Electronic Supplementary Material (ESI) for Chemical Science.


# Supporting Information

# Macroscopic handedness inversion of terbium coordination polymers achieved by doping homochiral ligand analogues

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# Experimental procedures

## General materials and measurements

All starting materials were used as purchased from commercial sources without further purification. (*R*)- or (*S*)-(1-cyclohexyl-ethylamino)methylphosphonic acid (*R*- or *S*-cyampH$_2$),[1] (*R*)- or (*S*)-(1-phenylethylamino)methylphosphonic acid (*R*- or *S*-pempH$_2$),[2] and (*R*)-(4-X-phenylethylamino)methylphosphonic acid (*R*-XpempH$_2$, X = F, Cl, Br) were synthesized according to a literature method[3] with (*R*)- or (*S*)-cyclohexylethyl-1-amine, (*R*)- or (*S*)-phenylethyl-1-amine and (*R*)-4-X-phenylethyl-1-amine as the reactant respectively as well as paraformaldehyde and diethyl phosphite. The pH value was measured by using a Sartorius PB-10 pH metre. Powder X-ray diffraction (PXRD) data were collected on Bruker D8 advance diffractometer with Cu-Kα radiation in a range of 4–50°. The infrared spectra were recorded by using Bruker Tensor 27 spectrometer in a 4000–400 cm$^{-1}$ region with pressed KBr pellets of the analytes. Scanning electron microscope (SEM) imaging and energy dispersive X-ray (EDX) analysis were carried out on Hitachi S-4800. Fluorescence spectra were obtained by using an Edinburgh FLS980 spectrofluorometer and the circularly polarized luminescence (CPL) spectra by using a JASCO CPL-300 CPL spectrophotometer. The ECD spectra were measured on a JASCO J-810 spectropolarimeter and the VCD spectra on a Bruker VERTEX 80V FT-IR spectrometer using KBr pellets at room temperature. The elemental analysis was done be using an Elemetar Vario MICRO cube elemental analyzer. The thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC STARe thermal analyzer under a nitrogen gas flow at a heating rate of 5 °C/min in the range of 25–600 °C.

## Synthetic procedures

***R*-** and ***S*-Tb(cyamp)$_{3a}$(pemp)$_{3(1-a)}$·3H$_2$O** (the molar ratio $a \approx x$ and the doping ratio $x$ = 5%, 10% or 20%) (***R*-** and ***S*-1H-*x***). The compound ***R*-** and ***S*-1H-*x*** was prepared through the similar procedures except the molar ratio of the ligands according to the value of $x$. A typical procedure for the synthesis of ***R*-1H-5%** is described below. *R*-cyampH$_2$ (0.285 mmol, 63.1 mg), *R*-pempH$_2$ (0.015 mmol, 3.2 mg) and Tb(OAc)$_3$·3H$_2$O (0.1 mmol, 39.0 mg) were added in 8.5 mL deionized water and stirred for 5 h until the solution turned white and opaque. Afterwards, 0.5 M NaOH solution was used to adjust pH of the suspension to 5.0. Then the suspension was kept in a Teflon-lined autoclave at 100 °C for 1 d. After being cooled to room temperature, the precipitates of ***R*-1H-5%** were collected by centrifugation and washed three times with water and then dried in air. Yield: 73.0% based on Tb. Elemental analysis (%) calcd for C$_{27}$H$_{61.8}$N$_3$O$_{11}$P$_3$Tb: C 37.17, H 7.14, and N 4.82; found: C 36.84, H 6.90, and N 4.64. IR (KBr, cm$^{-1}$): 3680(w), 3420(w),

2986(w), 2928(s), 2853(m), 2793(w), 2670(w), 2523(w), 2405(w), 1618(m), 1450(m), 1392(w), 1344(w), 1308(w), 1275(w), 1234(w), 1153(s), 1072(s), 1024(s), 989(s), 893(w), 860(w), 783(w), 763(m), 702(w), 613(w), 567(m), 517(w), 483(m), 457(w).

For ***S*-1H-5%**. Yield: 68.3% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{62.0}N_3O_{11}P_3Tb$: C 37.16, H 7.16, and N 4.82; found: C 36.84, H 7.04, and N 4.71. IR (KBr, $cm^{-1}$): 3733(w), 3680(w), 3420(w), 2986(w), 2928(s), 2853(m), 2793(w), 2670(w), 2523(w), 2405(w), 2351(w), 2323(w), 1618(m), 1450(m), 1392(w), 1344(w), 1308(w), 1275(w), 1234(w), 1153(s), 1072(s), 1024(s), 989(s), 893(w), 860(w), 783(w), 763(m), 702(w), 613(w), 567(m), 517(w), 483(m), 457(w).

For ***R*-1H-10%**. Yield: 69.7% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{60.7}N_3O_{11}P_3Tb$: C 37.22, H 7.02, and N 4.82; found: C 36.71, H 6.78, and N 4.40. IR (KBr, $cm^{-1}$): 3733(w), 3680(w), 3420(w), 2986(w), 2928(s), 2853(m), 2793(w), 2670(w), 2523(w), 2405(w), 2351(w), 2323(w), 1618(m), 1450(m), 1392(w), 1344(w), 1308(w), 1275(w), 1234(w), 1153(s), 1072(s), 1024(s), 989(s), 893(w), 860(w), 783(w), 763(m), 702(w), 613(w), 567(m), 517(w), 483(m), 457(w).

For ***S*-1H-10%**. Yield: 62.1% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{61.0}N_3O_{11}P_3Tb$: C 37.21, H 7.06, and N 4.82; found: C 36.82, H 6.96, and N 4.68. IR (KBr, $cm^{-1}$): 3733(w), 3680(w), 3420(w), 2986(w), 2928(s), 2853(m), 2793(w), 2670(w), 2523(w), 2405(w), 2351(w), 2323(w), 1618(m), 1450(m), 1392(w), 1344(w), 1308(w), 1275(w), 1234(w), 1153(s), 1072(s), 1024(s), 989(s), 893(w), 860(w), 783(w), 763(m), 702(w), 613(w), 567(m), 517(w), 483(m), 457(w).

For ***R*-1H-20%**. Yield: 68.1% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{59.4}N_3O_{11}P_3Tb$: C 37.27, H 6.89, and N 4.83; found: C 37.27, H 6.58, and N 4.71. IR (KBr, $cm^{-1}$): 3733(w), 3680(w), 3420(w), 2986(w), 2928(s), 2853(m), 2793(w), 2670(w), 2523(w), 2405(w), 2351(w), 2323(w), 1618(m), 1450(m), 1392(w), 1344(w), 1308(w), 1275(w), 1153(s), 1072(s), 1024(s), 989(s), 893(w), 860(w), 763(m), 702(w), 613(w), 567(m), 517(w), 477(m), 457(w).

For ***S*-1H-20%**. Yield: 68.3% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{59.3}N_3O_{11}P_3Tb$: C 37.28, H 6.87, and N 4.83; found: C 36.98, H 6.73, and N 4.69. IR (KBr, $cm^{-1}$): 3733(w), 3680(w), 3420(w), 2986(w), 2928(s), 2853(m), 2793(w), 2670(w), 2523(w), 2405(w), 2351(w), 2323(w), 1618(m), 1450(m), 1392(w), 1344(w), 1308(w), 1275(w), 1153(s), 1072(s), 1024(s), 989(s), 893(w), 860(w), 763(m), 702(w), 613(w), 567(m), 517(w), 477(m), 457(w).

***R*-Tb(cyamp)$_{3a}$(Fpemp)$_{3(1-a)}$** (the molar ratio $a \approx x$ and the doping ratio $x$ = 5% and 10%) (***R*-2F-*x***). The compounds ***R*-2F-*x*** were prepared through the similar procedures to ***R*-1H-*x*** except that *R*-pempH$_2$ were replaced by *R*-FpempH$_2$. For ***R*-2F-5%**. Yield: 65.1% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{62.1}N_3O_{12}P_3F_{0.13}Tb$: C, 37.05; H, 7.15; N, 4.80; found: C, 36.73; H, 6.73; N, 4.64. IR (KBr, $cm^{-1}$): 3732(w), 3674(w),

3425(w), 2984(w), 2928(s), 2855(m), 2793(w), 2669(w), 2519(w), 2401(w), 2353(w), 2324(w), 1618(m), 1514(w), 1450(m), 1391(w), 1344(w), 1308(w), 1275(w), 1229(w), 1153(s), 1074(s), 1022(s), 988(s), 891(w), 856(w), 841(w), 810(w), 781(w), 764(m), 730(w), 613(w), 565(m), 515(w), 484(m), 476(m), 457(w), 419(w).

For ***R*-2F-10%**. Yield: 61.6% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{61.0}N_3O_{12}P_3F_{0.29}Tb$: C, 36.97; H, 7.01; N, 4.79; found: C, 36.89; H, 7.19; N, 4.68. IR (KBr, $cm^{-1}$): 3732(w), 3674(w), 3425(w), 2984(w), 2928(s), 2855(m), 2793(w), 2669(w), 2519(w), 2401(w), 2353(w), 2324(w), 1618(m), 1514(w), 1450(m), 1391(w), 1344(w), 1308(w), 1275(w), 1229(w), 1153(s), 1074(s), 1022(s), 988(s), 891(w), 856(w), 841(w), 810(w), 781(w), 764(m), 730(w), 613(w), 565(m), 515(w), 484(m), 476(m), 457(w), 419(w).

***R*-Tb(cyamp)$_{3a}$(ClpempH)$_{3(1-a)}$** (the molar ratio $a \approx x$ and the doping ratio $x$= 5% and 10%) (***R*-3Cl-*x***). The compounds ***R*-3Cl-*x*** were prepared through the similar procedures to ***R*-1H-*x*** except that *R*-pempH$_2$ were replaced by *R*-Cl-pempH$_2$. For ***R*-3Cl-5%**. Yield: 62.2% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{62.1}N_3O_{12}P_3Cl_{0.13}Tb$: C, 36.97; H, 7.14; N, 4.79; found: C, 36.60; H, 6.77; N, 4.55. IR (KBr, $cm^{-1}$): 3732(w), 3674(w), 3424(w), 2984(w), 2928(s), 2853(m), 2791(w), 2669(w), 2517(w), 2399(w), 2353(w), 2324(w), 1618(m), 1450(m), 1391(w), 1346(w), 1308(w), 1275(w), 1234(w), 1153(s), 1072(s), 1022(s), 988(s), 891(w), 858(w), 781(w), 764(m), 615(w), 565(m), 517(w), 484(m), 476(m), 457(w), 419(w).

For ***R*-3Cl-10%**. Yield: 69.4% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{61.1}N_3O_{12}P_3Cl_{0.27}Tb$: C, 36.80; H, 6.99; N, 4.77; found: C, 36.53; H, 7.19; N, 4.66. IR (KBr, $cm^{-1}$): 3732(w), 3674(w), 3424(w), 2984(w), 2928(s), 2853(m), 2791(w), 2669(w), 2517(w), 2401(w), 2353(w), 2324(w), 1620(m), 1450(m), 1391(w), 1344(w), 1308(w), 1275(w), 1234(w), 1153(s), 1074(s), 1022(s), 988(s), 891(w), 858(w), 783(w), 764(m), 615(w), 565(m), 517(w), 484(m), 474(m), 457(w), 419(w).

***R*-Tb(cyamp)$_{3a}$(BrpempH)$_{3(1-a)}$** (the molar ratio $a \approx x$ and the doping ratio $x$= 5% and 10%) (***R*-4Br-*x***). The compounds ***R*-4Br-*x*** were prepared through the similar procedures to ***R*-1H-*x*** except that *R*-pempH$_2$ were replaced by *R*-Br-pempH$_2$. For ***R*-4Br-5%**. Yield: 53.7% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{62.2}N_3O_{12}P_3Br_{0.11}Tb$: C, 36.60; H, 6.77; N, 4.55; found: C, 36.40; H, 6.73; N, 4.29. IR (KBr, $cm^{-1}$): 3732(w), 3674(w), 3422(w), 2984(w), 2928(s), 2853(m), 2791(w), 2669(w), 2517(w), 2399(w), 2353(w), 2322(w), 1620(m), 1450(m), 1391(w), 1344(w), 1308(w), 1275(w), 1234(w), 1153(s), 1072(s), 1022(s), 988(s), 891(w), 858(w), 783(w), 764(m), 615(w), 565(m), 517(w), 484(m), 474(m), 457(w), 419(w).

For ***R*-4Br-10%**. Yield: 59.6% based on Tb. Elemental analysis (%) calcd for $C_{27}H_{60.6}N_3O_{12}P_3Br_{0.36}Tb$: C, 36.02; H, 6.77; N, 4.67; found: C, 35.61; H, 6.53; N, 4.25. IR (KBr, $cm^{-1}$): 3732(w), 3674(w), 3420(w), 2984(w), 2928(s), 2853(m), 2793(w),

2669(w), 2519(w), 2399(w), 2351(w), 2324(w), 1620(m), 1450(m), 1391(w), 1346(w), 1308(w), 1277(w), 1232(w), 1153(s), 1074(s), 1022(s), 988(s), 891(w), 858(w), 818(w), 779(w), 762(m), 615(w), 565(m), 517(w), 484(m), 474(m), 457(w), 420(w).

## References


1 Z.-S. Cai, S.-S. Bao, M. Ren, L.-M. Zheng, *Chem. Eur. J.*, 2014, **20**, 17137-17142.

2 (a) X.-G. Liu, S. Bao, Y.-Z. Li and L.-M. Zheng, *Inorg. Chem.*, 2008, **47**, 5525; (b) J.-G. Jia, J.-S. Feng, X.-D. Huang, S.-S. Bao and L.-M. Zheng, *Chem. Commun.*, 2019, **55**, 2825-2828.

3 J.-G. Jia, C.-C. Zhao, S.-S. Bao, L.-Q. Wu, G.-H. Wen, A. J. Jacobson, J. Ma and L.-M. Zheng, *J. Am. Chem. Soc.,* 2021, **143**, 17587-17598.

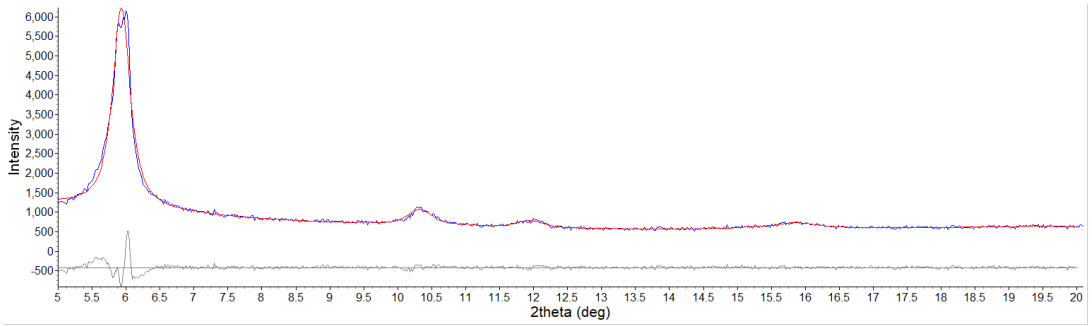


**Figure S1** Pawley fit of powder samples of ***R*-1H-5%** using Topas 5.0 program. Fitted cell parameters ($R_{wp}$ = 5.30): $P6_5$, $a$ = 17.01 Å, $c$ = 23.53 Å, $V$ = 5898.8 Å$^3$.

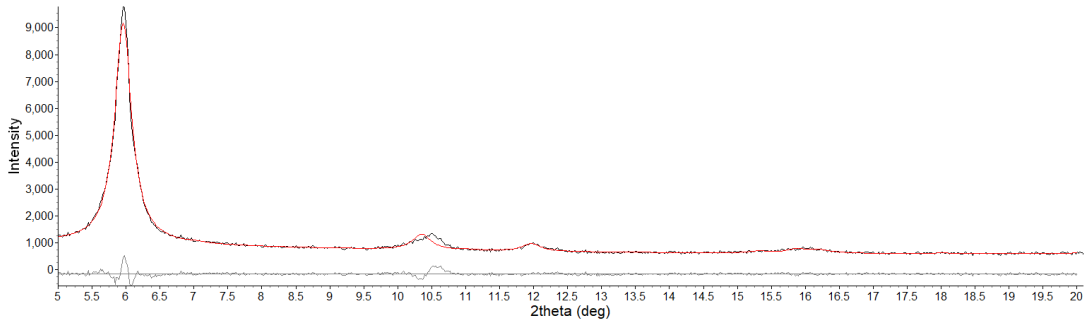


**Figure S2** Pawley fit of powder samples of ***R*-1H-10%** using Topas 5.0 program. Fitted cell parameters ($R_{wp}$ = 5.16): $P6_5$, $a$ = 17.01 Å, $c$ = 23.53 Å, $V$ = 5898.8 Å$^3$.

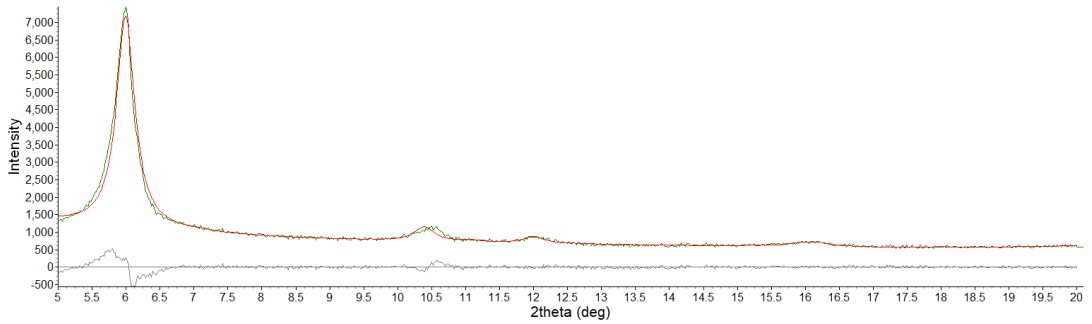


**Figure S3** Pawley fit of powder samples of ***R*-1H-20%** using Topas 5.0 program. Fitted cell parameters ($R_{wp}$ = 5.96): $P6_5$, $a$ = 17.01 Å, $c$ = 23.53 Å, $V$ = 5898.8 Å$^3$.

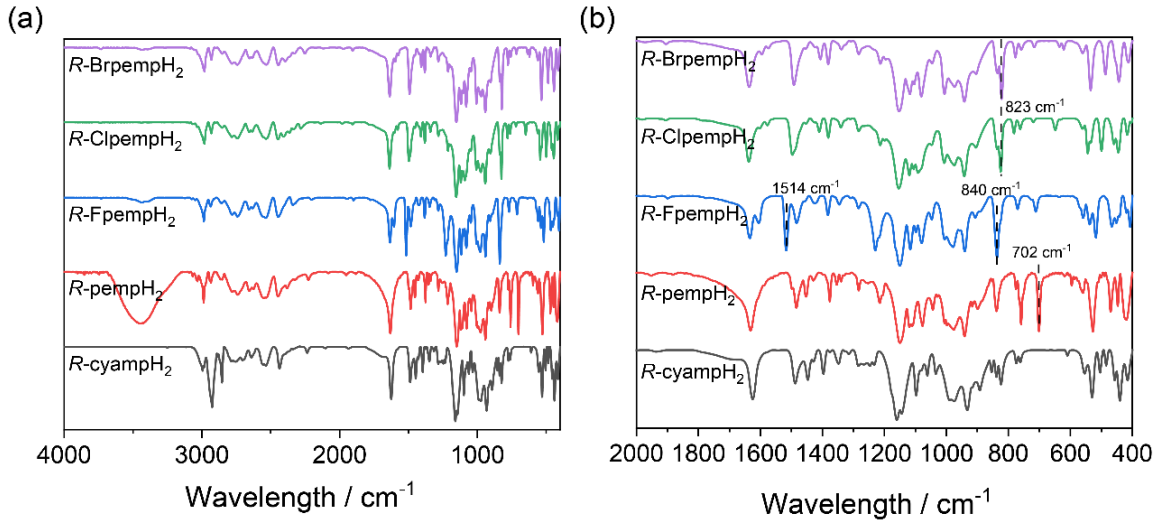


**Figure S4** IR spectra (4000–400 $cm^{-1}$ (a) and 2000–400 $cm^{-1}$ (b)) of the ligands *R*-cyampH$_2$, *R*-pempH$_2$, *R*-FpempH$_2$, *R*-ClpempH$_2$, and *R*-BrpempH$_2$, which are used in the syntheses of superhelices ***R*-1H-*x***, ***R*-2F-*x***, ***R*-3Cl-*x***, and ***R*-4Br-*x***.

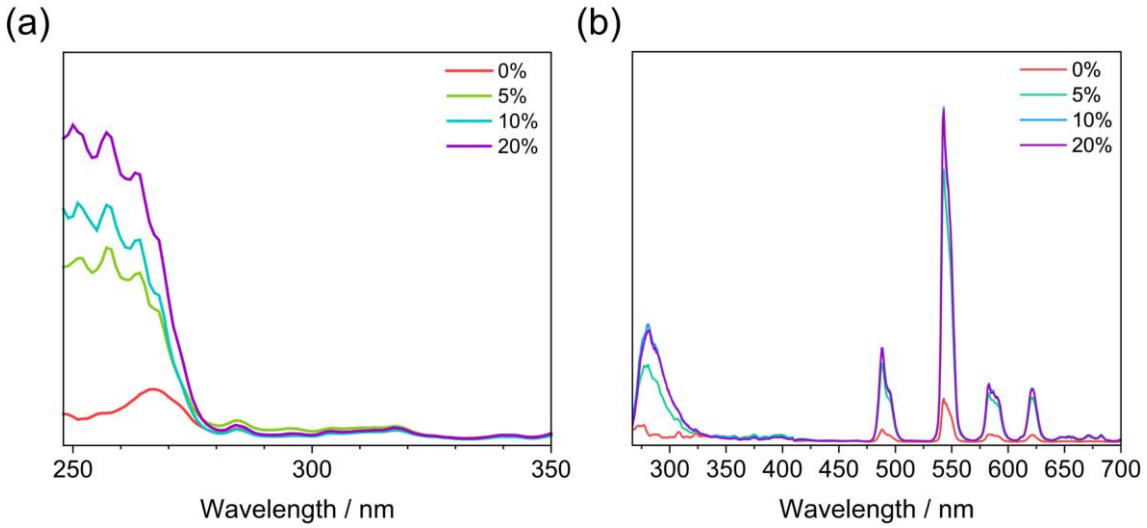


**Figure S5** (a) Excitation spectra (with emission at 543 nm) and (b) emission spectra excited at 247 nm of ***R*-1H-*x*** (*x* = 0%, 5%, 10%, 20%) obtained at pH = 5.0.

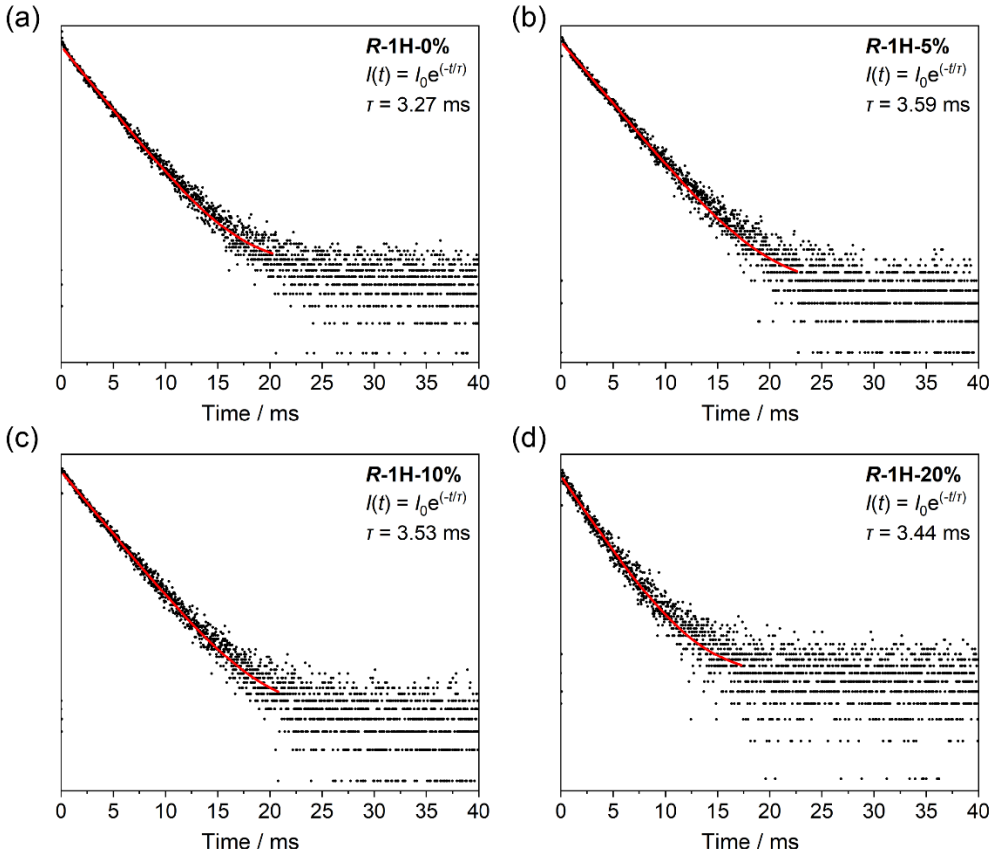


**Figure S6** Transient emission decay spectra of ***R*-1H-*x*** ($x$ = 0%, 5%, 10%, 20%).

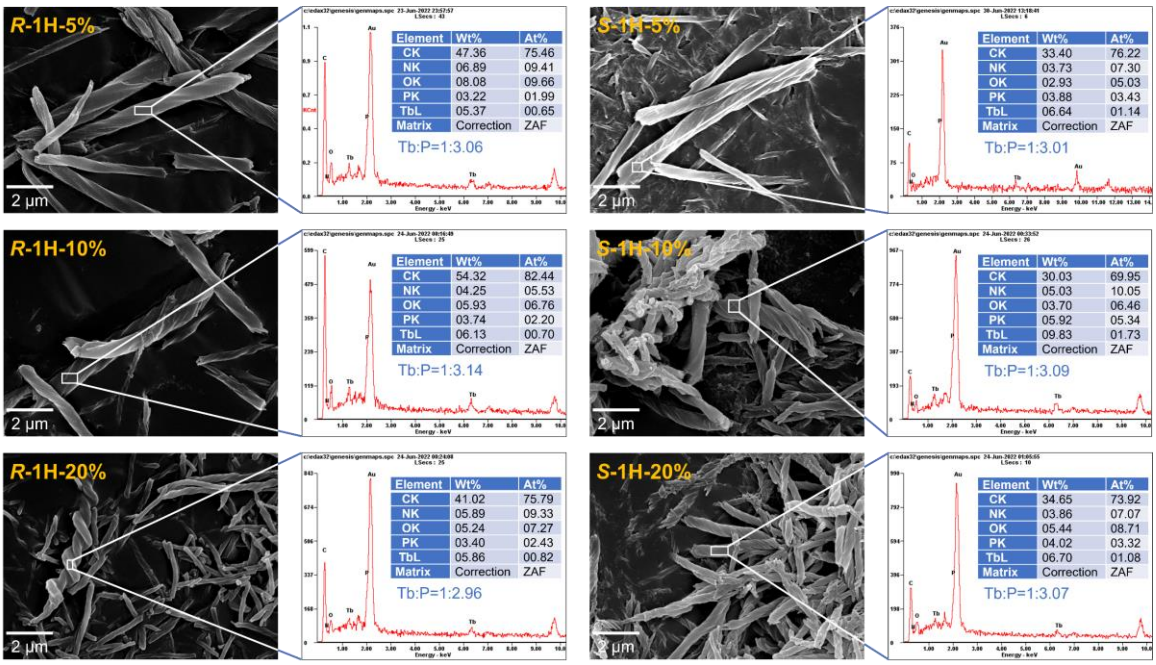


**Figure S7** EDX spectra of ***R*-** and ***S*-1H-*x*** ($x$ = 5%, 10%, 20%) superhelices.

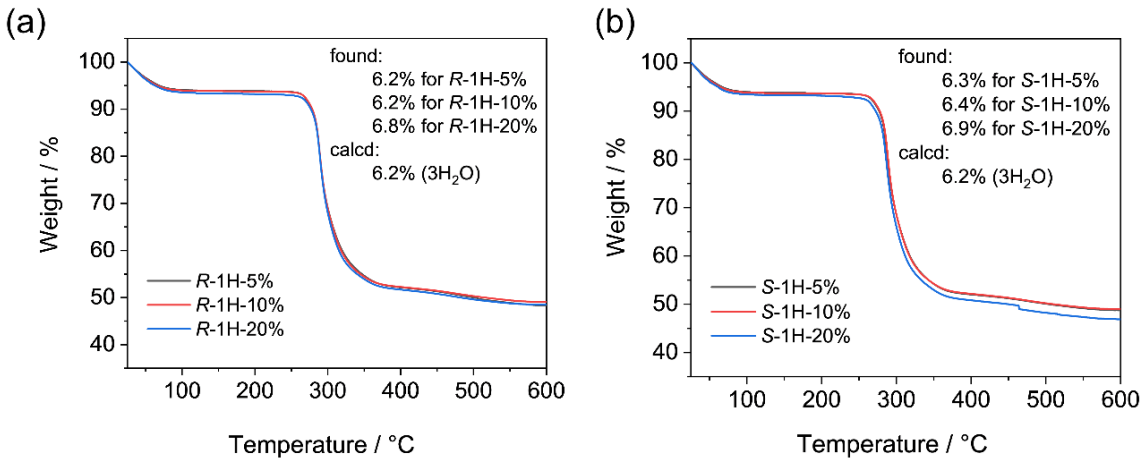


**Figure S8** TG analyses of ***R-*** and ***S*-1H-*x*** (*x* = 5%, 10%, 20%) obtained at pH = 5.0.

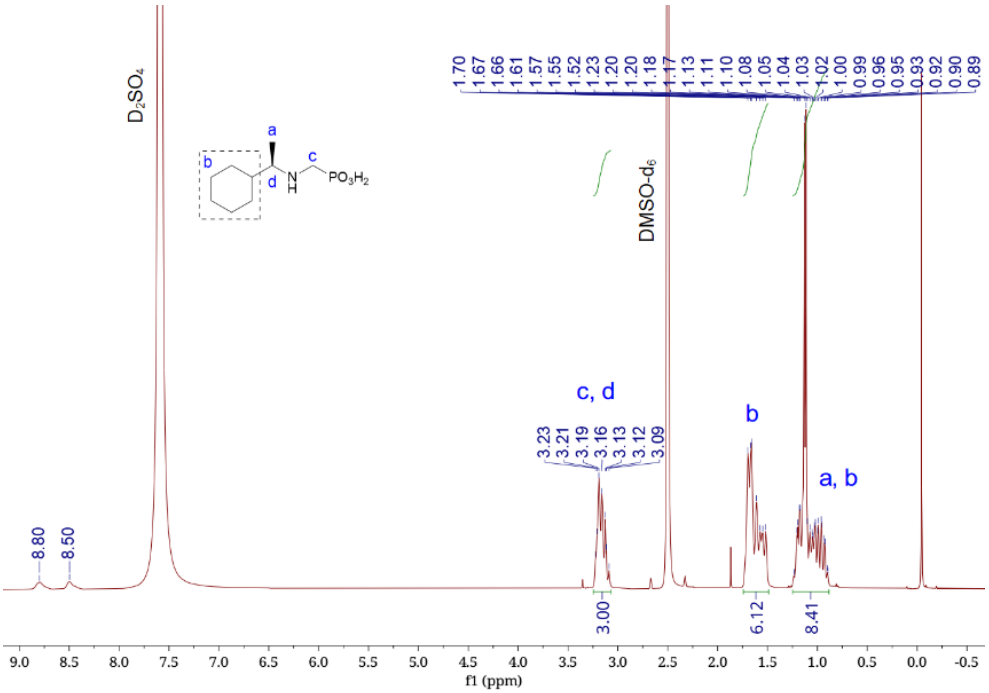


**Figure S9** 1H-NMR spectra of ***R*-1H-0%** obtained at pH = 5.0. The peaks at 8.5 and 8.8 ppm are attributed to the H atoms adjacent to N and O atoms of the ligand.

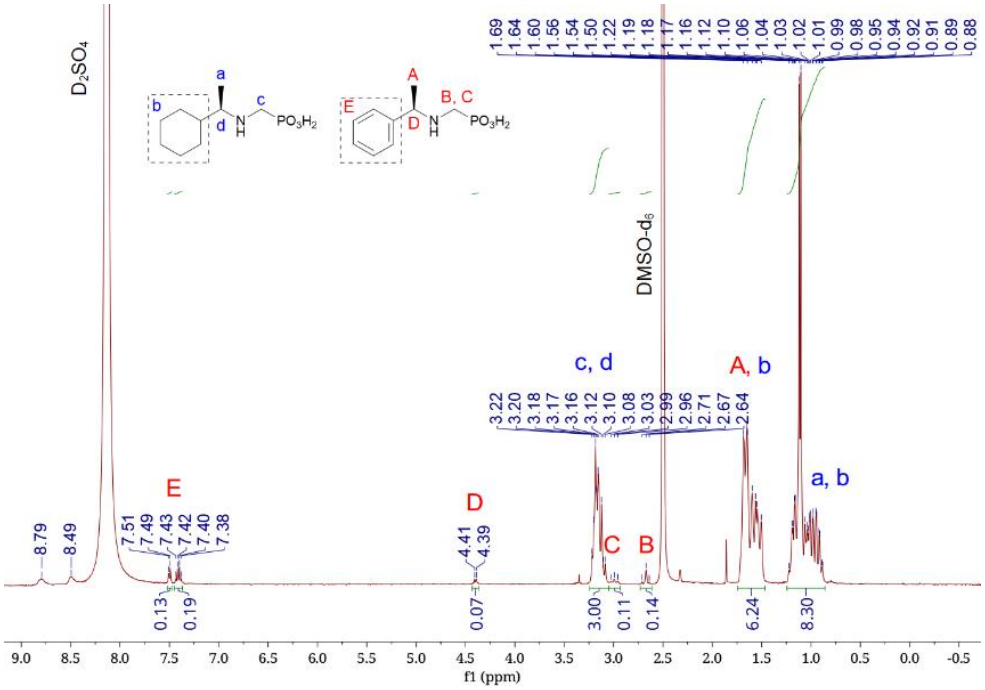


**Figure S10** 1H-NMR spectra of ***R*-1H-5%** obtained at pH = 5.0.

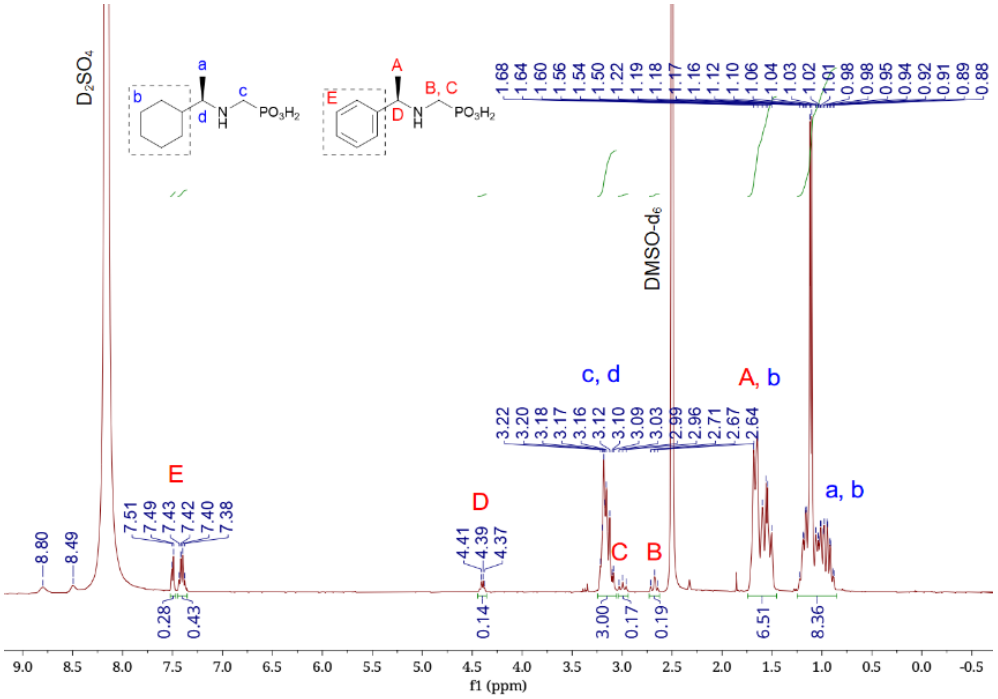


**Figure S11** 1H-NMR spectra of ***R*-1H-10%** obtained at pH = 5.0.

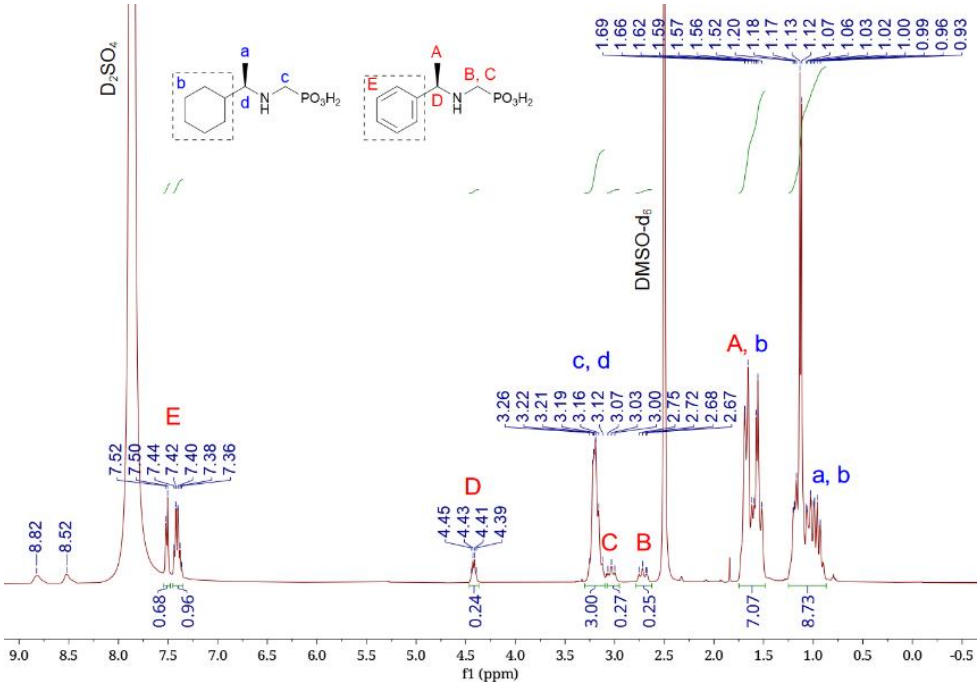


**Figure S12** 1H-NMR spectra of ***R*-1H-20%** obtained at pH = 5.0.

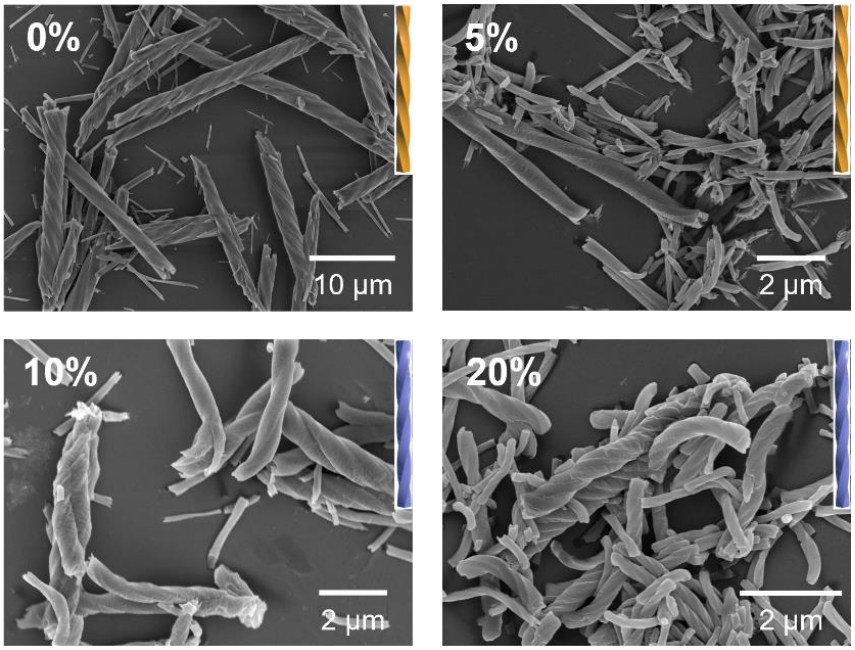


**Figure S13** SEM images of ***S*-1H-*x*** (*x* = 0%, 5%, 10%, and 20%) obtained at pH 5.0.

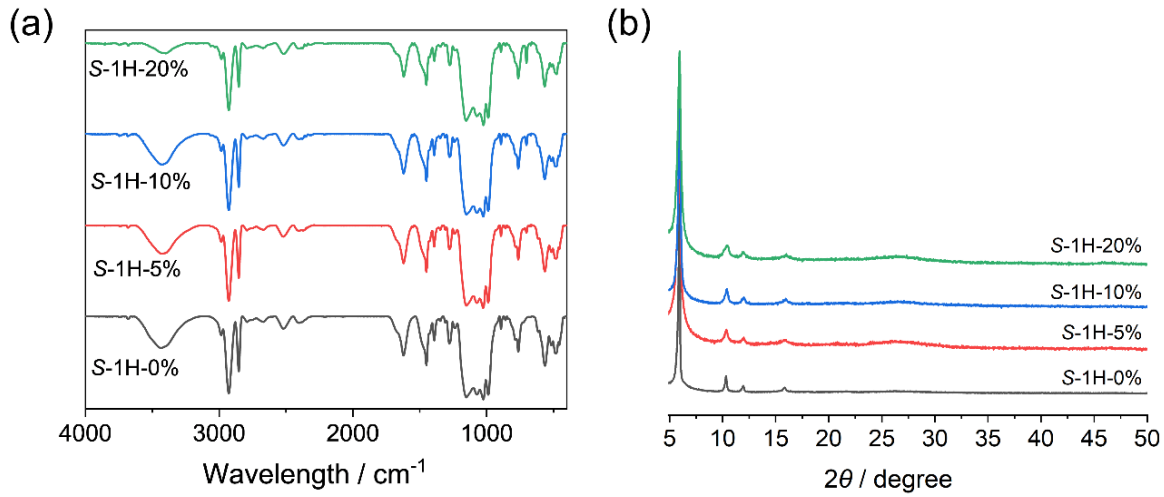


**Figure S14** IR spectra (4000–400 $cm^{-1}$) (a) and PXRD patterns (b) of ***S*-1H-*x*** (*x* = 0%, 5%, 10%, 20%) obtained under pH 5.0.

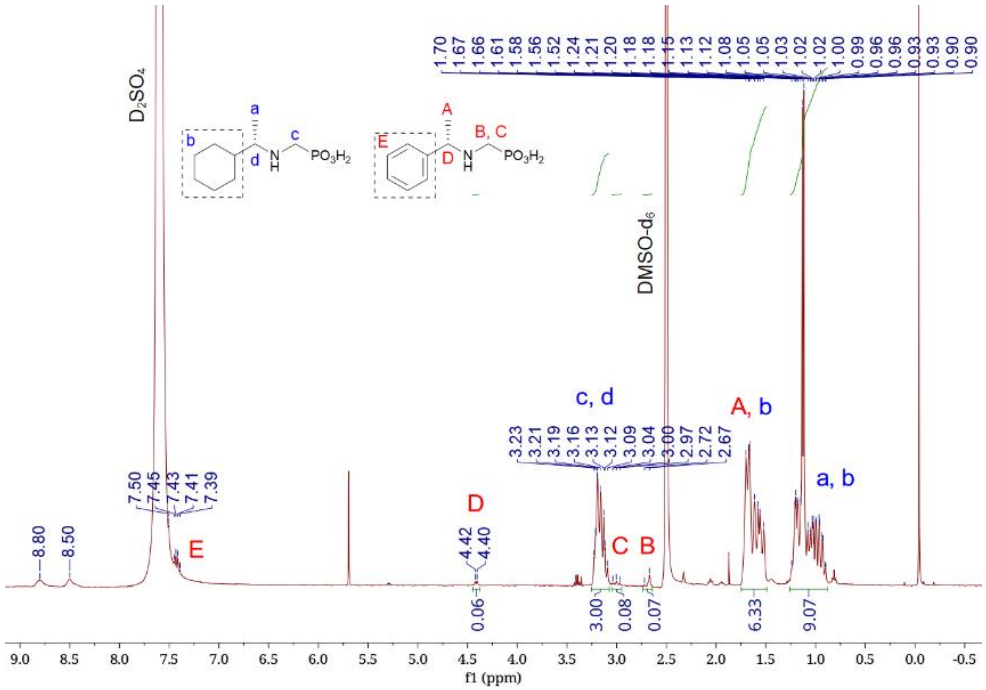


**Figure S15** 1H-NMR spectra of ***S*-1H-5%** obtained at pH = 5.0.

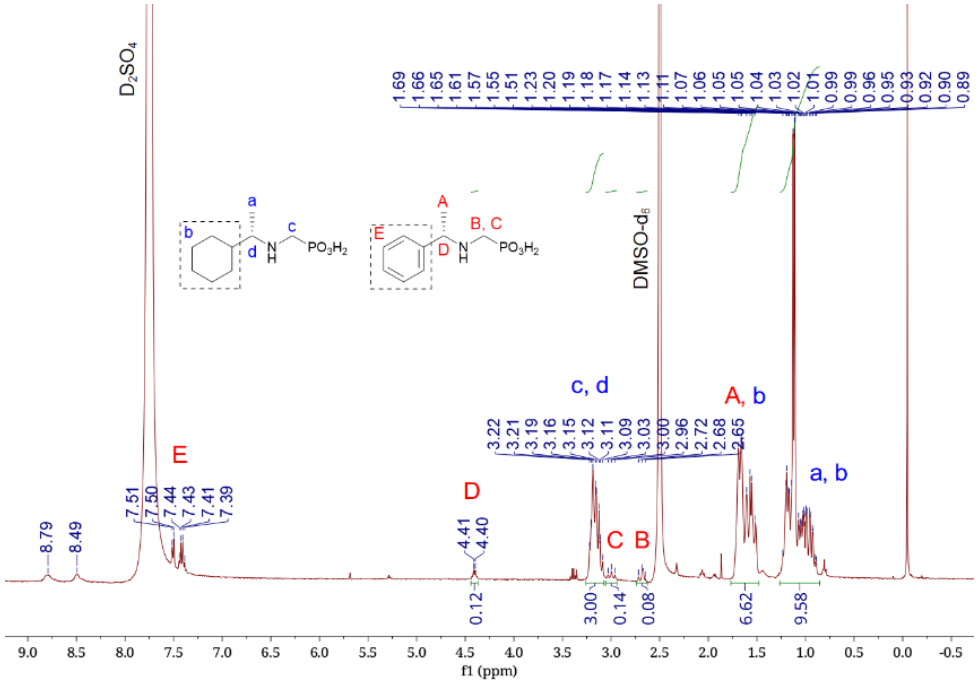


**Figure S16** 1H-NMR spectra of ***S*-1H-10%** obtained at pH = 5.0.

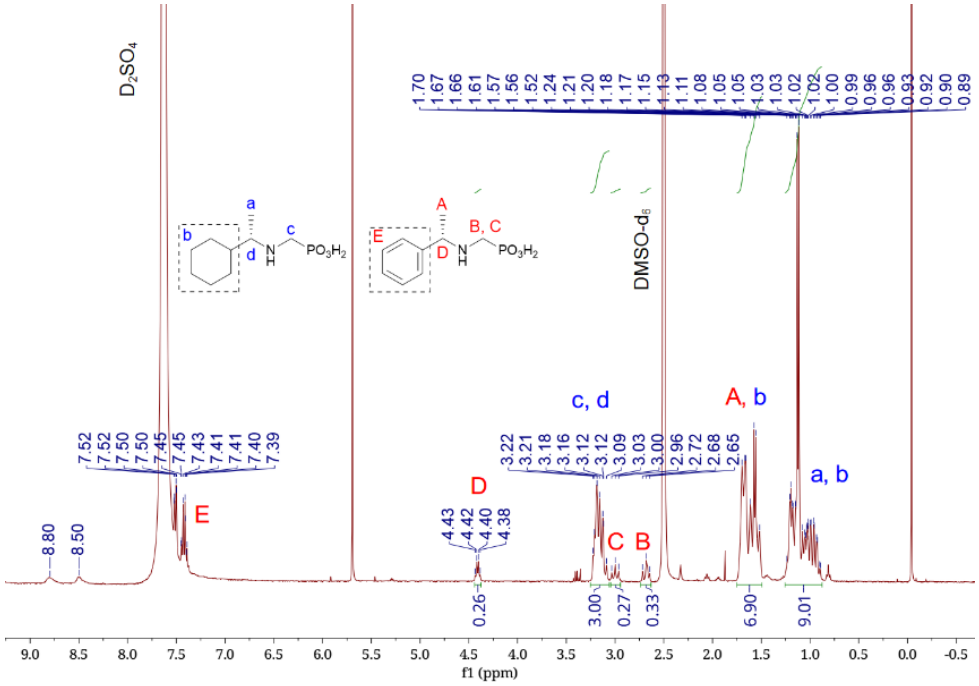


**Figure S17** 1H-NMR spectra of ***S*-1H-20%** obtained at pH = 5.0.

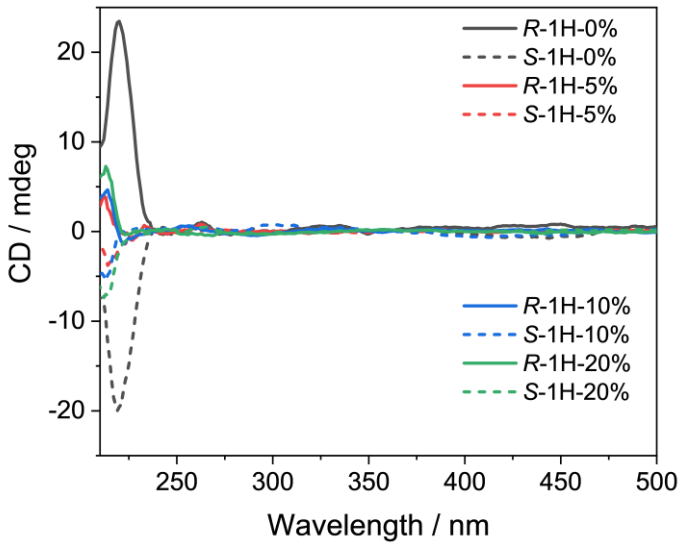


**Figure S18** The ECD spectra of ***R*-** and ***S*-1H-*x*** (*x* = 0%, 5%, 10%, and 20%) obtained under pH 5.0.

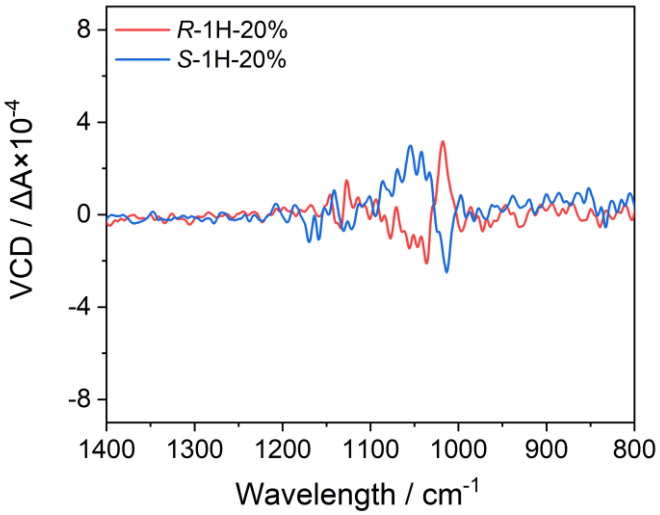


**Figure S19** The VCD spectra of ***R*-** and ***S*-1H-20%** obtained under pH 5.0.

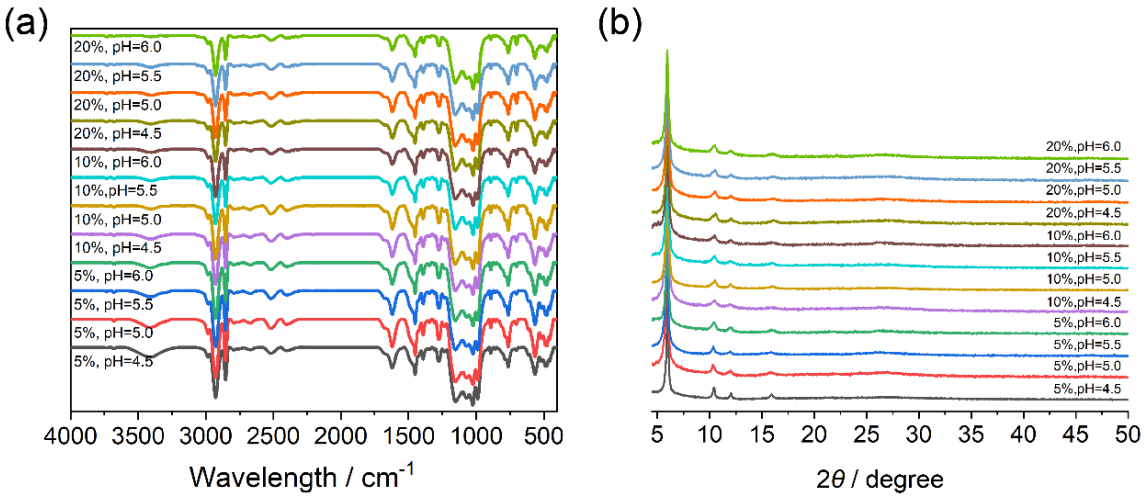


**Figure S20** IR spectra (4000–400 $cm^{-1}$) (a) and PXRD patterns (b) of ***R*-1H-*x*** (*x* = 5%, 10%, 20%) obtained under 100 °C and different pH.

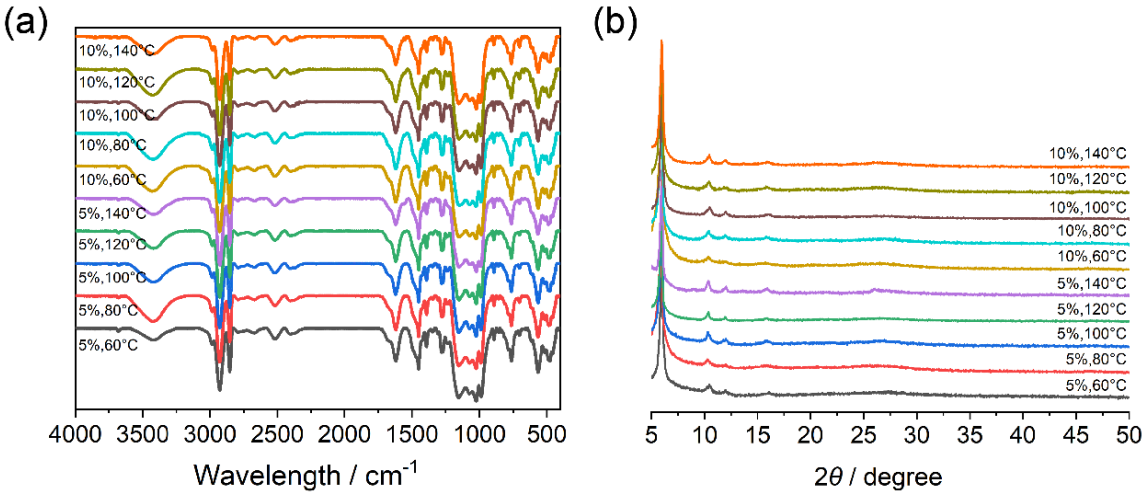


**Figure S21** IR spectra (4000–400 $cm^{-1}$) (a) and PXRD patterns (b) of ***R*-1H-*x*** (*x* = 5%, 10%) obtained under pH 5.0 and different temperatures.

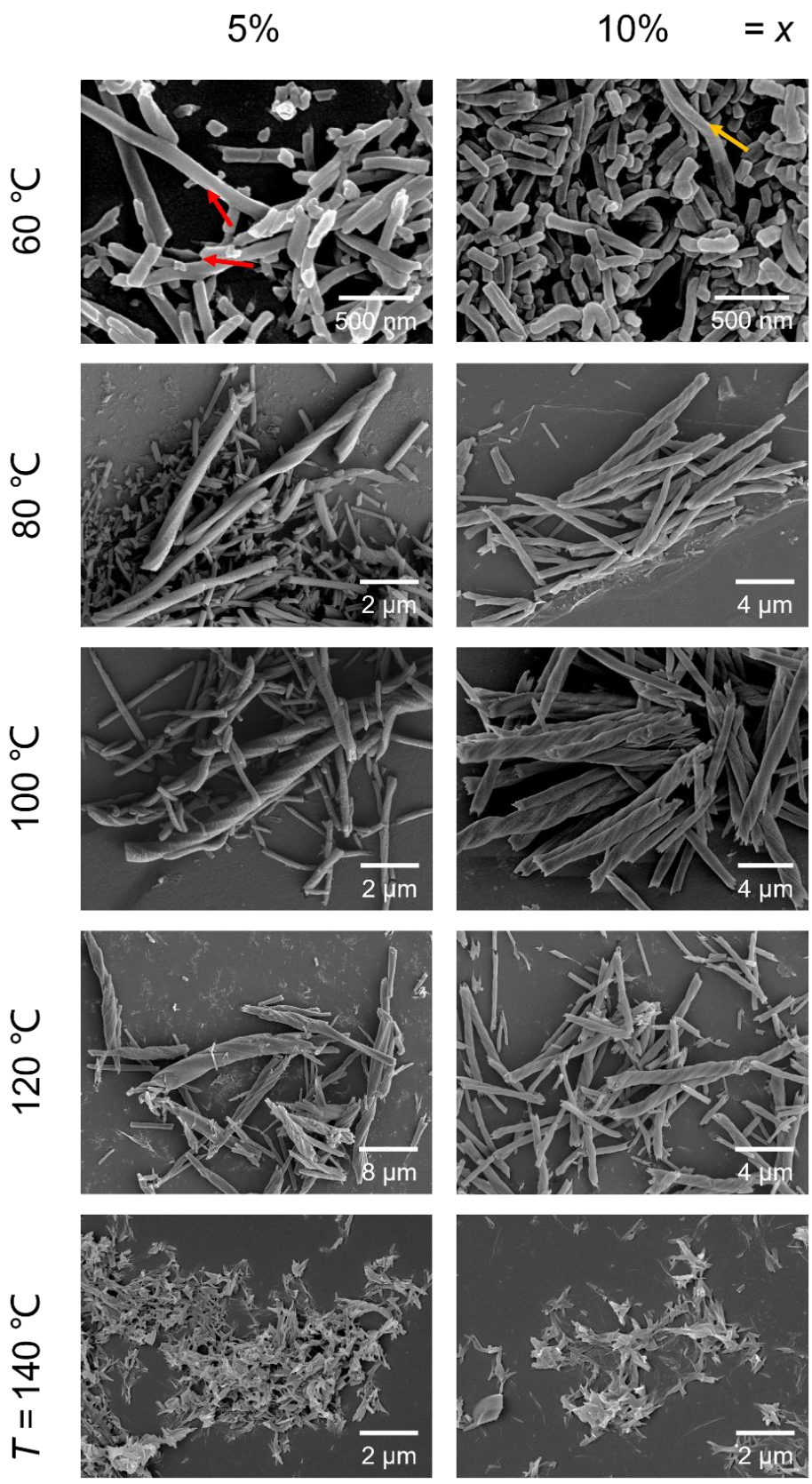


**Figure S22** SEM images of ***R*-1H-*x*** (*x* = 5% and 10%) obtained at pH 5.0 under hydrothermal reaction in different temperatures *T* (from 60 °C to 140 °C).

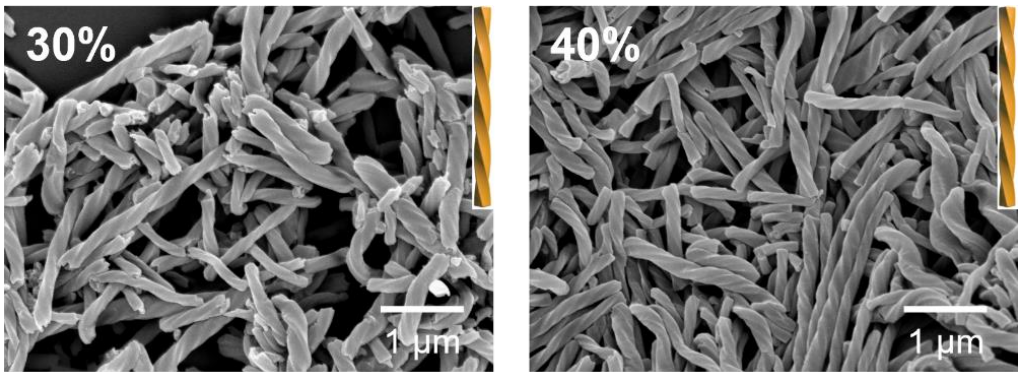


**Figure S23** SEM images of ***R*-1H-*x*** (*x* = 30% and 40%) obtained at pH 5.0.

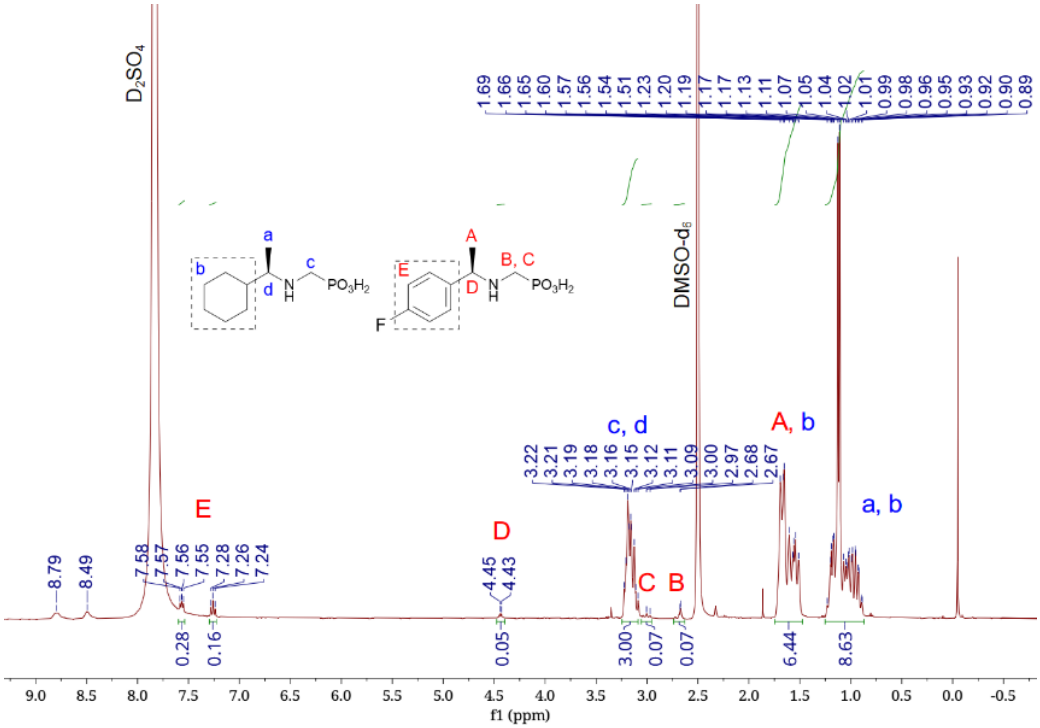


**Figure S24** 1H-NMR spectra of ***R*-2F-5%** obtained at pH = 5.0.

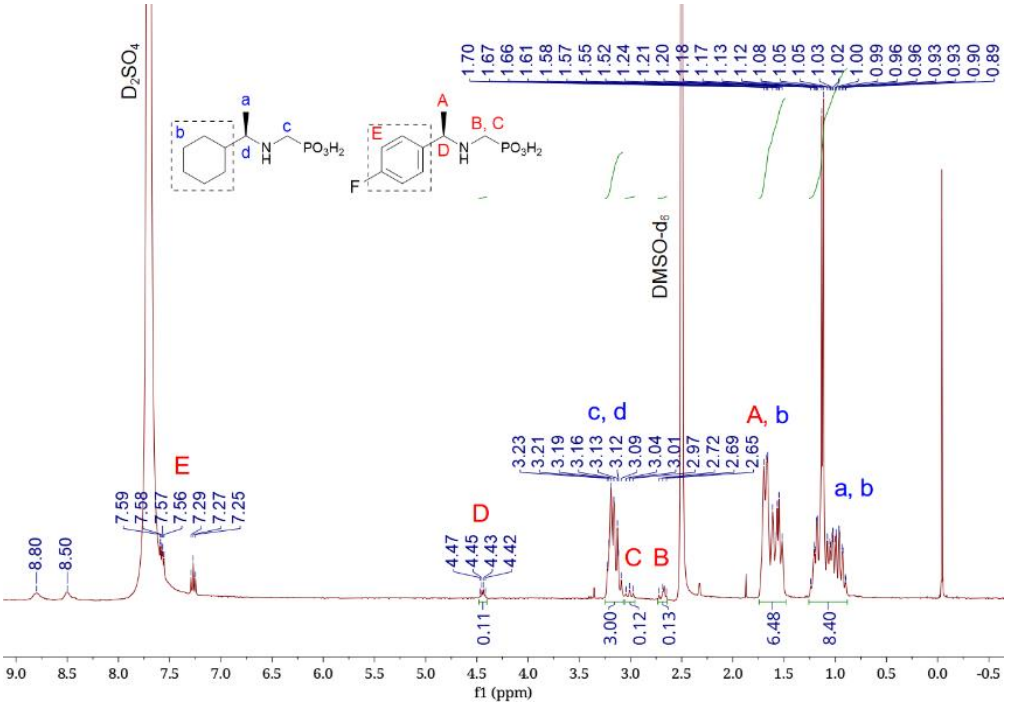


**Figure S25** 1H-NMR spectra of ***R*-2F-10%** obtained at pH = 5.0.

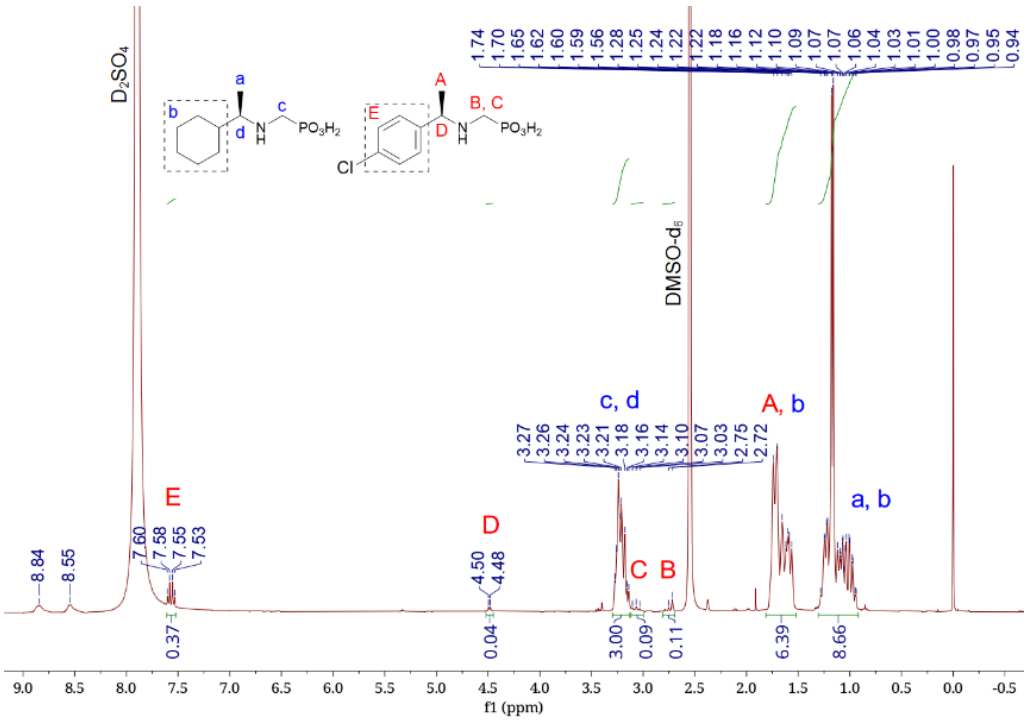


**Figure S26** 1H-NMR spectra of ***R*-3Cl-5%** obtained at pH = 5.0.

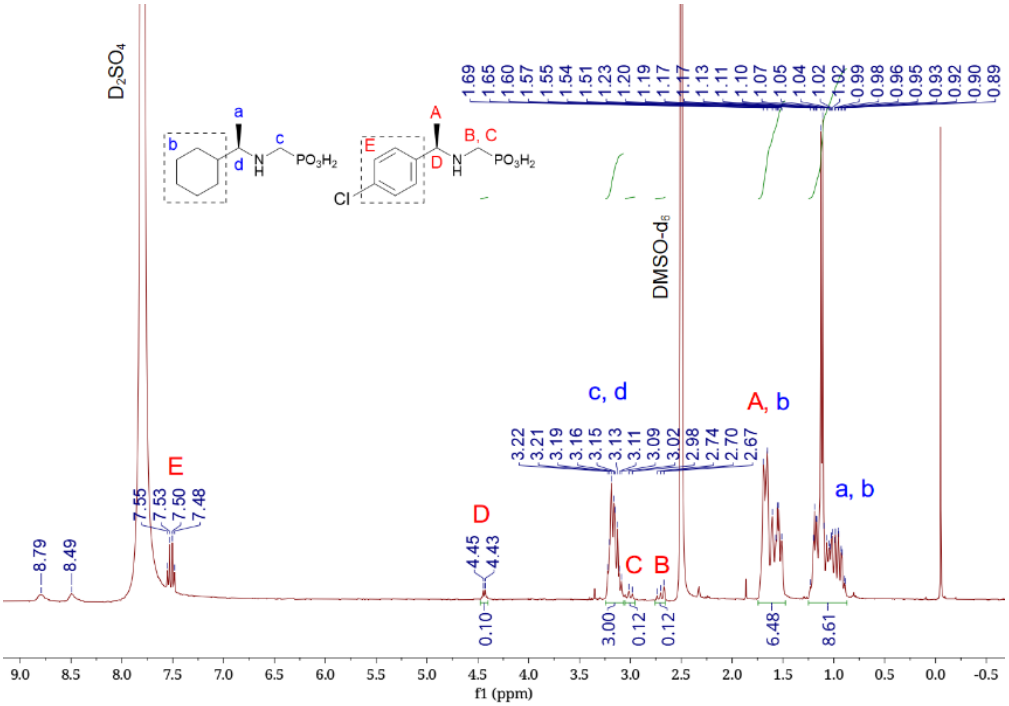


**Figure S27** 1H-NMR spectra of ***R*-3Cl-10%** obtained at pH = 5.0.

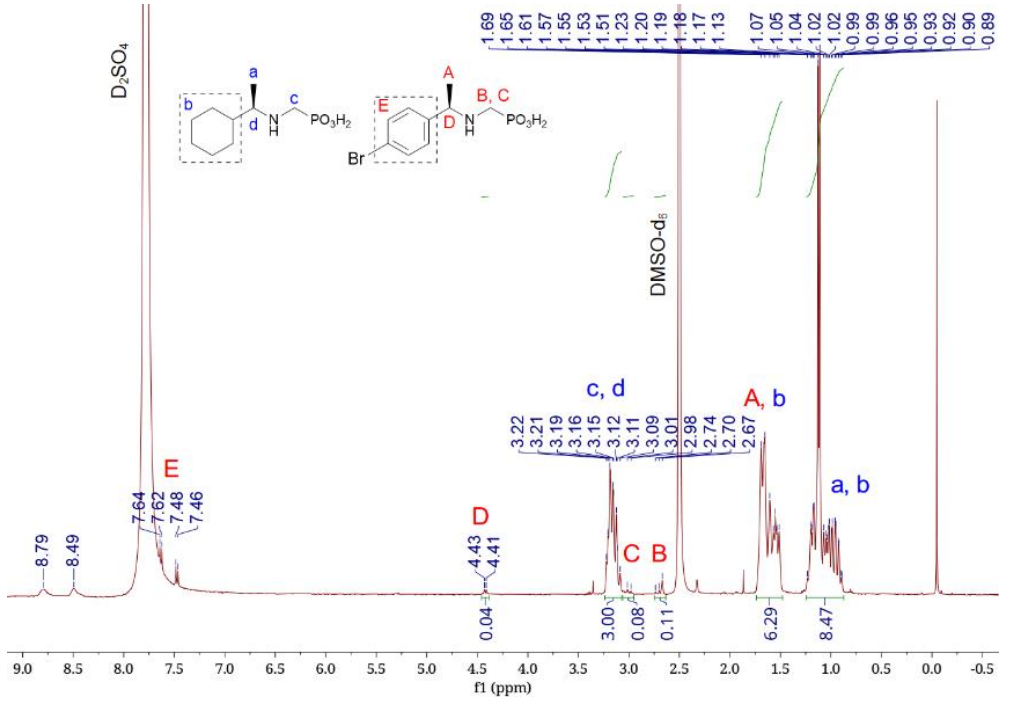


**Figure S28** 1H-NMR spectra of ***R*-4Br-5%** obtained at pH = 5.0.

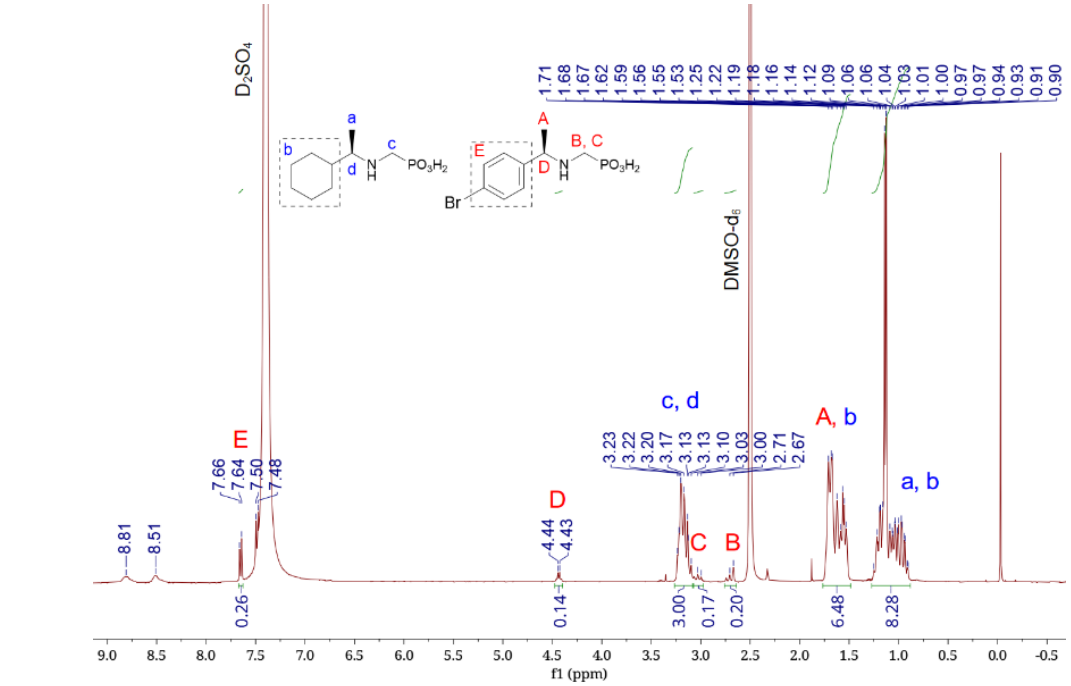


**Figure S29** 1H-NMR spectra of ***R*-4Br-10%** obtained at pH = 5.0.

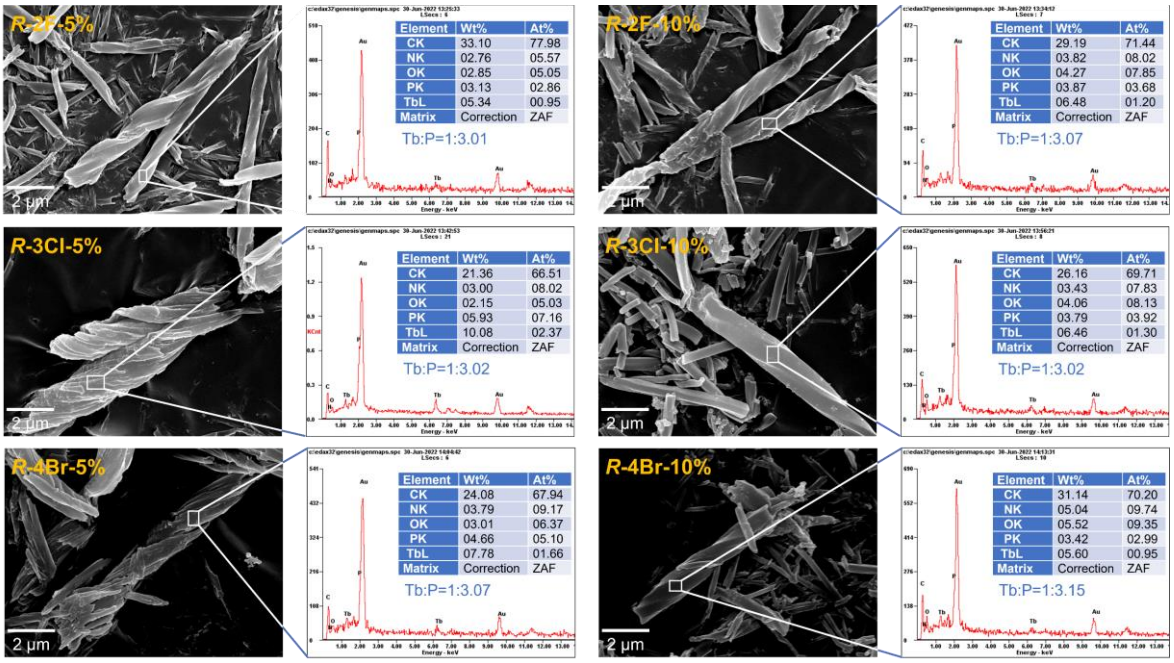


**Figure S30** EDX spectra of ***R*-2F-*x***, ***R*-3Cl-*x*** and ***R*-4Br-*x*** (*x* = 5%, 10%) superhelices.

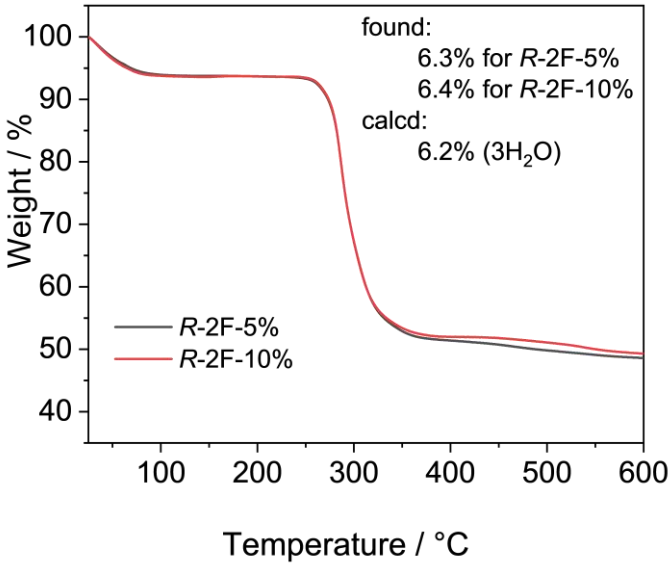


**Figure S31** TG analyses of ***R*-2F-*x*** (*x* = 5%, 10%) obtained at pH = 5.0.

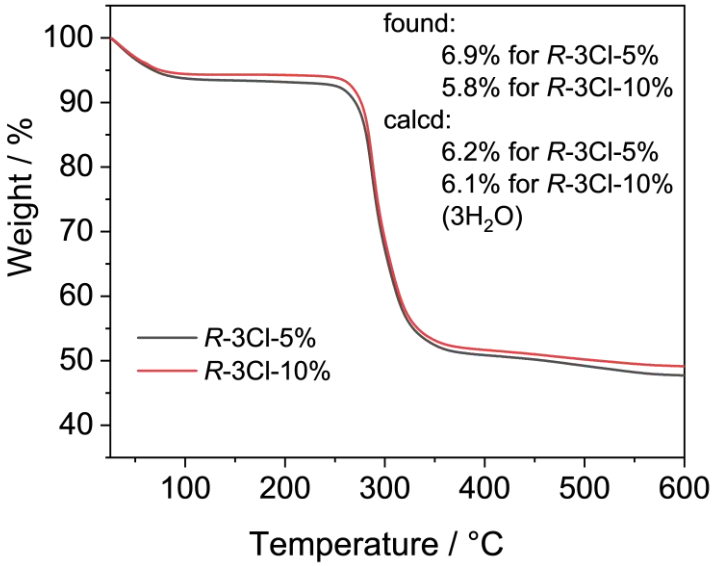


**Figure S32** TG analyses of ***R*-3Cl-*x*** (*x* = 5%, 10%) obtained at pH = 5.0.

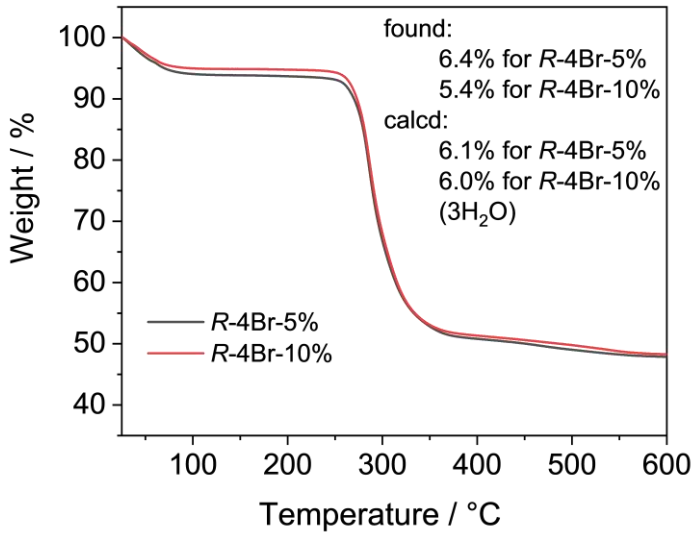


**Figure S33** TG analyses of ***R*-4Br-*x*** (*x* = 5%, 10%) obtained at pH = 5.0.

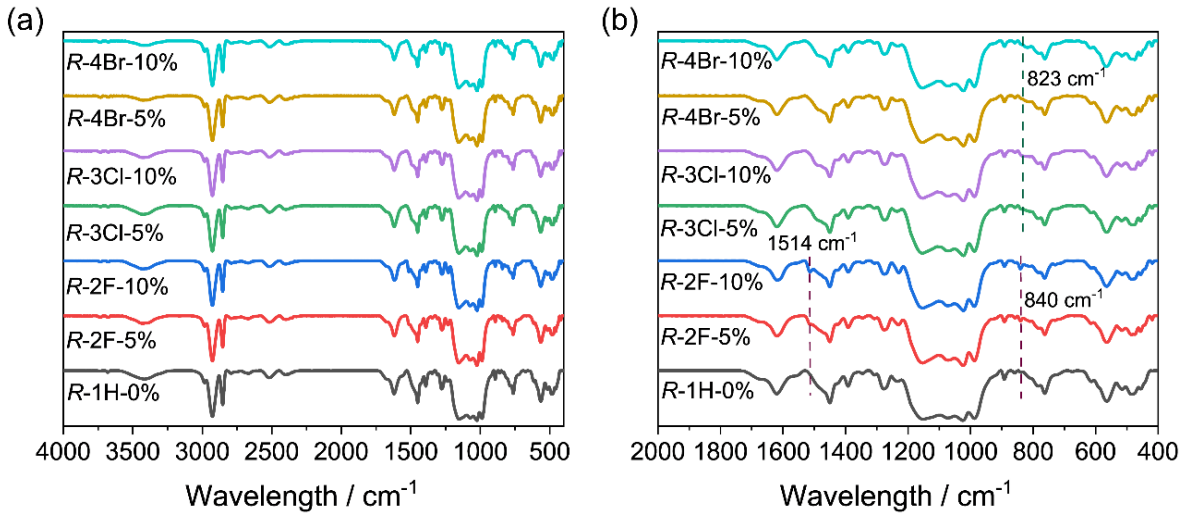


**Figure S34** IR spectra (4000–400 $cm^{-1}$ (a) and 2000–400 $cm^{-1}$ (b)) of ***R*-2F-*x***, ***R*-3Cl-*x***, and ***R*-4Br-*x*** (*x* = 5%, 10%) obtained under pH 5.0. The marked peak positions are the IR signal peaks of the doped ligands X-pemp$H_2$, which are indicated in Figure S4.

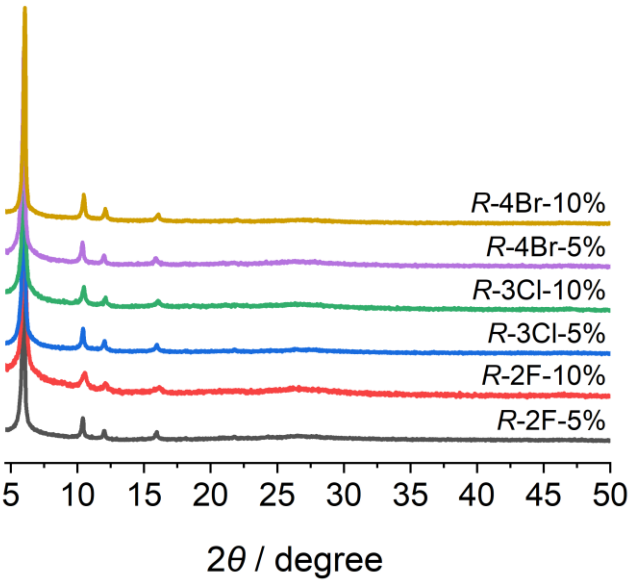


**Figure S35** PXRD patterns of ***R*-2F-*x***, ***R*-3Cl-*x***, and ***R*-4Br-*x*** (*x* = 5%, 10%) obtained under pH 5.0.