chemistry and materials science communities during the past two decades.<sup>1</sup> They have shown promising applications spanning areas from gas and metal capture to optoelectronics and catalysis, among others. Dynamic covalent chemistry (DCC)<sup>2</sup> is a key feature in the synthesis of these systems; the reversibility of the reactions provides self-correcting behavior which, in turn, allows the formation of high-quality, low-defect materials. Despite their interesting properties, the lability of most of the linkages (e.g., imine, boronate ester, and boroxine) used to construct these materials under self-correcting conditions makes them unstable toward moderately harsh media (e.g., water, pH, temperature, and pressure), often hampering downstream application. For this reason, the synthesis of analogous yet more stable materials containing stronger covalent bonds in a DCC-like manner is highly attractive. Ideally, such new materials should, despite their high chemical strength, be recyclable to their monomers to allow for their circular use in accordance with sustainable chemistry goals.<sup>3</sup>

Sulfur-containing 1D-polymers like poly(phenylene sulfide) (PPS) have seen widespread use in industry as insulators and replacements for metal parts due to their extremely high chemical, thermal, and mechanical resistance, as illustrated by the large number of patents (>100000) in this area.<sup>4</sup> However,

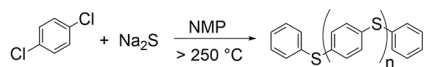
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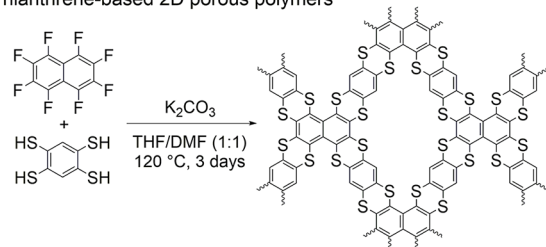


**Scheme 1. Synthesis and Structure of (a) PPS and (b) Thianthrene-Based 2D Polymers;<sup>10</sup> (c) Experiment Showing the Reversibility of the C–S/C–S Metathesis Reaction: Equilibrium Is Reached Starting from Both Sides;<sup>11</sup> (d) Approach Followed in This Work Showing Hypothetical Polymer Structures**

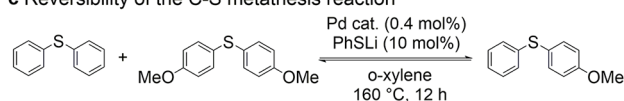
a Polyphenylene sulfide (PPS)



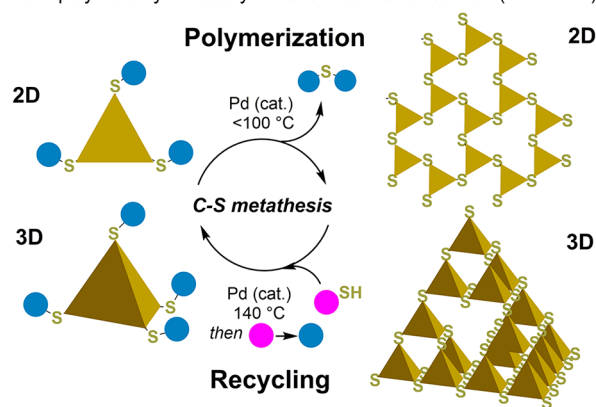
b Thianthrene-based 2D porous polymers



c Reversibility of the C–S metathesis reaction



d Porous polymers by Pd-catalyzed C–S metathesis reaction (this work)



- Novel synthetic procedure • Porosity • Control of the properties
- Mild reaction conditions • Recyclable • Chemical & thermal stability
- Promising applications: • metal capture • metal sensing • catalysis

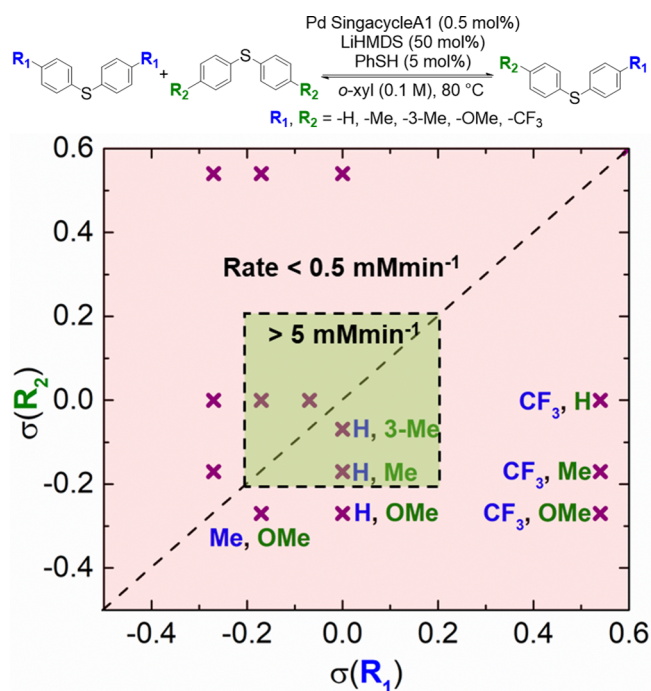
can be easily degraded.<sup>7</sup> While several sulfur-containing porous materials have been reported in the literature,<sup>8</sup> examples of porous materials containing aryl thioether linkages in the backbone are extremely scarce.<sup>9</sup> Swager and co-workers reported the synthesis of thianthrene-based 2D polymers with high surface areas and interesting redox properties by using dynamic  $S_NAr$  reactions of thiocatechols and perfluorinated aromatic compounds (Scheme 1b).<sup>10</sup> While this synthetic method provides an exciting new approach, it is limited to specific monomers (1,2,4,5-benzenetetrathiol with hexafluorobenzene or octafluoronaphthalene) that can participate in the  $S_NAr$  reaction. Moreover, potential applications of these materials have not yet been extensively explored, and their recyclability has not been demonstrated. Therefore, there is a critical need to develop new, complementary approaches to fully harness the potential of porous poly(aryl thioether)s in advanced materials and catalytic applications with a focus on recyclability.

Our group has previously developed transition-metal-catalyzed C–S/C–S single-bond metathesis reactions and

showcased their utility in small molecule synthesis.<sup>11</sup> These reactions allow the facile synthesis of a number of thioether-containing molecules from the corresponding thiols as nucleophiles and aryl–SR (R = H, Me) compounds as electrophiles by driving the equilibrium toward product formation (using an excess of nucleophile and precipitation of LiSMe or Li<sub>2</sub>S salts as a driving force). Interestingly, depolymerization of PPS was achieved in 85% yield, showing the potential of the reaction for polymer recycling. In addition, full reversibility was demonstrated at high temperatures (160 °C) by scrambling of the aryl groups, giving a statistical mixture of products in both the forward and reverse reactions (Scheme 1c). As mentioned previously, full reversibility of the reaction is highly desirable for materials synthesis to obtain high quality polymers with fine-tuned properties. Additionally, it inherently opens the door for the material's recycling after use. While transition-metal catalysis is widely applied to make conventional 1D polymers, including reversible reactions such as olefin metathesis,<sup>12</sup> their use in the synthesis of 2D and 3D porous polymers is much less developed. Some remarkable examples include the report from Dichtel and co-workers using catalytic amounts of metal triflates to make imine COFs<sup>13</sup> or the use of alkyne metathesis by Zhang and co-workers.<sup>2,14</sup> On the basis of these considerations, we decided to harness the potential of reversible Pd-catalyzed C–S/C–S metathesis to not only synthesize novel 2D and 3D porous polymers but also readily recycle them after use. Herein, we report the synthesis of a new family of aryl thioether-based porous organic polymers from simple building blocks enabled by a fully reversible version of the Pd-catalyzed C–S/C–S metathesis reaction with excellent control over the physical properties of the resulting materials (Scheme 1d). Importantly, the new polymers can be recycled to the monomers and reveal promising applications in metal capture, metal sensing, and heterogeneous catalysis.

## RESULTS AND DISCUSSION

**Preliminary Kinetic Study.** Translating a reversible catalytic reaction from small molecule synthesis to materials preparation is a daunting task encompassing many challenges such as catalyst deactivation and insufficient self-correcting ability due to unfavorable kinetics. In this context, our previous work showing one example of the fully reversible C–S/C–S metathesis of diaryl thioethers at high temperatures (160 °C) needed careful re-evaluation.<sup>11</sup> Under such harsh conditions, side reactions and catalyst decomposition become problematic and can hamper the synthesis of the materials. To address these issues, we studied the effect of the electronic properties on the reaction rate by performing a 2D Hammett analysis using various symmetric aryl thioethers bearing different substituents. Interestingly, the reaction is extremely fast, even at much lower temperatures than previously reported (80 vs 160 °C), in a small, optimal range of matching electronic properties (Figure 1 and Figure S1,  $-0.2 < \sigma(Ar_1 \text{ and } Ar_2) < 0.2$ ). We can thus conclude that the design of the optimal building blocks should rely on electronically neutral, minimally biased aromatic monomers. Noteworthy, the C–S/C–S metathesis reaction rate is in the same order of magnitude as imine condensation used for COFs synthesis (70 °C, 3.0 vs 10.0 mM min<sup>-1</sup>, respectively, Figure S2)<sup>15</sup> and can reach the equilibrium, which further supports its potential in the synthesis of materials following a DCC approach. The effects of different parameters on the reaction rate and catalyst

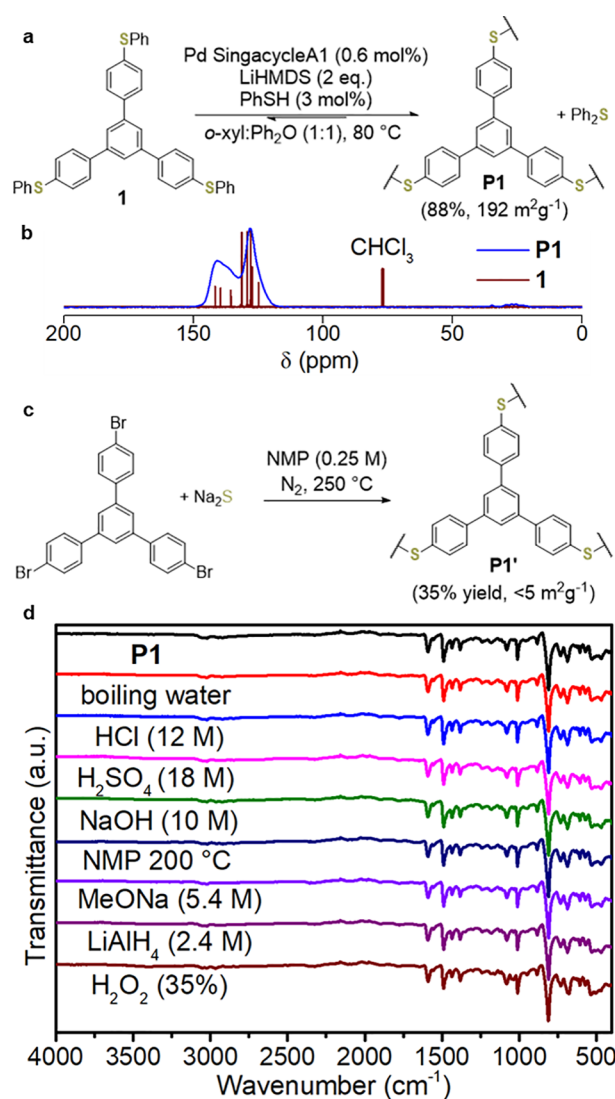


**Figure 1.** Preliminary mechanistic studies. Kinetics of C–S/C–S metathesis (top) in the scrambling of aryl groups with different electronic properties. See the Supporting Information for full kinetic data (Figure S1).

lifetime were also evaluated to find the optimal range of conditions for the reaction (see Table S1 and Figure S3 for the full study).

#### Synthesis and Characterization of the Polymers.

Using the information gathered from the preliminary kinetic experiments, we designed the model monomer **1** containing an 1,3,5-triphenylbenzene core with  $D_{3h}$  geometry bearing three electronically neutral phenyl thioether functional groups. The optimal polymerization conditions were found by performing a screening within the narrow set of conditions obtained from the preliminary kinetic study ( $[1]$ ,  $[\text{PhSH}]$ ,  $[\text{LiHMDS}]$ ,  $[\text{Pd}]$ ,  $T$ , solvent, and stirring, Table S2). With the optimized conditions in hand, we performed the gram-scale synthesis of **P1** in excellent yield (Figure 2a), in good agreement with the conversion measured as yield of byproduct ( $\text{Ph}_2\text{S}$ ) by GC analysis (Table S7). Magic angle spinning,  $^{13}\text{C}$  solid-state NMR shows the presence of aromatic carbons in **P1**, associated with those measured for the monomer **1** (Figure 2b). In addition, FT-IR shows the disappearance of the bands associated with the pendant  $-\text{SPh}$  groups of the monomers, indicating a high degree of polymerization (Figure S17). Elemental analysis of the synthesized structure showed good agreement between the measured and calculated amount of C, H, and S (Table S8). As expected, controls performed without Pd catalyst or base gave neither solid formation nor conversion. These results are remarkable, as examples of reversible, metal-catalyzed syntheses of porous materials are scarce in the literature<sup>13,14,16</sup> due to the challenge posed by the potential irreversible deactivation of the catalyst by trapping inside the pores. The choice of the solvent system is extremely important in the synthesis of porous polymeric structures: stabilization of oligomers and formation of colloids in the solution during the first stages of the reaction is proposed to prevent a premature precipitation of the particles, ensuring



**Figure 2.** (a) Synthesis of a model poly(aryl thioether) **P1** by reversible C–S metathesis reaction. Values in parentheses show yield by mass and surface area of the polymer. (b) Solid-state  $^{13}\text{C}$  CP-MAS NMR spectra of **P1** and liquid  $^{13}\text{C}$  NMR spectra of the monomer **1** ( $\text{CDCl}_3$ ). (c) Synthesis of **P1'** via nonreversible polycondensation reaction. Values in parentheses show yield by mass and surface area of the polymer. (d) FT-IR spectra of **P1** after 24 h in contact with different chemicals.

continuous growth and self-correction which lead to low-defect materials.<sup>17</sup> We decided to use  $\text{Ph}_2\text{O}$  as cosolvent due to its ability to partially solubilize PPS<sup>18</sup> (Figure S4). Indeed, using a one-to-one mixture of *o*-xylene/ $\text{Ph}_2\text{O}$  as solvent, we obtained **P1** as a colloidal suspension after 20 h, in contrast to pure *o*-xylene that formed a precipitate, supporting the stabilizing effect of  $\text{Ph}_2\text{O}$  (in both cases, turbidity appeared after 20 min). Field emission scanning electron microscopy (FESEM) showed a remarkable difference in **P1** particle size for both solvent systems (50 vs 200 nm, for *o*-xylene/ $\text{Ph}_2\text{O}$  and *o*-xylene, respectively, Figures S39 and S44). Moreover, the surface area of **P1** was inferior for the synthesis in pure *o*-xylene ( $29 \text{ m}^2 \text{ g}^{-1}$ ) than for the *o*-xylene/ $\text{Ph}_2\text{O}$  (1:1) mixture ( $192 \text{ m}^2 \text{ g}^{-1}$ ) (Figures S29 and S30). Temperature had also a big impact on the surface area ( $192$  vs  $36 \text{ m}^2 \text{ g}^{-1}$  for 80 and 120 °C, respectively, Figures S29 and S31) and particle size (50 vs 500 nm for 80 and 120 °C, respectively, Figures S39



and S45). Thus, by modification of the temperature and the solvent system, we were able to control the physicochemical properties of the material. Considering the flexibility of the C–S–C linkage, the surface area of **P1** is comparable to other porous organic materials containing flexible linkers<sup>19</sup> and is more than 6 times higher than the only other porous polymer containing monoaryl thioether linkers in the skeleton ( $30 \text{ m}^2 \text{ g}^{-1}$ ) reported up to date.<sup>9</sup>

Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements of the digested polymers detected some remaining Pd in the polymers even after washing the solids with a chelating agent (1,3-propanodiamine, Table S9).<sup>20</sup> The Pd remaining in the structure is likely to be trapped in closed pores and stay inaccessible to the chelating agent under such conditions. Pd–K edge extended X-ray absorption fine structure (EXAFS) measurements of the materials synthesized employing different reaction conditions showed that the remaining metal embedded within the structure is coordinated to sulfur ( $R = 1.8 \text{ \AA}$ ) and carbon ( $R = 1.4 \text{ \AA}$ ) atoms (Figures S66 and S67).

To demonstrate the importance of the reaction's reversibility for the synthesis of the materials, an alternative synthesis of **P1** was attempted following the most common procedure to prepare sulfur-based polymers: polycondensation reaction of aryl halides with  $\text{Na}_2\text{S}$  at elevated temperatures ( $250 \text{ }^\circ\text{C}$ ). The material **P1'** was indeed obtained according to the FT-IR spectra (Figure S22), albeit in considerably lower yield of solid than **P1** (35% vs 88%, Figure 2c; full conversion of the monomer was observed in both cases), and more importantly, **P1'** was nonporous ( $<5 \text{ m}^2 \text{ g}^{-1}$  vs  $192 \text{ m}^2 \text{ g}^{-1}$  for **P1**), indicative of an amorphous, interlinked polymer formed under complete kinetic control. These results highlight that while the standard polycondensation reaction can somewhat enable the low-yielding formation of a similar structure, the reversibility of the C–S/C–S metathesis is a crucial factor in the synthesis of these materials providing self-correction characteristics that lead to the formation of pores and well-defined particle sizes, two important features for downstream applications.

Thermal stability of the polymer by thermogravimetric analysis (TGA) under a  $\text{N}_2$  atmosphere showed that **P1** is highly temperature resistant up to  $450 \text{ }^\circ\text{C}$  (Figure S38a). Moreover, **P1** also exhibits high thermal stability (up to  $300 \text{ }^\circ\text{C}$ ) under air with no apparent signs of sulfur atom oxidation (Figure S38b). Remarkably, **P1** displays similar thermal stability as PPS. Chemical resistance of the material **P1** was next tested by immersion in different solutions for 24 h: boiling water, NMP at  $200 \text{ }^\circ\text{C}$ , strong acids, bases, reducing agents, and oxidizing agents. The FT-IR spectra before and after exposing the materials to these conditions were compared (Figure 2d). Very small differences were observed between the spectra (see Figure S23 for subtracted spectra), demonstrating the extremely high stability of the materials against harsh chemicals and conditions, comparable to poly(aryl ether)-based COFs.<sup>21</sup> Moreover, adsorption isotherms of **P1** after 24 h contact with the harshest chemicals according to the FT-IR spectra:  $\text{H}_2\text{SO}_4$  (18 M) and  $\text{H}_2\text{O}_2$  (35% v/v) showed that most of the porosity is retained (Figures S32 and S33, Table S12) as well as the mass balance (98% and 80%, respectively), further confirming the exceptional chemical stability of the porous poly(aryl thioether)s. These results altogether further support the original hypothesis that the materials prepared by this synthetic method combine the robustness of PPS with the characteristics of porous materials.

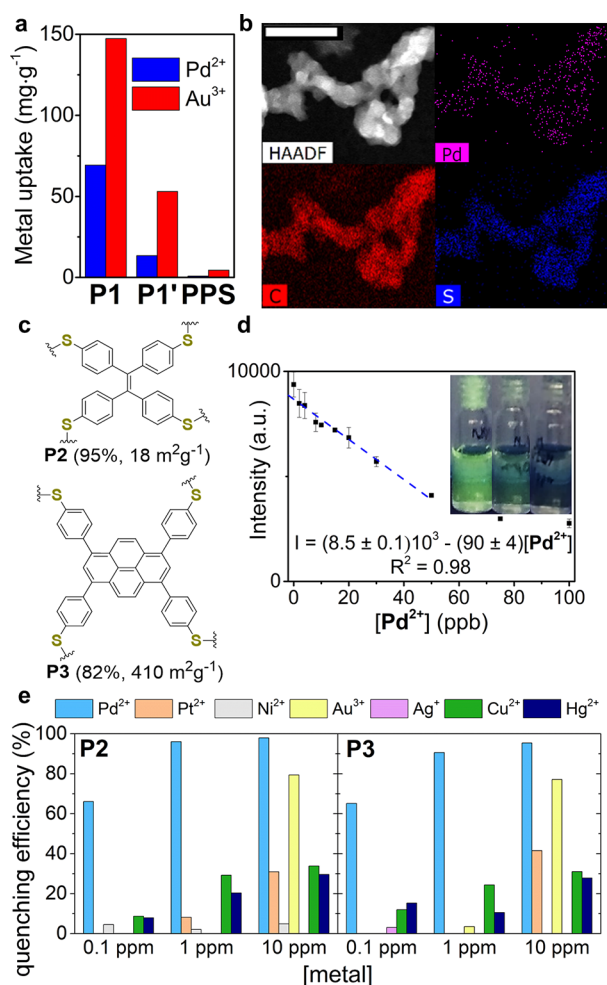
## Design of Fluorescent Polymers for Noble Metal Sensing and Capture.

Given the simplicity and mild conditions of our synthetic method, we hypothesized that by using monomers containing different functionalities, we could easily access a variety of new functional materials. One straightforward application for porous, sulfur-containing materials would be in detection and capture of noble metals from water. Water contamination by noble metal cations is an environmental challenge due to its harmful effects on human health and ecosystems.<sup>22</sup> In addition to that, efficient recovery of expensive metals like Pd, Au, and Pt from industrial waste waters can have a huge economic impact due to their scarcity and high price. The porosity of the polymers and the high density of sulfur atoms (10–20 wt %) with high affinity for noble metals can enable the capture of the metal ions from water, while a built-in fluorescent functionality can potentially enable metal sensing by fluorescence quenching, one of the methods of choice to detect metal cations in aqueous solutions due to its high sensitivity.<sup>23</sup> Indeed, several porous materials have already been used for metal capture and sensing including MOFs,<sup>8d,24</sup> COFs,<sup>25</sup> and polymers.<sup>26</sup>

To get further insight about the benefits of our synthetic method over traditional polycondensation reactions toward their application, we evaluated the capacity of **P1** for  $\text{Au}^{3+}$  and  $\text{Pd}^{2+}$  capture—two common and valuable pollutants in industrial wastewaters (Figure 3a). In the case of palladium, **P1** was able to capture up to  $69 \text{ mg g}^{-1}$  of  $\text{Pd}^{2+}$  from a 100 ppm  $\text{PdCl}_2$  solution, which could be increased to  $94 \text{ mg g}^{-1}$  starting from a 500 ppm  $\text{PdCl}_2$  solution. The amount of Au captured by **P1** from a 500 ppm  $\text{AuCl}_3$  solution was  $147 \text{ mg g}^{-1}$ , which is comparable to that of other reported porous materials containing thioether moieties ( $150\text{--}200 \text{ mg g}^{-1}$ ).<sup>24</sup> **P1'** and commercial PPS, on the other hand, showed much lower capacity for metal uptake, further highlighting the importance of our synthetic method with regard to the polymers properties and applications. Importantly, most of the metal cations could be easily removed from **P1** by washing with 1,3-diaminopropane, and it could be reused to almost full capacity over three cycles (Figure S7).

We next sought to experimentally confirm that the structural thioether groups are indeed responsible for the metal binding properties of the material. High-resolution transmission electron microscopy (HR-TEM) and high-angle annular dark-field (HAADF) coupled to EDX images showed the good dispersion of the metals in the material (Figure 3b). Pd–K edge EXAFS measurements indicated that the adsorbed  $\text{Pd}^{2+}$  is directly bound to the sulfur sites ( $R = 1.8 \text{ \AA}$ ) with different degrees of hydration<sup>27</sup> ( $R = 1.5 \text{ \AA}$ , Figure S68). Moreover, the  $\text{Pd}^{2+}$  uptake capacity was not affected by different amounts of PhSH in the synthesis of **P1** (69.3, 69.0, and  $72.3 \text{ mg g}^{-1}$  respectively for 2, 5, and 10 mol % of PhSH), clearly pointing toward structural thioethers, and not residual thiols, acting as binding sites. In contrast to our new materials, commonly used metal absorbents based on porous materials traditionally rely on pendant thiol groups to adsorb higher amounts of metals.<sup>8d,25</sup> However, these free thiols have to be introduced in an additional postsynthetic modification step that significantly increases the complexity of the material's preparation. In addition, the strong metal–thiol interaction makes it difficult to recover the metals from the solid without damaging the structure.

To develop materials for metal sensing, two new polymers **P2** and **P3** were synthesized containing well-studied



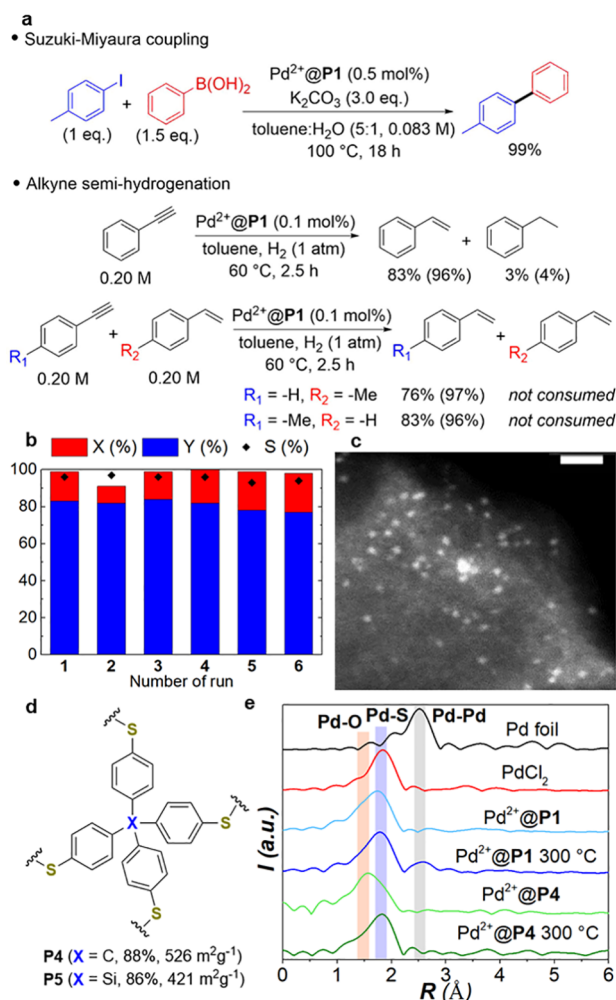
**Figure 3.** (a) Pd<sup>2+</sup> and Au<sup>3+</sup> uptake capacity from aqueous solutions containing PdCl<sub>2</sub> (100 ppm) and AuCl<sub>3</sub> (500 ppm). (b) HAADF image and EDX mapping of Pd<sup>2+</sup>@P1 (1 wt %, bar represents 200 nm). (c) Structures of the polymers P2 and P3. Values in parentheses show yields by mass and surface area. (d) Fluorescence emission intensity of P2 in water (2 ppm) at 540 nm (excitation at 370 nm) vs [Pd<sup>2+</sup>]. The inset shows the quenching of fluorescence in a dispersion of P2 (10 ppm) after adding Pd<sup>2+</sup> (from left to right: 0, 0.1, and 1.0 ppm). (e) Fluorescence quenching of P2 and P3 (10 ppm) by different metal cations (0.1, 1.0, and 10 ppm).

fluorophore cores including tetraphenylethylene and tetraphenylpyrene,<sup>28</sup> respectively (Figure 3c). In this case, the interaction of the polymers with metals in solution would be used along with their built-in fluorescence (Figure S27). Both polymers were synthesized in high yields with P3 displaying a higher surface area, which can be explained either by the increased rigidity of the monomer core, therefore decreasing the flexibility of the polymer, or by the  $\pi$ - $\pi$  stacking interactions between the pyrene-containing cores, which has been proven relevant in the synthesis of COFs, contributing to the increase in the rate of polymerization and the quality and surface area of the final materials.<sup>29</sup> Notably, both materials P2 and P3 were extremely sensitive for Pd<sup>2+</sup> detection by fluorescence quenching,<sup>30</sup> with P2 being able to sense down to 2 ppb or 0.019  $\mu$ M (Figure 3d), making it considerably more sensitive than other solid materials like polymers<sup>31</sup> or MOFs<sup>32</sup> (400 and 44 ppb of Pd<sup>2+</sup>, respectively) and are even at the level of the best small molecule sensors reported.<sup>33</sup> Moreover, the response was fast (within seconds),

and both materials were extremely selective for Pd<sup>2+</sup>; the fluorescence was not significantly affected by other cations such as Pt<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>, or Hg<sup>2+</sup> (Figure 3e, Figures S8–S13) and just slightly by Au<sup>3+</sup>—10 ppm of Au<sup>3+</sup> induces similar response as 0.1 ppm of Pd<sup>2+</sup>—demonstrating the great potential of the materials as very sensitive and selective sensors for Pd<sup>2+</sup> traces in water.

**Expansion to 3D Geometries and Catalytic Application of Pd<sup>2+</sup>@P1/P4.** Given the high capacity of the polymers to adsorb and disperse noble metals, we decided to test the hybrid material Pd<sup>2+</sup>@P1 (1 wt % Pd) as heterogeneous catalyst. One of the key features of a good catalyst support is the ability to stabilize metals without binding too strongly and thus reducing catalytic activity. Considering the characteristics of our new materials—porosity, good dispersion of the metals, and reversible binding to the metal cations—we hypothesized that they could be efficient supports for noble metal catalysts. Similar materials including carbon nitride<sup>34</sup> or even PPS<sup>35</sup> have been used as supports to stabilize and modify catalytic activity of Pd in catalysis. Gratifyingly, Pd<sup>2+</sup>@P1 showed good catalytic activity for classical Pd-catalyzed reactions, i.e., Suzuki–Miyaura coupling and the industrially relevant semihydrogenation of terminal alkynes (Figure 4a).<sup>36</sup> Notably, Pd<sup>2+</sup>@P1 could perform the semihydrogenation of phenylacetylene to styrene under mild conditions with high selectivity (>95%) and could be reused over six cycles (TON = 5860) without significant loss of activity (Figure 4b). Moreover, the hot-filtration test showed that the Suzuki and semihydrogenation reactions stopped when the solid was filtered from the solution (Figures S14 and S16), indicating that the reaction takes place in the solid/liquid interface and not in the solution through leaching of metal species. Control experiments without catalyst or using the as-synthesized and the washed materials prior to supporting Pd<sup>2+</sup> did not give any activity, confirming that the Pd traces trapped inside the polymer after synthesis (analyzed by ICP-OES) are not accessible to the reagents under the reaction conditions. HR-TEM and EXAFS after the Suzuki and hydrogenation reactions show that the support can prevent agglomeration of Pd, and only small amounts of subnanometer Pd clusters were detected (Figure 4c).

Analogously, as previously done for the fluorophores in P2 and P3, harnessing the versatility of the reaction, we can design monomers with T<sub>d</sub> geometry to expand the family of porous poly(aryl thioether)s to 3D structures. These structures can be ideal supports for single atom catalysts (SACs) due to their usually higher porosity than the corresponding 2D analogues, providing better stabilization of the metals and improving diffusion of the reactants and products under reaction conditions. We designed the polymers P4 and P5 (Figure 4d) containing tetraphenylmethane and silane, respectively. These materials were synthesized in excellent yields and, in fact, showed the highest surface areas of all the family due to the 3D geometry of the nodes. We compared P1 and P4 as supports for single atom catalysts (SACs) under reducing gas-phase reaction conditions (H<sub>2</sub> atmosphere, up to 400 °C). Pd–K EXAFS in situ measurements of Pd<sup>2+</sup>@P1 and Pd<sup>2+</sup>@P4 (1.0 and 0.6 wt % Pd<sup>2+</sup>, respectively) suggested that the materials were able to stabilize and isolate the Pd atoms, preventing agglomeration even up to 300 °C under a H<sub>2</sub> atmosphere (Figure 4e)—only a small Pd–Pd contribution appears for P1, whereas no Pd–Pd feature appears for P4, consistent with the higher surface area of the latter. The X-ray absorption near edge structure (XANES) region indicates

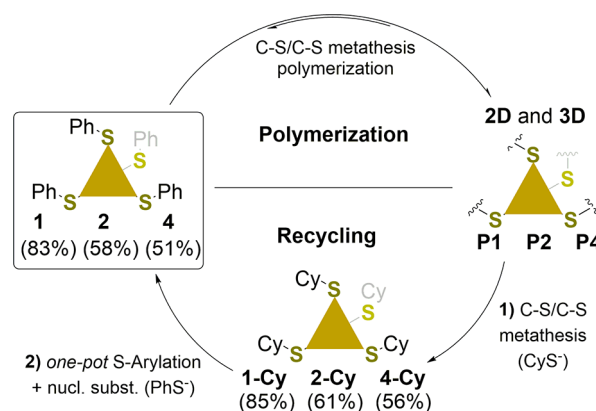


**Figure 4.** (a) Reactivity of the Pd<sup>2+</sup>@P1 (1 wt % Pd) as heterogeneous catalyst. Yields are shown, and values in parentheses stand for selectivity of semi- vs complete hydrogenation. (b) Reusability of Pd<sup>2+</sup>@P1 over six cycles of phenylacetylene semi-hydrogenation (X - conversion, Y - yield, S - selectivity). (c) HAADF image of Pd<sup>2+</sup>@P1 after Suzuki reaction (bar represents 10 nm). (d) Structures of the polymers P4 and P5. Values in parentheses show yield by mass and surface area. (e)  $k^2$ -weighted Fourier transform of the EXAFS function for Pd<sup>2+</sup>@P1 and Pd<sup>2+</sup>@P4 at RT and 300 °C under H<sub>2</sub> stream and selected references. The Pd–O interaction is due to the hydration of the Pd<sup>2+</sup>.

reduction of the Pd already at 100 °C (Figures S69 and S70).<sup>37</sup> These results reinforce the potential of the sulfur-containing porous polymers as supports for gas-phase heterogeneous catalysts. Further reactivity tests are underway in our laboratories to unlock the full potential of this new family of materials in catalysis.

**Recyclability of the Polymers.** Being able to recycle polymeric materials to the original monomers at the end of their life cycle is one of the biggest challenges in sustainable chemistry. Decomposition and revalorization of polymers have been extensively studied in the past decades; however, recovery of the original monomers from the polymers is still rare and usually requires the design of polymers that are labile under acidic conditions (acetal, ester, amide, etc.).<sup>38</sup> Moreover, despite some relevant efforts to depolymerize linear polymers synthesized by reversible alkyne metathesis to macrocycles,<sup>39</sup> recovery of the original monomers from porous polymers has

not yet been demonstrated. Given the extraordinary chemical stability of the porous poly(aryl thioether)s reported in this work, recycling them to the monomers poses an evident challenge; however, since they were synthesized by a reversible reaction, the same reaction should, in principle, give the monomers back under suitable conditions. Unfortunately, the C–S metathesis reaction with excess of thiophenol was not effective to directly recycle the polymers, probably due to the low reactivity of the thiophenol toward transmetalation that kinetically prevents any efficient degradation. Gratifyingly, when a more nucleophilic thiol, cyclohexanethiol, is used, the polymers P1, P2, and P4 could all be readily depolymerized in high yields to close analogues of the original monomers (1-Cy, 2-Cy and 4-Cy, Figure 5). Subsequent S-arylation via



**Figure 5.** Recyclability of the polymers to the initial monomers. Percentages in parentheses indicate isolated yields starting from the polymers.

diphenyliodonium hexafluorophosphate led to the formation of the corresponding sulfonium salts, which were reacted in one pot with thiophenol in a nucleophilic substitution reaction, yielding the original monomers through a direct Cy to Ph switch. These proof-of-principle results demonstrate how, thanks to transition-metal catalysis, polymeric materials can be designed to be extremely stable and, at the same time, be easily recycled back to the starting monomers.

## CONCLUSIONS AND OUTLOOK

We have developed a new methodology to synthesize previously unknown porous polymers linked by strong thioether bonds, which would be difficult to access by traditional synthetic methods, by using the reversible Pd-catalyzed C–S/C–S metathesis reaction. The materials were obtained in good yields with high surface areas and are extremely resistant against several harsh conditions including highly reactive chemicals. We have demonstrated the importance of the reaction's reversibility to produce high quality materials and good control over their properties. In addition, the polymers are highly modular, as several functionalities can be introduced, enabling their application to different environmentally relevant fields: metal capture, metal sensing, and heterogeneous catalysis, in both the liquid and gas phase. In particular, P2 outperforms previously reported materials in Pd<sup>2+</sup> sensing, detecting down to 2 ppb with great selectivity. Importantly, the polymers have been designed to be recycled after use by degrading them back to the monomers by using palladium catalysis, taking advantage of



the reaction's reversibility. This conceptual design is highly relevant in the context of a circular economy. Besides these exciting preliminary results, and given the novelty as well as modularity of this family of materials, we believe that many more applications can be developed in different fields such as photo/electrocatalysis or gas capture by introducing new functionalities. In a broader context, we believe this work demonstrates the untapped potential of emerging single-bond metathesis reactions for the synthesis of robust yet recyclable materials.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c09884>.

Details of experimental procedures and characterization techniques (PDF)

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