Electronic Supplementary Information

Self-assembly ionic nanofibers derived from amino acid for high-performance particulate matter removal

Lei Zhang, Wen-Li Yuan, Zhang Zhang, Guo-Hao Zhang, Hao Chen, Nanrong Zhao, Ling He and Guo-Hong Tao**

College of Chemistry, Sichuan University, Chengdu 610064, China.

E-mail address: lhe@scu.edu.cn, taogh@scu.edu.cn

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Experimental section

Materials: *L*-Phenylalanine methyl ester hydrochloride ([*L*-PheC_1]Cl) (98%) and *D*-phenylalanine methyl ester hydrochloride ([*D*-PheC_1]Cl) (98%) were purchased from J&K Scientific Ltd. (China). Acetonitrile (MeCN) (>99.8%) and ethanol (EtOH) (>99.8%) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). All reagents were used as received. Solvents were dried using standard procedures.

General methods: Infrared spectra (IR) were obtained from Bruker ALPHA infrared spectrometer. Raman spectra were obtained from Bruker BRAVO. Powder X-Ray Diffraction (PXRD) was recorded on Schimadzu-xrd-6100. ^{1}H and ^{13}C NMR spectra were taken on Bruker 400 MHz nuclear magnetic resonance spectrometer operating at 400 and 100 MHz, respectively, with d_6-DMSO as the locking solvent. The ^{1}H and ^{13}C chemical shifts are reported in ppm relative to TMS. Coupling constants are given in Hertz. Elemental analysis (H, C, N) was taken at an Elementar Vario MICRO CUBE elemental analyzer. Thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60H thermal analyser. Measurements were accomplished by heating the samples at a heating rate of 10 °C min^{-1} from ambient temperature to 600 °C. Melting points were determined by differential scanning calorimetry (DSC) on a TA Q20 calorimeter calibrated with standard pure indium. Measurements were performed at a heating rate of 10 °C min^{-1} with a nitrogen flow rate of 20 mL min^{-1}. The reference sample was an Al container with nitrogen. Microscopic morphologies of the ionic fibers were observed with a HLP-85C polarizing microscope equipped with a KER 3100-08S hotstage and a CCD video camera. SEM images were obtained using a Hitachi TM3000 scanning electron microscope. PM counts were measured using a BR-smart-126 laser PM detector. Pressure drop were measured by Differential Pressure AS8520 from SMART SENSOR.

Preparation of ionic fibers: In a 20 mL vial, 50 mg, 75 mg, 100 mg, 100 mg, and 100 mg [*L*-$PheC_1$]Cl (or [*D*-$PheC_1$]Cl) were added into different volume ethanol solution (200 mL, 200 mL, 200 mL, 300 mL, 400 mL), respectively. The resulting mixture was sonicated for one minute. Then various volume acetonitrile (800 mL, 800 mL, 800 mL, 700 mL, and 600 mL) were added to ethanol solution of [*L*-$PheC_1$]Cl (or [*D*-$PheC_1$]Cl). These vials containing the solutions were stoppered and were allowed to stand for about a few minutes at ambient temperature. Then white organic gel were formed. The organic gels were dried in vacuum under ambient conditions for at least one hour to yield white ionic fibers.

Preparation of ionic fiber composites: Solution of [*L*-$PheC_1$]Cl were prapred at room temperature in ethanol. (Concentration: 100 mg mL^{-1}, $V_{(Ethanol)}$: $V_{(aetonitrile)}$ = 2:8) The porous skeleton (Melamine formaldehyde resin foam, Nylon nonwoven, polyurethane foam, and polypropylene nonwoven) of 4 mm was placed into ethanol solution of [*L*-$PheC_1$]Cl. Add acetonitrile to the ethanol solutions and let stand for a few minutes. Then the porous composites was removed from the gels and dried in vacuum under ambient conditions for at least an hour.

X-ray Crystallography: Single crystals of [*L*-$PheC_1$]Cl and [*D*-$PheC_1$]Cl were removed from the flask, and a suitable crystal was selected and attached to a glass fiber. The data were collected by a New Gemini, Dual, EosS2 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal was held at 293 K during data collection. Using Olex2,[1]

the structure was solved with the ShelXT[2] structure solution program using Direct Methods and refined with the XL[3] refinement package using least squares minimization. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and refined. No decomposition was observed during data collection.

Theoretical Study: The quantitative analysis of molecular surface is significant to study non-covalent interaction. Electrostatic potential (ESP) can be written as:

$$V_{Total}(r) = V_{Nuc}(r) + V_{Elec}(r) = \sum_{A} \frac{Z_A}{\sqrt[2]{(r - R_A)^2}} - \int \frac{\rho(r')}{\sqrt[2]{(r - r')^2}} dr'$$

where Z and **R** denote nuclear charge and nuclear position, respectively. Then the $\bar{V}_S^+$, $\bar{V}_S^-$ and $\bar{V}_S$, denoting average of positive, negative and overall ESP on van der Waals (vdW) surface respectively, can be expressed as:[4]

$$\bar{V}_S^+ = (\frac{1}{m}) \sum_{i=1}^{m} V(r_i)$$

$$\bar{V}_S^- = (\frac{1}{n}) \sum_{j=1}^{n} V(r_j)$$

$$\bar{V}_S = (\frac{1}{z}) \sum_{k=1}^{n} V(r_k)$$

where *i*, *j* and *k* are indices of sampling points in positive, negative and entire regions respectively, *t* is the total number of surface vertices. A positive (negative) value means that current position is dominated by nuclear (electronic) charges.

The structure of 2-methylpentane (simplified sutrcture of polypropylene), 2,4-dimethylpentanedinitrile (simplified sutrcture of polyacrylonitrile), and phenylalanine methyl ester were optimized in gas phase at B3LYP/6-311++G** level. The quantitative analysis of molecular surface for 2-methylpentane, phenylalanine methyl ester and the cluster conformers in the [*L*-PheC_1]Cl and [*D*-PheC_1]Cl crystal structure at the B3LYP/6–311++G(d, p) level was performed by the Gaussian09 (Revision A.02) suite of programs.[5] The Gaussian output wfn files were used as inputs for Multiwfn to perform the quantitative analysis.[6] The color mapped isosurface graphs of ESP were rendered by VMD 1.9 program.[7] Followed by Bader and coworkers,[8] the vdW surface referred throughout this paper denotes the isosurface of r = 0.001 e bohr^{-3}.

Figure S1 Morphological characterization of self-assembled [*D*-PheC$_1$]Cl fibers formed at different conditions. (All the experiments were done at room temperature. **D1**: 50 mg mL^{-1}, $V_{(EtOH)}$:$V_{(MeCN)}$ = 2:8. **D2**: 75 mg mL^{-1}, $V_{(EtOH)}$:$V_{(MeCN)}$ = 2:8. **D3**: 100 mg mL^{-1}, $V_{(EtOH)}$:$V_{(MeCN)}$ = 2:8. **D4**: 100 mg mL^{-1}, $V_{(EtOH)}$:$V_{(MeCN)}$ = 3:7. **D5**: 100 mg mL^{-1}, $V_{(EtOH)}$:$V_{(MeCN)}$ = 4:6. EtOH: ethanol, MeCN: acetonitrile) a) Microscopy image of [*D*-PheC$_1$]Cl fibers. b) Polarizing optical microscopy (POM) images of [*D*-PheC$_1$]Cl fibers. c) SEM images of the [*D*-PheC$_1$]Cl fibers. d) The corresponding histograms of the fiber diameters based on the evaluation of at least 100 fibers. (The average fiber diameter of the ionic fibers **D1**-**D5** are 1.2±0.8 μm, 1.2±0.9 μm, 1.1±0.9 μm, 1.1±0.9 μm, and 1.1±0.8 μm, respectively)

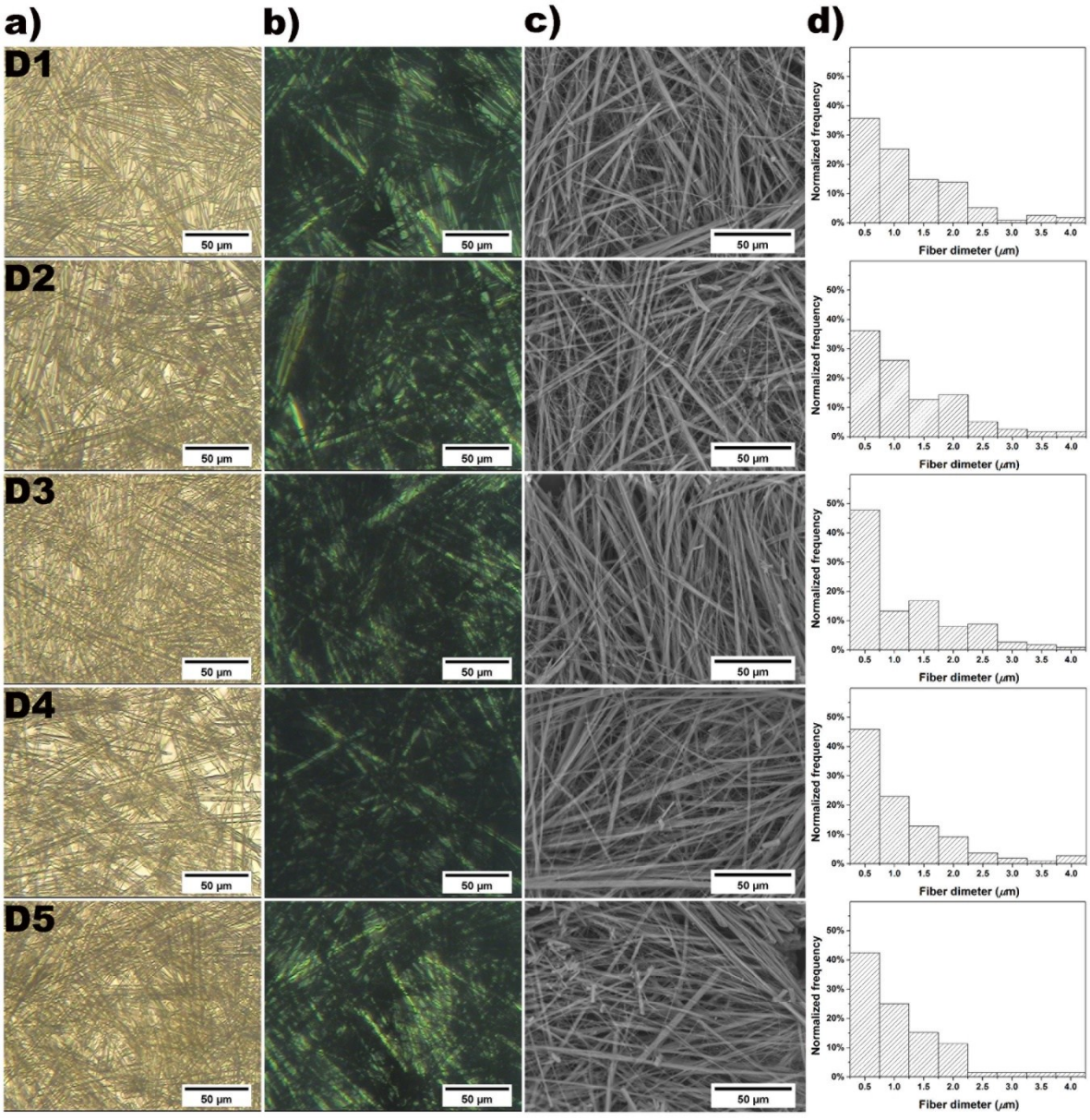


Figure S2 Powder X-ray diffraction (PXRD) patterns of [*L*-PheC$_1$]Cl fibers, [*L*-PheC$_1$]Cl crystals, [*D*-PheC$_1$]Cl fibers and [*D*-PheC$_1$]Cl crystals.

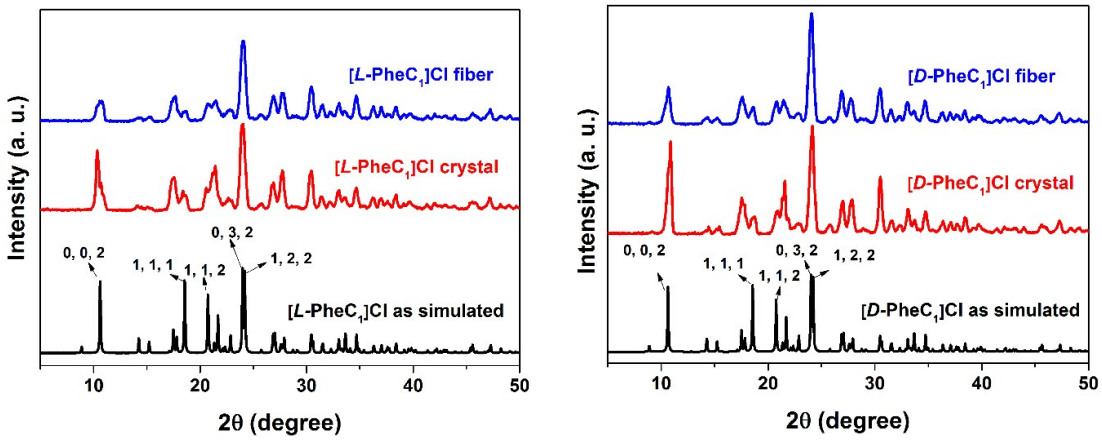


Figure S3 Fourier transform infrared spectroscopy (FTIR) spectra of [*L*-PheC$_1$]Cl fibers, [*L*-PheC$_1$]Cl crystals, [*D*-PheC$_1$]Cl fibers and [*D*-PheC$_1$]Cl crystals.

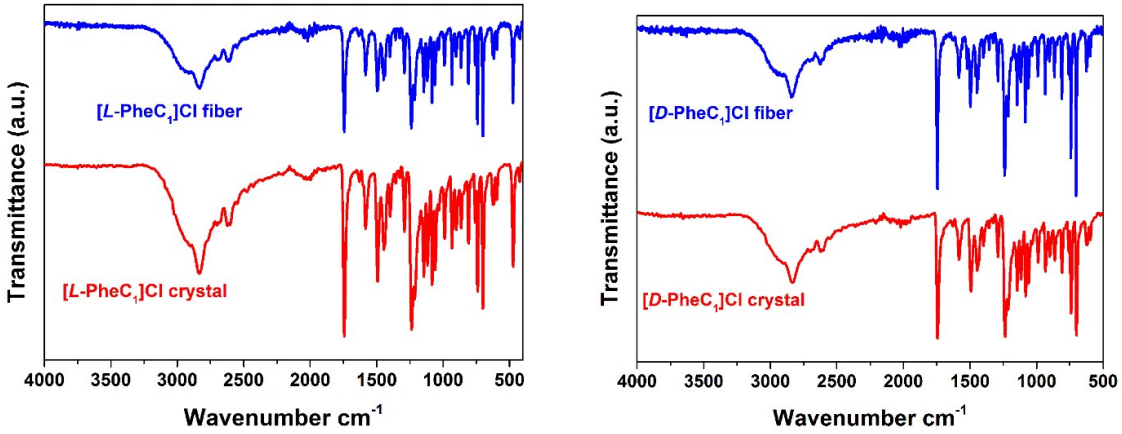


Figure S4 Raman spectra of [*L*-PheC$_1$]Cl fibers, [*L*-PheC$_1$]Cl crystals, [*D*-PheC$_1$]Cl fibers and [*D*-PheC$_1$]Cl crystals.

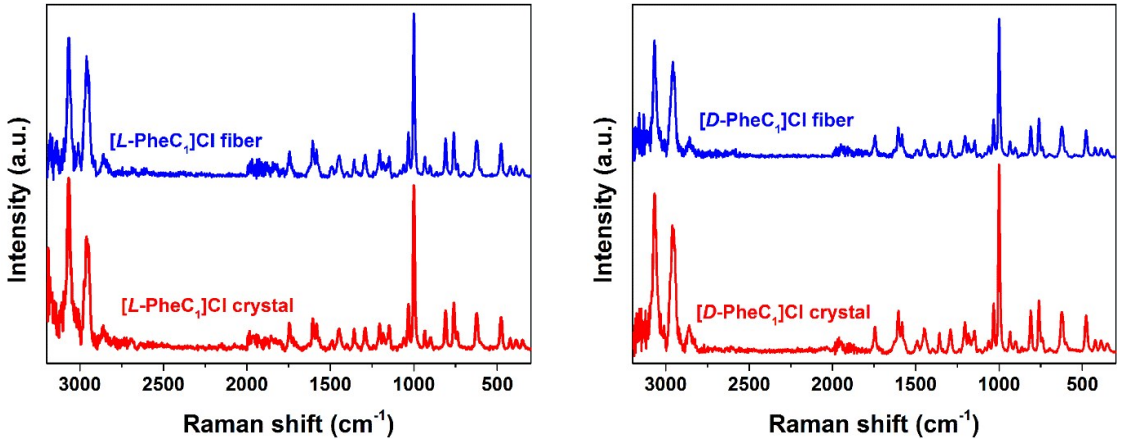
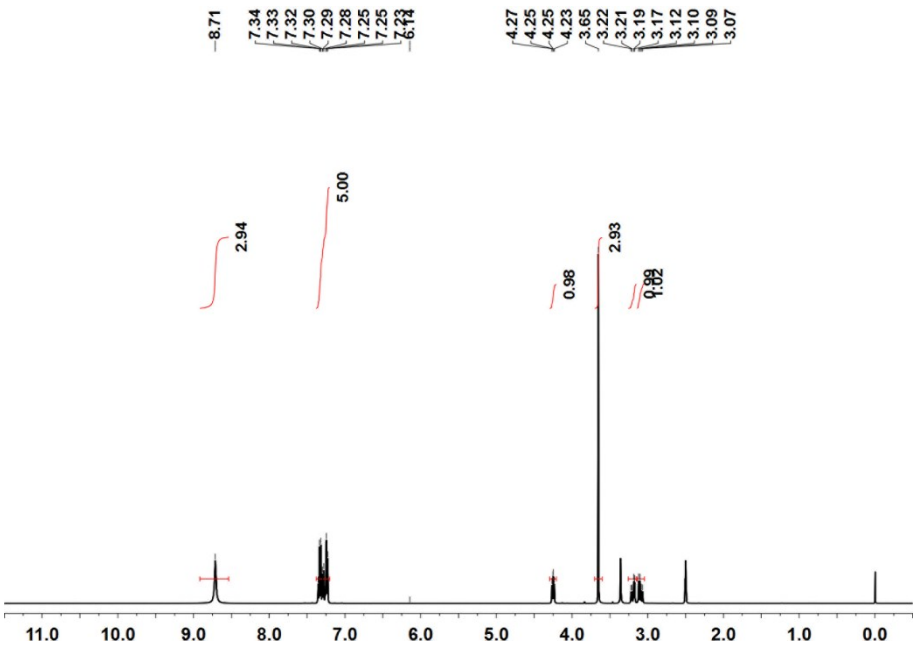
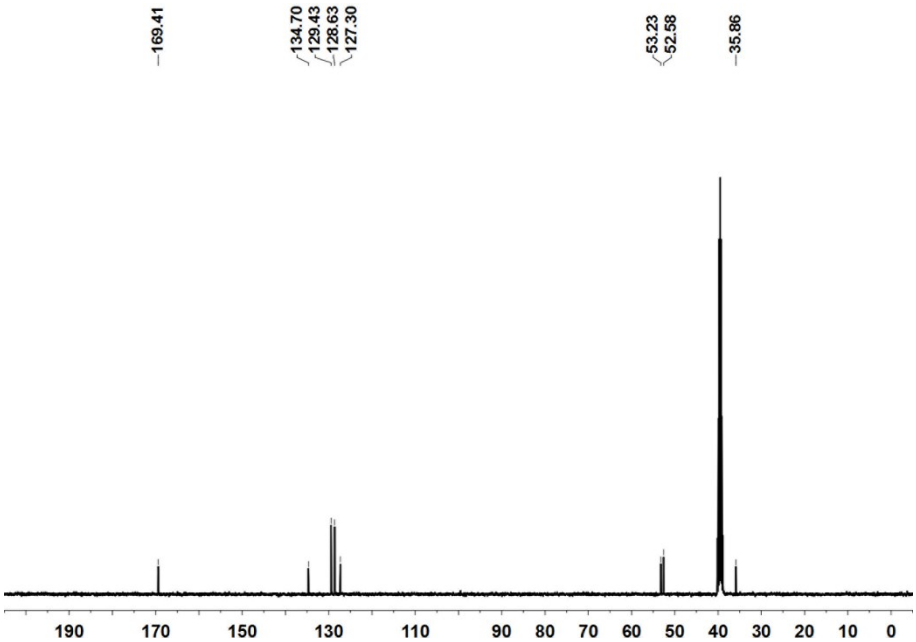


Figure S5 ^{1}H NMR spectrum of fibrous [*L*-PheC$_1$]Cl in d_6-DMSO.



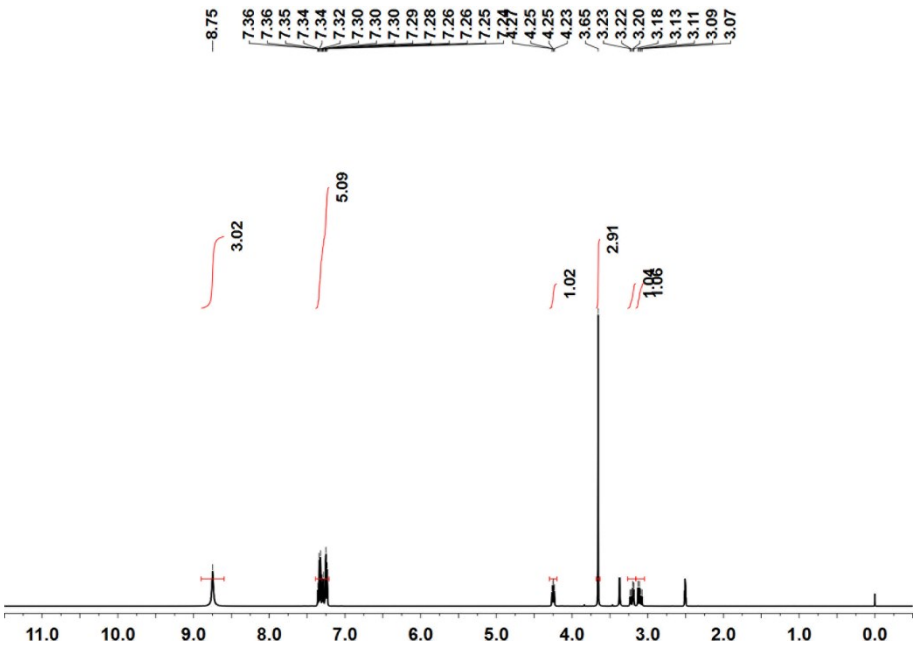
^{1}H NMR (400 MHz, DMSO) δ 8.71 (s, 3H), 7.38–7.20 (m, 5H), 4.25 (dd, *J* = 7.3, 5.9 Hz, 1H), 3.65 (s, 3H), 3.20 (dd, *J* = 14.0, 5.8 Hz, 1H), 3.09 (dd, *J* = 14.0, 7.4 Hz, 1H).

Figure S6 ^{13}C NMR spectrum of fibrous [*L*-PheC$_1$]Cl in d_6-DMSO.



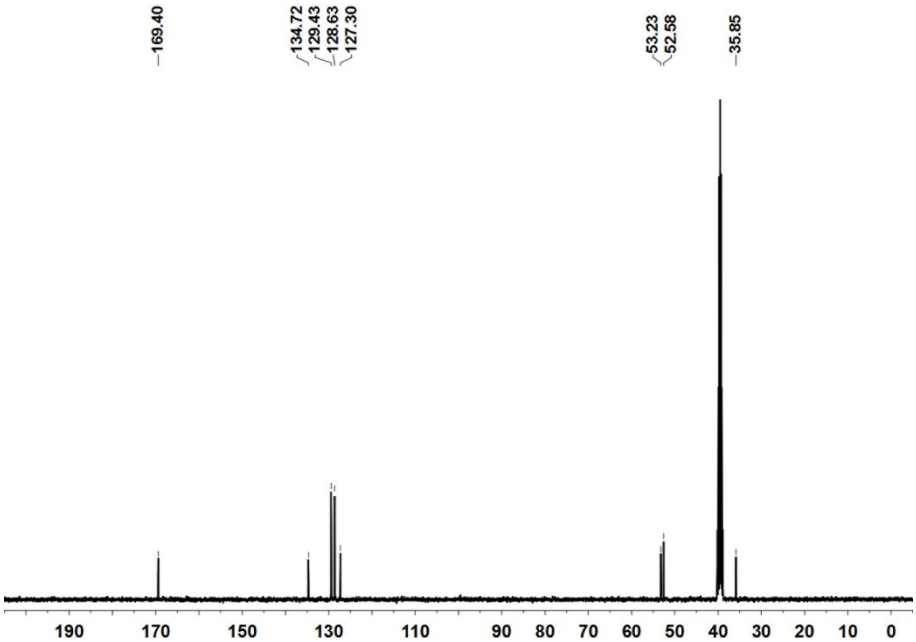
^{13}C NMR (100 MHz, DMSO) δ 169.41, 134.70, 129.43, 128.63, 127.30, 53.23, 52.58, 35.86.

Figure S7 ^{1}H NMR spectrum of crystalline [*L*-PheC$_1$]Cl in d_6-DMSO.



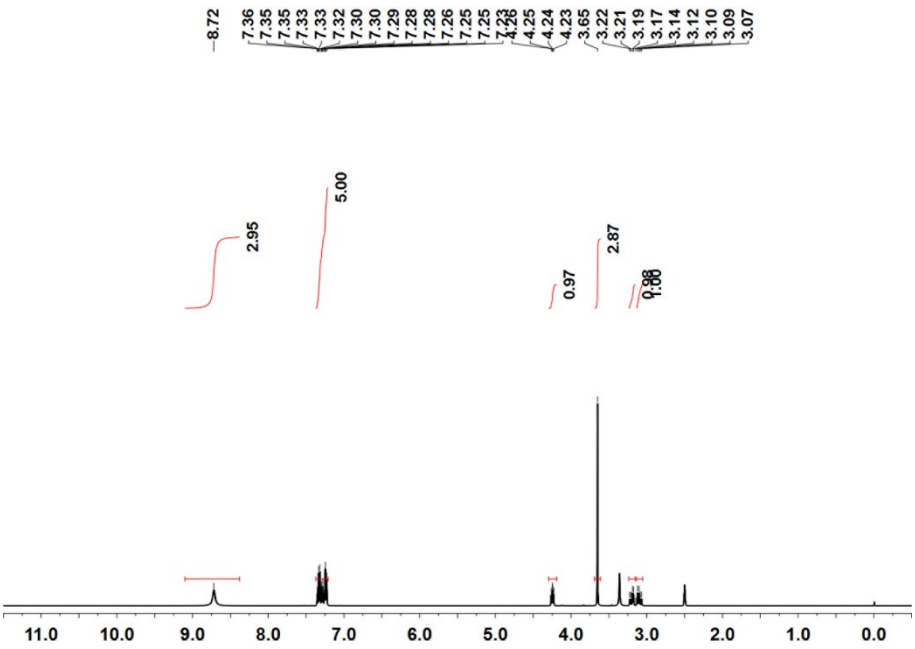
^{1}H NMR (400 MHz, DMSO) δ 8.75 (s, 3H), 7.39–7.21 (m, 5H), 4.25 (dd, *J* = 7.3, 5.8 Hz, 1H), 3.65 (s, 3H), 3.37 (s, 1H), 3.21 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.10 (dd, *J* = 14.0, 7.4 Hz, 1H).

Figure S8 ^{13}C NMR spectrum of crystalline [*L*-PheC$_1$]Cl in d_6-DMSO.



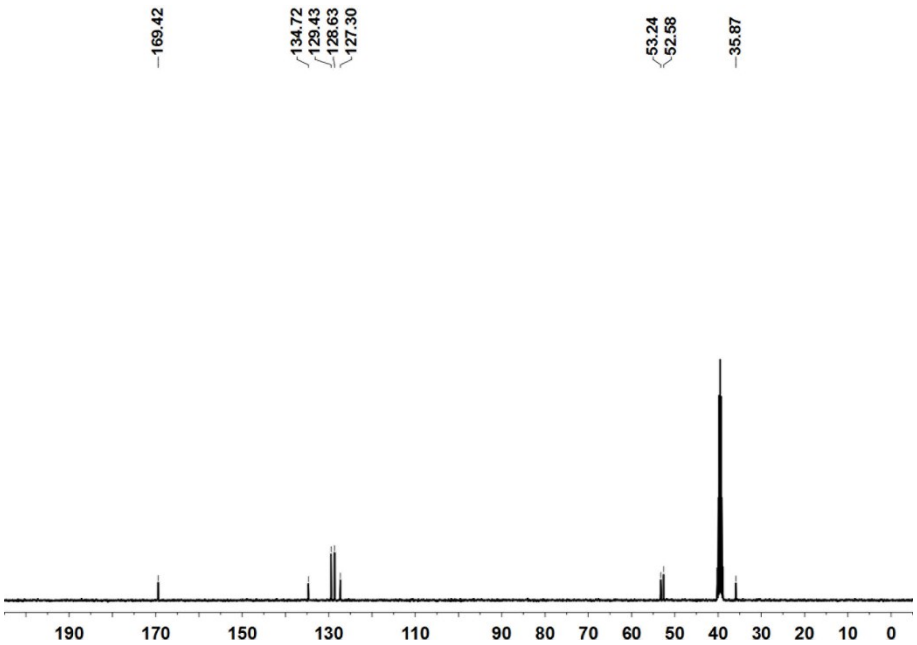
^{13}C NMR (100 MHz, DMSO) δ 169.40, 134.72, 129.43, 128.63, 127.30, 53.23, 52.58, 35.85.

Figure S9 ^{1}H NMR spectrum of fibrous [*D*-PheC$_1$]Cl in d_6-DMSO.



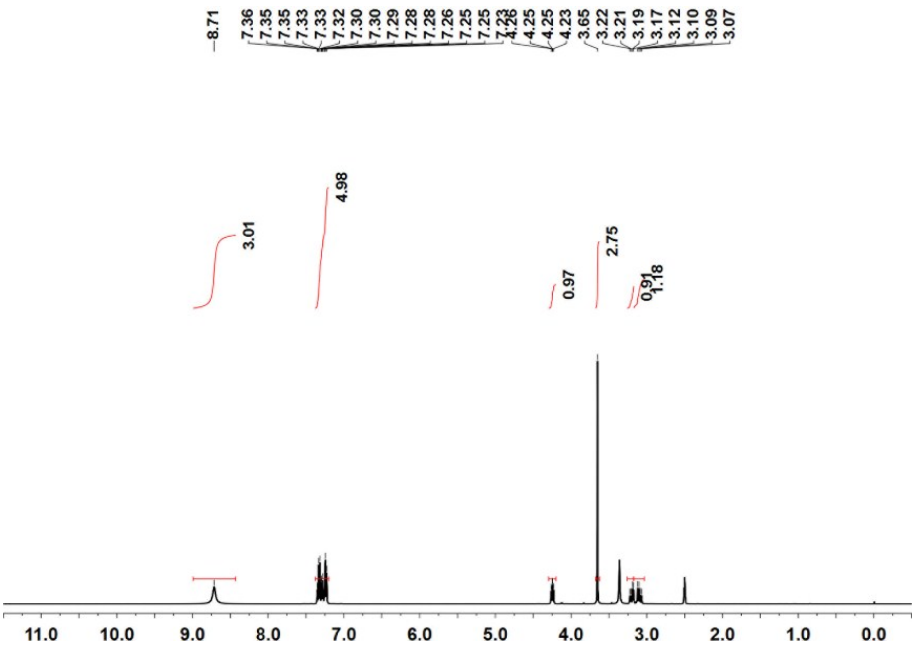
^{1}H NMR (400 MHz, DMSO) δ 8.72 (s, 3H), 7.37–7.21 (m, 5H), 4.25 (dd, J = 7.3, 5.9 Hz, 1H), 3.65 (s, 3H), 3.20 (dd, J = 14.0, 5.8 Hz, 1H), 3.09 (dd, J = 14.0, 7.4 Hz, 1H).

Figure S10 ^{13}C NMR spectrum of fibrous [*D*-PheC$_1$]Cl in d_6-DMSO.



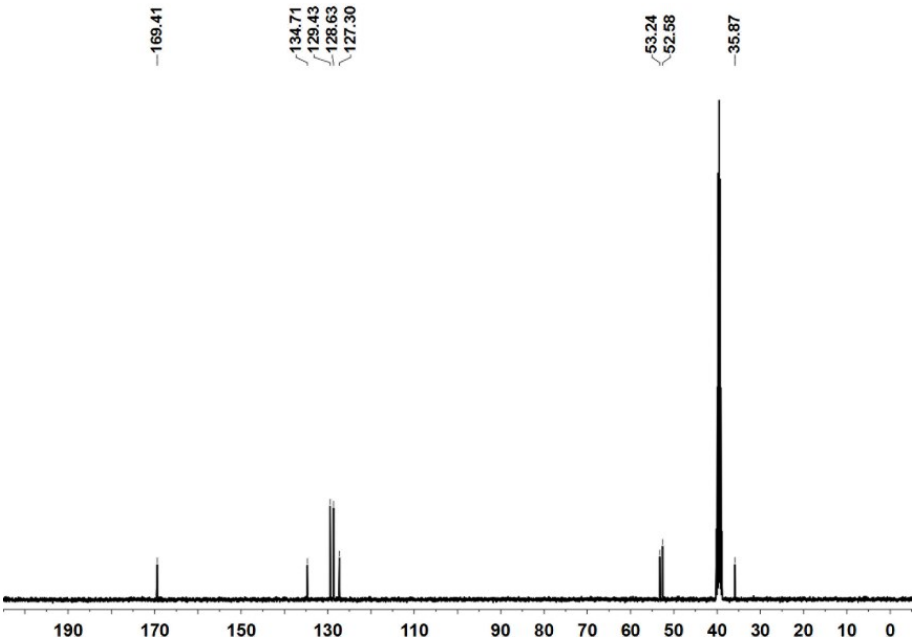
^{13}C NMR (100 MHz, DMSO) δ 169.42, 134.72, 129.43, 128.63, 127.30, 53.24, 52.58, 35.87.

Figure S11 ^{1}H NMR spectrum of crystalline [*D*-PheC$_1$]Cl in d_6-DMSO.



^{1}H NMR (400 MHz, DMSO) δ 8.71 (s, 3H), 7.38–7.20 (m, 5H), 4.25 (dd, J = 7.3, 5.9 Hz, 1H), 3.65 (s, 3H), 3.20 (dd, J = 14.0, 5.8 Hz, 1H), 3.09 (dd, J = 14.0, 7.4 Hz, 1H).

Figure S12 ^{13}C NMR spectrum of crystalline [*D*-PheC$_1$]Cl in d_6-DMSO.



^{13}C NMR (100 MHz, DMSO) δ 169.41, 134.71, 129.43, 128.63, 127.30, 53.24, 52.58, 35.87.

Figure S13 ESP-mapped molecular vdW surface of *L*-phenylalanine methyl ester (*L*-PheC$_1$).

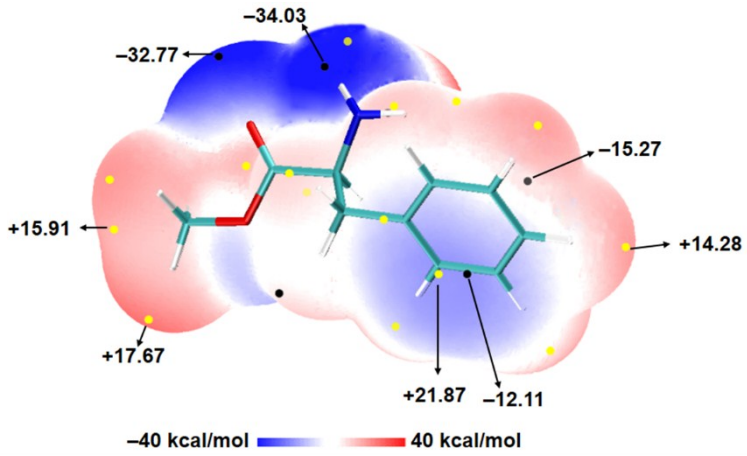


Figure S14 ESP-mapped molecular vdW surface of *D*-phenylalanine methyl ester (*D*-PheC$_1$).

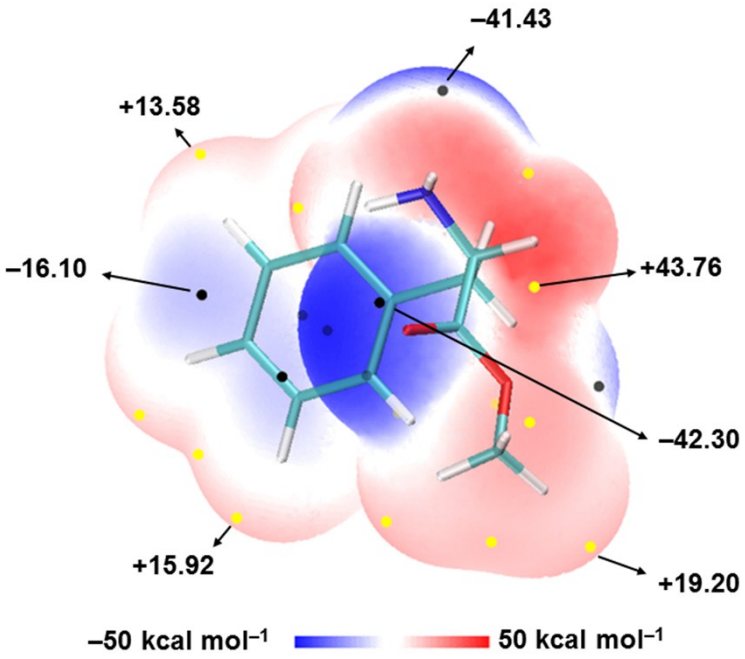


Figure S15 POM micrographs of self-assembled [*D*-PheC_1]Cl fibers at different temperatures.

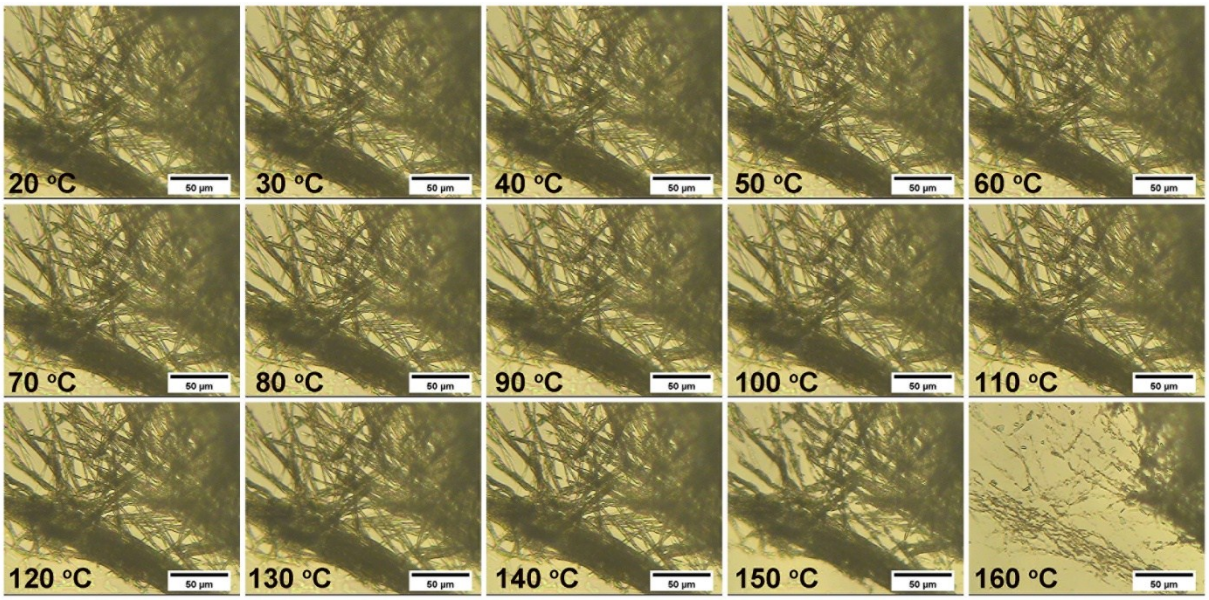


Figure S16 PXRD patterns of ionic fiber composites and porous skeletons.

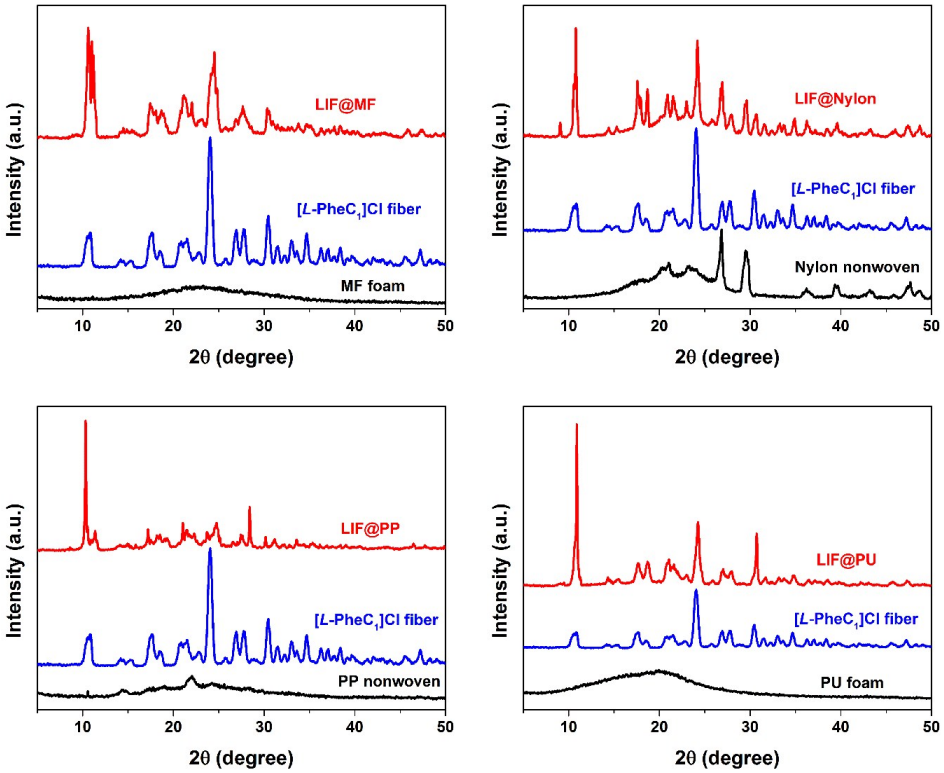


Figure S17 FTIR spectra of composites.

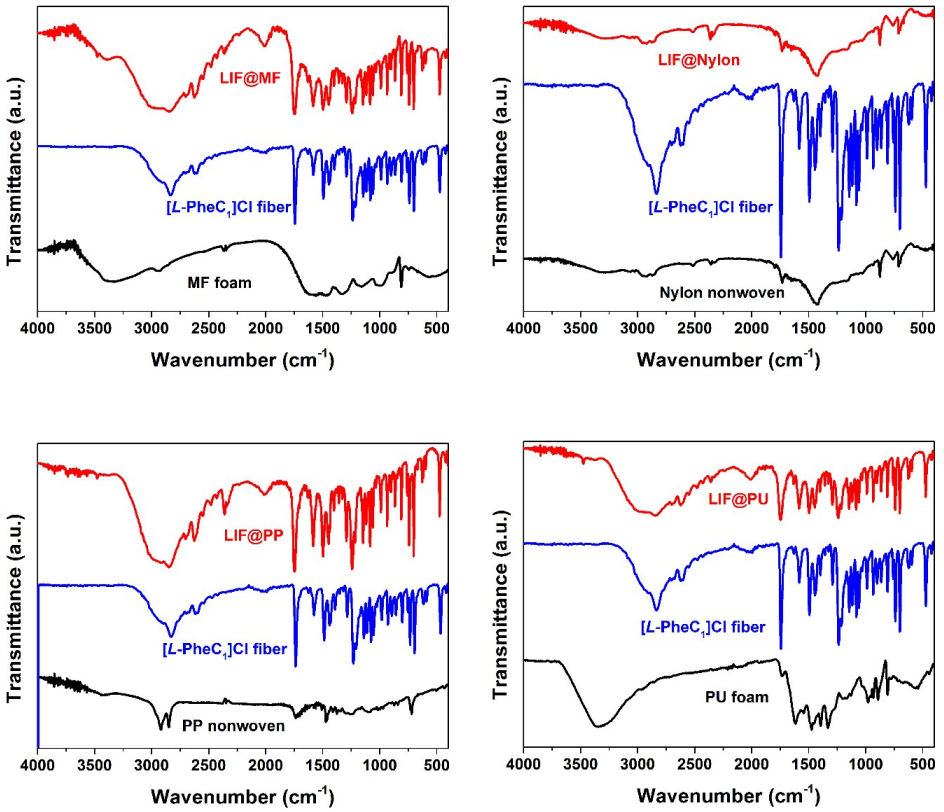


Figure S18 The histograms of the fiber diameters in a) LIF@MF, b) LIF@Nylon, c) LIF@PU, and d) LIF@PP.

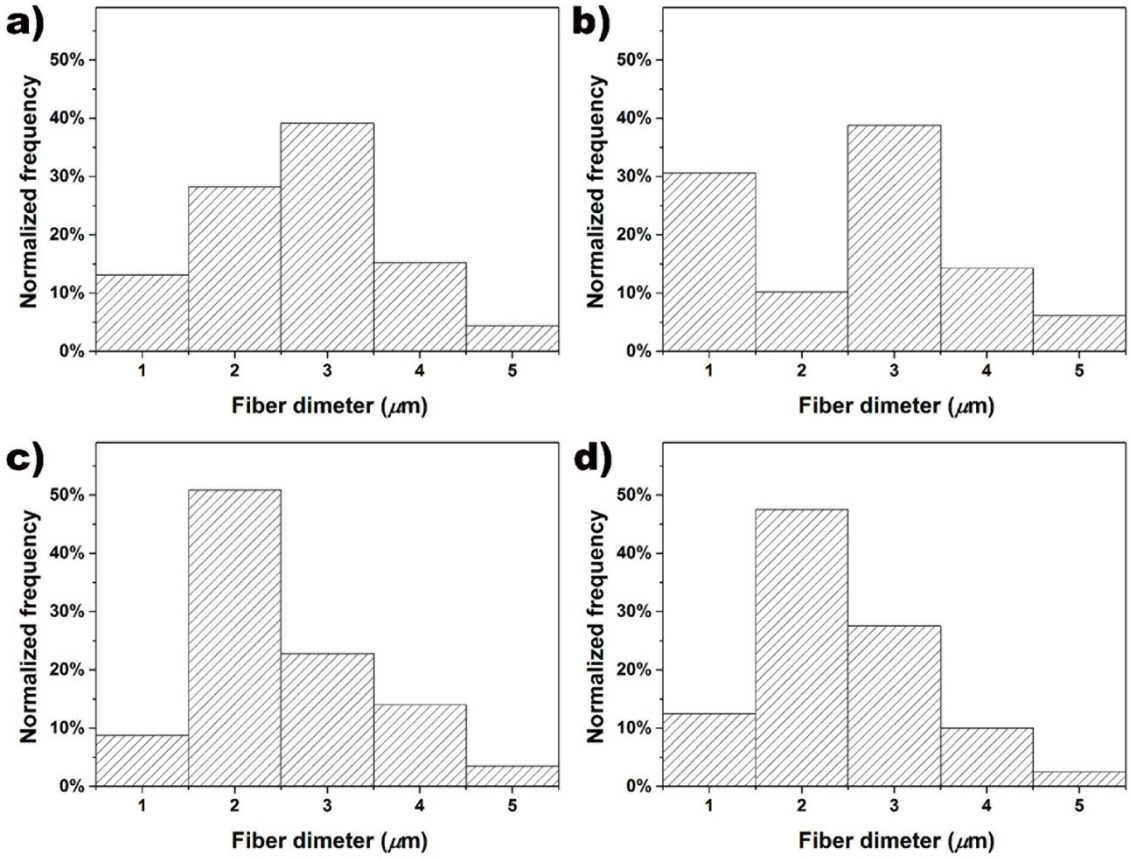


Figure S19 Photograph of [*L*-PheC$_1$]Cl fibers.

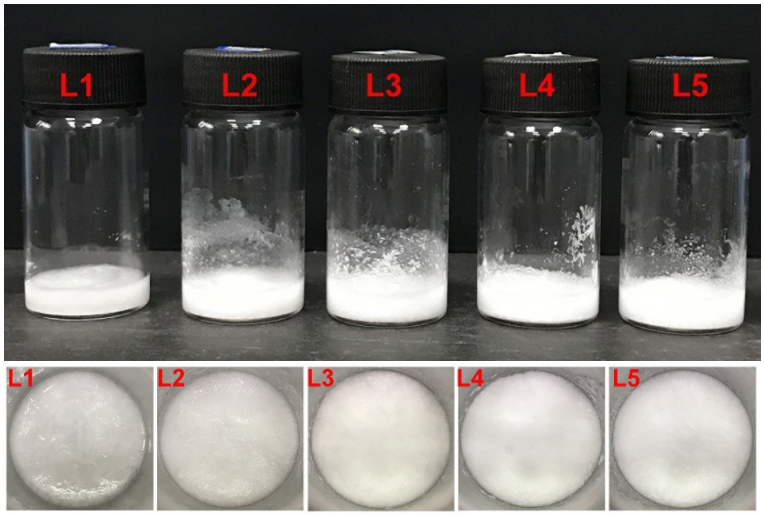


Figure S20 SEM images of porous skeletons. a) melamine formaldehyde resin (MF) foam, b) nylon nonwoven, c) polyurethane (PU) foam, d) polypropylene (PP) nonwoven.

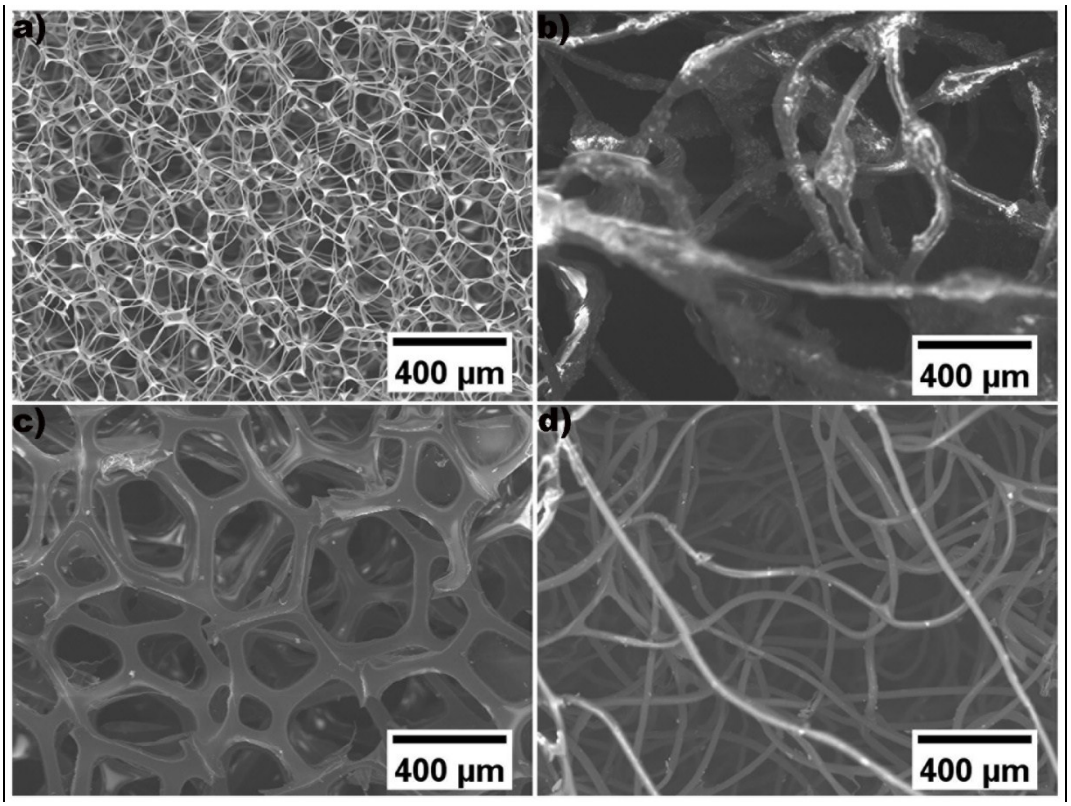


Figure S21 Filtration efficiencies of [*L*-PheC$_1$]Cl ionic fiber MF foam composite (LIF@MF).

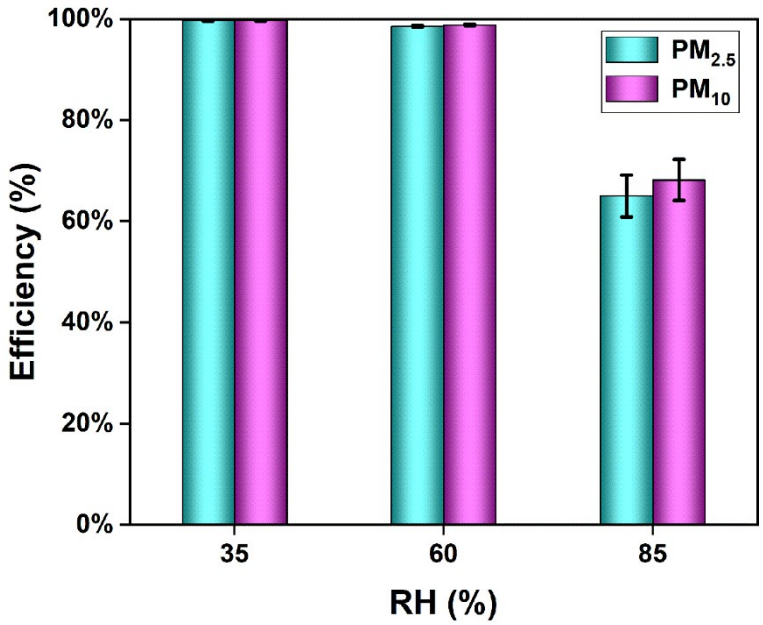


Figure S22 Filtration efficiencies of [*L*-PheC$_1$]Cl ionic fiber PU foam composite (LIF@PU).

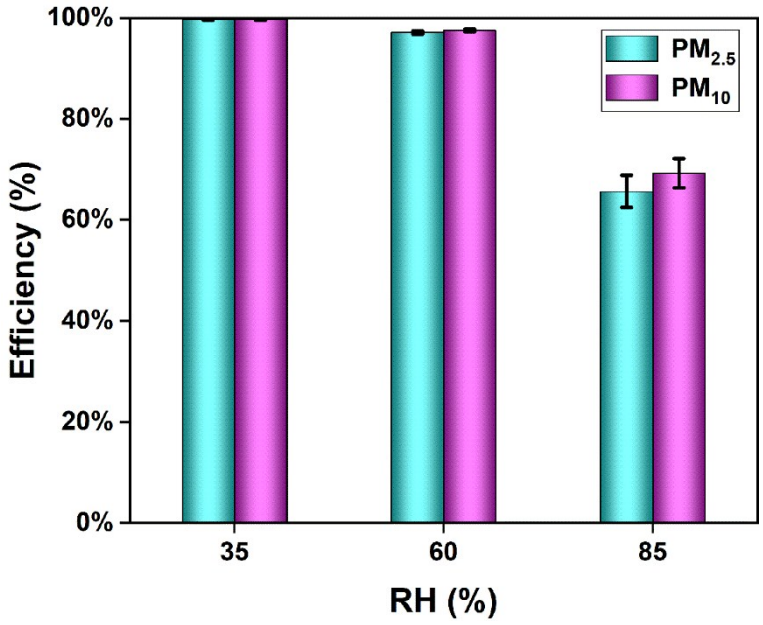


Figure S23 Filtration efficiencies of [*L*-PheC$_1$]Cl ionic fiber Nylon nonwoven composite (LIF@Nylon).

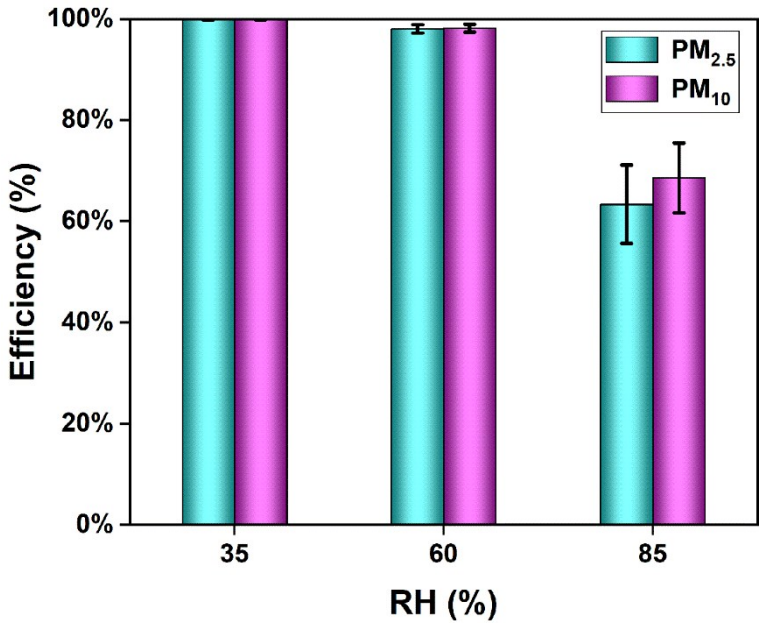


Figure S24 FTIR spectra of composites after filtration experiments.

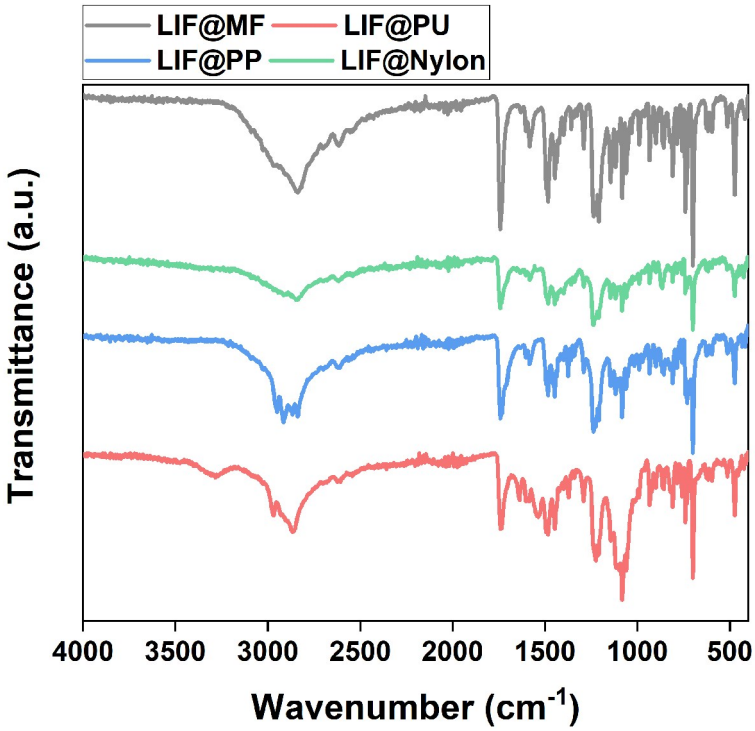


Figure S25 SEM images of composites after filtration experiments.

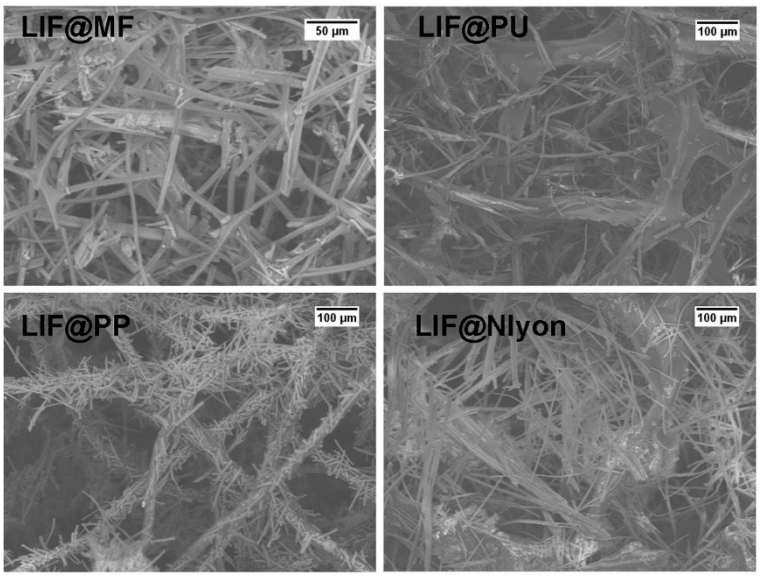


Table S1 Crystal data and structure refinement for [*L*-PheC$_1$]Cl and [*D*-PheC$_1$]Cl.

Compound	[*L*-PheC$_1$]Cl	[*D*-PheC$_1$]Cl
Empirical formula	$C_{10}H_{14}ClNO_2$	$C_{10}H_{14}ClNO_2$
Formula weight	215.67	215.67
Temperature/K	293.15	293.15
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.4485(3)	5.4456(4)
b/Å	12.4239(9)	12.4023(13)
c/Å	16.6464(11)	16.6206(14)
α/°	90.00	90.00
β/°	90.00	90.00
γ/°	90.00	90.00
Volume/Å^3	1126.81(13)	1122.52(17)
Z	4	4
ρ_{calc}/g cm^{-3}	1.271	1.276
μ/mm^{-1}	0.315	0.316
F(000)	456.0	456.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.9 to 52.74	5.9 to 52.68
Index ranges	-6≤h≤6, -15≤k≤ 8, -20≤l≤20	-6≤h≤6, -13≤k≤15, -19 ≤l≤20
Reflections collected	3210	4891
Independent reflections	2065 [R_{int} = 0.0206, R_{sigma} = 0.0479]	2281 [R_{int} = 0.0480, R_{sigma} = 0.0662]
Data/restraints/parameters	2065/0/129	2281/0/129
Goodness-of-fit on F^2	1.040	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.0677	R_1 = 0.0776, wR_2 = 0.1819
Final R indexes [all data]	R_1 = 0.0542, wR_2 = 0.0748	R_1 = 0.0944, wR_2 = 0.2067
Largest diff. peak/hole / e Å^{-3}	0.17/-0.13	0.58/-0.34
Flack parameter	0.05(8)	0.01(15)

Table S2 Bond lengths for [*L*-PheC$_1$]Cl.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.386(3)	C7	C8	1.532(3)
C1	C6	1.379(3)	C8	C9	1.507(3)
C1	C7	1.510(3)	C8	N1	1.490(3)
C2	C3	1.381(4)	C9	O1	1.199(3)
C3	C4	1.378(4)	C9	O2	1.318(3)
C4	C5	1.362(4)	C10	O2	1.458(3)
C5	C6	1.382(4)			

Table S3 Bond angles for [*L*-PheC$_1$]Cl.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C7	121.9(2)	C1	C7	C8	115.84(19)
C6	C1	C2	117.8(2)	C9	C8	C7	114.8(2)
C6	C1	C7	120.3(2)	N1	C8	C7	111.6(2)
C3	C2	C1	121.5(3)	N1	C8	C9	108.2(2)
C4	C3	C2	119.8(3)	O1	C9	C8	124.6(2)
C5	C4	C3	119.0(3)	O1	C9	O2	125.2(2)
C4	C5	C6	121.4(3)	O2	C9	C8	110.2(2)
C1	C6	C5	120.5(3)	C9	O2	C10	117.2(2)

Table S4 Bond lengths for [*D*-PheC$_1$]Cl.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.504(6)	C5	C6	1.394(6)
C1	O1	1.203(6)	C5	C10	1.368(6)
C1	O2	1.316(5)	C6	C7	1.371(7)
C2	C4	1.530(5)	C7	C8	1.379(7)
C2	N1	1.488(5)	C8	C9	1.356(9)
C3	O2	1.457(6)	C9	C10	1.388(8)
C4	C5	1.510(6)			

Table S5 Bond angles for [*D*-PheC$_1$]Cl.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	C2	124.1(4)	C10	C5	C4	120.4(4)
O1	C1	O2	125.1(4)	C10	C5	C6	118.1(4)
O2	C1	C2	110.8(4)	C7	C6	C5	120.8(5)
C1	C2	C4	115.0(3)	C6	C7	C8	120.3(5)
N1	C2	C1	108.4(3)	C9	C8	C7	119.2(5)
N1	C2	C4	111.7(4)	C8	C9	C10	120.9(5)
C5	C4	C2	115.9(3)	C5	C10	C9	120.7(5)
C6	C5	C4	121.5(4)	C1	O2	C3	117.0(4)

Table S6 Surface area in each ESP range on the vdW surface for [*L*-PheC$_1$]Cl-A.

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–100	–80	15.21	5.97
–80	–60	24.94	9.79
–60	–40	13.55	5.32
–40	–20	14.75	5.79
–20	0	31.13	12.22
0	20	58.93	23.13
20	40	56.85	22.32
40	60	13.72	5.39
60	80	12.81	5.03
80	100	12.84	5.04
Sum:		254.73	100.00

Table S7 Surface area in each ESP range on the vdW surface for [*L*-PheC$_1$]Cl-B.

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–100	–80	1.08	0.42
–80	–60	29.79	11.64
–60	–40	14.46	5.65
–40	–20	11.97	4.68
–20	0	15.28	5.97
0	20	64.01	25.01
20	40	81.98	32.03
40	60	18.70	7.31
60	80	10.92	4.27
80	100	7.74	3.02
Sum:		255.92	100.00

Table S8 Surface area in each ESP range on the vdW surface for [*L*-PheC$_1$]Cl-C.

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–100	–80	0.00	0.00
–80	–60	25.57	10.10
–60	–40	13.86	5.48
–40	–20	7.52	2.97
–20	0	34.19	13.51
0	20	73.20	28.92
20	40	67.08	26.50
40	60	12.56	4.96
60	80	14.17	5.60
80	100	4.95	1.96
Sum:		253.10	100.00

Table S9 Surface area in each ESP range on the vdW surface for [*D*-PheC$_1$]Cl-A.

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–100	–80	15.40	6.06
–80	–60	24.76	9.75
–60	–40	13.63	5.37
–40	–20	14.57	5.74
–20	0	31.37	12.35
0	20	58.63	23.08
20	40	56.04	22.06
40	60	13.74	5.41
60	80	12.74	5.01
80	100	13.12	5.17
Sum:		254.01	100.00

Table S10 Surface area in each ESP range on the vdW surface for [*D*-PheC$_1$]Cl-B.

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–100	–80	0.54	0.21
–80	–60	29.91	11.71
–60	–40	14.48	5.67
–40	–20	12.16	4.76
–20	0	15.23	5.96
0	20	65.06	25.48
20	40	81.11	31.76
40	60	18.38	7.20
60	80	10.97	4.29
80	100	7.58	2.97
Sum:		255.39	100.00

Table S11 Surface area in each ESP range on the vdW surface for [*D*-PheC$_1$]Cl-C.

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–100	–80	0.00	0.00
–80	–60	25.49	10.09
–60	–40	13.91	5.50
–40	–20	7.53	2.98
–20	0	34.55	13.68
0	20	73.70	29.17
20	40	65.79	26.04
40	60	12.37	4.90
60	80	14.23	5.63
80	100	5.06	2.00
Sum:		252.62	100.00

Table S12 Surface area in each ESP range on the vdW surface for *L*-PheC_1.

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–60	–40	0.00	0.00
–40	–20	18.78	8.08
–20	0	71.71	30.87
0	20	141.07	60.73
20	40	0.73	0.32
40	60	0.00	0.00
Sum:		232.29	100.00

Table S13 Surface area in each ESP range on the vdW surface for simplified sutrcture of PP (2-methylpentane).

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–20	–10	0.00	0.00
–10	0	53.98	33.40
0	10	107.67	66.60
10	20	0.00	0.00
Sum:		161.65	100.00

Table S13 Surface area in each ESP range on the vdW surface for simplified sutrcture of PAN (2,4-dimethylpentanedinitrile).

Begin/kcal mol^{-1}	End/kcal mol^{-1}	Area/Å^2	%
–60	–40	0.00	0.00
–40	–20	28.62	15.25
–20	0	28.49	15.17
0	20	98.83	52.64
20	40	31.80	16.94
40	60	0.00	0.00
Sum:		187.74	100.00

Table S14 Surface local minima of ESP for [*L*-PheC$_1$]Cl-A.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	–11.01	–3.96	–2.82	0.08
2	–44.85	–2.51	1.02	–0.85
3	–7.99	–2.06	–3.38	–0.56
4	–85.35	–1.14	4.53	–2.53
5	–5.73	3.08	–2.67	0.87

Table S15 Surface local maxima of ESP for [*L*-PheC$_1$]Cl-A.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	14.95	–3.31	–1.96	–2.85
2	–41.56	–1.82	0.82	–0.84
3	13.46	–0.10	0.62	–0.58
4	98.33	0.01	0.82	3.33
5	32.21	0.70	–2.70	0.26
6	33.81	1.20	–1.04	–1.69
7	97.00	2.49	1.72	2.13
8	27.71	4.27	–1.89	–2.77
9	28.49	4.53	–3.35	–1.45

Table S16 Surface local minima of ESP for [*L*-PheC$_1$]Cl-B.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	–80.44	–6.27	–1.38	–0.81
2	–18.60	–2.13	2.07	2.26
3	7.88	1.81	1.00	–2.30
4	6.72	3.58	–1.58	–2.45
5	3.37	3.86	1.54	1.20
6	1.91	5.12	–0.18	1.05

Table S17 Surface local maxima of ESP for [*L*-PheC$_1$]Cl-B.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	28.41	–2.66	0.61	0.93
2	24.14	–1.44	4.91	–0.52
3	23.52	–1.17	5.13	1.24
4	96.31	0.12	–2.91	0.93
5	43.44	0.40	2.19	–0.75
6	83.06	0.46	–1.90	–1.58
7	36.48	1.28	1.66	1.71
8	32.62	4.87	1.27	–1.96

Table S18 Surface local minima of ESP for [*L*-PheC$_1$]Cl-C.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	–77.26	–5.27	–3.06	–0.81
2	–3.59	–1.91	2.97	2.34
3	–10.16	–1.72	3.93	–1.62
4	–7.50	–1.61	1.80	–2.34
5	6.72	0.99	2.34	2.01
6	–8.62	2.62	–1.37	–2.46
7	–14.67	3.02	–0.58	2.96

Table S19 Surface local maxima of ESP for [*L*-PheC$_1$]Cl-C.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	13.50	–4.04	3.40	0.62
2	12.52	–3.74	1.80	0.07
3	80.77	–0.14	0.09	2.20
4	27.03	0.42	4.99	1.04
5	95.20	0.93	–3.01	1.12
6	30.39	1.61	0.76	–1.77
7	49.07	2.66	0.92	0.37
8	32.33	5.65	–0.31	–1.92
9	35.36	5.74	–0.14	–0.15

Table S20 Surface local minima of ESP for [*D*-PheC_1]Cl-A.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	–5.93	–3.09	–2.67	0.88
2	–85.48	1.15	4.47	–2.56
3	–8.17	2.10	–3.34	–0.51
4	–45.44	2.49	1.02	–0.84
5	–11.14	3.86	–2.88	–0.01

Table S21 Surface local maxima of ESP for [*D*-PheC_1]Cl⁻A.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	28.53	–4.73	–3.22	–1.34
2	27.63	–4.31	–1.85	–2.75
3	97.75	–2.48	1.65	2.20
4	32.17	–1.21	–1.03	–1.70
5	31.41	–0.62	–2.82	0.41
6	98.04	–0.05	0.83	3.33
7	8.81	0.11	0.69	–0.59
8	–42.76	1.84	0.84	–0.84
9	14.60	3.35	–1.95	–2.83

Table S22 Surface local minima of ESP for [*D*-PheC_1]Cl-B.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	1.78	–5.11	–0.17	1.06
2	3.17	–3.78	1.68	1.20
3	6.50	–3.52	–1.57	–2.44
4	7.32	–1.80	0.98	–2.30
5	–18.25	2.06	2.10	2.30
6	–80.22	6.23	–1.37	–0.94

Table S23 Surface local maxima of ESP for [*D*-PheC_1]Cl⁻B.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	32.27	–4.83	1.29	–1.97
2	35.72	–1.29	1.65	1.72
3	41.59	–0.45	2.27	–0.72
4	96.51	–0.14	–2.88	0.94
5	23.98	1.40	4.91	–0.52
6	22.94	1.35	5.09	1.32
7	30.06	2.63	0.68	1.00

Table S24 Surface local minima of ESP for [*D*-PheC_1]Cl-C.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	–14.46	–3.02	–0.49	2.94
2	–8.74	–2.59	–1.28	–2.49
3	6.23	–0.97	2.25	2.00
4	–7.62	1.55	1.97	–2.30
5	–10.30	1.81	3.95	–1.60
6	–3.79	1.92	3.01	2.33
7	–77.15	5.25	–3.15	–0.78

Table S25 Surface local maxima of ESP for [*D*-PheC_1]Cl⁻C.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	32.32	–5.77	–0.57	–1.78
2	35.30	–5.73	–0.12	–0.13
3	47.41	–2.68	0.91	0.37
4	29.51	–1.62	0.77	–1.75
5	95.64	–0.91	–3.02	1.05
6	26.63	–0.44	5.00	1.01
7	80.32	0.20	0.10	2.19
8	12.33	3.73	1.82	0.06
9	13.50	4.04	3.40	0.61

Table S26 Surface local minima of ESP for *L*-PheC_1.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	–32.77	–4.25	2.61	–0.33
2	–11.36	–1.94	–2.53	–0.17
3	3.02	–0.91	1.68	–2.59
4	–34.04	–0.77	3.00	1.14
5	–12.11	3.25	0.78	–1.87
6	–15.27	3.75	–1.09	1.69

Table S27 Surface local maxima of ESP for *L*-PheC_1.

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	17.67	–5.96	–1.63	0.59
2	15.91	–5.58	–1.25	–1.63
3	15.06	–5.38	–0.29	2.23
4	19.70	–4.60	–3.50	1.01
5	15.22	–2.41	–0.37	–1.96
6	11.40	–2.24	0.49	1.63
7	15.70	–1.73	3.27	–1.81
8	13.54	–0.72	–0.76	–2.62
9	7.74	–0.46	0.67	2.93
10	15.46	0.54	–3.00	–1.37
11	21.87	1.16	2.32	–1.89
12	9.00	1.76	2.55	2.41
13	–14.38	2.96	–1.22	1.58
14	14.85	4.16	–3.03	–2.12
15	13.62	5.00	2.55	1.45
16	14.28	6.51	–0.17	–0.71

Table S28 Surface local minima of ESP for simplified sutrcture of PAN (2,4-dimethylpentanedinitrile).

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	8.92	–3.96	0.00	0.55
2	9.68	–3.61	2.24	1.85
3	–38.05	–2.89	–2.86	–2.40
4	14.64	0.07	–0.02	3.00
5	–38.06	2.94	2.83	–2.40
6	9.68	3.57	–2.26	1.88
7	8.93	4.01	–0.03	0.64

Table S29 Surface local maxima of ESP for simplified sutrcture of PAN (2,4-dimethylpentanedinitrile).

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	19.69	–3.90	1.96	–0.60
2	22.40	–2.38	1.32	–1.32
3	26.63	–1.83	–1.15	1.44
4	21.48	–1.49	2.11	–1.47
5	24.77	–0.07	–2.06	2.10
6	23.01	–0.07	0.11	–1.78
7	24.78	0.06	2.06	2.09
8	21.48	1.38	–2.14	–1.49
9	26.70	1.87	1.10	1.47
10	22.39	2.34	–1.33	–1.34
11	19.69	3.93	–1.89	–0.61

Table S30 Surface local minima of ESP for simplified sutrcture of PP (2-methylpentane).

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	–2.08	–4.08	–1.15	–0.71
2	–3.12	–3.26	–0.22	–2.42
3	–3.79	–2.22	0.82	2.45
4	–4.79	0.84	–2.20	1.55
5	–2.70	1.84	3.22	0.56
6	–2.32	2.42	–1.55	–2.16
7	–2.87	3.37	0.71	0.36
8	–3.06	3.74	–1.94	–0.17

Table S31 Surface local maxima of ESP for simplified sutrcture of PP (2-methylpentane).

Number	Value/kcal mol^{-1}	Coordinate/Å		
		x	y	z
1	7.77	–4.58	0.90	–0.47
2	6.42	–2.96	–1.25	2.23
3	7.87	–2.50	–2.40	–1.43
4	8.70	–0.93	1.05	–2.42
5	9.09	–0.98	2.69	0.11
6	6.34	–0.46	–2.96	–0.15
7	6.58	1.00	–0.34	2.75
8	7.46	1.52	–3.13	–0.96
9	8.13	1.95	1.39	2.40
10	7.77	2.89	–0.68	2.08
11	8.06	2.94	2.15	–1.47
12	7.87	3.69	0.24	–1.82

The geometry coordinates (Å) of the four cluster conformers in [*L*-PheC$_1$]Cl.

[*L*-PheC$_1$]Cl-A

C	-3.52460000	-7.33770000	-9.70900000
C	-2.40820000	-8.11280000	-9.43400000
H	-2.17610000	-8.27680000	-8.54790000
C	-1.63350000	-8.64450000	-10.44540000
H	-0.87880000	-9.14770000	-10.23920000
C	-1.98050000	-8.42840000	-11.76130000
H	-1.47160000	-8.79240000	-12.44980000
C	-3.07950000	-7.67420000	-12.03970000
H	-3.32250000	-7.53260000	-12.92590000
C	-3.84120000	-7.11390000	-11.03260000
H	-4.57290000	-6.58220000	-11.24800000
C	-4.39530000	-6.77600000	-8.61080000
H	-4.59310000	-7.48910000	-7.98360000
H	-5.23600000	-6.49270000	-9.00240000
C	-3.80630000	-5.59700000	-7.82930000
H	-4.49500000	-5.29010000	-7.20290000
C	-2.57880000	-5.92500000	-7.01980000
C	-1.75170000	-7.33760000	-5.30720000
H	-1.06080000	-7.71030000	-5.86120000
H	-2.07370000	-8.01090000	-4.70260000
H	-1.39700000	-6.59960000	-4.80580000
N	-3.48100000	-4.45110000	-8.72540000
H	-4.14850000	-4.32600000	-9.30030000
H	-2.73240000	-4.62790000	-9.17380000
H	-3.36770000	-3.71600000	-8.23660000
O	-1.51690000	-5.38200000	-7.14350000
O	-2.84900000	-6.87310000	-6.14620000
Cl	-0.72640000	-3.85020000	-10.24840000

[*L*-PheC$_1$]Cl-B

C	-3.52460000	-7.33770000	-9.70900000
C	-2.40820000	-8.11280000	-9.43400000
H	-2.17610000	-8.27680000	-8.54790000
C	-1.63350000	-8.64450000	-10.44540000
H	-0.87880000	-9.14770000	-10.23920000
C	-1.98050000	-8.42840000	-11.76130000
H	-1.47160000	-8.79240000	-12.44980000
C	-3.07950000	-7.67420000	-12.03970000
H	-3.32250000	-7.53260000	-12.92590000
C	-3.84120000	-7.11390000	-11.03260000
H	-4.57290000	-6.58220000	-11.24800000
C	-4.39530000	-6.77600000	-8.61080000
H	-4.59310000	-7.48910000	-7.98360000
H	-5.23600000	-6.49270000	-9.00240000
C	-3.80630000	-5.59700000	-7.82930000

H	-4.49500000	-5.29010000	-7.20290000
C	-2.57880000	-5.92500000	-7.01980000
C	-1.75170000	-7.33760000	-5.30720000
H	-1.06080000	-7.71030000	-5.86120000
H	-2.07370000	-8.01090000	-4.70260000
H	-1.39700000	-6.59960000	-4.80580000
N	-3.48100000	-4.45110000	-8.72540000
H	-4.14850000	-4.32600000	-9.30030000
H	-2.73240000	-4.62790000	-9.17380000
H	-3.36770000	-3.71600000	-8.23660000
O	-1.51690000	-5.38200000	-7.14350000
O	-2.84900000	-6.87310000	-6.14620000
Cl	-3.45060000	-2.36180000	-6.39800000

[*L*-PheC_1]Cl-C

C	-3.52460000	-7.33770000	-9.70900000
C	-2.40820000	-8.11280000	-9.43400000
H	-2.17610000	-8.27680000	-8.54790000
C	-1.63350000	-8.64450000	-10.44540000
H	-0.87880000	-9.14770000	-10.23920000
C	-1.98050000	-8.42840000	-11.76130000
H	-1.47160000	-8.79240000	-12.44980000
C	-3.07950000	-7.67420000	-12.03970000
H	-3.32250000	-7.53260000	-12.92590000
C	-3.84120000	-7.11390000	-11.03260000
H	-4.57290000	-6.58220000	-11.24800000
C	-4.39530000	-6.77600000	-8.61080000
H	-4.59310000	-7.48910000	-7.98360000
H	-5.23600000	-6.49270000	-9.00240000
C	-3.80630000	-5.59700000	-7.82930000
H	-4.49500000	-5.29010000	-7.20290000
C	-2.57880000	-5.92500000	-7.01980000
C	-1.75170000	-7.33760000	-5.30720000
H	-1.06080000	-7.71030000	-5.86120000
H	-2.07370000	-8.01090000	-4.70260000
H	-1.39700000	-6.59960000	-4.80580000
N	-3.48100000	-4.45110000	-8.72540000
H	-4.14850000	-4.32600000	-9.30030000
H	-2.73240000	-4.62790000	-9.17380000
H	-3.36770000	-3.71600000	-8.23660000
O	-1.51690000	-5.38200000	-7.14350000
O	-2.84900000	-6.87310000	-6.14620000
Cl	-6.17490000	-3.85020000	-10.24840000

The geometry coordinates (Å) of the four cluster conformers in [*D*-PheC$_1$]Cl.

[*D*-PheC$_1$]Cl-A

C	2.58770000	5.90850000	7.00230000
C	3.80810000	5.58230000	7.81830000
H	4.49920000	5.27590000	7.19510000
C	1.74480000	7.31610000	5.29700000
H	2.07860000	7.91140000	4.62220000
H	1.09840000	7.77620000	5.83880000
H	1.33040000	6.55710000	4.87980000
C	4.39620000	6.75800000	8.60120000
H	5.23650000	6.47400000	8.99510000
H	4.59660000	7.47110000	7.97460000
C	3.52600000	7.32110000	9.69980000
C	2.40210000	8.09370000	9.41390000
H	2.16630000	8.25130000	8.52800000
C	1.63860000	8.62460000	10.42280000
H	0.88440000	9.12810000	10.21670000
C	1.98490000	8.41620000	11.74080000
H	1.47470000	8.78450000	12.42560000
C	3.07840000	7.66590000	12.02670000
H	3.32020000	7.52820000	12.91420000
C	3.84020000	7.10280000	11.01280000
H	4.57210000	6.57070000	11.22890000
N	3.48360000	4.43630000	8.71090000
H	3.41550000	3.69340000	8.22550000
H	2.71140000	4.59130000	9.12470000
H	4.12940000	4.33830000	9.31420000
O	1.51880000	5.37520000	7.14390000
O	2.84750000	6.86590000	6.13730000
Cl	0.72970000	3.84510000	10.23480000

[*D*-PheC$_1$]Cl-B

C	2.58770000	5.90850000	7.00230000
C	3.80810000	5.58230000	7.81830000
H	4.49920000	5.27590000	7.19510000
C	1.74480000	7.31610000	5.29700000
H	2.07860000	7.91140000	4.62220000
H	1.09840000	7.77620000	5.83880000
H	1.33040000	6.55710000	4.87980000
C	4.39620000	6.75800000	8.60120000
H	5.23650000	6.47400000	8.99510000
H	4.59660000	7.47110000	7.97460000
C	3.52600000	7.32110000	9.69980000
C	2.40210000	8.09370000	9.41390000
H	2.16630000	8.25130000	8.52800000
C	1.63860000	8.62460000	10.42280000
H	0.88440000	9.12810000	10.21670000

C	1.98490000	8.41620000	11.74080000
H	1.47470000	8.78450000	12.42560000
C	3.07840000	7.66590000	12.02670000
H	3.32020000	7.52820000	12.91420000
C	3.84020000	7.10280000	11.01280000
H	4.57210000	6.57070000	11.22890000
N	3.48360000	4.43630000	8.71090000
H	3.41550000	3.69340000	8.22550000
H	2.71140000	4.59130000	9.12470000
H	4.12940000	4.33830000	9.31420000
O	1.51880000	5.37520000	7.14390000
O	2.84750000	6.86590000	6.13730000
Cl	3.45250000	2.35610000	6.38580000

[*D*-PheC_1]Cl-C

C	2.58770000	5.90850000	7.00230000
C	3.80810000	5.58230000	7.81830000
H	4.49920000	5.27590000	7.19510000
C	1.74480000	7.31610000	5.29700000
H	2.07860000	7.91140000	4.62220000
H	1.09840000	7.77620000	5.83880000
H	1.33040000	6.55710000	4.87980000
C	4.39620000	6.75800000	8.60120000
H	5.23650000	6.47400000	8.99510000
H	4.59660000	7.47110000	7.97460000
C	3.52600000	7.32110000	9.69980000
C	2.40210000	8.09370000	9.41390000
H	2.16630000	8.25130000	8.52800000
C	1.63860000	8.62460000	10.42280000
H	0.88440000	9.12810000	10.21670000
C	1.98490000	8.41620000	11.74080000
H	1.47470000	8.78450000	12.42560000
C	3.07840000	7.66590000	12.02670000
H	3.32020000	7.52820000	12.91420000
C	3.84020000	7.10280000	11.01280000
H	4.57210000	6.57070000	11.22890000
N	3.48360000	4.43630000	8.71090000
H	3.41550000	3.69340000	8.22550000
H	2.71140000	4.59130000	9.12470000
H	4.12940000	4.33830000	9.31420000
O	1.51880000	5.37520000	7.14390000
O	2.84750000	6.86590000	6.13730000
Cl	6.17530000	3.84510000	10.23480000

The optimized geometry coordinates of *L*-PheC_1.

N	-0.60940900	1.82413100	-0.55030000
H	-1.35632300	2.33429900	-1.00885400
C	-0.94668900	0.41108300	-0.43189800
H	-0.77140500	-0.15481800	-1.36371400
C	-0.11020900	-0.26527800	0.68246100
C	-2.44911700	0.28984500	-0.19355300
H	-0.30686400	0.26426900	1.61833300
H	-0.45256300	-1.29492200	0.80017100
C	1.37237800	-0.24944500	0.38140800
O	-3.24265700	1.18450900	-0.35933400
C	2.20073900	0.76615700	0.87246200
C	1.94640600	-1.24669800	-0.41720200
H	1.77240900	1.54615900	1.49231000
C	3.56254600	0.78619900	0.57258300
C	3.30639300	-1.22981000	-0.71977900
H	1.32348100	-2.05063700	-0.79787800
H	4.18808900	1.58011000	0.96587100
C	4.11997900	-0.21082200	-0.22578700
H	3.73180600	-2.01522000	-1.33494400
H	5.17930700	-0.19785000	-0.45641700
O	-2.80291800	-0.95645900	0.17360900
C	-4.21392700	-1.18463500	0.35783700
H	-4.75289200	-1.00267700	-0.57289000
H	-4.30177200	-2.22713000	0.65515100
H	-4.60676000	-0.52791700	1.13470700
H	0.25296400	1.95344400	-1.06514000

The optimized geometry coordinates of simplified sutrcture of PAN (2,4-dimethylpentanedinitrile).

C	1.20652400	-0.49198500	0.08922100
H	0.86048900	-1.26368200	-0.60817400
C	0.00001100	-0.00110000	0.92023200
H	-0.32173900	-0.82194800	1.56783800
H	0.32167800	0.81806200	1.57000900
C	-1.20649100	0.49192600	0.09039700
H	-0.86048200	1.26567600	-0.60472000
C	-2.30847800	1.09280400	0.98470100
H	-1.90751300	1.94393700	1.53923200
H	-3.15181500	1.43925400	0.38538500
H	-2.67767400	0.35405900	1.69977800
C	1.74585600	0.60432800	-0.72458300
C	-1.74558700	-0.60222900	-0.72645200
N	2.16344600	1.48269100	-1.34509400
N	-2.16333200	-1.47919800	-1.34882800
C	2.30821300	-1.09570000	0.98198500
H	1.90696900	-1.94838100	1.53392000

H	3.15162000	-1.44054700	0.38184300
H	2.67738800	-0.35914300	1.69933700

The optimized geometry coordinates of simplified sutrcture of PP (2-methylpentane).

C	-1.60614700	0.02368500	0.62876100
H	-2.22161200	-0.47452900	1.38639500
H	-1.53100500	1.06854000	0.94935400
C	-0.21482600	-0.63045600	0.64058700
H	0.17428200	-0.61345200	1.66746400
H	-0.32707100	-1.69046800	0.37798300
C	0.84802000	-0.00940000	-0.28784600
H	0.46343200	-0.03447600	-1.31525100
C	2.13316700	-0.84921600	-0.25829100
H	1.93821600	-1.88625000	-0.54780200
H	2.88715000	-0.44695100	-0.94156600
H	2.56891700	-0.86112500	0.74703100
C	-2.32926800	-0.04666900	-0.72107000
H	-3.33826200	0.36896600	-0.64816600
H	-1.80116100	0.51256400	-1.49838700
H	-2.42164200	-1.08229500	-1.06483400
C	1.15188600	1.45339900	0.06623100
H	0.26964500	2.09244400	-0.02258700
H	1.52080100	1.53567600	1.09500700
H	1.92131700	1.86329400	-0.59486600

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