

Supporting information

A succinct *amine-first* strategy suitable for preparing both functional and engineering biopolyamides: Furfurylamine as the sole furan source of bisfuranic diamine/diacid monomers

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S1 Abbreviation list of all compounds and polymers in this study

Table S1 Bisfuranic diamine and its hydrochlorides

Structure	Name	Abbreviation
	(propane-2,2-diylbis(furan-5,2-diyl))dimethanamine	PDFDA
	(butane-2,2-diylbis(furan-5,2-diyl))dimethanamine	BDFDA
	(pentane-3,3-diylbis(furan-5,2-diyl))dimethanamine	PeDFDA
	methyl 4,4-bis(5-(aminomethyl)furan-2-yl)pentanoate	MDFDA
	((1-phenylethane-1,1-diyl)bis(furan-5,2-diyl))dimethanamine	PhDFDA
	((5-chloropentane-2,2-diyl)bis(furan-5,2-diyl))dimethanamine	ChDFDA
	(methylenebis(furan-5,2-diyl))dimethanaminium chloride	MeDFDAc
	(propane-2,2-diylbis(furan-5,2-diyl))dimethanaminium chloride	PDFDAc
	(butane-2,2-diylbis(furan-5,2-diyl))dimethanaminium chloride	BDFDAc
	(pentane-3,3-diylbis(furan-5,2-diyl))dimethanaminium chloride	PeDFDAc
	((5-methoxy-5-oxopentane-2,2-diyl)bis(furan-5,2-diyl))dimethanaminium chloride	MDFDAc
	((1-phenylethane-1,1-diyl)bis(furan-5,2-diyl))dimethanaminium chloride	PhDFDAc
	((4-carboxybutane-2,2-diyl)bis(furan-5,2-diyl))dimethanaminium chloride	CDFDAc
	((5-chloropentane-2,2-diyl)bis(furan-5,2-diyl))dimethanaminium chloride	ChDFDAc

Table S2 Bisfuranic diacid monomers

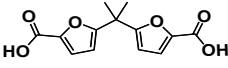
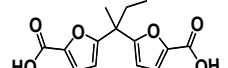
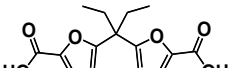
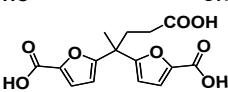
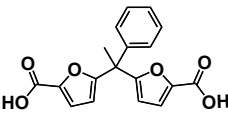
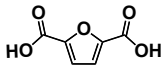
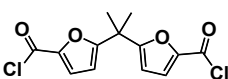
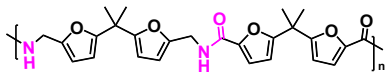
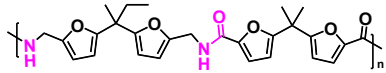
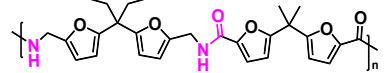
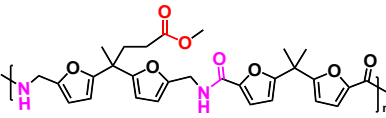
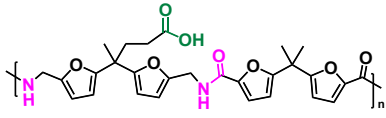
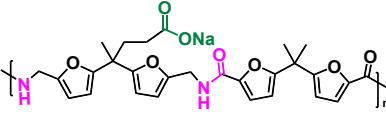
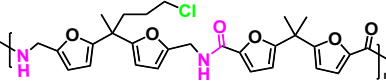
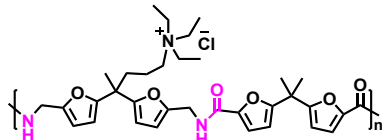
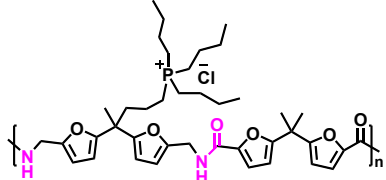
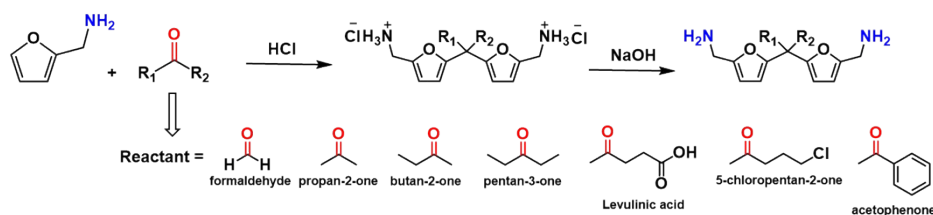
Structure	Name	Abbreviation
	5,5'-(propane-2,2-diyl)bis(furan-2-carboxylic acid)	PDFDC
	5,5'-(butane-2,2-diyl)bis(furan-2-carboxylic acid)	BDFDC
	5,5'-(pentane-3,3-diyl)bis(furan-2-carboxylic acid)	PeDFDC
	5,5'-(4-carboxybutane-2,2-diyl)bis(furan-2-carboxylic acid)	CDFDC
	5,5'-(1-phenylethane-1,1-diyl)bis(furan-2-carboxylic acid)	PhDFDC
	furan-2,5-dicarboxylic acid	FDC
	5,5'-(propane-2,2-diyl)bis(furan-2-carbonyl chloride)	PDFDCc

Table S3 Bisfuranic-based Polyamides

Polymer	Monomer combination	Abbreviation
	PDFDA/ PDFDCc	PA-P
	BDFDA/ PDFDCc	PA-B
	PeDFDA/ PDFDCc	PA-Pe
	PDFDA/ PDFDCc	PA-M
	PDFDA/ PDFDCc	PA-C
		PA-Na
	PDFDA/ PDFDCc	PA-Cl
		PA-T _n
		PA-T _p

S2 Synthesis of bisfuran-based diamine hydrochlorides and diamine monomers

S2-1 Synthesis of bisfuran-based diamine hydrochlorides



Scheme S1 Synthesis of bisfuranic diamines by Mannich condensation

General method for preparing bisfuranic diamine hydrochlorides

A typical synthetic procedure was as follows: 20 mL of hydrochloric acid (37%) was added to a 100 mL round-bottom flask, which was cooled in an ice bath. Furfurylamine (0.1 mol, 9.72 g) was dropped into flask under stirring, and the inner temperature of the flask was maintained below 5 °C during addition. After stirring for 30 min, acetone (0.05 mol, 2.9 g) was added to the flask and the temperature was gradually increased to 45 °C. After stirring at 45 °C overnight, the reaction mixture was brought back to ambient temperature, then the mixture was poured into 200 mL of ethanol. The precipitated product was collected by filtration and dried under vacuum at 50 °C to obtain a white powder in 69% yield (PDFDac).

(Propane-2,2-diylbis(furan-5,2-diyl)) dimethanaminium chloride (PDFDac). ^1H NMR (DMSO- d_6), δ (TMS, ppm): 8.486 (s, 6H), 8.07 (s, 1H), 6.448, 6.440 (d, 2H), 6.176, 6.168 (d, 2H), 4.009 (s, 4H), 1.593 (s, 6H). ^{13}C NMR (DMSO- d_6), δ (TMS, ppm): 159.986, 146.755, 111.205, 106.067, 37.384, 35.476, 26.617.

(Butane-2,2-diylbis(furan-5,2-diyl)) dimethanaminium chloride (BDFDac) was obtained as a white powder in 69% yield. ^1H NMR (DMSO- d_6), δ (TMS, ppm): 8.597 (s, 6H), 6.457, 6.452 (d, 2H), 6.200, 6.192 (d, 2H), 3.996 (s, 4H), 2.028, 2.010, 1.991, 1.974 (dd, 2H), 1.535 (s, 3H), 0.756, 0.737, 0.719 (t, 3H). ^{13}C NMR (DMSO- d_6), δ (TMS, ppm): 159.256, 146.747, 111.107, 106.929, 41.411, 35.511, 31.721, 22.332, 9.189.

(Pentane-3,3-diylbis(furan-5,2-diyl)) dimethanaminium chloride (PeDFDac) was obtained as a white powder in 65% yield. ^1H NMR (DMSO- d_6), δ (TMS, ppm): 8.464 (s, 6H), 6.467, 6.459 (d, 2H), 6.262, 6.254 (d, 2H), 3.997 (s, 4H), 2.021, 2.003, 1.985, 1.967 (dd, 4H), 0.688, 0.670, 0.651 (t, 6H). ^{13}C NMR (DMSO- d_6), δ (TMS, ppm): 158.175, 146.696, 111.082, 108.122, 45.716, 35.551, 27.586, 8.750.

((4-carboxybutane-2,2-diyl)bis(furan-5,2-diyl)) dimethanaminium chloride (CDFDAC) was obtained as a white powder in 62% yield. ^1H NMR (DMSO- d_6), δ (TMS, ppm): 12.141 (s, 1H), 8.515 (s, 6H), 6.464, 6.456 (d, 2H), 6.215, 6.207 (d, 2H), 4.016 (s, 4H), 2.243 (m, 2H), 2.118 (m, 2H), 1.552 (s, 3H). ^{13}C NMR (D_2O), δ (TMS, ppm): 178.15 (-COOH), 159.25, 145.58, 111.91, 107.48, 40.63, 36.05, 33.13, 29.63, 22.20.

((5-chloropentane-2,2-diyl)bis(furan-5,2-diyl)) dimethanaminium chloride (ChDFDAC), a white powder was obtained in 60% yield. ^1H NMR (DMSO- d_6), δ (TMS, ppm): 8.565 (s, 6H), 6.464, 6.456 (d, 2H), 6.213, 6.206 (d, 2H), 4.007 (s, 4H), 3.632, 3.616, 3.600 (t, 2H), 2.080 (m, 4H), 1.566 (s, 3H). ^{13}C NMR (DMSO- d_6), δ (TMS, ppm): 158.853, 146.927, 111.161, 106.991, 46.081, 40.731, 36.359, 35.452, 27.940, 23.021.

((1-phenylethane-1,1-diyl)bis(furan-5,2-diyl)) dimethanaminium chloride (PhDFDAC), a light-yellow powder was obtained in 49% yield. ^1H NMR (DMSO- d_6), δ (TMS, ppm): 8.609 (s, 6H), 7.305-7.043 (m, 5H, Ph-H), 6.530, 6.524 (d, 2H), 6.213, 6.207 (d, 2H), 4.023 (s, 4H), 1.959 (s, 3H). ^{13}C NMR (DMSO- d_6), δ (TMS, ppm): 158.208, 147.561, 145.020, 128.726, 127.272, 172.194, 111.289, 108.890, 46.317, 35.465, 26.189.

((5-methoxy-5-oxopentane-2,2-diyl)bis(furan-5,2-diyl)) dimethanaminium chloride (MDFDAC), a light yellow powder was obtained in 98% yield. ^1H NMR (DMSO- d_6), δ (TMS, ppm): 8.537 (s, 6H), 6.465, 6.457 (d, 2H), 6.222, 6.214 (d, 2H), 4.018, 4.007 (d, 4H), 2.214-2.194 (m, 4H), 1.552 (s, 3H). ^{13}C NMR (D_2O), δ (TMS, ppm): 176.71 (COOCH_3), 159.16, 145.55, 111.78, 107.37, 52.43, 40.54, 35.90, 32.97, 29.45, 21.19.

methylenebis(furan-5,2-diyl)) dimethanaminium chloride (MeDFDAC)^[1], ^1H NMR (DMSO- d_6), δ (TMS, ppm): 8.5575 (s, 6H), 6.488, 6.480 (d, 2H), 6.249, 6.241 (d, 2H), 4.037 (s, 2H), 4.009 (s, 4H).

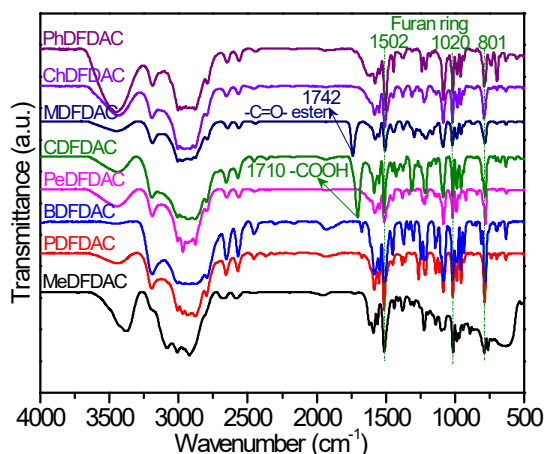


Fig. S1 FT-IR spectra of bisfurannic diamine hydrochlorides

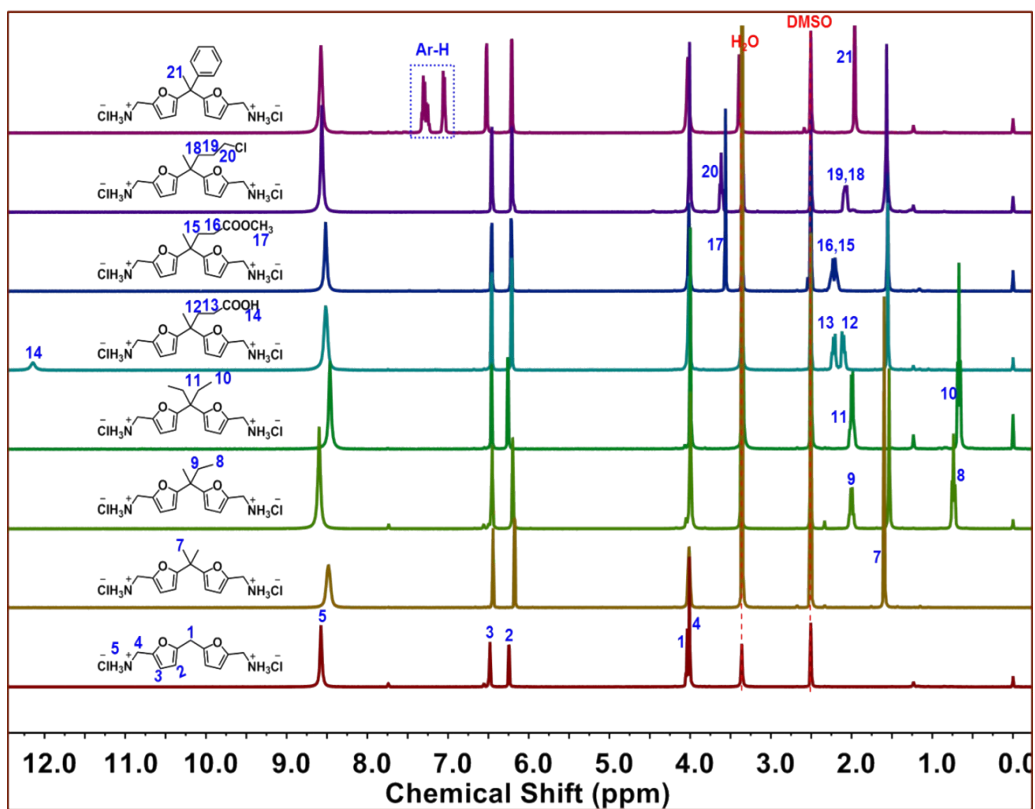


Fig. S2 ^1H NMR of bisfurannic diamine hydrochlorides

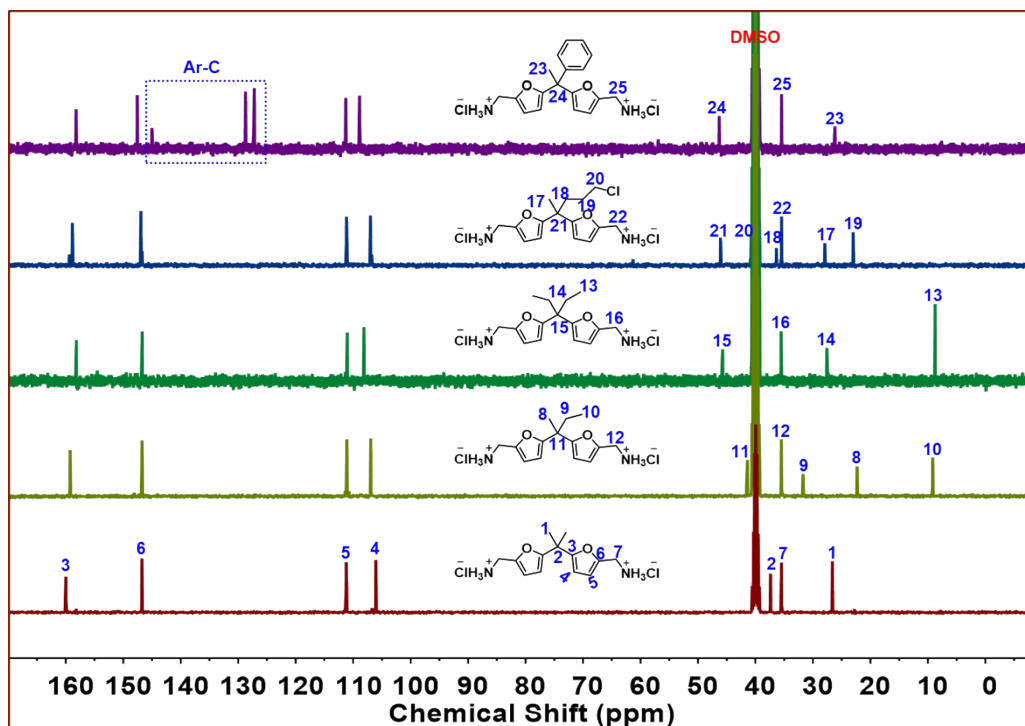


Fig. S3 ^{13}C NMR of bisfurannic diamine hydrochlorides

S2-2 Synthesis, characterization of bisfuranic diamine monomers

General method: 10.0 g of bisfuranic diamine hydrochloride was dissolved in 80 mL distilled water. Under stirring, 20 mL of NaOH solution (2.0 eq) was added to the diamine hydrochloride solution. Diamine was extracted using dichloromethane (DCM, 20 mL × 3). The combined organic layer was dried overnight over anhydrous Na₂SO₄ and then concentrated to obtain a liquid product with a near quantitative yield.

(propane-2,2-diylbis(furan-5,2-diyl))dimethanamine (PDFDA): ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.070, 6.062 (d, 2H), 5.981, 5.974 (d, 2H), 3.594 (s, 4H), 2.034 (s, 4H, -NH₂), 1.593 (s, 6H). ¹³C NMR (DMSO-*d*₆), δ (TMS, ppm): 158.419, 156.360, 105.721, 105.034, 39.276, 37.161, 26.733.

(butane-2,2-diylbis(furan-5,2-diyl))dimethanamine (BDFDA): ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.063, 6.057 (d, 2H), 6.002, 5.994 (d, 2H), 3.583 (s, 4H), 1.971, 1.952, 1.934, 1.915 (dd, 2H), 1.473 (s, 3H), 0.733, 0.715, 0.696 (t, 3H). ¹³C NMR (DMSO-*d*₆), δ (TMS, ppm): 157.567, 156.571, 105.883, 105.499, 41.158, 39.372, 31.701, 22.546, 9.172.

(pentane-3,3-diylbis(furan-5,2-diyl))dimethanamine (PeDFDA): ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.079, 6.072 (d, 2H), 6.068, 6.060 (d, 2H), 3.576 (s, 4H), 1.960, 1.942, 1.924, 1.905 (dd, 4H), 1.668 (s, 4H, -NH₂), 0.663, 0.645, 0.627 (t, 6H). ¹³C NMR (DMSO-*d*₆), δ (TMS, ppm): 156.508, 156.394, 107.067, 105.408, 45.406, 39.367, 27.507, 8.700.

methyl 4,4-bis(5-(aminomethyl)furan-2-yl)pentanoate (MDFDA): ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.079, 6.071 (d, 2H), 6.027, 6.019 (d, 2H), 3.589 (s, 4H), 3.546 (s, 3H), 2.198-2.157 (m, 4H), 1.669 (s, 4H, -NH₂), 1.490 (s, 6H). ¹³C NMR (DMSO-*d*₆), δ (TMS, ppm): 173.522 (COOCH₃), 156.914, 156.733, 106.221, 105.563, 51.785, 40.384, 39.347, 33.991, 39.594, 23.054.

((5-chloropentane-2,2-diyl)bis(furan-5,2-diyl))dimethanamine (ChDFDA): ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.080, 6.073 (d, 2H), 6.015, 6.007 (d, 2H), 3.594 (s, 4H), 3.600, 3.583, 3.566 (t, 2H), 2.605 (s, 4H, -NH₂), 2.040, 1.549 (m, 4H), 1.502 (s, 3H). ¹³C NMR (DMSO-*d*₆), δ (TMS, ppm): 157.569, 154.624, 106.793, 106.204, 46.032, 40.552, 38.512, 36.363, 28.051, 23.218.

((1-phenylethane-1,1-diyl)bis(furan-5,2-diyl))dimethanamine (PhDFDA): ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 7.218-6.985 (m, 5H, Ph-H), 5.993, 5.985 (d, 2H), 5.843, 5.835 (d, 2H), 3.685 (s, 4H), 1.920 (s, 3H), 1.697 (s, 4H, -NH₂). ¹³C NMR (CDCl₃), δ (TMS, ppm): 157.296, 155.890, 145.271, 128.115, 126.997, 126.690, 107.713, 105.536, 46.405, 39.376, 25.774.

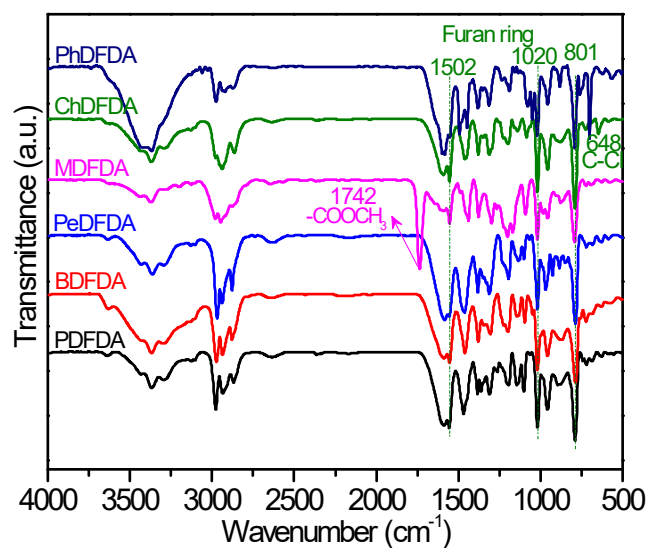


Fig. S4 FT-IR spectra of bisfuranic diamine monomers

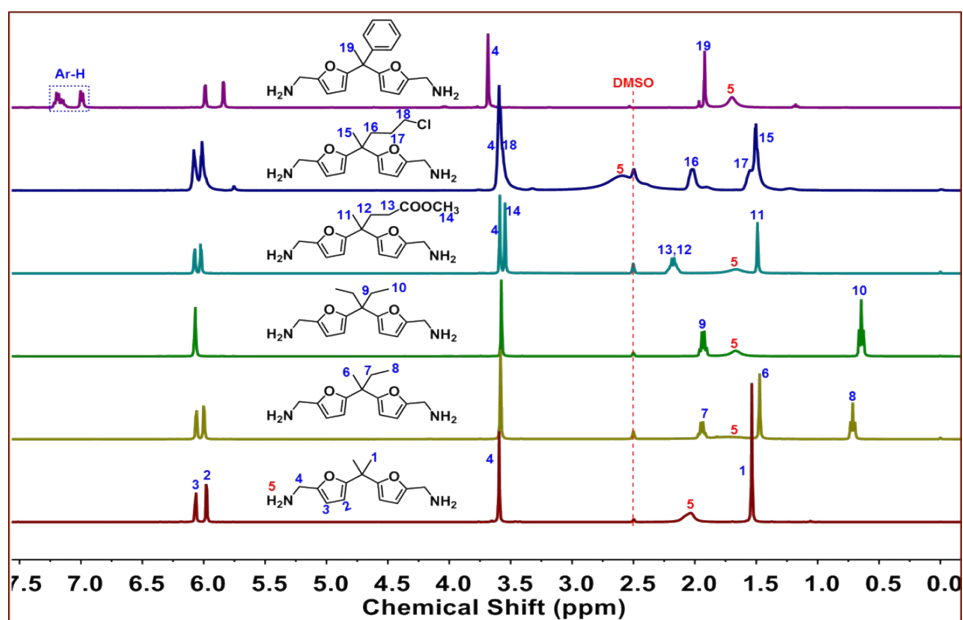


Fig. S5 ¹H NMR spectra of bisfuranic diamine monomers

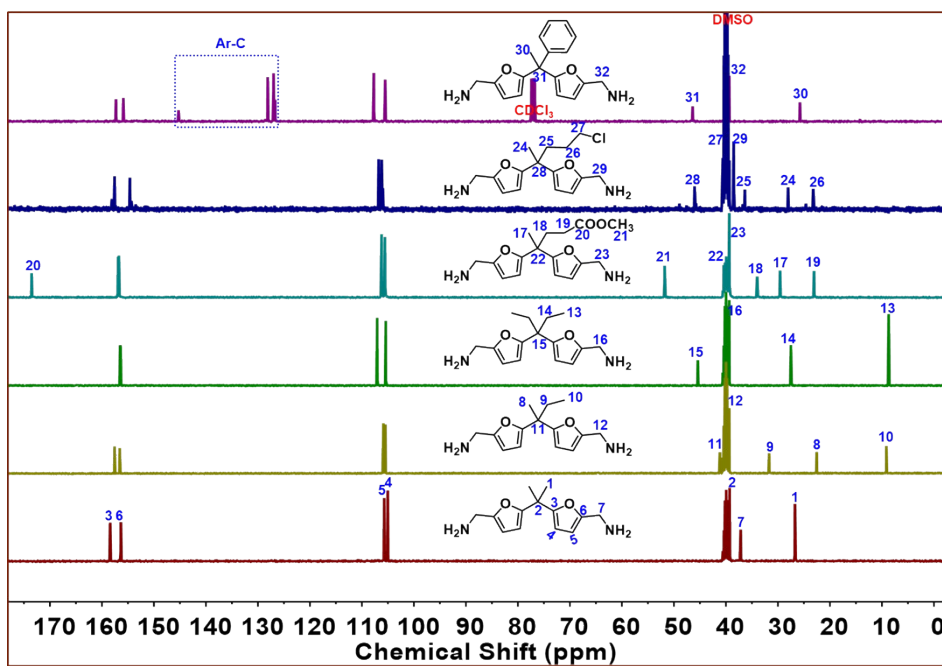
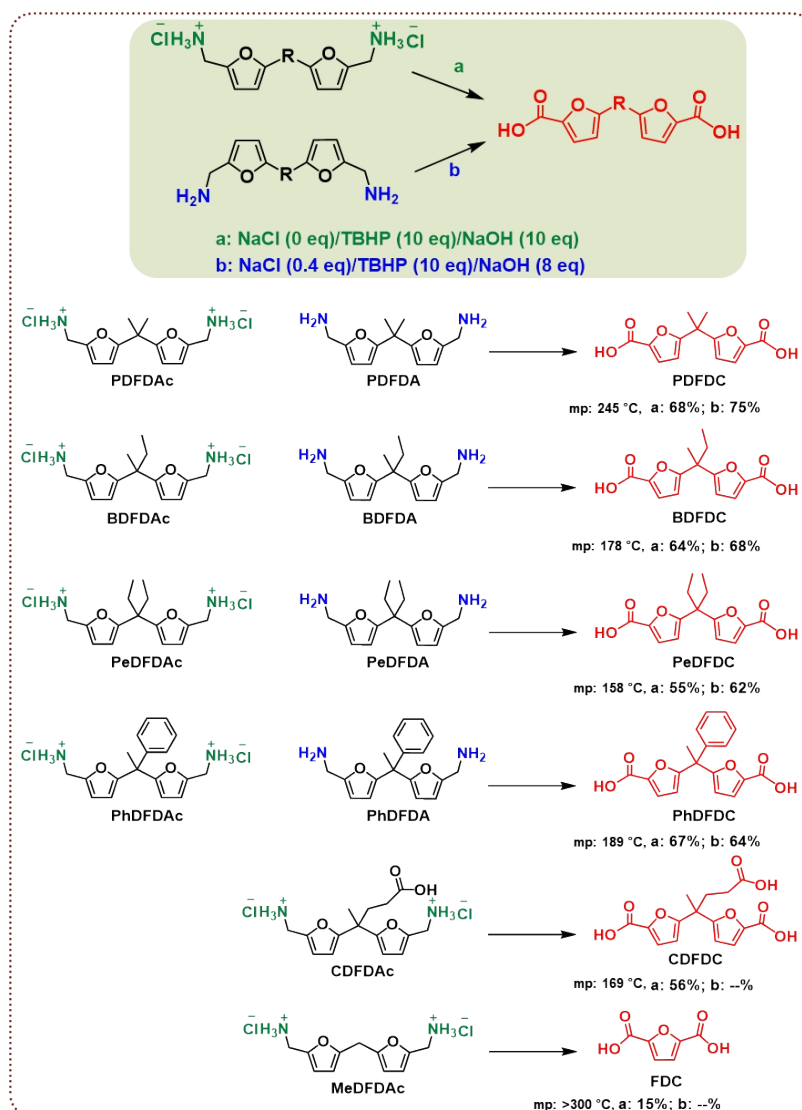


Fig. S6 ^{13}C NMR spectra of bisfuranic diamine monomers

S3 Preparation of bisfuranic diacid monomers via THBP/NaCl oxidative reaction and structure characterization



Scheme S2 Synthesis of bisfuran-based diacid

5,5' - (propane-2,2-diyl) bis (furan-2-carboxylic acid) (PDFDC), yield 75%, M.p 245 °C. MS (*m/z*): [M+Na]⁺: 287.06, calculated: 264.23. ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 13.015 (s, 2H, -COOH), 7.153, 7.144, 6.435, 6.425 (dd, 4H, =CH-CH=), 1.647 (s, 6H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 162.952, 159.666, 144.308, 119.065, 107.990, 37.996, 26.100.

5,5'-(butane-2,2-diyl)bis(furan-2-carboxylic acid) (BDFDC), yield 68%, M.p 178 °C. MS (*m/z*): [M+Na]⁺: 301.07, calculated: 278.26. ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 13.025 (s, 2H, -COOH), 7.163, 7.154, 6.454, 6.446 (dd, 4H, =CH-CH=), 2.096, 2.078, 2.059, 2.041 (m, 2H, -CH₂-), 1.593 (s, 3H, -CH₃), 0.764, 0.745, 0.727 (t, 3H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 162.227, 159.667, 144.327, 118.999, 108.834, 42.065, 31.250, 22.065, 8.939.

5,5'-(pentane-3,3-diyl)bis(furan-2-carboxylic acid) (PeDFDC), yield 62%, M.p 158 °C. MS (*m/z*):

[M+Na]⁺: 315.08, calculated: 292.29. ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 13.016 (2H, -COOH), 7.176, 7.167, 6.519, 6.510 (4H, =CH-CH=), 2.088, 2.070, 2.052, 2.034 (4H, -CH₂-), 0.682, 0.664, 0.645 (6H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 161.280, 159.678, 144.304, 118.900, 109.925, 46.293, 27.043, 8.431.

5,5'-(1-phenylethane-1,1-diyl)bis(furan-2-carboxylic acid) (*PhDFDC*), yield 64%, M.p 189 °C. MS (*m/z*): [M+Na]⁺: 349.07, calculated: 326.08. ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 13.099 (2H, -COOH), 7.378-7.319 (3H, Ph-H), 7.057, 7.038 (2H, Ph-H), 7.206, 7.197, 6.337, 6.329 (4H, =CH-CH=), 2.035 (3H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 161.096, 159.651, 144.888, 143.332, 128.999, 127.762, 127.101, 118.934, 110.522, 46.950, 25.745.

Furan-2,5-dicarboxylic acid, (*FDC*), yield 15%, M.p>300 °C. MS (*m/z*): [M+H]⁺: 157.01, calculated: 156.09. ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 13.632 (2H, -COOH), 7.299 (4H, =CH-CH=); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 159.348, 147.471, 118.874

5,5'-(4-carboxybutane-2,2-diyl)bis(furan-2-carboxylic acid), (*CDFDC*), yield 56%, M.p 169 °C. MS (*m/z*): [M+Na]⁺: 345.06, calculated: 322.07. ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 12.758 (3H, -COOH), 7.170, 7.161, 6.469, 6.461 (4H, =CH-CH=), 2.317, 2.299, 2.278, 2.119, 2.098, 2.080 (4H, -CH₂-CH₂-), 1.613 (3H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 174.210, 161.539, 159.635, 144.502, 118.997, 108.971, 41.265, 33.381, 29.500, 22.517.

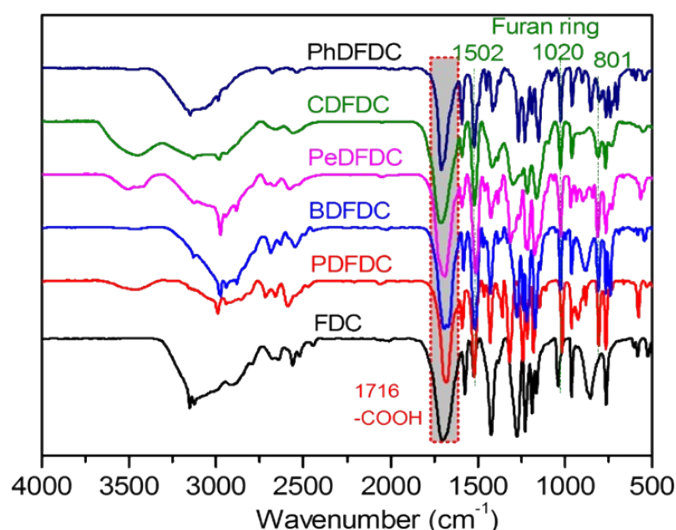
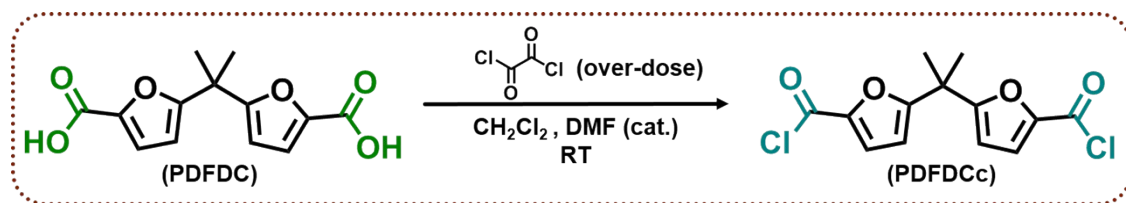


Fig. S7 FT-IR spectra of bisfuranic diacid monomers

S4 Preparation and characterization of 5,5'-(propane-2,2-diyl)di(furan-2-carbonyl chloride) (PDFDCc)



Scheme S3 Synthetic route of PDFDCc

Experimental detail: Into dried a 250 mL flask, was added 100.0 mL of dry dichloromethane and 0.15 mL of dry DMF. Under well-stirring 8.0 mL (excess) oxalyl chloride was added slowly, then add 13.20 g (0.05 mol) of a 5,5'-(propane-2,2-diyl)di(furan-2-carboxylic acid) (PDFDC) was added into the stirring mixture. The reaction mixture was stirred at room temperature with protection of argon gas. The solid the solid slowly dissolved and a yellow clear solution was obtained. After finishing the reaction, the dichloromethane was removed under vacuum at room temperature. The remaining crude product was dissolved in dried n-hexane and then filtered while hot to remove the insoluble impurity. The desired PDFDCc precipitated gradually from the hexane solution as crystals when the temperature dropped down. The product was collected by filtration, the remaining solvent was removed under vacuum dried to obtain 8.91 g of yellowish powder.

5,5'-(propane-2,2-diyl) bis(furan-2-carbonyl chloride) (PDFDCc) a yield of 60%. ¹H NMR (CDCl₃, TMS, δ ppm): 7.372, 7.362, 6.317, 6.307 (4H, =CH-CH=), 1.701 (6H, -CH₃); ¹³C NMR (CDCl₃, TMS, δ ppm): 166.221, 154.968, 144.998, 126.134, 109.318, 38.840, 25.599.

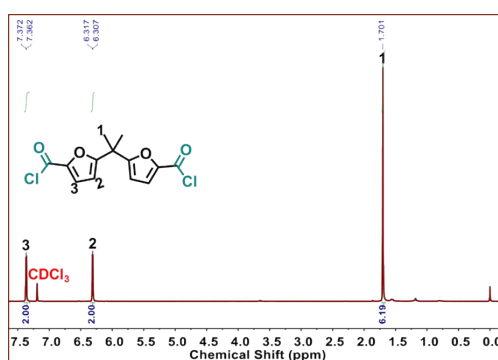


Fig. S8 ¹H NMR spectrum of PDFDCc

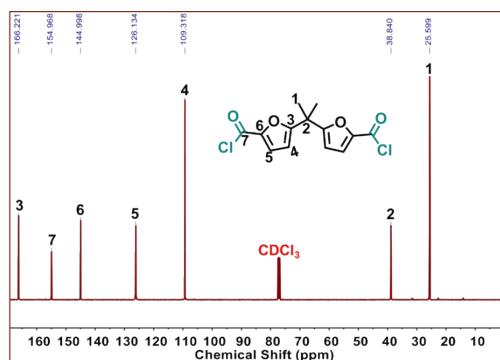
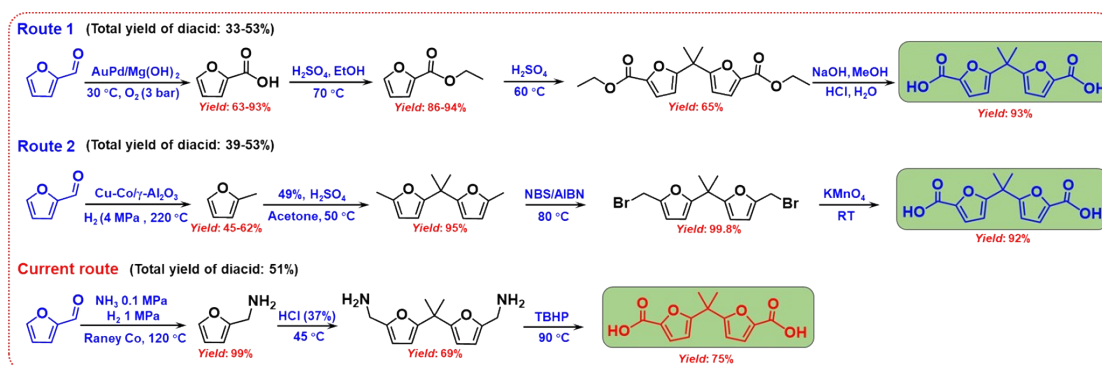


Fig. S9 ¹³C NMR spectrum of PDFDCc

S5 Summary the preparation methods of bisfuranic diacid in literatures

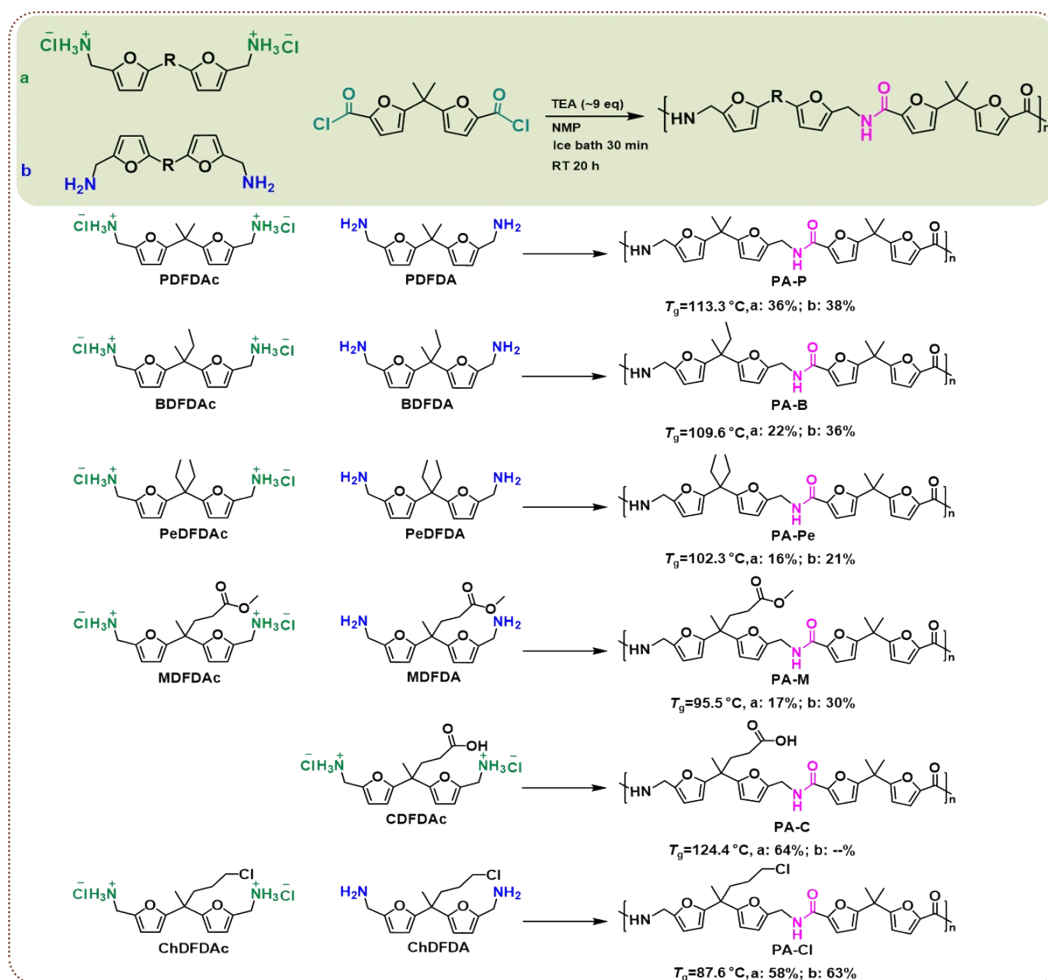


Scheme S4 The reported methods of preparing bisfuranic diacid monomers and their comparison with current one

Table S4 Synthetic routes of bisfuranic diacid

Route 1	
1.1	$\text{O}_2/\text{H}_2\text{O}$, AuPd/Mg(OH) ₂ , 110 °C [2]
1.2	H_2SO_4 , Ethanol, 70 °C, 3 h [3]
1.3	H_2SO_4 , Acetone, 60 °C [4]
1.4	NaOH/ H_2O / CH_3OH , HCl/ H_2O [5]
Route 2	
2.1	① Cu-Co/ γ - Al_2O_3 , 220 °C and 4 MPa H_2 [6] ② Cu- SiO_2 , 270 °C and 5 vol% H_2/N_2 gas mixture [7] ③ Ru/ RuO_2/C , alcohols [8]
2.2	① 49% H_2SO_4 , Acetone, 50 °C, 20 h [9] ② Nafion-212 resin, 50 °C [10] ③ Hydrochar (HC) was functionalized with sulfonic (SHC), 50 °C 5 h [11]
2.3	Cyclohexane, NBS, and AIBN, N_2 , 80 °C for 5 h [9]
2.4	KMnO_4 , NaOH, H_2O /dioxane, RT for 2 h [9]
Route 3	
3.1	Ammonia 0.1 MPa, H_2 1 MPa, Roney Co, 120 °C
3.2	37% HCl, Acetone, 45 °C, 4 h
3.3	NaOH/ H_2O This work
3.3.1	TBHP, NaOH/ H_2O , 90 °C, 20 h
3.4	TBHP, NaOH/ H_2O , NaCl, 90 °C, 20 h

S6 Polycondensation and structure characterization of biopolyamides



Scheme S5 Polycondensation of various kinds of bisfuranic diamine monomers with PDFDCc

Polymerization details: All glassware and solvents used in polymerization were thoroughly dried before use. Taking PA-M preparation as an example, 0.9185 g (0.003 mol) of MDFDA was added to a 100 mL flask containing 4.0 mL NMP and 4.0 mL TEA, and then 0.9034 g (0.003 mol) PDFDCc in 8.0 mL NMP was added to a flask under stirring. The reaction was performed for 20 h at room temperature under an argon atmosphere. At the end of polymerization, the reaction mixture was poured into an excess amount of deionized water to obtain a white solid. The crude product was washed used with deionized water (3 times), acetone (3 times), and then vacuum-dried for 24 h at 60 °C, yielding 0.59 g of PA-M (36% yield).

PA-P: ^1H NMR (DMSO- d_6 , TMS, δ ppm): 8.718 (2H, -NH-), 7.030-5.994 (8H, =CH-CH=), 4.305 (4H, -CH₂-), 1.638 (6H, -CH₃), 1.510 (6H, -CH₃); ^{13}C NMR (DMSO- d_6 , TMS, δ ppm): 161.246, 158.732, 158.052 (-C(O)NH-), 151.370, 146.865, 114.740, 107.739, 107.451, 105.507, 37.888, 37.200, 35.921, 26.649, 26.124.

PA-B: ^1H NMR (DMSO- d_6 , TMS, δ ppm): 8.715 (2H, -NH-), 7.028-6.016 (8H, =CH-CH=), 4.307 (4H, -

CH₂-), 1.920, 1.902 (2H, -CH₂-), 1.638 (6H, -CH₃), 1.451 (3H, -CH₃), 0.674 (3H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 161.229, 158.051 (-C(O)NH-), 157.941, 151.358, 146.893, 114.703, 107.595, 107.434, 106.342, 41.215, 37.890, 35.923, 31.150, 26.107, 22.501, 9.073.

PA-Pe: ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 8.697 (2H, -NH-), 7.017-6.080 (8H, =CH-CH=), 4.299 (4H, -CH₂-), 1.908, 1.890 (4H, -(CH₂)₂-), 1.634 (6H, -CH₃), 0.599 (6H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 161.201, 158.038 (-C(O)NH-), 156.792, 151.316, 146.905, 114.663, 107.471, 107.417, 45.482, 37.886, 35.925, 27.687, 26.089, 8.628.

PA-M: ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 8.712 (2H, -NH-), 7.026-6.044 (8H, =CH-CH=), 4.311 (4H, -CH₂-), 3.481 (3H, -COOCH₃), 2.175, 2.150 (4H, -CH₂-CH₂-), 1.639 (6H, -CH₃), 1.474 (3H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 173.378 (-COOCH₃), 161.242, 158.055 (-C(O)NH-), 157.111, 151.659, 146.867, 114.718, 107.696, 107.442, 106.679, 51.743, 48.941, 37.902, 35.924, 34.025, 29.482, 26.117, 23.038.

PA-C: ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 12.484 (H, -COOH), 8.727 (2H, -NH-), 7.026-6.032 (8H, =CH-CH=), 4.306 (4H, -CH₂-), 2.156- 1.918 (4H, -CH₂-CH₂-), 1.643 (6H, -CH₃), 1.465 (3H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 174.623 (-COOH), 161.274, 158.103 (-C(O)NH-), 157.327, 151.664, 146.861, 114.772, 107.706, 106.583, 106.477, 40.472, 37.923, 35.959, 34.094, 29.765, 26.137, 22.876.

PA-CI: ¹H NMR (DMSO-*d*₆, TMS, δ ppm): 8.723 (2H, -NH-), 7.028-6.037 (8H, =CH-CH=), 4.304 (4H, -CH₂-), 3.489 (2H, -CH₂-), 2.041-1.980 (4H, -CH₂-CH₂-), 1.642 (6H, -CH₃), 1.488 (3H, -CH₃); ¹³C NMR (DMSO-*d*₆, TMS, δ ppm): 161.246, 158.078 (-C(O)NH-), 157.576, 151.511, 146.861, 114.738, 107.685, 107.432, 106.428, 45.821, 40.573, 37.888, 36.397 35.908, 29.994, 26.112, 23.242.

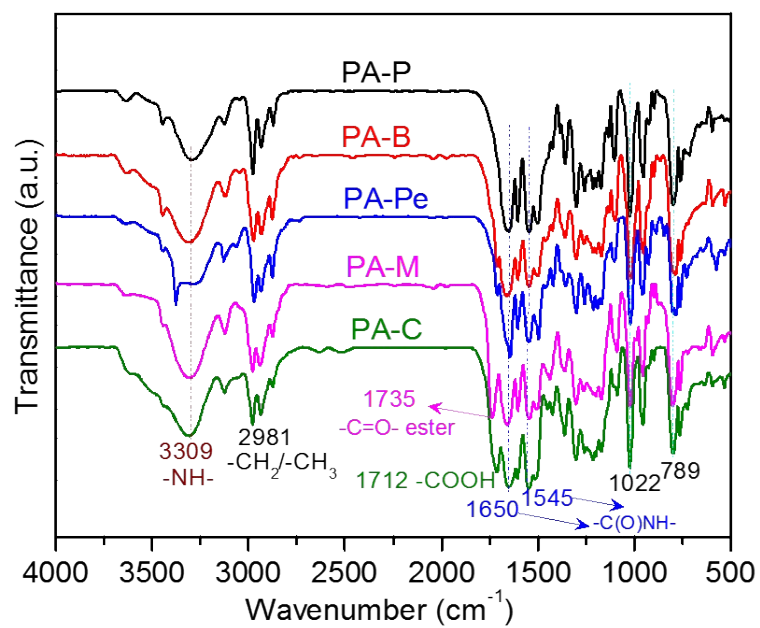


Fig. S10 FTIR spectra of all bisfuran-based bioPAs

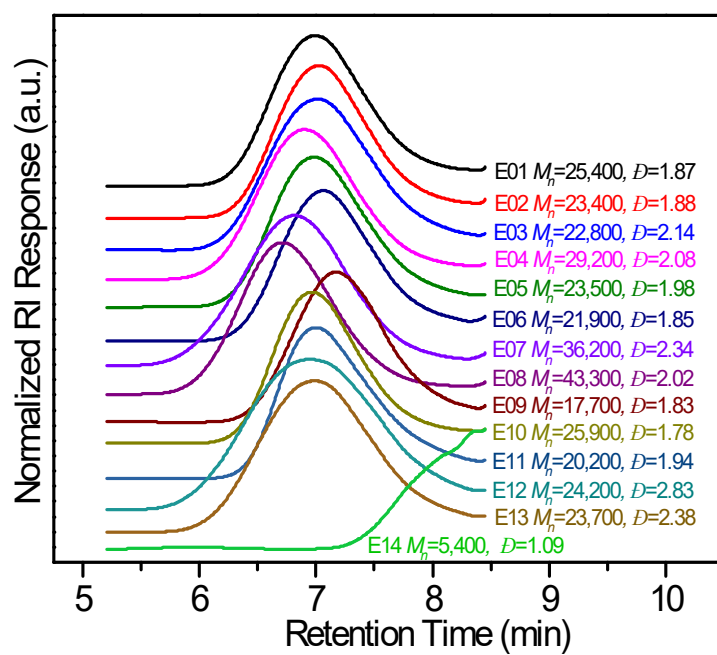


Fig. S11 GPC curves of purified bioPAs

S7 NMR studied the Diels -Alder reaction characters of PA-P with BMI

Screening DA reaction conditions

Into 1.0 mL DMSO-d₆ in NMR tube was added 0.03 g of polymer PA-P, 0.02 g BMI (N,N'-4,4'-diphenylmethane-bismaleimide). The mixture was left at ambient temperature for 20 h to obtain a clear solution, and the ¹H NMR spectrum of the mixture was recorded as NMR20. The tube was then heated at 50 °C and the NMR signal was recorded at a fixed time span.

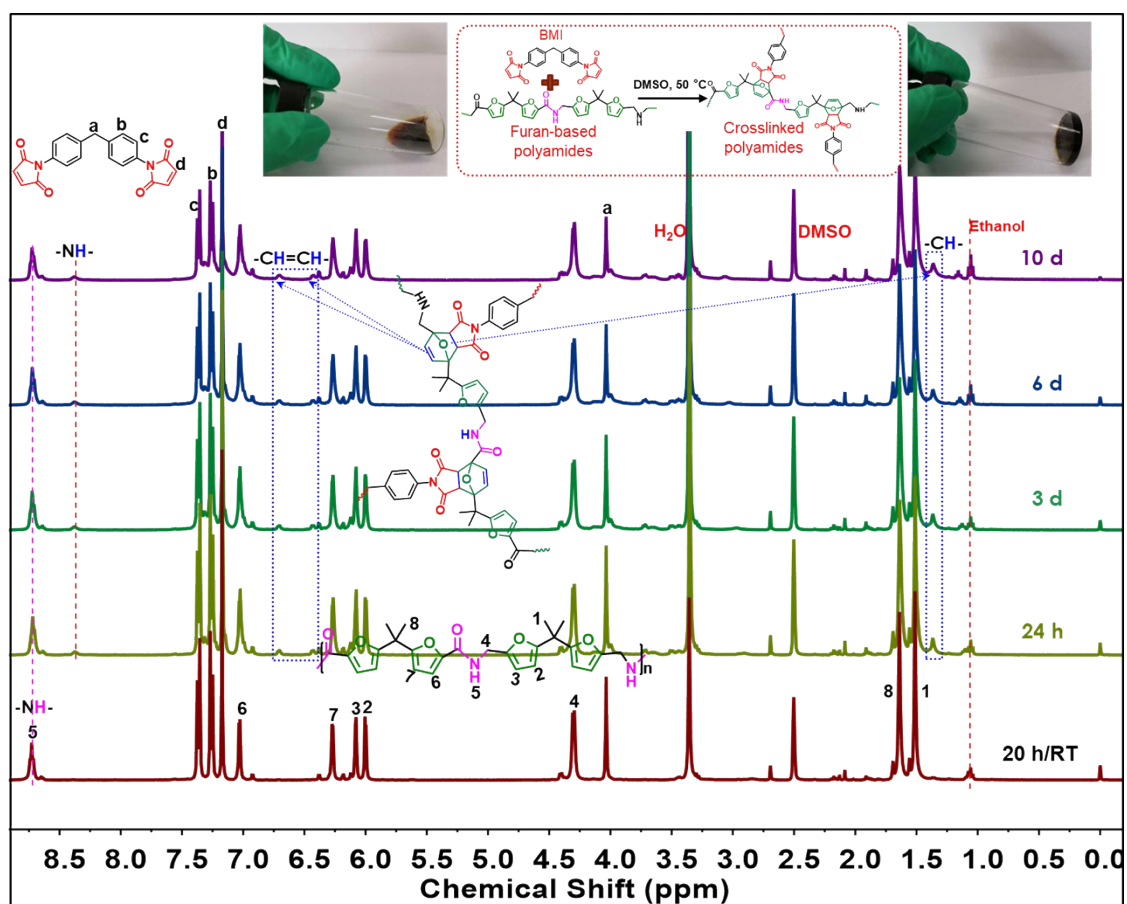
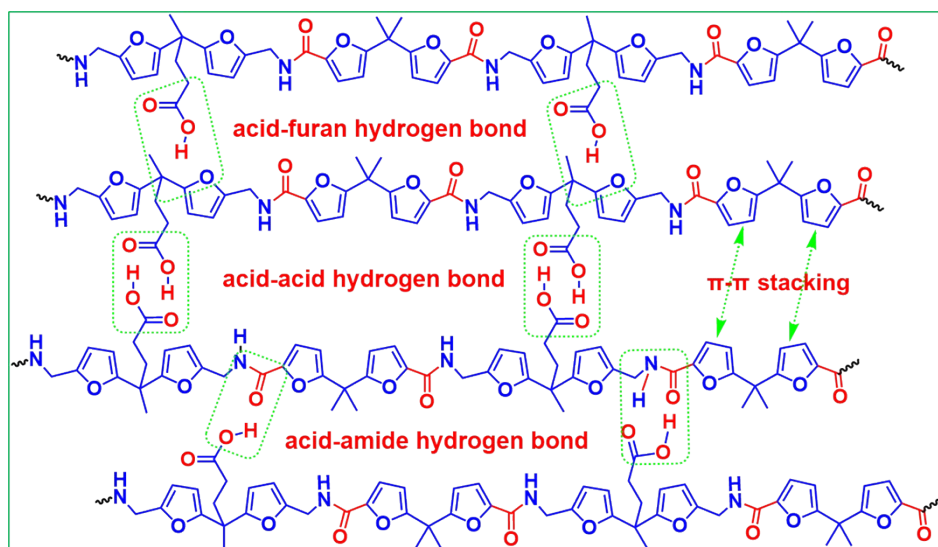


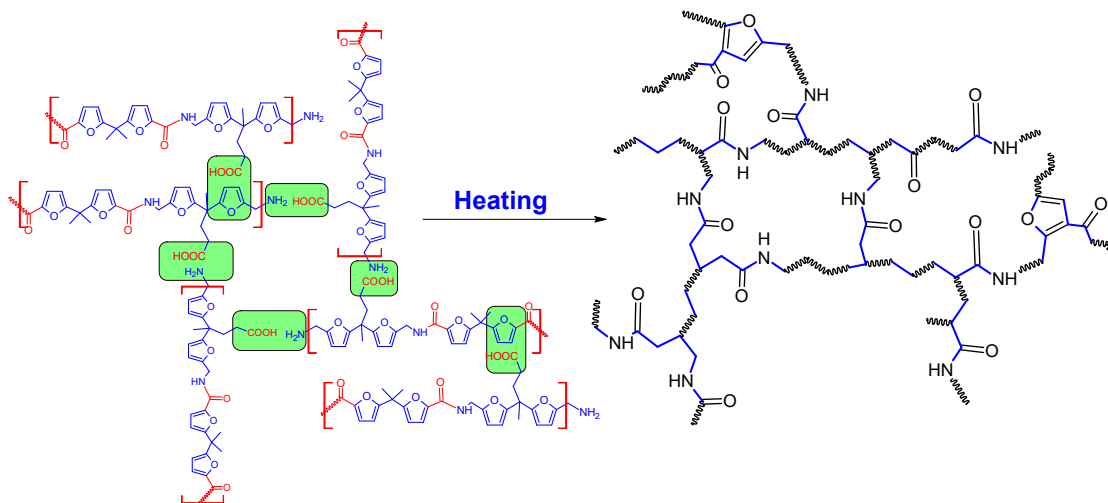
Fig. S12 ¹H NMR spectra of DA reaction mixture at different reaction time under 50 °C

S8 Proposed interchain hydrogen bond interactions and π - π stacking among acid-functionalized polyamides (PA-C)



Scheme S6 H-bond formation among pendent acid groups, furan oxygen, amide group and furan-furan π - π stacking

S9 Proposed crosslinking reaction mechanism of acid-functionalized PA (PA-C) under high temperature range



Scheme S7 The reaction between pendent acid groups of PA-C with end amine groups and furan ring under heating

S10 Hydrolytic resistance of PA-P

Description of testing method: 0.2 g PA-P powder was added to 20 mL of 5% NaOH solution and stirred for 15 days at 80 °C. The undissolved polymer was collected via filtration and washed with water. The dried samples were subjected to GPC and FTIR tests.

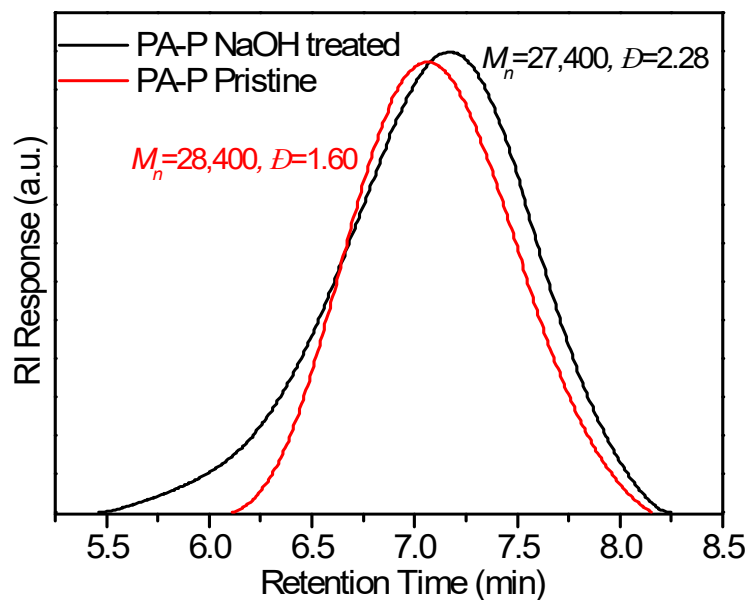


Fig. S13 GPC curves of PA-P and its hydrolytic product

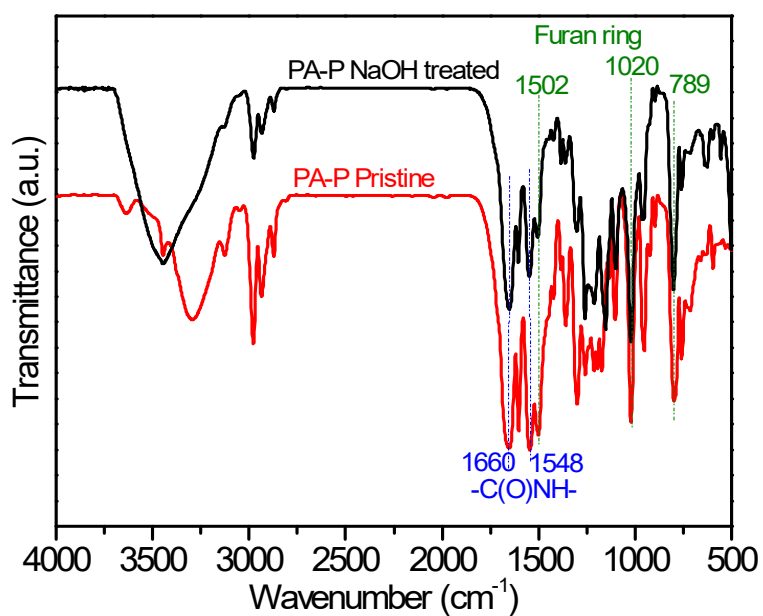
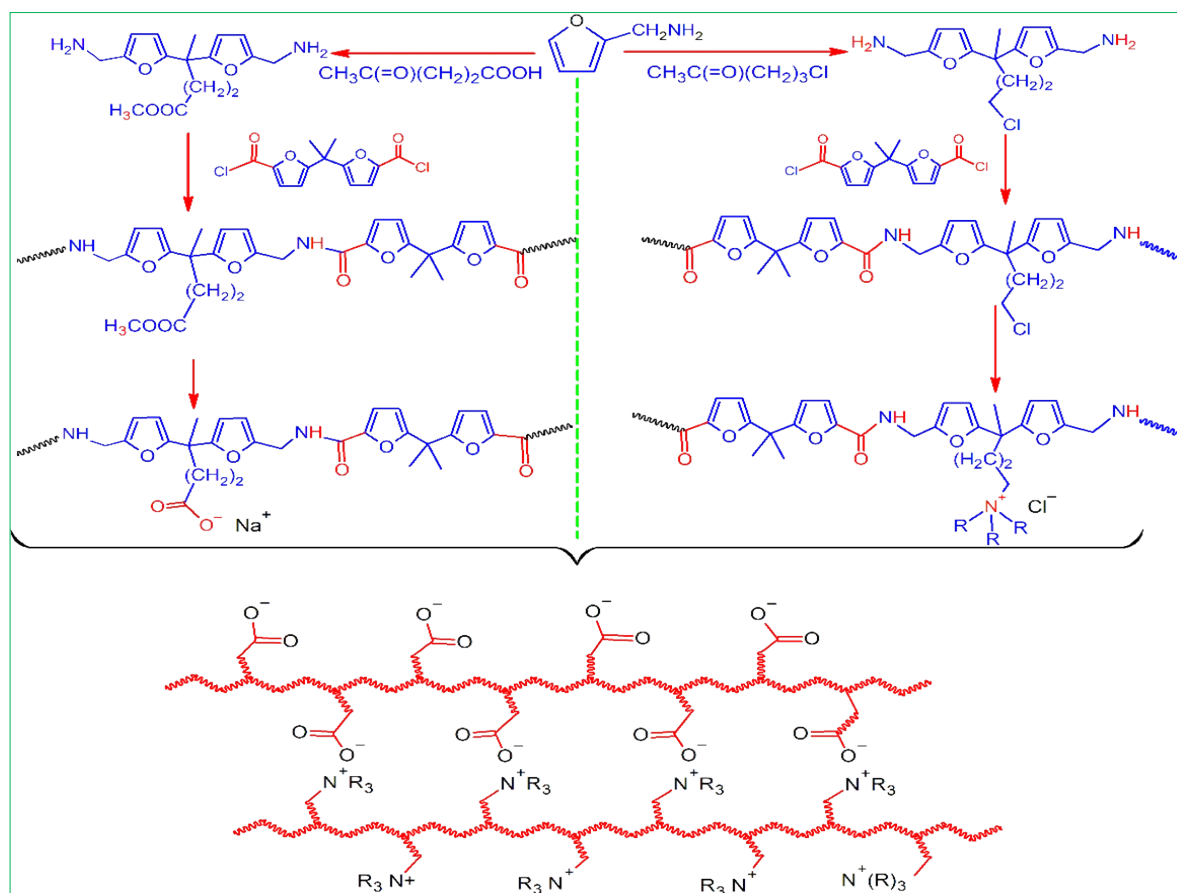


Fig. S14 FT-IR of PA-P and its hydrolytic Product

S11 Preparation of PA-C by postpolymerization hydrolysis and anionic polyelectrolyte PA-Na:

The synthetic route was shown in Scheme S11-1, and the details as following: 0.2 g ester-functionalized polyamide PA-M was added to 40 mL 5% NaOH solution (v (H₂O): v (THF) =50:50), the mixture was stirred at 50 °C for 24 h, the solid completely dissolved after hydrolysis reaction. Then the solvent was removed by rotary evaporation under vacuum and a yellow solid was left. The solid was washed with THF for 3 times and then vacuum dried at 50 °C overnight to obtain the anionic polyelectrolyte PA-Na with yield of 92%. For preparation of acid-functionalized PA-C, the reaction mixture was acidified with concentrated HCl after hydrolysis, and the PA-C was precipitated from the solution. Crude PA-C was washed with THF and dried under vacuum to obtain the desired polymer in 90% yield.



Scheme S8 Synthetic route of cationic/anionic polyelectrolytes and their complexes

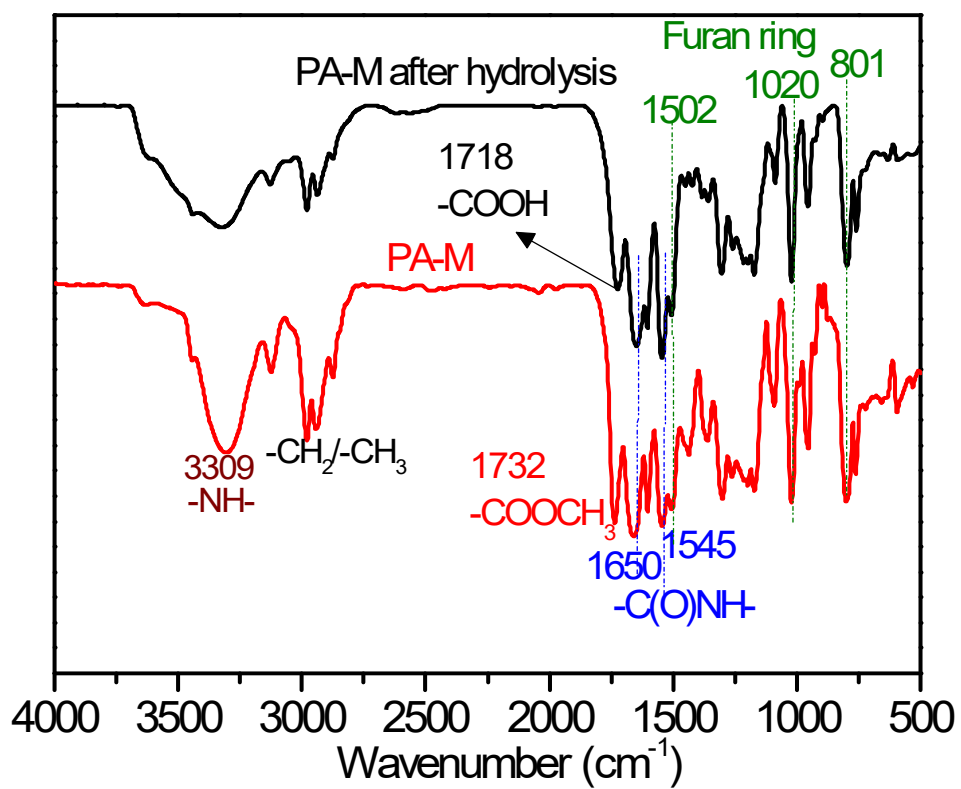


Fig. S15 The FT-IR spectra of PA-M and PA-C

S12 Preparation of polyelectrolyte complex:

Equal molar of PA-T and PA-Na were dissolved separately in deionized water under heating. Then, the PA-T solution was added to the PA-Na solution under stirring, and the polyelectrolyte complex formed immediately as the two oppositely charged polymer solutions met together. After complete addition, 1 mL of the suspension was removed and diluted with ethanol; this solution was used as the SEM sample. The remaining suspension was filtered to obtain the polyelectrolyte complex as a white powder. The solid was washed with deionized water and then freeze-dried to obtain a lyophilized sample for the SEM test. Electrolyte complex was obtained by filtration and drying.

S13 Video of the electrolyte complex preparation



静电复合.mp4

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