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Gold Recovery from E-Waste by Porous Porphyrin–Phenazine Network Polymers

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ABSTRACT: Gold recovery from electronic waste could prevent excessive mining with toxic extractants and provide a sustainable path for recycling precious metals. Unfortunately, no viable recycling is practiced, except burning electronic circuit boards in underdeveloped countries, mainly because of the lack of chemical scavengers as adsorbents. Here, we report the synthesis of a family of porphyrin–phenazine-based polymers and their gold-capturing properties as well as application in gold recovery from actual e-waste. The polymers show high selectivity toward gold as well as other precious metals. The Au(III) adsorption isotherms were well-fitted to the Langmuir adsorption model and proportionality between porosity and uptake capacity was observed. Solution pH values and illumination conditions were shown to have influences on the performance of the adsorbents with the highest capacity of 1.354 g/g obtained in acidic pH and under continuous UV irradiation. Such a remarkable capacity of 7 times the theoretical estimate was achieved through photochemical adsorption−reduction mechanism supported by the observed suppressing effect of oxidant on gold-capturing ability. The adsorbents are robust and recyclable, a significant advantage over other emerging materials.
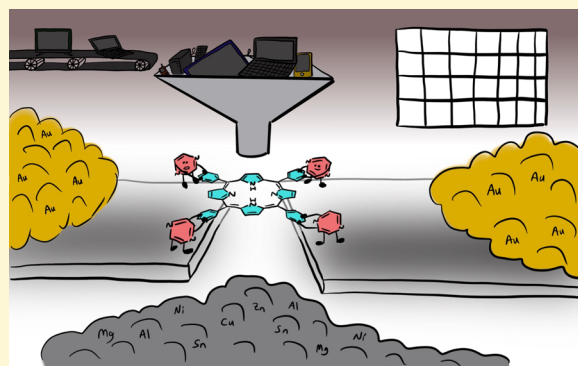
INTRODUCTION

Gold, a precious metal, has been extensively used in catalysis, jewelry, medicine, and electronics.[1−3] The demand for gold has been increasing with the growing need for device manufacturing. The majority of the gold supply comes from ore mining, about 75% of the total volume each year. The conventional mining process requires a leaching process involving the use of toxic cyanide solution.[4] This may raise questions regarding the environmental impact and safety issues. Furthermore, mining activities including exploration, mine construction with essential infrastructure, ore extraction, and processing necessitate a considerable capital investment. An alternative way to produce gold is through recycling, which actually makes up the rest of the annual gold supply. About 90% of the recycled gold comes from jewelry, and only 10% is from technological products. This share from technology-derived gold could be enhanced given the high content of gold in electronic devices such as mobile phones, television sets, and refrigerators. In fact, one ton of ore contains as much gold as only 40 mobile phones combined.[5] Taking the increasing generation of e-waste (∼50 Mt/year) into consideration together with the above-mentioned economic perspective of gold recovery from electronics, urban mining,[6,7] a process of retrieving valuable elements from e-waste, is expected to play a more important role both in fulfilling the global gold need and in affording efficient waste treatments.

Methods to extract gold from electronic waste primarily include pyrometallurgy and hydrometallurgy.[1] While pyrometallurgical processes in most cases implement direct incineration of the e-waste that could then generate secondary pollutants and other hazardous substances, hydrometallurgical methods employ a more environment-friendly treatment when using digestive solutions to assimilate electronic parts prior to the recovery of the targeted elements. The solutions are then subjected to the process of extraction and purification. To this end, an effective and convenient strategy is to use an adsorbent tailored to selectively pick up the metal of interest in the matrix of different elements. Many adsorbents have been attempted for the purpose of capturing gold species from a complex solution. The literature includes biomaterials such as lignin-based[8−10] and chemically modified polysaccharide adsorbents,[11−13] chelating resins,[14−16] functionalized silica,[17,18] nanoparticles,[19,20] metal−organic frameworks (MOFs),[5,21] and porous organic polymers.[22] In general, a common strategy for designing an adsorbent is to incorporate electron-rich
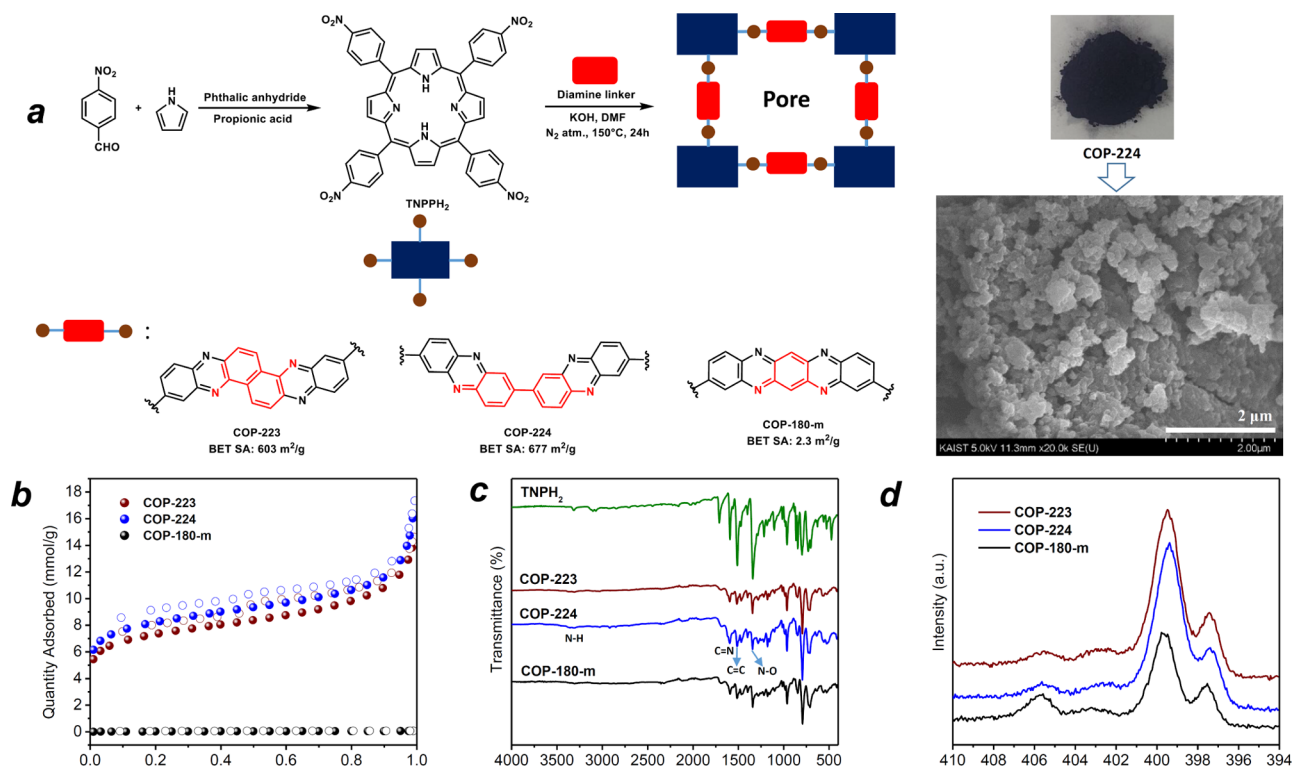
Figure 1. (a) Synthesis, (b) N_2 adsorption−desorption isotherms, (c) attenuated total reflectance (ATR) spectra, and (d) N 1s X-ray photoelectron spectroscopy (XPS) spectra of the porphyrin−phenazine-based polymers COP-223, COP-224, and COP-180-m.

atoms such as oxygen, nitrogen, and sulfur to take advantage of their ability to coordinate or chelate metal ions. Porphyrins are known as great complexing agents for a variety of metal ions due to the inherent cavity, and the chelating nitrogen atoms that could provide a strong binding effect.[23−25] A number of porphyrin-based polymers have in fact been reported.[26−28] Yet, none of them has been employed for recovering valuable metals from electronic waste. Therefore, in this work, we would like to report the synthesis as well as the gold-capturing activity of a novel family of porous porphyrin-based polymers. The selective adsorption of gold was investigated from a mixed-metal solution containing various common elements. The adsorption property was further evaluated upon the adsorption isotherms, illumination dependence, and pH dependence studies. Finally, the potential application of the adsorbent in the practical recovery of gold from electronic waste was assessed using one of the materials with an e-waste solution.

RESULTS AND DISCUSSION

Synthesis and Characterization. The porphyrin-containing polymers, covalent organic polymers, COP-223, COP-224, and COP-180-m, were obtained using the Wohl-Aue coupling reaction from TNPPH2 monomer and different diamine−arene linkers (Figure 1a). The monomer was accessed via a well-established cyclization protocol from pyrrole and 4-nitrobenzaldehyde (see the Supporting Information for details). The polymers were subsequently formed by stirring TNPPH2 (1 g, 1.26 mmol), diamine (2.54 mmol), and potassium hydroxide (12.6 mmol) in N,N-dimethylformamide (DMF, 250 mL) at room temperature under a N_2 atmosphere for 1 h, followed by the elevation of temperature to reflux for 24 h. The generated polymers were then thoroughly washed

with water and acetone before being dried in a vacuum oven at 150 °C for 24 h.

Porosity is anticipated as a critical factor governing the gold-capturing efficiency of the materials. The porosity differences observed in the obtained adsorbents (Figure 1b) would unravel the significance of porosity in the gold uptake capacity. In particular, while COP-223 and COP-224 possessed high Brunauer−Emmett−Teller (BET) surface areas of 603 and 677 m^2/g, respectively, COP-180-m appeared to be non-porous. The two former polymers were constructed against geometrically similar diamine linkers that possessed two amino groups aligned in para and para-like arrangements. This allows the propagation to proceed along the inherent perpendicular axes of the porphyrin core, which could sterically minimize the clash of the growing branches for a productive network building process. A similar building direction could not be achieved in the case of COP-180-m as the diamine unit had the amino groups positioned at meta position from each other. Such an arrangement formed a cis-like linkage (Figure 1a) and thus hampered the extensive generation of the polymer.

Aside from the difference in the porosity resulting from different constructing orientations, the polymers shared common structural characteristics as expressed in the Fourier transform infrared (FT-IR) and XPS spectra (Figure 1c,d). The FT-IR spectra of the materials showed a perfect resemblance (Figure 1c), and this served to confirm their structural relationship. A closer examination highlighted some unique porphyrin signals including (1) the out-of-plane C−H bending vibrations of the pyrrole ring at 795, 726, and 710 cm^{-1}, (2) the in-plane modes at 1015, 990, 980, and 964 cm^{-1}, and (3) the skeletal vibrations of the pyrrole ring at 1470, 1400, and 1340 cm^{-1}. In addition, the C≡N stretching
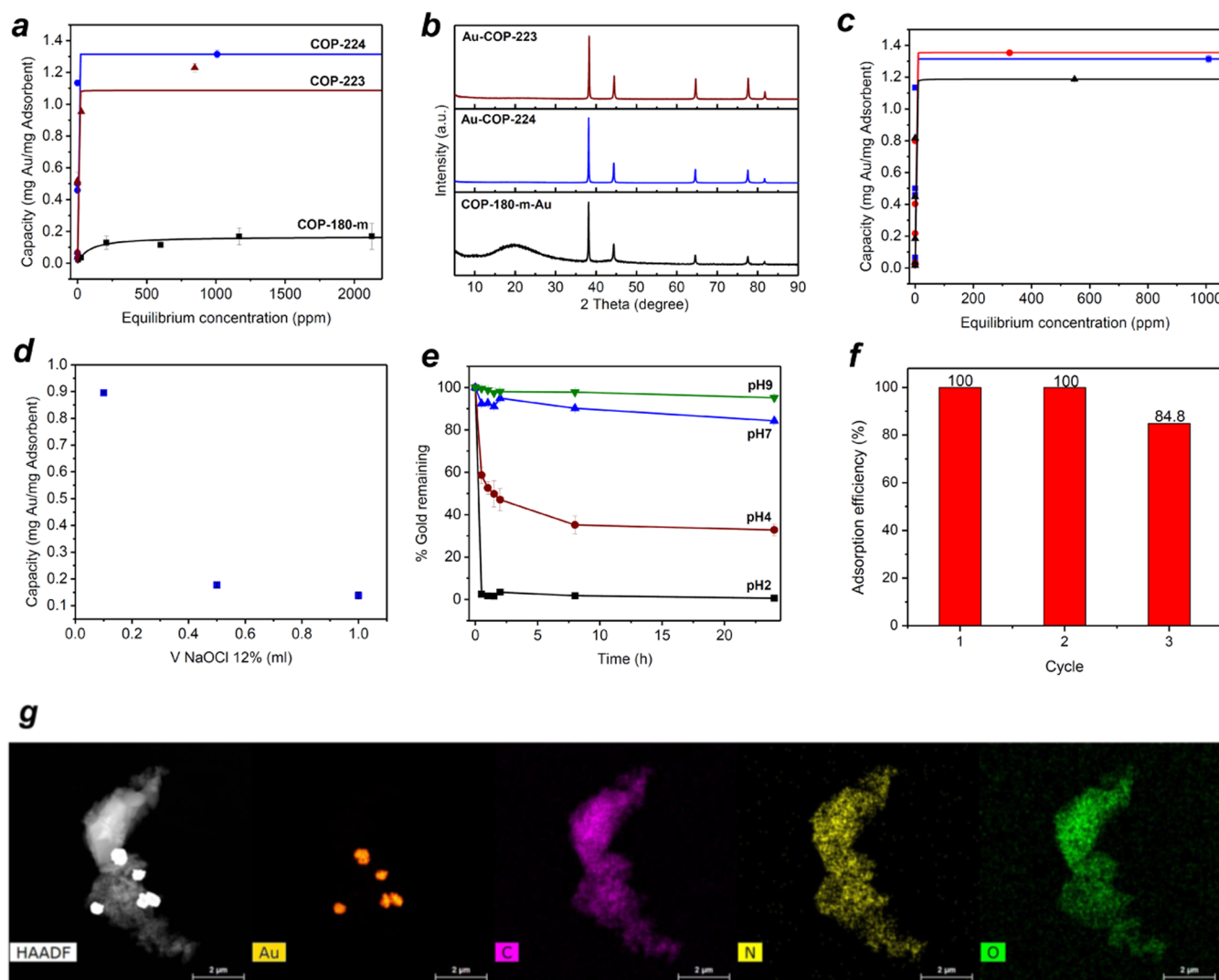
Figure 2. (a) Gold uptake isotherms of COP-223, COP-224, and COP-180-m, (b) XRD patterns of the gold-loaded adsorbents, (c) light effect on the adsorption of COP-224, (d) effect of oxidant on the adsorption of COP-224, (e) pH effect on the adsorption of COP-224, (f) desorption of the gold-loaded COP-224, and (g) transmission electron microscopy (TEM) and elemental mapping of the gold-loaded COP-224.

vibration, which was present in both porphyrin macrocycle and phenazine linkage, was also observed at 1680 cm^{-1}.

XPS data was also in accordance with the proposed structure when signals from the N 1s spectra of all of the absorbents revealed the existence of the corresponding pyrrole and aza nitrogens at 399.5 and 397.5 eV, respectively (Figure 1d). The aza nitrogens could be from either the porphyrin ring or the phenazine moiety. After the gold adsorption, all porphyrin nitrogens became equivalent and converged at 399 eV (Figure S1). This caused the intensity of the 397.5 eV signal to decrease to the point that reflexed only the phenazine nitrogen. Besides, the unreacted nitro and amine nitrogens were also recorded at 405 and 402 eV, respectively. The intensity of the NO$_2$ signal in COP-180-m appeared to be higher than those in COP-223 and COP-224, indicating a lower polymerization degree in its synthesis. Lastly, the temperature stability of the polymers was found to exceed 300 °C by thermogravimetric analysis (TGA) (Figure S2).

Gold Uptake Activity. The adsorption efficiency of the adsorbents was assessed based on the gold adsorption isotherms assembled upon various gold solutions of different concentrations at pH 2. As shown in Figure 2a, the adsorption

curves were well-fitted to the Langmuir model, and a correlation between porosity and uptake capacity was observed. The nonporous COP-180-m exhibited negligible adsorption, whereas COP-224 and COP-223 captured significant amounts of gold ions with the capacities of 1.315 and 1.087 g/g, respectively. These values corresponded well to the observed X-ray diffraction (XRD) spectra of the gold-loaded materials (Figure 2b). With high quantities of the absorbed gold, the Au-COP-223 and Au-COP-224 showed characteristic and distinct gold crystal patterns in contrast to a much higher extent of the amorphous character of the polymer Au-COP-180-m (see Figure S3 for XRD of the untreated polymers).

Although the remarkable capacities of COP-223 and COP-224 definitely derived from the porous nature of the polymers, they also significantly exceeded the theoretical capacity of 0.1934 g/g calculated upon the assumption that each porphyrin unit would host one gold ion. The adsorptive−reductive mechanism was thus considered to play a key role in the uptake activity of these adsorbents. This phenomenon was commonly observed in a number of adsorbents where the actual capacities exceeded the theoretical values. As exempli-

fied in the recent literature reports, gold particles can be produced inside the network of porous materials via the reduction of gold ions by the reductive nitrogen centers. Hence, this enabled effective gold recovery processes[5] or a powerful heterogeneous gold-catalyzed transformation.[29] The Au 3f XPS spectrum of Au-COP-224 (Figure S1) asserted the occurrence of Au(0), whose signals appeared at 84 and 87 eV, as the major gold component along with the less abundant Au(III) species observed at 91.48 eV. As Au(I) characteristic signals conventionally reside in almost the same region as Au(0), its presence should not be excluded, although the observed signals appeared to be made up more from elemental gold. Furthermore, the gold clusters were visually observed by TEM analysis and elemental mapping, as demonstrated in Figure 2g. These large-sized gold clusters resulted from the treatment of COP-224 with a highly concentrated Au(III) solution. After the reduction instance, close-by Au(0) species aggregated to form larger particles, which then parted the adsorption sites and made room for the solution gold ions to fill the post.

To seek further support for the reductive mechanism, a light-dependent gold uptake test was carried out in dark and under constant irradiation with COP-224 (Figure 2c). As a result, light exposure proved to have an effect on the performance of the polymer. In particular, without a light source, the adsorbent exhibited a diminished capacity with a value of 1.188 g/g, while an enhancement to 1.354 g/g was obtained with continuous illumination from a halogen light. The UV−vis spectrum of COP-224 (Figure S4) revealed a strong absorbance in the range of 300−900 nm. Therefore, under ambient and UV lighting conditions, the porphyrin core could receive a photoinduction for the reduction of gold ions to elemental gold, which possessed a weaker binding to the porphyrin than the coming gold ions in the solution. However, the capacity increase is not high enough to make light irradiation industrially viable.

The control experiment in which a strong oxidant, in particular NaOCl, was introduced to the adsorption test showed that increasing the amount of oxidant in the gold solution could inhibit the sorption ability (Figure 2d). The IR spectrum of the gold-loaded COP-224 and that of the NaOCl-treated COP-224 appeared to be similar in a way that most of the signals from the original COP-224 appeared in much lower intensities (Figure S5). The Au-COP-224's IR spectrum, however, showcased a greater change in the pyrrole ring skeletal vibrations region primarily due to the binding of the porphyrin unit to gold. Such a similarity between Au-COP-224 and oxidized COP-224 implied the oxidation of COP-224 during the gold-capturing process and hence further supported the reductive adsorption scenario.

Effect of Solution pH. The adsorption behavior of COP-224 appeared to show a significant dependence on the solution pH (Figure 2e). As the pH went from acidic to basic, the uptake activity declined with a rapid adsorption rate at pH 2 (over 90% after 30 min) and only a diminutive uptake at pH 9 after 24 h. Such a pH dependence could be considered advantageous in e-waste treatment since the e-waste is commonly digested in strong acid solutions. It is noteworthy that many reported adsorbents shared dependence on solution pH. The effect could be proportional or inverse according to the chemical behavior of the adsorptive sites on the adsorbent's surface and the form of the metal ions at a given pH. At low pH below 3, gold ions exist predominantly in the

form of $AuCl_4^-$ complex and the basic sites on COP-224's surface would be ionized, enabling the initial ionic attraction at the adsorption point and the subsequent photoreduction to yield elemental gold. At higher pH values (above 8), due to the high content of OH^-, gold ions were cast in hydroxo-containing complexes such as $Au(OH)_4^-$, which had a weaker interaction with now neutral coordinating sites of the adsorbent, yielding the observed lower adsorption power.

Desorption and Reusability. Given the photoreductive adsorption mode of the adsorbent, an appropriate desorption method with reducing capability should be considered. The acidic thiourea solution hence chosen for this reagent has been widely used for many desorption processes. In addition, it could reduce the adsorbent, which had been oxidized during the adsorption phase, to regenerate the effective adsorptive sites. The desorption study was carried out using COP-224, which was loaded with gold by shaking with a 600 ppm gold solution. Thiourea solution (0.1 M) in acidic pH (0.1 M H_2SO_4) was used at the dose of 1 mL/1 mg Au-COP-224, and the mixture was heated at 80 °C for 6 h. As shown in Figure 2f, after the first two cycles of maximum adsorption efficiency, the adsorbent lost about 15% gold-capturing power. This could be due to the strong binding of the porphyrin core to gold ions from the initial adsorption cycles, which survived through desorption processes and hence limited the open sites for the incoming gold ions. Lastly, we calculated that the single use of the adsorbent would be profitable (Table S4) if the gold price remained higher than $ 39/g.

Gold Adsorption Selectivity. As mentioned earlier, the designed adsorbent was aimed for gold recovery from electronic waste. In fact, the electronic waste contains a variety of metals other than gold. Therefore, to implement an adsorbent for the recovery of gold from e-waste solutions, it should exhibit considerable preference toward gold ions in the solution of various metal ions. The preliminary mixed-metal adsorption test was hence performed to evaluate the selective affinity for gold ions in the presence of other metal species in the solution. The test was carried out at low concentrations to ensure sufficient adsorption sites for all participating metal ions. Commercial standard solutions that contained the most common elements were utilized for this purpose. As a result, COP-224 showed a significant preference for precious metals such as gold, platinum, palladium, silver, and copper (Figure S6) in that over 99% of gold, platinum, and palladium ions were captured after 24 h.

E-Waste Treatment. The next phase was the gold extraction from the actual e-waste solution (Figure 3. To achieve this goal, a computer processing unit (CPU) was exclusively removed from the printed circuit board (PCB) and subsequently leached into a solution. For leaching purposes, Yang et al.'s method was chosen for it employed mild and environmentally benign conditions.[30] In particular, the mixture of N-bromosuccinimide (NBS) and pyridine in an aqueous solution at almost neutral pH proved to have leaching power comparable to that of traditional methods that normally utilized toxic cyanide solutions or dangerous extreme pH values. In this solution, CPU was treated for 3 days at ambient temperature and the resulting e-waste solution was acidified to pH 2 for more efficient preservation of the solution metal ions. The final solution contained a number of different elements including primarily Mg, Al, Ni, Cu, Zn, Sn, and Au. While copper appeared to be the major component (416 ppm), gold existed as the least abundant metal among the present
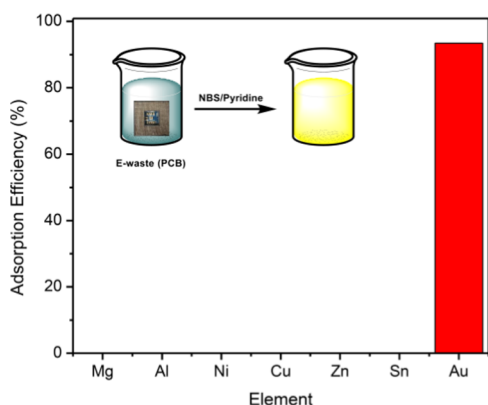
Figure 3. Gold recovery from actual e-waste using COP-224.

elements (31 ppb) (see Table S1 for the concentration of each element in the e-waste solution). Despite that, COP-224 demonstrated a great selectivity toward gold ions when it only chose to capture gold (93.4%) and almost ignored all other metal components. This would make adsorbent a promising agent to recover gold from e-waste.

Reported Adsorbents. A quick look at the reported gold adsorbents provided relative information on the practicality of the working polymer. As demonstrated in Table S5, the sorbents generally fall into two main groups: biomaterial-derived sorbents and synthetic sorbents. While higher capacities could be obtained with biosorbents such as the cross-linked cellulose gel (Pangeni et al.; 1.49 g/g) and the tannin gel adsorbent (Otaga et al.; 8 g/g), the recyclability of these materials has not been sufficiently reported. On the other hand, synthetic sorbents exhibited lower gold recovery but showed greater reusability. The robustness of the synthetic frameworks especially in harsh media like acidic e-waste solutions and destructive desorbing reagents could account for such high recyclability. In such a consideration, COP-224 appeared to possess both capacity and reusability. Additionally, along with its synthetic accessibility through commercially obtainable starting materials together with the high gold recovery performance, COP-224 proved that the porous phenazine-linked porphyrin polymer family could provide high potential candidates for capturing precious metals.

CONCLUSIONS

A family of porphyrin-based polymers was constructed and systematically studied for gold-capturing properties. While the porphyrin core provided the necessary selectivity, the porosity enhanced the interfacial contact between gold ions and adsorption centers for a more effective binding interaction. The main governing factor, however, was the reduction process that produced elemental gold whose coordinative interaction with the porphyrin unit was less efficient than that of incoming gold ions, and this raised the capturing performance of the adsorbent (COP-224) to a substantially higher level than predicted theoretically. Furthermore, practical application was examined, showing the promising ability of the material in the selective extraction of gold from real e-waste.

METHODS

General Procedure for the Synthesis of Porphyrin-Based Polymers. (**1**) **Monomer synthesis**: 5,10,15,20-tetrakis(4-nitrophenyl)-21H,23H-porphyrin (TNPPH2) was synthesized according to the literature with a slight modification: 4-nitrobenzaldehyde (110

g, 727.9 mmol) and phthalic anhydride (1.75 equiv) were dissolved in propionic acid (3 L) at 141 °C and pyrrole (1 equiv) was added dropwise for 30 min. The mixture was stirred at reflux for another 1 h. The mixture was then cooled to room temperature and the precipitate was filtered and washed with water and methanol and dried under vacuum. The obtained dark powder was dissolved in pyridine (800 mL) and refluxed for 1 h. The final product was collected by vacuum filtration, washed with acetone, and further purified by Soxhlet washing with acetone. Yield: 26.1537 g (18%). 1H NMR (CDCl$_3$, 300 MHz, ppm): δ 8.40 (d, 8H, J = 8.3 Hz), 8.67 (d, 8H, J = 8.4 Hz), 8.82 (s, 8H). Anal. calcd for C$_{44}$H$_{26}$N$_8$O$_8$: C, 66.50; H, 3.30; N, 14.10; O, 16.10%. Found: C, 66.53; H, 3.33; N, 14.48; O, 16.02%. (**2**) **Polymer synthesis**: the polymers were synthesized following a modified method from the literature: TNPPH2 (1g, 1.26 mmol), diaminoarene (2 equiv), and KOH (10 equiv) were mixed in DMF (250 mL) under nitrogen atmosphere. The mixture was stirred at room temperature under nitrogen for 1 h. The reaction was then heated to 150 °C and allowed to stir at this temperature for 24 h. The mixture was cooled to room temperature and water (1 L) was added, and the resulting mixture was further stirred at room temperature for 1 h. The crude product was filtered under vacuum and washed with water and acetone. The polymer was then thoroughly washed with acetone by Soxhlet washing before being dried in a vacuum oven at 120 °C for 15 h.

Metal Selectivity Test. The multielement calibration standard solution at 10 ppm for each metal was diluted to 100 ppb with deionized (DI) water. The dilute solution was then used for three samples of the control group (10 mL each sample) and three samples of the experimental group (10 mL each). To the samples of the experimental group were added 10 mg of the adsorbent. All of the samples were tumbled at 8 rpm for 24 h and filtered using syringe filters (ADVANTEC, pore size = 0.50 μm). The concentration of the metals in the samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

Gold Adsorption Isotherms. The gold solutions in the range of 30–2000 ppm were obtained by diluting the stock solution of gold(III) chloride trihydrate. At each concentration, one control and two experimental samples were prepared. Ten milliliters of the solution was added to each sample in a 15 mL conical tube. The adsorbent (10 mg each) was added to the experimental group. After shaking the mixtures for 48 h at 8 rpm, the polymer was filtered off and the gold concentrations were measured by ICP-MS. The captured metal amounts were calculated by concentration comparison between control and experimental groups. To examine the effect of light on gold adsorption, the same experiment was conducted under light irradiation (halogen lamp, 42 W, 630 lm) and in dark condition using COP-224 as the adsorbent. Two separate sets of each concentration were used in which transparent vials were utilized in one set and aluminum-foil-covered conical tubes were used in the other set to protect the solutions from light. All tubes were tumbled for 48 h at 8 rpm. The polymer was then filtered off, and the gold concentrations were measured by ICP-MS.

pH Effect. The gold stock solution was diluted to 50 ppb, and the solution pH was adjusted by NaOH (1 M, 3 M) and HCl (1 M) to pH values of 2, 4, 7, and 9. At each pH, one control and two experimental samples were prepared. To each sample was added 10 mL of the solution, and 10 mg of COP-224 was added to each experimental sample. The tubes were shaken at 8 rpm for 30 min, 1, 1.5, 2, 6, and 24 h. The polymer was then filtered off and the remaining gold concentrations were determined by ICP-MS.

Desorption and Recyclability. The gold solution at 600 ppm was used for adsorption steps. The adsorption was performed as described in the gold adsorption isotherm experiment above. For desorption, 0.1 M thiourea solution in acidic pH (0.1 M H$_2$SO$_4$) was used at the loading of 1 mL per each milligram of gold-loaded materials. The mixture was heated at 80 °C for 6 h. The filtrate was separated from the adsorbent by filtration, and the concentration was determined by ICP-MS. The adsorbent was dried in a convection oven at 70 °C for 15–24 h before being subjected to another adsorption process.

Metal Capture from Electronic Waste. Electronic waste was obtained from a local junk store. The CPU was manually removed from the PCB, and the metal scraps were also removed from the CPU. The leaching solution was prepared by mixing 0.966 μL of pyridine and 750 mg of NBS in 120 mL of deionized water. Solid metal scrap (0.32 g) was introduced to the solution, and the mixture was allowed to stand for 3 days. The resulting e-waste solution was then separated from the remaining solid by filtration and acidified by 1 M HCl to pH 2. The metal content of the solution was determined by ICP-MS analysis. The adsorption experiment with COP-224 was then performed following the procedure described in the metal selectivity test mentioned above.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01734.

> Materials synthesis and optimization, gold recovery methods, and analysis (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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