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Metal-Backboned Polymer: Conception, Design and Synthesis

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Electronic Supplementary Information

Abstract The backbones of polymers are generally composed of non-metal elements such as C, N, O and Si. Here we propose and synthesize a new class of polymers whose backbones are completely made from metal atoms connected by chemical bonds, and they are thus named metal-backboned polymers. As a demonstration, nickel is selected as the metal to construct the nickel-backboned polymers with varied lengths, which are verified by mass spectrometry and studied by ultraviolet-visible spectroscopy. These metal-bonded polymers open up a new avenue to develop functional polymers in the future.

Keywords Metal-backboned; Nickel; Functional; Polymer

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INTRODUCTION

Polymers have played essential roles in the history of human kinds due to a variety of attractive properties.[1−6] Natural polymers such as wool, silk and cellulose have been used for tens of centuries.[7−9] After the pioneer study by Hermann Staudinger in 1920,[10] general polymers mainly including plastics, rubbers and chemical fibers were discovered to revolutionize the world in many directions in the past century.[11−13] Natural and general polymers share non-conjugated backbones and are typically insulating. Conducting polymers with conjugated backbones have been later investigated to greatly expand the application scope of polymers in the recent decade.[14−16] The backbones of all types of polymers mentioned above are typically based on C, N, O and Si, although the other elements have been also incorporated together to improve their properties.[17] However, metal elements, the major components of the periodic table of elements, are less studied for polymer backbones; to the best of our knowledge, it is not available to construct polymer backbones completely with metal atoms.

Herein, we propose such a new type of polymers whose backbones are composed of metal atoms, *i.e.*, metal-backboned polymers. Fig. 1 shows a representative example with metal atoms linearly bonded like a chain as the backbone. In a typical synthesis, multidentate scaffold ligands that consist of four poly(2-aminopyridine) chains and a calix[4]arene unit act as an ideal one-dimensional tunnel-like host to hold the single chain of nickel atoms, and the resulting nickel-backboned polymer (**NBP**) has been characterized by matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectrometry and studied by ultraviolet-visible (UV-Vis) spectroscopy.

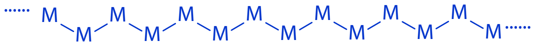

Fig. 1 Molecular structure of the backbone of metal-backboned polymer. "M" represents metal atom.

EXPERIMENTAL

General Considerations

All solvents and reagents including anhydrous *N*,*N*-dimethylformamide, 4-*tert*-butylcalix[4]arene, 6-bromopyridin-2-amine, 2-aminopyridine, tris(dibenzylideneacetone) dipalladium, 1,3-bis(diphenylphosphino)propane and toluene were purchased from Adamas with reagent grade, and they were used without any further purification.

^{1}H-nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III HD 400 MHz spectrometer at 25 °C and processed by MestReNova software. HRMS was measured using a Bruker McriOTOF11 spectrometer. MALDI-TOF mass spectra were measured by AB SCIEX 5800 mass spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]m-alononitrile as matrix and sodium trifluoroacetate as ionizer (when necessary). Fourier transform infrared spectroscopy (FTIR) spectra were recorded in the region of 400–4000 cm^{-1} by Thermo-fisher Nicolet 6700 FTIR instrument (KBr Discs). UV-Vis spectrometry was recorded on a Perkin-Elmer Lambda750 spectrophotometer with 10 mm width quartz cell using CH_2Cl_2 as solvent. The Ni K-edge X-ray absorption spectroscopy (XAS) was recorded in a transmission mode at 1W1B beamline in Beijing Synchrotron Radi-

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ation Facility (BSRF). For Ni K-edge data, the absorption edge energy E_0 of pure Ni foil was aligned to 8333 eV. E_0 of Ni foil was assigned by the first maximum of first-derivative X-ray absorption near-edge structures (XANES) spectrum. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA 1 and SDT Q600 TG-DTA analyzer under N_2 atmosphere from 30 °C to 800 °C along with a ramp rate of 10 °C·min^{-1}. Before carrying out the TGA, the samples were activated at 100 °C for 30 min to eliminate water in the samples.

Synthesis of Poly(2-aminopyridine) 1

To a refluxing pyridine (60 mL) solution of 2-aminopyridine (1.00 g, 10.63 mmol), a pyridine (40 mL) solution of 2-amino-6-bromopyridine (11.03 g, 63.78 mmol) and a catalyst solution of $Pd_2(dba)_3$ (366 mg, 0.39 mmol), 1,3-bis(diphenyphosphino)propane (327 mg, 0.78 mmol), *t*-BuOK (14.32 g, 127.56 mmol) and pyridine (40 mL) were added by syringe pumps at 80 μL/min under N_2. After filtration and concentration, the residue was dissolved in methanol (40 mL) solution acidified with HCl aqueous solution (0.1 mol/L) and then filtered. The filtration was further neutralized with saturated $NaHCO_3$ aqueous solution, filtered, washed with water and ethanol, and finally dried at 120 °C in a vacuum oven to produce poly(2-aminopyridine) **1** as dark yellow solid, 4.67 g, 68% yield. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 9.35 (s, —NH—), 9.11–8.96 (m, —NH—), 8.78 (s, —NH—), 8.26–8.20 (m, Py-H), 7.94 (d, Py-H), 7.69–7.59 (m, Py-H), 7.59–7.41 (m, Py-H), 7.38–7.16 (m, Py-H), 7.13–7.07 (m, Py-H), 6.99–6.94 (m, Py-H), 6.89–6.81 (m, Py-H), 5.98 (d, Py-H), 5.62 (m, —NH_2). MS (MALDI-TOF, *m/z*): [M+H]$^+$ calcd. for $C_{5n}H_{4n+3}N_{2n}$, 371.1, 463.2, 555.2, 647.3, 739.3, 831.4, 923.4; Found, 371.1, 463.1, 555.2, 647.2, 739.3, 831.3, 923.4. FTIR (KBr, cm^{-1}): 3477, 3395, 3197, 3021, 1603, 1575, 1507, 1422, 1249, 1152, 987, 876, 776, 721, 615, 512.

Synthesis of Multidentate Scaffold Ligands 2

To a stirred dry *N*,*N*-dimethylformamide (150 mL) suspension of NaH (3.12 g, 60% suspension in paraffin liquid, 0.078 mol), 4-*tert*-butylcalix[4]arene (5.00 g, 0.008 mol) was added in small portions at 50 °C, and the solution was stirred for 30 min under N_2. 2,6-Dibromopyridine (29.13 g, 0.123 mol) was added and the mixture was heated at refluxing overnight. Ethanol was added slowly to quench the excess NaH, and the solvent was then removed by distillation under reduced pressure. The residue was washed with ethanol and methanol in order, extracted with acetone and then recrystallized from CH_2Cl_2/MeOH to produce **CPBr** (Fig. S1 in the electronic supplementary information, ESI) as white solid, 3.41 g, 34% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 7.60 (dd, J=8.2, 7.5 Hz, 4H), 7.37 (dd, J=8.2, 0.7 Hz, 4H), 7.08 (dd, J = 7.5, 0.6 Hz, 4H), 7.06 (s, 8H), 3.78 (d, J=13.0 Hz, 4H), 3.16 (d, J=13.0 Hz, 4H), 1.18 (s, 36H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): 164.2, 147.2, 145.6, 140.8, 138.5, 133.9, 125.6, 121.1, 110.4, 34.2, 31.4, 31.1. HRMS (ESI, *m/z*): [M+H]$^+$ calcd. for $C_{64}H_{64}Br_4N_4O_4$, 1273.1706; Found, 1273.1714. FTIR (KBr, cm^{-1}): 3077, 3049, 2962, 2933, 2903, 2866, 1577, 1557, 1480, 1429, 1405, 1362, 1301, 1283, 1261, 1236, 1192, 1157, 1137, 1118, 1076, 983, 924, 892, 879, 871, 821, 785, 740, 724, 670, 641, 540, 442.

A 100 mL Schlenk tube was charged with **CPBr** (400 mg, 0.31 mmol), poly(2-aminopyridine) **1** (2.05 g) and picoline (40 mL) under N_2, to which $Pd_2(dba)_3$ (14 mg, 0.02 mmol), dppp (13 mg, 0.03 mmol) and *t*-BuOK (278 mg, 2.48 mmol) were added quickly. After heating at refluxing for 12 h, the solution was poured into water (200 mL), filtered, washed with ethanol and CH_2Cl_2 and then dried at 80 °C in a vacuum oven to produce the crude product (2.12 g), which was used without further purification. MS (MALDI-TOF, *m/z*): [M+Na]$^+$ calcd. for $C_{54+5n}H_{60+4n}N_{2n}O_4Na$, 2451.3, 2545.1, 2637.2, 2729.2, 2821.3, 2913.3, 3005.3 3097.4, 3190.4, 3282.5, 3374.5, 3466.5, 3558.6; Found, 2451.5, 2544.6, 2636.7, 2728.8, 2821.8, 2913.9, 3005.9, 3098.0, 3190.1, 3282.1, 3374.2, 3466.2, 3558.3.

Synthesis of NBP

A mixture of **2** (40 mg), $Ni(OAc)_2·4H_2O$ (44 mg, 0.17 mmol) and naphthalene (20 g) was heated and stirred at 200 °C for 12 h. After cooling to 100 °C, petroleum ether (60 mL) was added and the hot solution was filtered quickly, followed by washing with petroleum ether to remove the residual naphthalene. Rinsing the filter cake with CH_2Cl_2 and then removing the solvent under reduced pressure produced the desired product of **NBP** (3.6 mg). MS (MALDI-TOF, *m/z*): [M]$^+$ calcd. for $C_{84+20n+5m}H_{80+12n+4m}N_{12+8n+2m}Ni_{3+2n}O_4$, 3218.5, 3310.6, 3402.6, 3494.6, 3586.7，3516.4, 3609.5, 3700.5, 3792.5, 3884.6, 3976.6，3997.4, 4089.5, 4182.5, found, 3218.0, 3310.1, 3402.1, 3494.2, 3586.2, 3515.9; 3609.0; 3700.0, 3792.1, 3884.1, 3976.1, 3996.9, 4089.0, 4182.1. FTIR (KBr, cm^{-1}): 2953, 2923, 2852, 1599, 1583, 1557, 1410, 1307, 1257, 1226, 1194, 1153, 1126, 1012, 842, 767, 722, 557.

RESULTS AND DISCUSSION

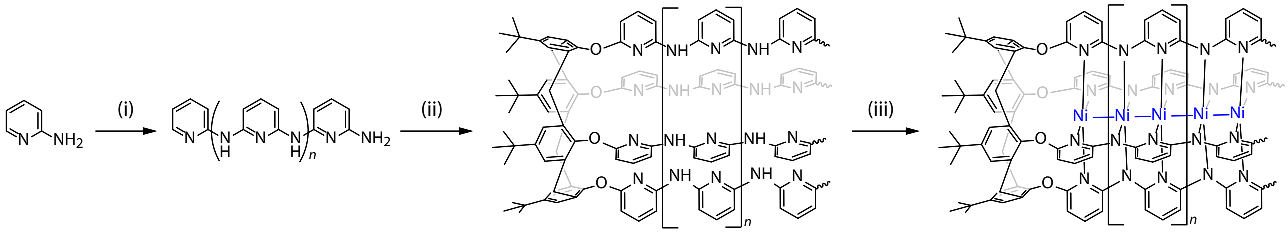
Design and Synthesis

In conventional polymers, non-metal atoms interlinked through strong covalent bonds to form stable polymers. However, when two metallic atoms bump into each other, the bond between them weakens a lot, resulting in the challenge to obtain stable metal-backboned polymers. To construct the **NBP**, poly(2-aminopyridine)s were rationally designed as multidentate ligands to hold the single chain of metal atoms in light of their regular intervals of N-donors comparable to metal-metal bond lengths, and every four of them are held together by a 4-*tert*-butylcalix[4]arene unit to form the one-dimensional tunnel-like structure in favor of the metal atoms to assemble into the linearly interconnected structure.[18−22]

A typical synthetic route for **NBP** is depicted in Fig. 2, and the resulting products were characterized with FTIR, NMR and mass spectrometry. Poly(2-aminopyridine)s **1** were polymerized and subsequently coupled with the calix[4]arene-based template **CPBr** produced from O-arylation reaction of 4-*tert*-butylcalix[4]arene with 2,6-dibromopyridines,[23] and the targeted **NBP** was then successfully synthesized by complexing the afforded multidentate ligands **2** with nickel salt. Nickel was selected as the metal for demonstration due to its mature in the synthesis of Ni—Ni bonds contained complexes.[24] In addition, once this synthetic strategy has been developed, the lengths of ligands and the types of metal atoms can be easily tuned to construct different metal-backboned or heterometal-backboned polymers with desired lengths.

Structural Characterization

The MALDI-TOF mass spectrum of **1** shows a series of peaks range mainly from 371 to 923 with intervals of *ca*. 92 that are molecular weights of repeating -pyridine-NH- unit (Fig. S2 in



1 **2** **NBP**

Fig. 2 Synthesis of **NBP**. Reaction conditions: (i) 2-amino-6-bromopyridine, $Pd_2(dba)_3$, dppp, *t*-BuOK, pyridine, 110 °C; (ii) CPBr, $Pd_2(dba)_3$, dppp, *t*-BuOK, picoline, 150 °C; (iii) $Ni(OAc)_2 \cdot 4H_2O$, naphthalene, 200 °C.

ESI), and higher molecular weights distributed in the range of 2542 to 3557 can be observed for **2** (Figs. S3 and S4 in ESI), corresponding to the targeted four poly(2-aminopyridine) chains-coupled structures. The shoulder peak around 2634 is resulted from the less poly(2-aminopyridine) chains-coupled by-products due to the unavoidable debromination side reaction during the cross-coupling reaction. The further increased molecular weights distributed in the range of 2990 to 4300 and increased numbers of isotopic peaks can be observed in the MALDI-TOF mass spectrum of **NBP**, suggesting the successful complexation of Ni ions with the ligands **2** (Fig. S4 in ESI). Through in-depth analysis on the MALDI-TOF mass spectrum of **NBP**, these peaks can be mainly divided into three groups, in each of which the peaks show similar intervals of *ca.* 92 and isotopic peak abundances, indicating that they bear the same nickel atoms but are different in ligand lengths (Fig. 3). As shown at Table S1 (in ESI), these peaks are well consistent with the **NBP** structures with increasing metal chain lengths in both molecular weights and isotope distribution patterns, rather than any of the possible non-nickel-backboned by-products.

The structures of **NBP** were further confirmed by FTIR (Fig. S5 in ESI). In the FTIR spectrum of **2**, the bands at 3406, 3278 and 3193 cm^{-1} that are characteristic N—H stretching modes and band at 1518 cm^{-1} that is characteristic N—H bending modes for secondary amines almost disappears in that of **NBP**, consistent with the structures of **NBP** whose N atoms were coordinated with Ni ions to form N—Ni coordinate bonds.

In addition, XAS was performed to provide further insight into the coordination structure of **NBP**. The X-ray absorption near edge structure (XANES) spectrum of **NBP** at the Ni K-edge was identical to that of NiO reference rather than that of Ni foil, which reflects the oxidation state of Ni in **NBP** (Fig. S6a in ESI). In the corresponding Fourier transforms of the extended X-ray absorption fine structure (EXAFS) spectra data (*r* space, Fig. S6b in ESI), there is a peak at 2.11 Å similar to that of Ni foil (2.16 Å), indicating the existences of Ni—Ni bonds in **NBP**.

Absorption Spectra of NBP

The UV-Vis absorption spectrum of **NBP** in CH_2Cl_2 is shown in Fig. 4. The absorption spectrum of **NBP** shows a broad absorption band in the range of 370–450 nm with maximal absorption wavelength at 414 nm, which can be ascribed to the π-π^* absorption band. This feature of NBP offers potential applications in the field of optoelectronics.

Solubility and Thermal Stability of NBP

Furthermore, the solubility and stability of **NBP** have also been investigated. The **NBP** exhibited outstanding solubilities in most polar organic solvents, such as dichloromethane, chloroform, methanol, tetrahydrofuran, dimethyl sulfoxide, *N*,*N*-dimethylformamide. The **NBP** also exhibits high thermal stability with decomposition temperature at 300 °C as shown in the TGA spectrum (Fig. S7 in ESI). These results revealed that this polymer is feasible and stable for practical applications.

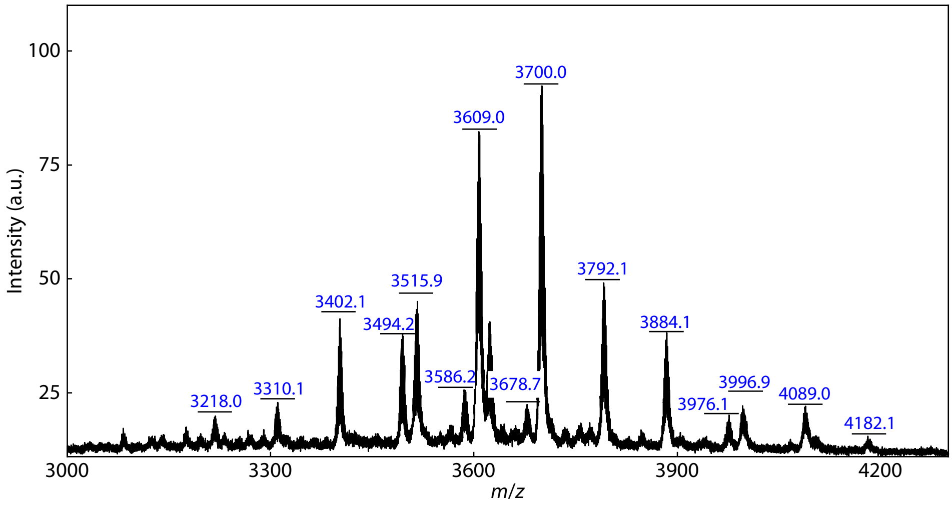


Fig. 3 MALDI-TOF mass spectrum of **NBP**.

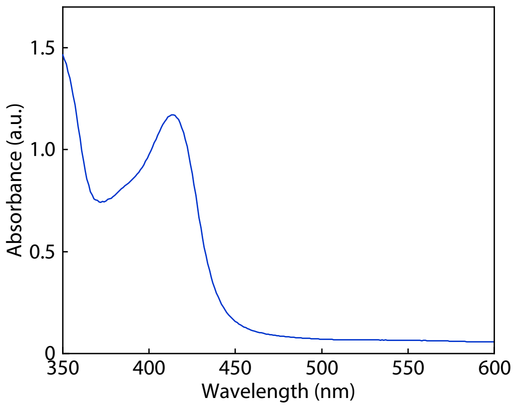


Fig. 4 Absorption spectrum of **NBP** in CH_2Cl_2 solution.

CONCLUSIONS

In conclusion, we present a new class of polymers whose backbones are made from metal atoms connected by chemical bonds. The nickel-backboned polymers of **NBP**s with varied lengths have been successfully synthesized and studied as a demonstration. The synthetic strategy developed in this work is convenient, and it provides opportunities to construct different metal-backboned or heterometal-backboned polymers with designed lengths. In short, we herein report metal-backboned polymer to open up a new avenue to design new functional polymers in the future.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-022-2887-x.

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