

Synthesis and Pyrolysis of Soluble Cyclic Hf-Schiff Base Polymers

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Abstract Soluble Hf-containing polymers are significant processable precursors for the fabrication of ultra-high temperature ceramics. In this work, cyclic Hf-Schiff base polymers were synthesized via direct polymerization of hafnium alkoxide and bis-salen monomers. The defined structure and molecular weight of the polymers were characterized by NMR spectroscopy, gel permeation chromatography and MALDI-TOF mass spectroscopy. The feed ratio of monomers regulated the molecular weight and solubility of the polymers. This synthetic strategy features simple operation under ambient conditions, efficient reaction with high yield and cyclic polymers as the main products. The Hf-Schiff base polymers were converted to HfC/C materials after pyrolysis under argon at 1600 °C, which was identified by XRD measurements, elemental analyses and Raman spectroscopy. This work will inspire more precise and efficient synthesis and applications of metallopolymer.

Keywords Hf-containing polymer; Schiff base; Cyclic polymer; Preceramic polymer; Hafnium carbide

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INTRODUCTION

Synthetic methodologies and potential applications of metallopolymer have attracted increasing attention during the past two decades.^[1–3] Because of the unique physical and chemical properties brought from various metals, metallopolymer have a wide application in the fields of catalysis,^[4] healthcare^[5] and ceramic materials.^[6] As an outstanding example, polyferrocenylsilanes showed typical properties of main-chain metallopolymer and were used to fabricate versatile functional materials.^[7–9] Among a great variety of metals in metallopolymer, most efforts have focused on late transition metals and their simple and stable complexes, while the research on the group 4 metals is very limited.^[10] However, soluble polymers containing group 4 metals like Zr and Hf are significant processable precursors to fabricate ultra-high temperature ceramics after pyrolysis.^[11] Hafnium carbide (HfC) with high melting point (>3900 °C), low vapor pressure and high chemical stability has become a promising material for applications in extreme environments.^[12,13]

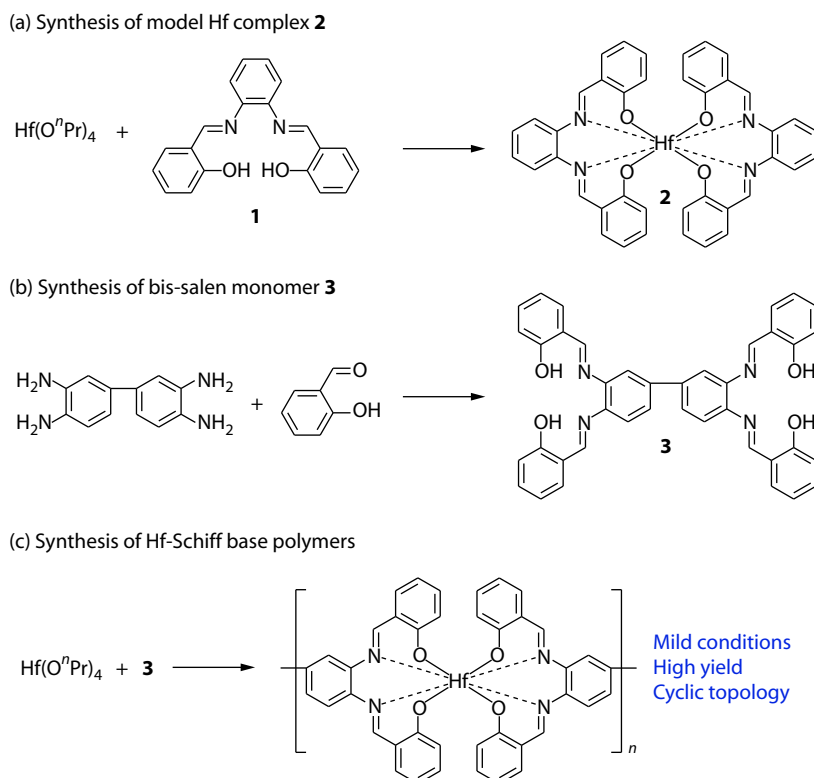
Only a few attempts on the synthesis of Hf-containing polymers have been reported so far, probably due to the high coordination number (up to eight) and complex reactivity of Hf. Initially, diols or diacids were used to polymerize with some Hf compounds like Cp_2HfCl_2 and HfCl_4 , forming polymers through Hf-O bonds.^[14–17] These solid products were insol-

uble in common solvents, so the characterizations were ambiguous. Alternatively, polymers containing Hf-C bonds were constructed through radical polymerization of alkenyl substituted hafnocene derivatives, or through nucleophilic reaction of Cp_2HfCl_2 with dilithioalkynyl compounds or Grignard reagents under strict anhydrous conditions.^[17–19] Only a small fraction of the product was soluble and characterized, while the structure of the polymers and the side reactions remained unclear. We hypothesize that the difficulty in the synthesis of Hf-containing polymers mainly comes from the high coordination number and crosslinking tendency of the Hf center, which inspires us to utilize stabilization of multidentate ligands derived from coordination chemistry to construct stable and soluble polymers.

Multidentate ligands such as terpyridine, porphyrin and hydroxyquinoline have been introduced into polymer science for the synthesis of polymers with diverse functions,^[20–22] demonstrating the strength of nitrogen-containing ligands. Salen-type Schiff bases represent one of the most widely utilized ligands to synthesize metal complexes and metallopolymer.^[23–25] The salen complexes of Zr and Hf are potent catalysts for ring-opening polymerization of lactones and copolymerization of epoxy with carbon dioxide.^[26–28] The linear eight-coordinate Zr-Schiff base polymers have been synthesized by imidization of tetra(salicylaldehydato)zirconium and tetraamine monomers under harsh conditions.^[29,30] In the present work, we synthesized soluble Hf-Schiff base polymers through direct polycondensation of hafnium alkoxide and bis-salen monomers (Scheme 1). To the best of our knowledge, this is the first example of soluble Hf-containing poly-

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Scheme 1 Synthetic strategy toward the model complex and Hf-Schiff base polymers.

mers with defined coordinate structure and cyclic topology. This synthetic strategy features simple operation under mild conditions and high yields. The obtained polymers possess high thermal stability and could be converted to HfC/C materials after pyrolysis at 1600 °C.

EXPERIMENTAL

Materials

Salicylaldehyde (99%, J&K Scientific), *o*-phenylenediamine (99%, J&K Scientific), 3,3'-diaminobenzidine (98%, Energy Chemical), HfCl₄ (98%, Alfa Aesar), Hf(acac)₃ (97%, Alfa Aesar), and all the solvents (>99%) were used as received without further purification. Hf(O^{*i*}Pr)₄ in *n*-propanol was synthesized from HfCl₄, *n*-propanol, and triethylamine according to the literature.^[31] The content of Hf was 31.64% determined gravimetrically as the oxides after calcination at 1000 °C.

Characterization

¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were collected on a Bruker Avance-400 spectrometer. Gel permeation chromatography (GPC) was performed on a Waters system equipped with a HPLC pump, a refractive index detector and three columns thermostated at 40 °C. *N*-methyl pyrrolidone (NMP) added LiBr (0.02 mol/L) was used as eluent at a flow rate of 0.8 mL/min. The calibration was made against linear polystyrene standards in the molecular weight range of 580–591000. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Autoflex III mass spectrometer equipped with a 355 nm laser. α -Cyano-4-hydroxycinnamic acid was used as the matrix and the

spectra were acquired in linear mode. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409 analyzer under nitrogen atmosphere (50 mL/min) at a heating rate of 10 °C/min. X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX 2500 diffractometer with Cu K α radiation and a scan speed of 5 (°)/min. The carbon, oxygen, and nitrogen content of the pyrolyzed ceramics were determined by a LECO CS844 carbon/sulfur analyzer and a LECO ON836 oxygen/nitrogen analyzer. The hafnium content of the pyrolyzed ceramics was determined by a Thermal IRIS Intrepid inductively coupled plasma (ICP) optical emission spectrometer. Raman spectra were recorded on a HORIBA LabRAM HR Evolution Raman spectrometer using a 532 nm laser as the excitation source.

Synthesis of Ligand 1

Salicylaldehyde (26.88 g, 0.22 mol) and *o*-phenylenediamine (10.81 g, 0.10 mol) were added into 100 mL of ethanol. The mixture was refluxed for 2 h and cooled to room temperature. The produced solid was collected by filtration and washed thoroughly with ethanol. The ligand **1** (30.58 g) was obtained as orange solid in 97% yield. ¹H-NMR (400 MHz, DMSO-*d*₆, δ , ppm) 12.93 (s, 2H), 8.94 (s, 2H), 7.67 (dd, *J*=7.6, 1.7 Hz, 2H), 7.50–7.45 (m, 2H), 7.45–7.39 (m, 4H), 7.03–6.92 (m, 4H). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ , ppm) 164.47, 160.85, 142.72, 133.87, 132.90, 128.23, 120.20, 119.96, 119.52, 117.13.

Synthesis of Complex 2

Ligand **1** (3.48 g, 11.0 mmol) and Hf(O^{*i*}Pr)₄ (2.82 g, 5.0 mmol) were added in 60 mL of toluene. The mixture was stirred at room temperature for 4 h. The produced solid was collected by

filtration and washed with 10 mL of toluene. The complex **2** (3.30 g) was obtained as yellow solid in 82% yield. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , δ , ppm) 8.75 (s, 4H), 7.64–7.56 (m, 4H), 7.53–7.46 (m, 4H), 7.33 (d, $J=7.7$ Hz, 4H), 7.00 (t, $J=8.4$ Hz, 4H), 6.43 (t, $J=7.3$ Hz, 4H), 5.77 (d, $J=8.3$ Hz, 4H). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6 , δ , ppm): 164.76, 161.38, 145.96, 135.16, 134.93, 128.47, 123.19, 120.18, 119.71, 116.43.

Synthesis of Monomer **3**

According to the literature,^[32] salicylaldehyde (29.31 g, 0.24 mol) and 3,3'-diaminobenzidine (6.42 g, 0.030 mol) were added in 100 mL of methanol and 100 mL of dichloromethane. The mixture was stirred at room temperature for 24 h. The produced solid was collected by filtration and washed thoroughly with methanol. The monomer **3** (18.39 g) was obtained as orange solid in 97% yield. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , δ , ppm): 12.99 (s, 4H), 9.10 (s, 2H), 9.04 (s, 2H), 7.93 (d, $J=1.8$ Hz, 2H), 7.90 (dd, $J=8.3$, 1.9 Hz, 2H), 7.71 (dd, $J=7.7$, 1.3 Hz, 4H), 7.63 (d, $J=8.3$ Hz, 2H), 7.48–7.40 (m, 4H), 7.04–6.95 (m, 8H). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6 , δ , ppm): 165.27, 164.19, 160.94, 160.90, 143.53, 141.97, 138.95, 133.99, 133.95, 133.05, 132.92, 126.27, 120.60, 120.04, 119.97, 119.58, 119.55, 118.48, 117.17.

General Procedure for the Synthesis of Hf-Schiff Base Polymers

Solution of monomer **3** (1.26 g, 2.0 mmol) in 10 mL of NMP was added in solution of $\text{Hf}(\text{O}^i\text{Pr})_4$ (1.13 g, 2.0 mmol) in 10 mL of tetrahydrofuran (THF) under stirring. The mixture was stirred at 50 °C for 6 h, while capping agents were added after different time if necessary. Thereafter the mixture was concentrated under reduced pressure to remove THF and added in methanol. The precipitation was collected by filtration and washed thoroughly with methanol. The polymer was obtained as yellow solid.

Pyrolysis of the Hf-Schiff Base Polymers

The polymers were pyrolyzed in a graphite furnace under argon atmosphere. The temperature was increased from room temperature to 1500 or 1600 °C at a rate of 5 °C/min and held for 2 h.

RESULTS AND DISCUSSION

At the outset of the investigation, three compounds were chosen as Hf sources to prepare model complexes with ligand **1**. As a result, HfCl_4 and $\text{Hf}(\text{acac})_4$ produced incompletely substituted and complicated products, while only $\text{Hf}(\text{O}^i\text{Pr})_4$

gave desired product in 4 h, referred to as model complex **2**. NMR spectra proved that the two ligands in complex **2** had the same chemical environment (Fig. S2 in the electronic supplementary information, ESI), so the eight-coordinate Hf was in a dodecahedral coordination sphere, similar to the Zr analogue.^[33] In this context, we proceeded to the polymerization of $\text{Hf}(\text{O}^i\text{Pr})_4$ with compound **3**. Bis-salen compound **3** was synthesized from 3,3'-diaminobenzidine with salicylaldehyde, which was then used as a polymerizable monomer with two coordination sites.

The polymerization of $\text{Hf}(\text{O}^i\text{Pr})_4$ with monomer **3** was investigated in detail. Solubility in DMSO, isolated yield, M_n , and PDI of the polymers under different reaction conditions are shown in Table 1. THF/NMP was found to be the optimal solvent (entries P3–P8), where homogenous solution was formed during the entire polymerization process. When THF was used as solvent (entry P1), the product precipitated quickly, which was insoluble in DMSO and partially soluble in NMP. When the reaction was carried out in NMP (entry P2), some gel appeared immediately after the addition of $\text{Hf}(\text{O}^i\text{Pr})_4$, yet the polymer product in the NMP solution was obtained after filtration. Based on these observations, a mixture of equal volume of THF and NMP was chosen as solvent for entry P3. Homogeneous solution was successfully obtained throughout the polymerization, and the reaction process of equivalent $\text{Hf}(\text{O}^i\text{Pr})_4$ and monomer **3** (entry P3) was monitored by GPC at different time (Fig. S4 in ESI). M_n increased from 2900 at 0.5 h to 3800 at 6 h, and the polymerization was almost completed after 4 h.

The poor DMSO solubility of the polymers synthesized from equivalent monomers (Table 1, entries P1–P3) probably came from the residual Hf end groups, which is difficult to characterize directly. Increasing the reaction temperature improved the solubility of the polymer and reduced its PDI value (entry P4). To eliminate the possible Hf end groups, we used an excess amount of monomer **3** (entry P5), and introduced capping agents (entry P6–P8). When 2.0 equiv. of monomer **3** was used to react with $\text{Hf}(\text{O}^i\text{Pr})_4$ (entry P5), soluble oligomer with lower M_n and phenolic hydroxyl end group was obtained at lower yield. When the amount of monomer **3** was obviously insufficient (entry P6), solids appeared in less than 1 h, which dissolved after adding ligand **1** as capping agent, indicating that it was the Hf end groups that reduced the solubility of the polymers. The polymerization of equivalent monomers with end capping of ligand **1** also produced soluble polymers with higher M_n (entry P7). In this context, addi-

Table 1 Optimization of polymerization conditions.

Entry ^a	solvent	<i>T</i> (°C)	Ratio ^b	Capping agents	Soluble in DMSO	Isolated yield	<i>M</i> _n ^c	PDI ^c
P1	THF	25	1.0:1.0	None	No	90	2990 ^d	3.93 ^d
P2	NMP	25	1.0:1.0	None	No	91	3280	2.92
P3	THF/NMP	25	1.0:1.0	None	No	93	3750	3.33
P4	THF/NMP	50	1.0:1.0	None	Yes	92	3600	2.84
P5	THF/NMP	50	1.0:2.0	None	Yes	77	1960	1.64
P6	THF/NMP	50	1.0:0.8	1 ^e	Yes	90	2460	2.64
P7	THF/NMP	50	1.0:1.0	1 ^f	Yes	92	3310	3.28
P8	THF/NMP	50	1.0:1.0	3 ^g	Yes ^h	95	4150	4.22

^a General reaction conditions: $\text{Hf}(\text{O}^i\text{Pr})_4$ (2.0 mmol), monomer **3** (2.0 mmol), solvent (20 mL), 6 h; ^b The molar ratio of $\text{Hf}(\text{O}^i\text{Pr})_4$ to monomer **3**; ^c Determined by GPC with NMP/LiBr (0.02 mol/L) as eluent; ^d Only the soluble part in NMP was determined; ^e Ligand **1** (0.8 equiv.) was added after 1 h; ^f Ligand **1** (0.3 equiv.) was added after 2 h; ^g Monomer **3** (0.1 equiv.) was added after 4 h; ^h The solubility of P8 was 0.02 g/g DMSO and 0.10 g/g NMP.

tional 0.1 equiv. of monomer **3**, used as capping and coupling agent, was added at the late stage of polymerization (entry P8), and the obtained polymer has the higher M_n value as expected. GPC traces of these polymers with complex **2** as reference (Fig. 1) demonstrate that the molecular weight could be adjusted by the ratio of monomers and adding capping agents. The high PDI values were due to the large polymeric unit with relatively low degree of polymerization, which will be discussed in detail below.

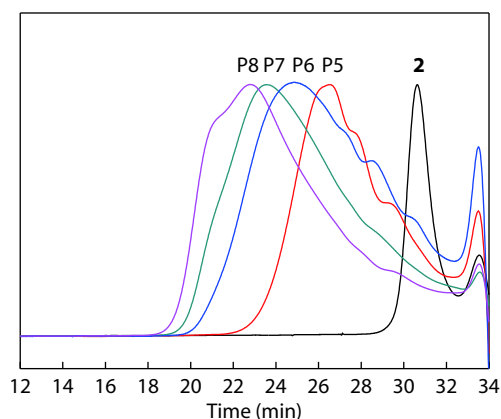


Fig. 1 GPC traces of polymers P5–P8 with complex **2** as reference.

The structures of the obtained Hf-Schiff base polymers were characterized by ^1H - and ^{13}C -NMR spectroscopy as shown in Fig. 2. All signals can be well assigned according to the NMR spectra of monomer **3** and Hf complex **2** (Figs. S2 and S3 in ESI), confirming the expected structural unit of the polymers. According to these spectra, the eight-coordinate Hf center in the polymers had the same coordinate structure as complex **2**, so the polymers should have linear topology. However, the signals of phenolic or other end groups in these polymers (except P5 and P6) are very small which cannot be integrated accurately, even in the case of P8 obtained from

excess monomer **3** (Fig. 2). The molecular weight estimated from the signals of end groups in the NMR results was much higher than that obtained from GPC measurements. Hence, we proposed that most of the polymers have cyclic structures.^[34]

MALDI-TOF-MS results provide another evidence of the cyclic structures. Fig. 3 shows the MALDI-TOF mass spectrum of P8 that identifies the polymer structure and end groups. A set of main peaks corresponded to cyclic polymers without end groups. In addition, there were some weak peaks assigned to linear oligomers and products derived from the elimination of salicyl group. The difference in molecular weight between adjacent peaks was consistent with the molecular weight of the structural unit of the polymers. Other polymers like P7 showed similar cyclic signals with little linear products containing ligand **1** as the end group (Fig. S5 in ESI). Combining the terminal analyses in NMR spectra and the MALDI-TOF-MS results, we conclude that most of these Hf-Schiff base polymers had cyclic topology, which is probably due to the angle between the two coordinate sites in monomer **3**.^[35] The molecular model of the dimer showed cyclic structure without much steric distortion (Fig. S6 in ESI). The easy cyclization of the polymers also explained their relatively low degrees of polymerization and the fact that polymerization conditions had limited influence on their molecular weights, even in the case of capping or coupling.

The Hf-Schiff base polymers had high thermal stability with 95% weight retention over 500 °C under nitrogen. The polymer P8 and the complex **2** gave 68.6% and 67.3% of the residual weight respectively at 1000 °C according to the TGA results (Fig. S7 in ESI). Their thermal stability, owing to the introduction of Hf, was much higher than that of the pure monomer **3**. Pyrolysis of the polymer P8 with complex **2** was conducted under argon atmosphere, producing black ceramic powders. Fig. 4 shows the XRD patterns of the ceramic products. The ceramics obtained from the complex **2** at 1600 °C and the polymer P8 at 1500 °C contained HfO_2 and

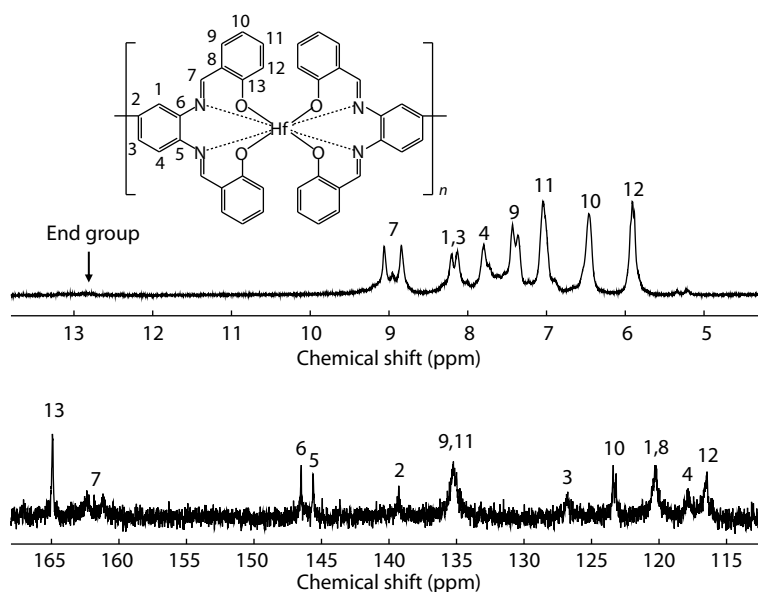


Fig. 2 ^1H -NMR and ^{13}C -NMR spectra of polymer P8 in DMSO-d_6 .

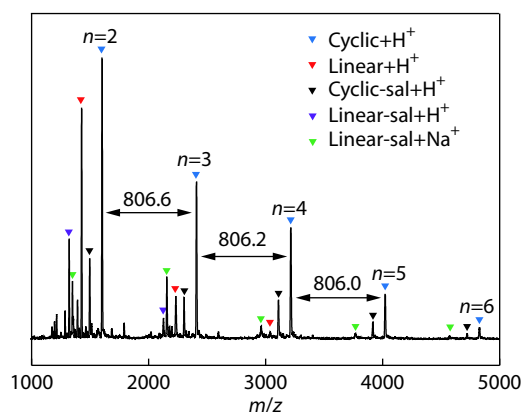


Fig. 3 MALDI-TOF mass spectrum of polymer P8.

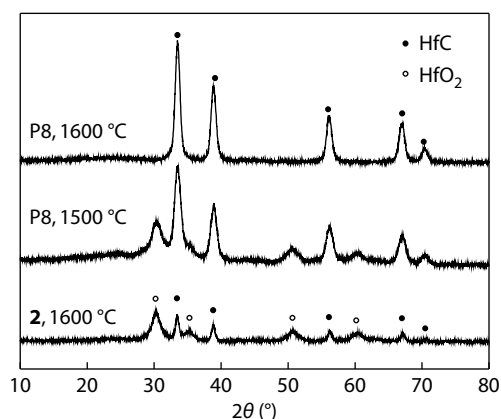


Fig. 4 XRD patterns of the ceramics obtained from polymer P8 and complex **2** at different temperatures.

HfC, while the pyrolyzed product of the polymer P8 at 1600 °C only contained crystalline phase of HfC, indicating that HfO₂ was generated at first and then carbothermally reduced to produce HfC during the pyrolysis process. The different compositions of the ceramics obtained from the polymer P8 and the complex **2** at 1600 °C demonstrated the advantages of Hf-containing polymers as precursors of HfC over small molecular complex. Elemental analysis of the P8 ceramics derived from 1600 °C at 59.4% yield gave an empirical formula of HfC_{28.8}O_{0.4} without nitrogen. The existence of free carbon was further confirmed by Raman spectroscopy (Fig. S8 in ESI). Two bands at 1342 and 1597 cm⁻¹ were attributed to disorder and graphite carbon, respectively. Therefore, the ceramics obtained from the pyrolysis of Hf-Schiff base polymers consisted of crystalline HfC and free carbon.

CONCLUSIONS

In conclusion, we have constructed cyclic Hf-Schiff base polymers from hafnium alkoxide and bis-salen monomer. This facile and efficient approach produced soluble metallopolymers with defined coordinate structures in high yield. Molecular weight and solubility of the polymers could be adjusted through the feed ratio and end capping. The Hf-Schiff base polymers had high thermal stability and could be converted to HfC/C materials after pyrolysis at 1600 °C. The synthetic strategy

described here innovates the toolbox toward preceramic polymers for the fabrications and applications of ultra-high temperature materials.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-021-2566-3>.

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