Functional polythioamides derived from thiocarbonyl fluoride

Haonan Xiang1,3, Jieping Wang1,3✉, Zihao Guo1, Yucong Chen1, Beihan Jiang1, Sitao Ye1, and Wenbin Yi1,2✉

1School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.
2 Key Laboratory of Organofluorine Chemistry, Shanghai Institute Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.
3 These authors contributed equally: H. Xiang, J. Wang. ✉ e-mail: jieping.wang@njjust.edu.cn; yiwb@njjust.edu.cn

Polythioamide is a unique type of sulfur-containing polymers with advanced functionalities. However, current synthetic approaches based on elemental sulfur, which could easily react with unsaturated functional groups, restrict the choice of substrates. Inspired by the highly efficient sulfur-fluoride exchange (SuFEx) polymerization through discrete hubs, we here report a novel and general method for the synthesis of polythioamides from diboronic acids, secondary diamines, and thiocarbonyl fluoride as the connective hub. Well-defined structures, including previously inaccessible unsaturated substrates, were realized with a narrow polydispersity. The polythioamides can efficiently and selectively bind to metal ions and were applied in precious metal recovery. Further development results in PdII-crosslinked single-chain nanoparticles acting as a recyclable homogeneous catalyst, demonstrating promising applications of these unprecedented polythioamides. We anticipate that thiocarbonyl fluoride could be a powerful hub for the challenging synthesis of sulfur-containing polymers.

Keywords: sulfur-containing polymers, polythioamides, thiocarbonyl fluoride, fluoride exchange, single-chain nanoparticles

Nature synthesizes its most essential molecules like polynucleotides, polypeptides, and polysaccharides of remarkable structural and functional perfection by using only a few simple and robust chemical reactions and a very small library of monomers.1 Inspired by this, polymer science has witnessed a broad adaption of simple and high-yielding chemistries to afford polymeric materials with precise control over architecture and functionality.2,3 Among these, the click chemistry, which is based on the concepts of modularity and orthogonality, has led to a significant change in design strategies and the overall approach to synthetic problems.4

Sulfur fluoride exchange (SuFEx)—the next-generation click chemistry, is possible to create novel polymers containing sulfone and sulfoxide building blocks with fascinating properties through discrete hubs such as sulfur fluoride (SO2F2),5,7 thionyl tetrafluoride (SOF4),8,10 and ethene-sulfonyl fluoride (ESF)11 (Fig. 1a). A similar compound, thiocarbonyl fluoride (CSF2), has been applied to prepare poly(thiocarbonyl fluoride) in the 1960s.12 However, the laborious low-yielding synthesis of CSF2 through fluorination of the toxic thiophosgene and the necessary low-temperature polymerization hampered further development.13 Until recently, the in-situ generation of CSF2 enables the successful functionalization of small molecules via fluoride exchange.14-18

Encouraged by these, we hypothesized that CSF2 could be a suitable hub to build sulfur-containing polymers. Among these, polythioamide is a unique type of material with selective metal coordination ability,19-21 high refractivity,22 and luminescence behavior.23 And the synthesis of polythioamides is highly demanding. Harsh conditions were required at the beginning.24-26 A breakthrough was realized by Tang et al. through a facile multicomponent polymerization directly from elemental sulfur and primary diamines (Fig. 1b).23,27-31 However, elemental sulfur is less selective and very susceptible to addition reactions with a large number of unsaturated functional groups,32-34 resulting in a limited choice of substrates. Besides, due to the site-blocking effects of condensation reactions, the synthesis of polythioamides via secondary diamines is rarely reported.29

Herein, we report a new and general method for the synthesis of unprecedented polythioamides from CSF2, diboronic acids, and secondary diamines via a facile Ni catalyzed C-F exchange process (Fig. 1c). Diverse and well-defined structures were realized with a narrow polydispersity. A DFT calculation indicates that the self-ligation of CSF2 can improve the selectivity of the reaction, while the short C-F bond is key to reducing the polymer molecular weight distribution. With selective coordination of metal ions, the polythioamides were applied in precious metal recovery. More noteworthy, PdII ions were directly incorporated into polymer chains, resulting in PdII-crosslinked single-chain nanoparticles (SCNPs),35 which were applied as a recyclable homogeneous catalyst for various catalytic reactions, demonstrating promising applications of these polythioamides.

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Results and discussion

Polymer synthesis. CSF\textsubscript{2} was in-situ generated by reducing Langlois’ reagent (CF\textsubscript{3}SO\textsubscript{2}Na) in the presence of triphenylphosphine and chlorodiphenylphosphine.\textsuperscript{17} Subsequent reaction with bis-secondary amines resulted in bis-substituted sulfuryl fluorides with 50-60% yield (Fig. 2a, 1a-8a). Piperazine-1,4-bis(carbothioyl) difluoride(1a) and commercially available 1,4-phenylenediboronic acid(1b) were selected as monomers to screen reaction conditions delicately. As the reaction progressed, the viscosity of the solution increased significantly and precipitates were observed after 12 h. So, we first screen the assistance of a phase-transfer catalyst (PTC). Among which, 18-crown-6 can significantly improve the yield to 63%. Other PTCs including n-Bu\textsubscript{4}PF\textsubscript{6} and 15-crown-6 also promoted the reaction, albeit in low yields (Table S1). Organic solvents were tested then, indicating that 1,3-dioxolane is a suitable solvent for polymerization (Table S2). Optimized monomer concentration (0.25 M) (Table S3) and feeding ratio (PTC : [1a] : [1b] = 3.0 : 1.0 : 1.5) were realized after an intensive investigation (Table S4). Ni(cod)\textsubscript{2} was selected as an efficient pre-catalyst in conjunction with a readily available phosphine ligand PCy\textsubscript{3},\textsuperscript{36} which is beneficial for a higher yield (Table S5). The reaction was heated to 100 °C until the weight-averaged molecular mass and the yield were no longer increased (Table S6). Finally, a yellow solid(P1) was isolated in 85% yield with a weight-averaged molecular mass (M\textsubscript{w}) of 7 kDa after 36 h (containing ~30 repeating units with an excellent polydispersity index (PDI) of 1.04).
Fig. 2 | Polythioamides derived from thio carbonyl fluoride. 

**a** Preparation of bis-substituted sulfuryl fluorides from thio carbonyl fluoride.  

**b** Synthesis of polythioamides from bis-substituted sulfuryl fluorides and diboronic acids.
We next explored the potential of this coupling polymerization to access structurally different polymers (Fig. 2b). First, piperazine-1,4-bis(carbothioyl) difluoride was examined with diboronic acids comprising both aromatics and heterocycles, giving the respective polymers P1-P6 in isolate yields 70–90%, with weight average molecular weights ranging from 3.8 to 8.1 kDa. A narrow polydispersity was realized except for P5, which might due to the large potential resistance of the diboronic acid structure. The C-F bond on the boronic acid substrate did not participate in the reaction (P6), showing a good selectivity of this C-F exchange process. Diboronic acids with a series of secondary aliphatic diamines, aromatic diamines and benzylamines were then explored (P7–P16), confirming the superioil construction of polythioamides via CSF hub, in terms of substrate range, selectivity and molecular weight distribution. Specifically, substrates containing unsaturated bonds, which were inaccessible before, were realized by a secondary amine with olefinic structure (P14).

The polymer structures were characterized through the comparison with a synthesized small molecular model compound M1. The single-crystal structure of M1 was obtained to confirm its structure, and the flexible chair-boat switching of piperazine was observed (Table S7). The IR spectrum of P1 is similar to that of M1: the absorption bands of the stretching vibration of the B(OH)2 group from 1b disappeared, and the stretching vibration peak of the C=S group from 1a at 1583 cm⁻¹ had shifted to 1624 cm⁻¹ of that of P1, indicating the consumption of monomers and the generation of thioamide groups (Fig. S1). In the 1H NMR spectrum of M1, the singlet peaks at δ 4.48, δ 3.64 and multiple peaks at δ 4.27-4.21 (dd 2H), δ 3.90-3.84 (dd, 2H) of the piperazine group are in good accordance with that of P1 at δ 3.5-4.5. In the 13C NMR spectra, the carbon resonance of the characteristic C=S carbon peak in compounds M1 and P1 at δ 199 both emerged, confirming their thioamide structures (Fig. S2).

The entire polymerisation process was tracked by 19F NMR spectroscopy. The gradual consumption of the thionyl fluoride (δ = 12.76-11.68 ppm) (Fig. S3) was observed, suggesting that it is a step-growth polymerization, same as normal cross-coupling polymerisations. Since homocoupling of electrophiles and nucleophiles are in competition to the cross-coupling process, which may result in homocoupling defects of copolymers. Three sets of parallel experiments between piperidine-1-carbothioyl fluoride, piperazine-1,4-bis(carbothioyl) difluoride, phenylboronic acid, and 1,4-phenylenediboronic acid were performed, and no homocoupling product was observed, highlighting the advantages of this C-F exchange reaction (Scheme S1).

A DFT calculation was performed to study the activation process of piperazine-1-thioborothioyl fluoride and phenylboronic acid (more details see SI). The reaction mechanism and the potential energy barrier diagram are shown in Fig. 3. The starting compound is NiIV intermediate IM-1 (0.00 kcal/mol), which was obtained by reacting piperazine-1-thioborothioyl fluoride with Ni(cod)2 and PCy3. Due to the coordination of sulfur to the metal, a new NiIV intermediate IM-2 (-5.82 kcal/mol) was subsequently generated. This self-ligating process of thiocarbonyl fluoride results in a more stable structure than the coupling of common metal insertions, which may be one of the reasons for the good selectivity of the reaction.

IM-2 reacted further with phenylboronic acid, resulted in IM-3 (-8.05 kcal/mol) with a Gibbs free energy difference of 2.23 kcal/mol. Then the cooperative reaction transition state TS-1 (13.04 kcal/mol) was formed with a Gibbs free energy barrier of 21.09 kcal/mol. This large energy barrier increase demonstrates that due to the short C-F bond, when phenylboronic acid participates in the reaction, the sterical hindrance becomes the main reason for the increased energy barrier. As the polymerisation proceeds, the steric hindrance of the polymorph reaches the limit of the energy barrier and the reaction then stops. This might be the main reason for a narrow polydispersity of this polymerisation. NiIII intermediate IM-4 (0.95 kcal/mol) was obtained through the dropping process of borofluoridic acid FB(OH)2. Finally, NiIII intermediate IM-4 proceeded Suzuki–Miyaura reaction, by undergoing the transition state TS-2 (14.26 kcal/mol) with a Gibbs free energy barrier of 13.31 kcal/mol, to generate the final product IM-5 (-15.13 kcal/mol). The hyperconjugation interactions in the Suzuki–Miyaura reaction were found to assist the reaction process between the C-H bonds’ ω-electrons and the benzene ring’s π-electrons of piperazine from IM-4 via TS-2 to IM-5, based on the IRI method in the Multiwfn program (Fig. S4).
**Polymer functionalization.** Selective recovery of precious metals by polymeric ligands coordination has received increasing attention in recent years. Polythioamides P1, P2, and P11 were selected as examples to investigate their metal coordination abilities. Different amounts of these polymers were added into the aqueous solutions of Au\(^{3+}\), Pd\(^{2+}\), and Pt\(^{4+}\), respectively. The solid was removed by centrifugation after being stirred at room temperature for 2 h, and the remaining metal ion concentrations were measured by ICP-OES to calculate the extraction efficiency. The extraction capacities of the polymers are 270 (P1), 120 (P2), and 76 (P11) mg·Au\(^{3+}\)/g, 85 (P1) and 306 (P2) mg·Pd\(^{2+}\)/g, 150 (P1), 215 (P2), and 10 (P11) mg·Pt\(^{4+}\)/g, respectively. (Fig. S5) The polythioamides prepared from aliphatic diamines show better performance as compared to the aromatic diamines. Surprisingly, the Pd\(^{2+}\) adsorption efficiency of P2 is twice higher than that of the previous reported sulfur-containing polymers. This might because the prepared polythioamides from secondary amines have no structural defects or hydrogen bonds interfering with the metal adsorption process. Besides, the adsorption rate of Au\(^{3+}\) is two times higher than that of Pd\(^{2+}\) and Pt\(^{4+}\) (Fig. S6). Since the adsorption of precious metals can often take place in extreme pH environments, we tested the adsorption ability of P1 and the stability of the coordinated metal complexes at different pH values, demonstrating a superior adsorption ability in a broad range of pH (Fig. S7).

To test the selectivity of the prepared polythioamides among different metal ions, P1 was added into the respective aqueous solutions of a variety of metal ions including Na\(^{+}\), K\(^{+}\), Mn\(^{2+}\), Cu\(^{2+}\), Cr\(^{3+}\), Cd\(^{2+}\), Fe\(^{2+}\), Pb\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Hg\(^{2+}\), Au\(^{3+}\), Pd\(^{2+}\), and Pt\(^{4+}\) with a metal ion concentration of 100 mg/L. The solid was removed by centrifugation after 2 h, and the remaining concentrations of metal ions in the supernatant were measured to calculate the extraction efficiency. Of all 16 metal ions, strong coordination between P1 and Au\(^{3+}\), Pd\(^{2+}\), Pt\(^{4+}\), and Hg\(^{2+}\) was observed. The colored metal ion solutions of Cu\(^{2+}\), Cr\(^{3+}\), Co\(^{2+}\), Fe\(^{3+}\), and Ni\(^{2+}\) showed no change after the treatment with
P1 (Fig. 4a). We next tried to recover the precious metals directly from pre-treated waste CPUs, platinum or palladium plated circuit boards with P1 respectively (Fig. S8 and Table S8-10). To our delight, gold, platinum and palladium were all successfully recovered from the e-waste by facile pyrolysis of the resulting P1-metal complexes with a metal content of more than 85 wt% measured by SEM-EDS (Fig. S9).

We further took advantage of the excellent precious metal adsorption properties of the polythioamides, incorporating palladium directly into polymer chains to form PdII-crosslinked single-chain nanoparticles (SCNPs) as a recyclable homogeneous catalyst. To demonstrate the feasibility of palladium as functional units and the working mechanism of the metal extraction process, XPS of P1 before and after its coordination with PdII was studied. From the XPS spectrum of P1 to that of P1−PdII, besides that the characteristic binding energy for Pd 3d (341.08, 335.78 eV) had emerged in the latter, the binding energy for S 2p had changed from 161.78, 160.58 eV to 162.08, 160.98 eV and a new characteristic peak at 401.28 eV in the spectrum of N 1S was also observed, indicating the coordination of tertiary amines with palladium (Fig. 4b).48,49 With these insights, it could be concluded that both N and S atoms from the polythioamide could form a strong binary coordination with PdII (Fig. 4c). Different from polythioamides prepared from primary amines, which possess a large number of inter- and intramolecular hydrogen bonds, decreasing the proportion of active coordination sites, weakening the coordination ability and reducing the solubility,31 polythioamides prepared by secondary amines are more soluble in organic solvents. Benefiting from this, PdII-SCNP were applied as a recyclable homogeneous catalyst, bridging the gap between homogeneous activity and heterogeneous recyclability. To develop the practicality of this catalyst, various reactions, such as Suzuki, Heck and nitroarene hydrogenation were realized in gram-scale with nearly 99% yield (Fig. 4d). Finally, we demonstrate that our current system allows for post-catalytic isolation and reuse of the PdII-SCNPs by precipitation in methanol. The activity of the recovered palladium complexes was investigated in a second cycle of Suzuki-Miyaura cross-coupling (Fig. S10). With a low catalyst loading (3 mol %), an approximately 77% conversion of 4-methyl-1,1′-biphenyl was realized, confirming its high catalytic activity.

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Fig. 4 | Application of Polythioamides. a Selective extraction by P1 in an aqueous solution with 16 mixed metal ions. Inset: Eight colored metal ion solutions before and after the treatment with P1. b XPS of P1 and P1−Pd2+. c The coordination process of Pd(NO3)2·2H2O with P1. d Catalytic reactions of PdII-SCNPs as a reusable homogeneous catalyst.
Conclusion

In conclusion, a facile synthesis of unprecedented polythioamides via thiocarbonyl fluoride, diboronic acids, and secondary diamines has been successfully established. Diverse and well-defined structures, including previously inaccessible unsaturated substrates, were realized with a narrow polydispersity. Different from previously reported polythioamides, both N and S atoms from the polythioamide could form a strong coordination with metal ions, enabling the successful recovery of precious metals from waste electronics. Further development results in PdII-crosslinked single-chain nanoparticles acting as a recyclable homogeneous catalyst. We anticipate that thiocarbonyl fluoride could be a powerful hub to achieve challenging sulfur-containing polymer syntheses.

Online content

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References


approximately 5 mL. A yellow solid was precipitated after adding MeOH (20 mL).

Methods

General synthesis of thiocarbonyl fluorides

CF3SO2Na (30 mmol, 3 equiv.), PPh3 (30 mmol, 3 equiv.), and secondary amine (10 mmol, 1.0 equiv.) were charged in a 100 mL round bottom flask. Ph3P (30 mmol, 3 equiv.) dissolved in MeCN (30 mL) was added dropwise to the flask. The resulting solution was stirred at room temperature for 30 min. The resulting solution was stirred at room temperature for 30 min before concentrating to

General synthesis of polythioamides

In a nitrogen-filled glovebox, dithiocarbamyl fluoride (1 mmol, 1 equiv.) was added into a 15 mL vial equipped with a 1 cm magnetic stir bar. A pre-mixed solution of N(cod): (0.1 mmol, 0.1 equiv.) and PCy3 (0.2 mmol, 0.2 equiv.) in 1,3-dioxolane (4 mL) was subsequently added. The aryl diboronic acid (1.5 mmol, 1.5 equiv.) and 18-Crown-6 (3 mmol, 3.0 equiv.) were added, and the vial was capped and removed from the glovebox. The reaction mixture was further stirred at 100 °C for 36 h before cooling down to room

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temperature, filtration and was diluted with 3 mL of DMF. The solvent was concentration with a rotary evaporator, which was then added into 50 mL of methanol dropwise through a cotton filter to precipitate. The precipitates were filtered and washed with methanol : H₂O = 1:1 for 2 times (2 × 20 mL), which were then dried under vacuum to a constant weight, and a polymer solid was obtained.

**Data availability**
All data supporting the findings of this study are available within the article and its Supplementary Information and can also be obtained from the corresponding author upon reasonable request. Metrical parameters for the structure of small molecular model compounds M1 are available free of charge from the Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/data_request/cif) under reference nos. CCDC 2244145).

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**Author contributions**
J.W. conceived the research. H. X. and J.W. carried out all the experiments and data analysis. Z.G. carried out density functional theory (DFT) calculations for the activation process. Y. C., B.J., and S.Y. carried out synthesis of various bis-substituted sulfuryl fluoride. H. X., J.W. and W.Y. wrote the manuscript with input from all authors. J.W. and W.Y. directed the project.

**Competing interests**
The authors declare no competing interests

**Additional information**
**Supplementary information** The online version contains supplementary material available at