Supporting Information

Metal-Coordination Crosslinked N-Polyindoles as Recyclable High-Performance Thermosets and Nondestructive Detection for Their Tensile Strength and Glass Transition Temperature

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1. Main materials and measurements

4,4'-Dibromo-2,2'-bipyridine was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification; 4,4'-difluorodiphenyl sulphone was purchased from J & K Technology Co., Ltd., and was purified by recrystallization from alcohol twice before use; p-Anisidine and 4-Bromoanisole were purchased from Tokyo Chemical Industry Co., Ltd. and Adamas Reagent Co., Ltd., respectively, and used without further purification. The rest of materials and reagents were obtained from different commercial sources and used without further purification.

FTIR spectra were recorded on a Nicolt 6700 FTIR spectrometer and a SPECTRUM ONE AUTOIMA FTIR spectrometer. NMR spectra were performed on Bruker AV-400 spectrometer. The glass transition temperature was obtained by DSC curve at a rate of 10 °C/min under flowing nitrogen gas. The thermogravimetric analysis (TGA) was performed on a Setarma TG-92 at a heating rate of 10 °C/min under nitrogen atmosphere. The stress-strain experiments were carried out on a universal testing machine (WDW-100, Changchun research institute of testing machines, Jilin, China) at a strain rate of 2 mm/min and a temperature of 25 °C. The 15×4 mm dumbbell-shaped specimens were prepared by cutting the material out of a polymer membrane, followed by precise

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machining. The stress at break and elongation at break were obtained from the stress-strain experiment with at least three identical specimens and reported as averaged values. ICP-MS experiments were performed on a Perkin Elmer ELAN® DRC II. The X-ray photoelectron spectroscopy (XPS) spectrum of the sample was obtained by using a Perkin-Elmer PHI 5000 C ESCA system equipped with Mg anode. The molecular weights and molecular weight distributions were estimated by gel permeation chromatography (GPC) on a Wyatt DAWNHELEOS using DMF (adding 1% LiBr) as an eluent, testing temperature 50 °C.

2. Synthesis and characterizations of DIN and IHQ

2.1. 4,4'-Diindole-2,2'-bipyridine (DIN):

To a flame-dried reaction vessel were added indole (22.5 mmol), Pd(OAc)₂ (0.75 mmol), K₂CO₃ (45 mmol), and PPh₃ (1.5 mmol). The reaction vessel was fitted with a silicon septum, evacuated, and back-filled with argon and this sequence was repeated three times. toluene (30 mL) and 4,4'- Dibromo-2,2'-bipyridine (7.5 mmol) were then added successively under a stream of argon at room temperature. The resulting mixture was refluxed under argon for 24 h at 110 °C. Afterwards, the resulting solution was allowed to slowly cool down to room temperature, and subsequently poured into cold water, filtered, washed with deionized water several times,

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and then the filtered products were recrystallized from DMF at 153 °C and dried under reduced vacuum to afford compound 4,4'-Diindole-2,2'bipyridine (62% yield). FT-IR spectrum (KBr pellet, cm⁻¹): 3439, 1588, 1467, 1337, 1207, 730; ¹H NMR (400 MHz, CDCl₃): δ = 8.82 (s, 1H), 8.76 (s, 1H), 7.89 (d, *J* = 8 Hz, 1H), 7.76 (d, *J* = 8 Hz, 1H), 7.60 (s, 1H), 7.39 (t, *J*₁ = 8 Hz, *J*₂ = 8 Hz, 1H), 7.29 (d, *J* = 12 Hz, 2H), 6.82 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =157.5, 150.7, 147.8, 135.1, 130.3, 125.8, 123.3, 121.5, 121.4, 117.3, 114.7, 110.9, 106.0 ppm.



Scheme S1. Synthetic route of 4,4'-Diindole-2,2'-bipyridine (DIN).



Figure S1. Characterizations of the 4,4'-Diindole-2,2'-bipyridine (DIN). (A) ¹H NMR, (B) ¹³C NMR, (C) FTIR.

2.2. 4,4'-Dihydroxydiphenylamine (IHQ)

To a three-necked flask (50 mL) equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, 4-Bromoanisole (0.017 mol), p-Anisidine (0.017 mol), Pd₂(dba)₃ (0.175 mmol), BINAP (0.52 mmol), NaOBu-t (4.9 mmol), DMAc (35 mL) were added. The reaction mixture was evacuated and flushed with high-purity argon. The reaction mixture was heated to 100 °C under stirring for 3 h. Next, the reaction mixture was heated to 165 °C under stirring for 5 h. Afterwards, the resulting solution was allowed to slowly cool down to room temperature, and subsequently

poured into cold water, filtered, washed with deionized water several times, and the filtered products were recrystallized from methanol at 65 °C and dried under reduced vacuum to afford 4,4'-dimethoxy aniline (97% yield).

To a stirred solution of 1.5 g of 4,4'-dimethoxy aniline in 22.5 mL of dichloromethane, under a nitrogen atmosphere, was slowly added 7.5 mL of 1.5 mL boron tribromide dissolved in 10 mL of dichloromethane at -80 °C. After the reaction mixture was stirred for 24 h, the reaction mixture was added 25 mL deionized water to afford white solid, filtered, washed with water several times, dried under reduced vacuum, and then purified by column chromatography 100-200 on mesh silica gel with dichloromethane/methanol=20:1 afford 4,4'-Dihydroxydiphenylamine (82%) yield). FT-IR spectrum (KBr pellet, cm⁻¹): 3329, 1669, 1523, 1251, 837; ¹H NMR (400 MHz, DMSO- d_6): δ = 8.76 (s, 2H, -OH), 7.16 (s, 1H, -NH-), 6.76 (d, J = 8 Hz, 4H, phenyl-H), 6.63 (d, J = 8 Hz, 4H, phenyl-H) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ =150.9, 137.4, 118.7, 116.0 ppm.



Scheme S2. Synthetic route of 4,4'-Dihydroxydiphenylamine (IHQ).



Figure S2. Characterizations of the 4,4'-Dihydroxydiphenylamine (IHQ). (A) ¹H NMR, (B) ¹³C NMR, (C) FTIR.

3. Preparation of the N-PIN and M-N-PINs

3.1. N-Polyindole (N-PIN)

To a three-necked flask (25 mL) equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, 4,4'-Dihydroxydiphenylamine (0.9 mmol), 4,4'-Diindole-2,2'-bipyridine (0.1 mmol), 4,4'-difluorodiphenyl sulphone (1 mmol), K₂CO₃ (3 mmol), and N-methylpyrrolidinone (NMP, 2.0 mL) were added. The reaction mixture was evacuated and flushed with high-purity argon. This procedure was repeated three times. The reaction

mixture was heated to 140 °C under stirring for 3 h, and then the temperature was subsequently brought to 185 °C and maintained at this temperature for 6 h. The resulting polymer solution was allowed to slowly cool to room temperature, and subsequently poured into cold water, filtered, washed with water and methanol several times, and then dried at 100 °C under vacuum (97% yield).

The synthesized N-Polyindole was characterized by Fourier transform infrared spectroscopy (FTIR) and ¹H nuclear magnetic resonance (¹H NMR), and the satisfactory analysis results were in good agreement with the proposed structure. In the FTIR spectrum (Fig. S3A), the band around 3380 cm⁻¹ is assigned to the stretching mode of N-H, and the characteristic peak at 1238 cm⁻¹ is assigned to the asymmetric stretching mode of C-O-C. The peak at 1484 cm⁻¹ is the axial C-N stretching. The characteristic peak at 1585 cm⁻¹ is the typical peak for C-C. In the ¹H NMR spectrum (Fig. S3B), the signal at δ 8.3 ppm is assigned to the NH proton, and the signals at around δ 6.9-7.9 ppm are assigned to the aromatic protons. There is no peak at δ 8.7 ppm, which is assigned to the resonance of OH proton of 4,4'-Dihydroxydiphenylamine. It is suggestive of the occurrence of the polymerization.



Figure S3. Characterizations of N-Polyindole (N-PIN). (A) FTIR, (B) ¹H NMR.

3.2. Preparation of N-Polyindoles (N-PIN) film

The polymer N-PIN was dissolved in 2.5 mL NMP to form a 2.5 wt % solution, the polymer solution was filtered and subsequently cast onto a clean, flat glass plate, and dried in a convection oven at 70 °C for 24 h, and then further dried under vacuum at 70 °C for another 24 h to afford the N-PIN polymer film.

3.3. Metal coordination networks (M-N-PINs)

Taking the synthesis of Cu-N-PIN film and other N-PIN+Cu²⁺ films as the example. 0.3125 g N-PIN was dissolved in 12.5 mL NMP to form a 2.5 wt % solution, the polymer solution was filtered. Next, this polymer solution was divided into five equal parts, 2.5 mL for each part. And then, the calculated volume of the Cu²⁺ solution in DMF (15 μ L 0.03 M, 30 μ L 0.03 M, 60 μ L 0.03 M, 12 μ L 0.3 M, 24 μ L 0.3 M) was added into each part of the N-PIN

polymer solution, respectively. The solution was subsequently cast onto five clean, flat glass plates, respectively, and dried in a convection oven at 70 °C for 24 h. Then further dried under vacuum at 70 °C for another 24 h to afford the crosslinking N-PIN+Cu²⁺ polymer films with different content Cu^{2+} ($n_{(Cu}^{2+})$: $n_{(bipyridine)} = 0.0312$, 0.0625, 0.125, 0.25, 0.5). For Cu-N-PIN film, the $n_{(Cu}^{2+})$: $n_{(bipyridine)} = 0.5$. Preparation of Zn-N-PIN, Fe-N-PIN and Co-N-PIN were carried out in the same manner.



Figure S4. Characterizations of Cu-N-PINs. (A) FTIR, (B) UV-vis spectra.

4. Solubility of the N-PINs and M-N-PINs

The solvent resistance is one of the key property of thermosets. In this part, we examined the solubility of N-PIN and M-N-PINs. The solubility was qualitatively determined by immersing an approximately 5 mg solid material in 1 mL of organic solvents at room temperature and 50 °C, respectively. We noted that N-PIN can be soluble in many solvents. In contrast, M-N-PINs are insolube in all solvents tested. The solubility test indicated that the

M-N-PINs are insoluble polymers and provided a solid evidence of crosslinking in bulk M-N-PINs that were removed after adding PPi. The crosslinking is relative to the metal coordination interaction.

Sample	DMAc	DMSO	DMF	NMP	THF	Chloroform
N-PIN	+ +	+ +	+ +	+ +		+-
Cu-N-PIN						
Zn-N-PIN						
Fe-N-PIN						
Co-N-PIN						

Table S1	. Solubility	of N-PIN	and I	M-N-PINs.
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+ +: The polymer can be completely dissolved at room temperature; + – : the polymer can only swelling but insoluble at both room temperature and 50 °C. - -: the polymer was insoluble at both room temperature and 50 °C.

5. The concentration of Cu(II) in the polymers

Table S2.	The concentration of Cu(II) in the crosslinked polymer Cu-N-PIN and the	Э
remaining	Cu(II) after each cycle.	

Sample	Cu-N-PIN	N-PIN N-PIN		N-PIN	N-PIN
Sample		(first cycle)	(second cycle)	(third cycle)	(fourth cycle)
Cu (%)	0.71	0.0020	0.0016	0.0021	0.0017

6. The XPS analysis



Figure S5. XPS analysis on Cu-N-PIN.

7. Molecular weights of original N-PIN and reclaimed N-PIN

Polymer	<i>M</i> n	M _w	<i>M</i> _w / <i>M</i> _n
N-PIN (original)	156200	408600	2.61
N-PIN (first cycle)	156300	415800	2.66
N-PIN (second cycle)	155800	409700	2.63
N-PIN (third cycle)	156000	411800	2.64
N-PIN (fourth cycle)	156500	422500	2.70

Table S3. Molecular weights of original N-PIN and reclaimed N-PIN in each cycle.

8. Thermal stability and mechanical property of the polymers



Figure S6. (A) TG curves of *N*-PIN and *Cu-N*-PIN. (B) TG curves of *Zn-N*-PIN, *Fe-N*-PIN and *Co-N*-PIN. (C) DSC curves of *Zn-N*-PIN, *Fe-N*-PIN and *Co-N*-PIN. (D) DMA curves of *Zn-N*-PIN, *Fe-N*-PIN and *Co-N*-PIN.



Figure S7. Thermal (A) and Mechanical (B) properties of the high performance polymers; PEEK, poly(ether ether ketone)^[1]; PI, polyimide^[2]; PHT, poly(hexahydrotriazine)^[3].

9. References

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