Electronic supplementary information for：

Construction of Flexible and Stable Near-Infrared Absorbing Polymer Films Containing Nickel-Bis(dithiolene) Moieties via Ligand-Exchange Post-Polymerization Modification

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4. Stress-strain curves of the polymers

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1. ^{1}H/^{13}C -NMR and HRMS of the monomers and polymers

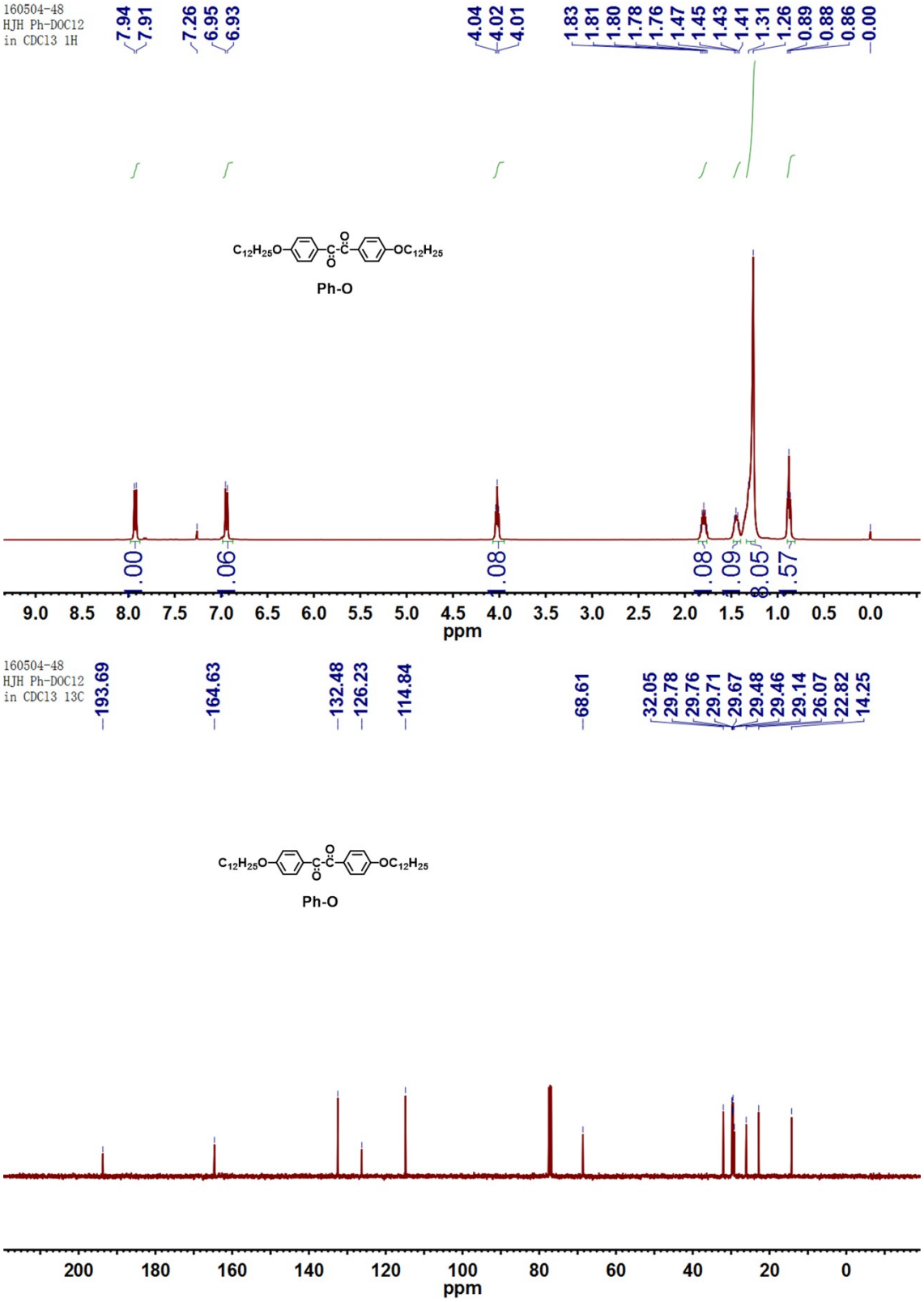


Figure S1. ^{1}H-NMR and ^{13}C-NMR of Ph-O

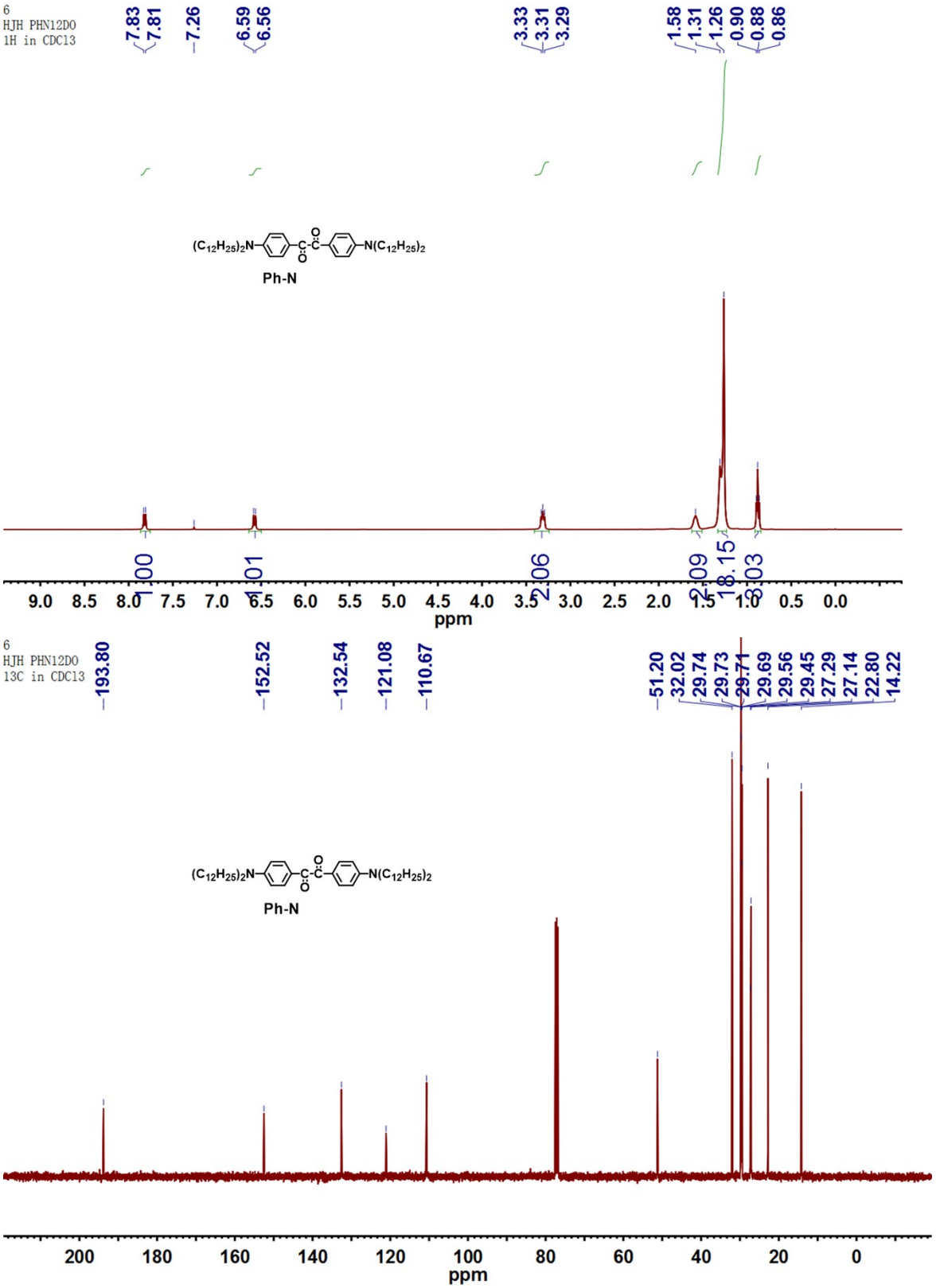


Figure S2. ^{1}H-NMR and ^{13}C-NMR of Ph-N

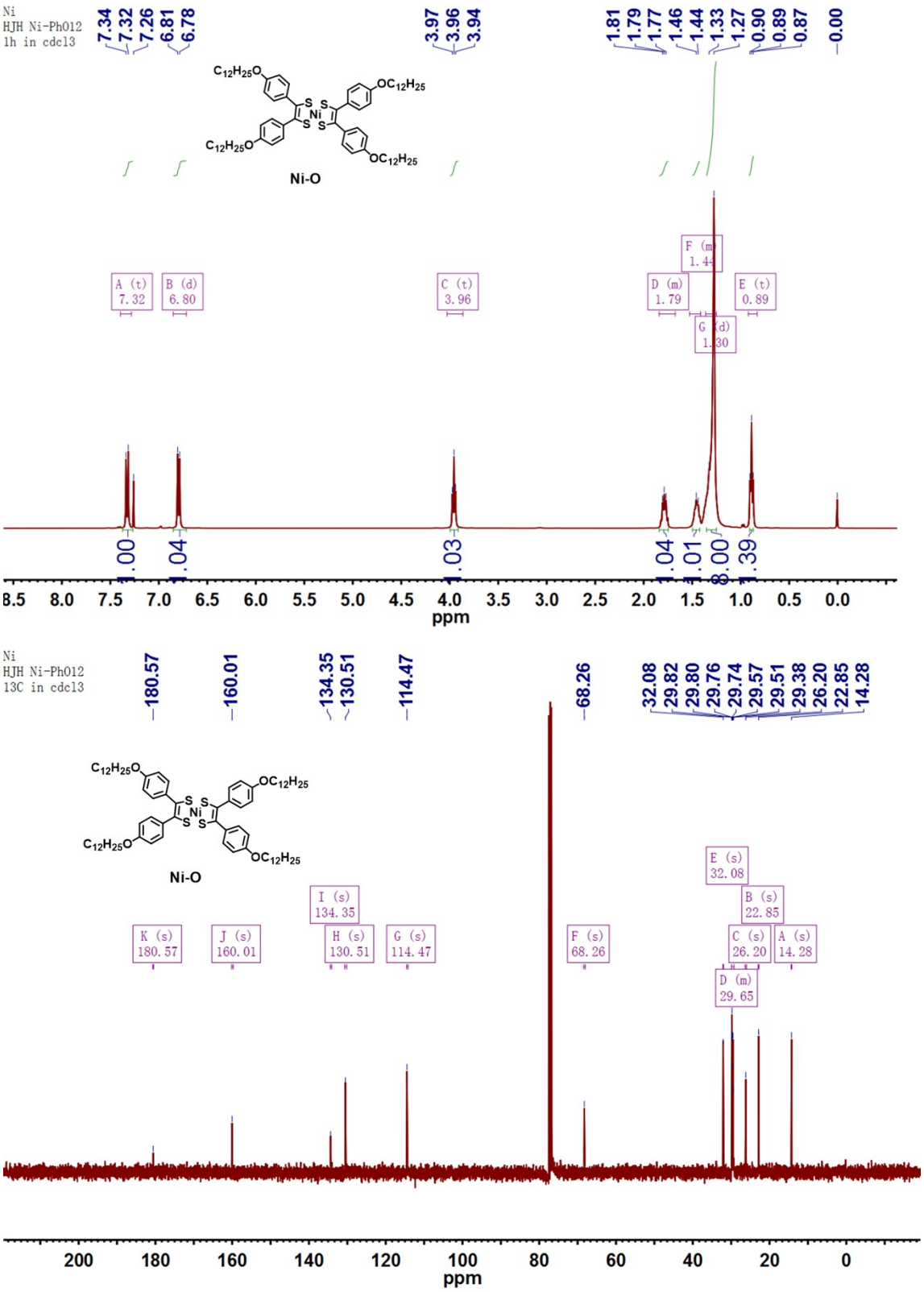


Figure S3. ^{1}H-NMR and ^{13}C-NMR of Ni-O

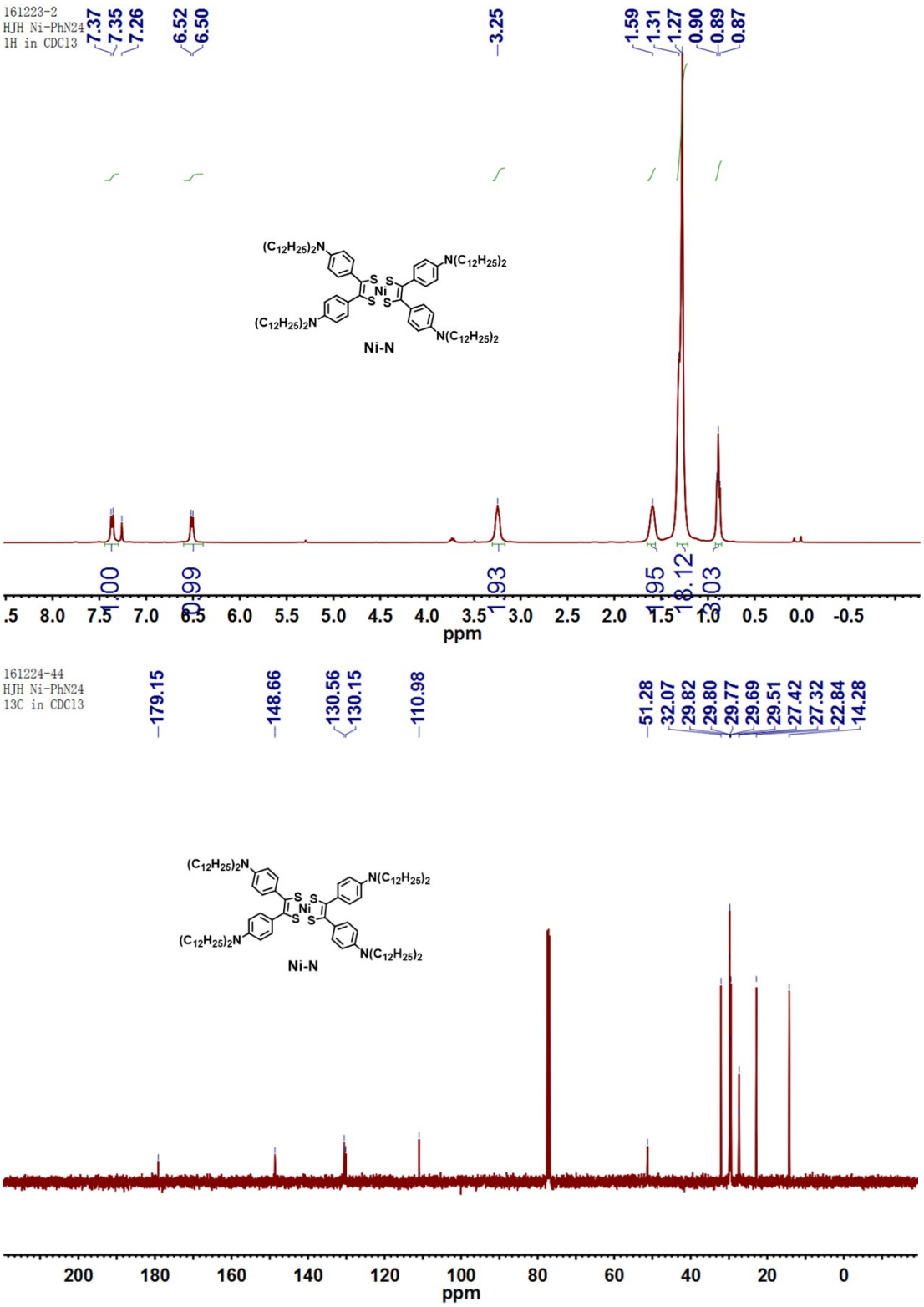
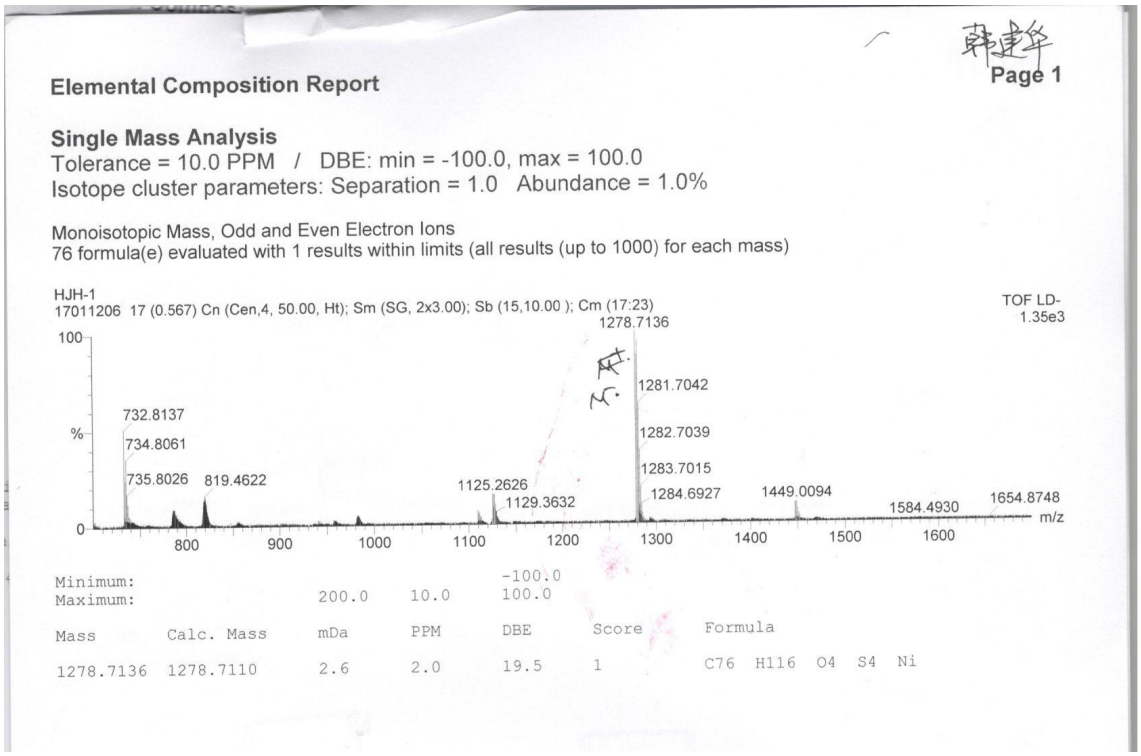


Figure S4. ^{1}H-NMR and ^{13}C-NMR of Ni-N



Elemental Composition Report Page 1

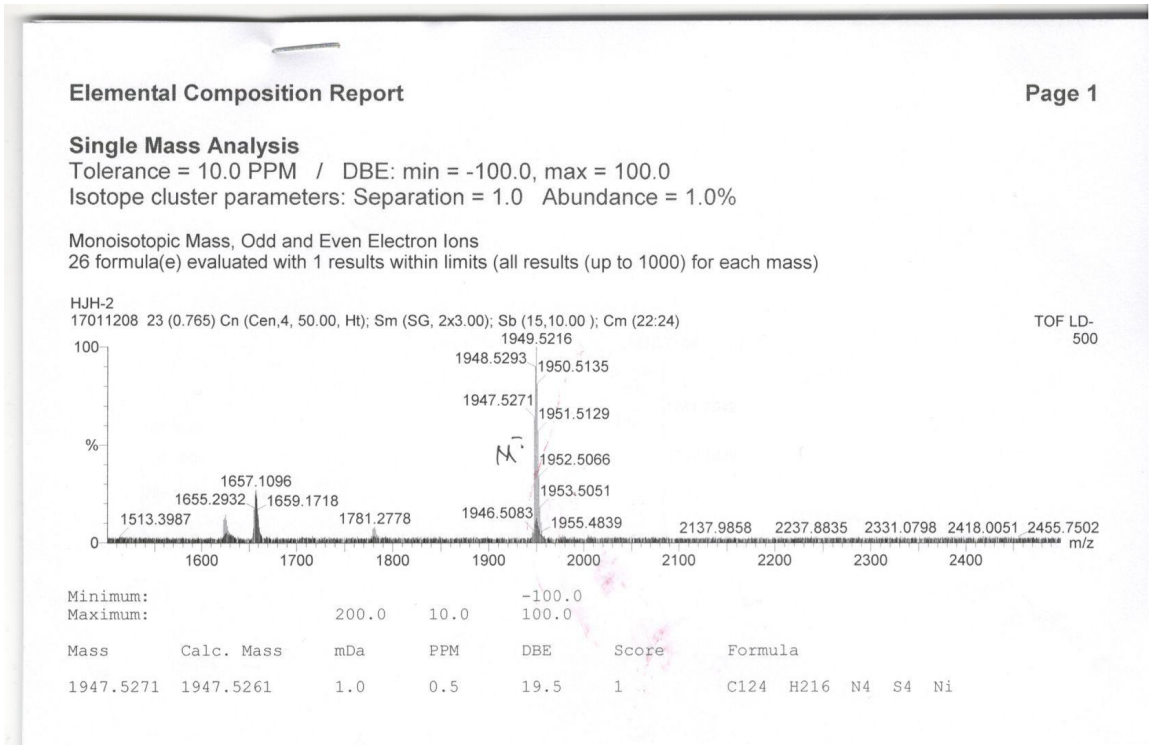
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 100.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
76 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

HJH-1
17011206 17 (0.567) Cn (Cen,4, 50.00, Ht); Sm (SG, 2x3.00); Sb (15,10.00); Cm (17:23)
TOF LD-1.35e3

Minimum:				-100.0		
Maximum:		200.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1278.7136	1278.7110	2.6	2.0	19.5	1	C76 H116 O4 S4 Ni

Figure S5. HRMS of Ni-O



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 100.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
26 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

HJH-2
17011208 23 (0.765) Cn (Cen,4, 50.00, Ht); Sm (SG, 2x3.00); Sb (15,10.00); Cm (22:24)
TOF LD-500

Minimum:				-100.0		
Maximum:		200.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1947.5271	1947.5261	1.0	0.5	19.5	1	C124 H216 N4 S4 Ni

Figure S6. HRMS of Ni-N

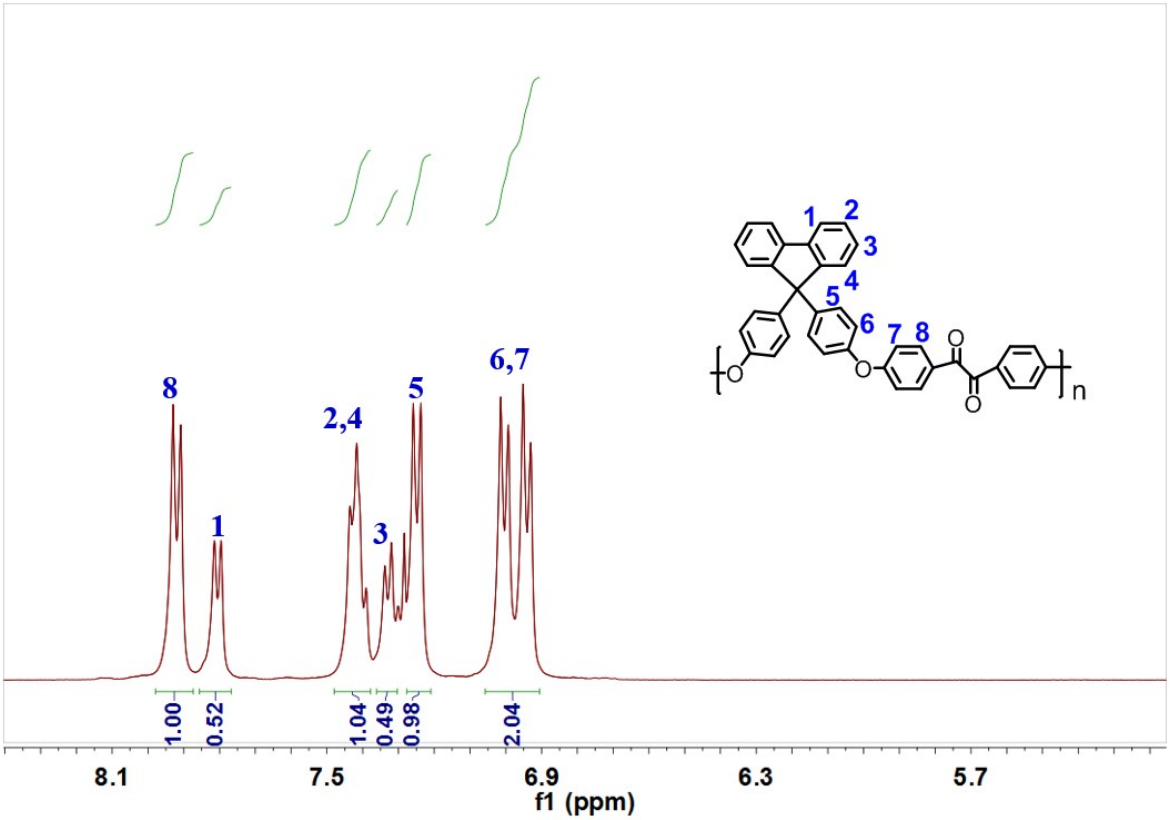


Figure S7. ^{1}H-NMR of PFO in $CDCl_3$

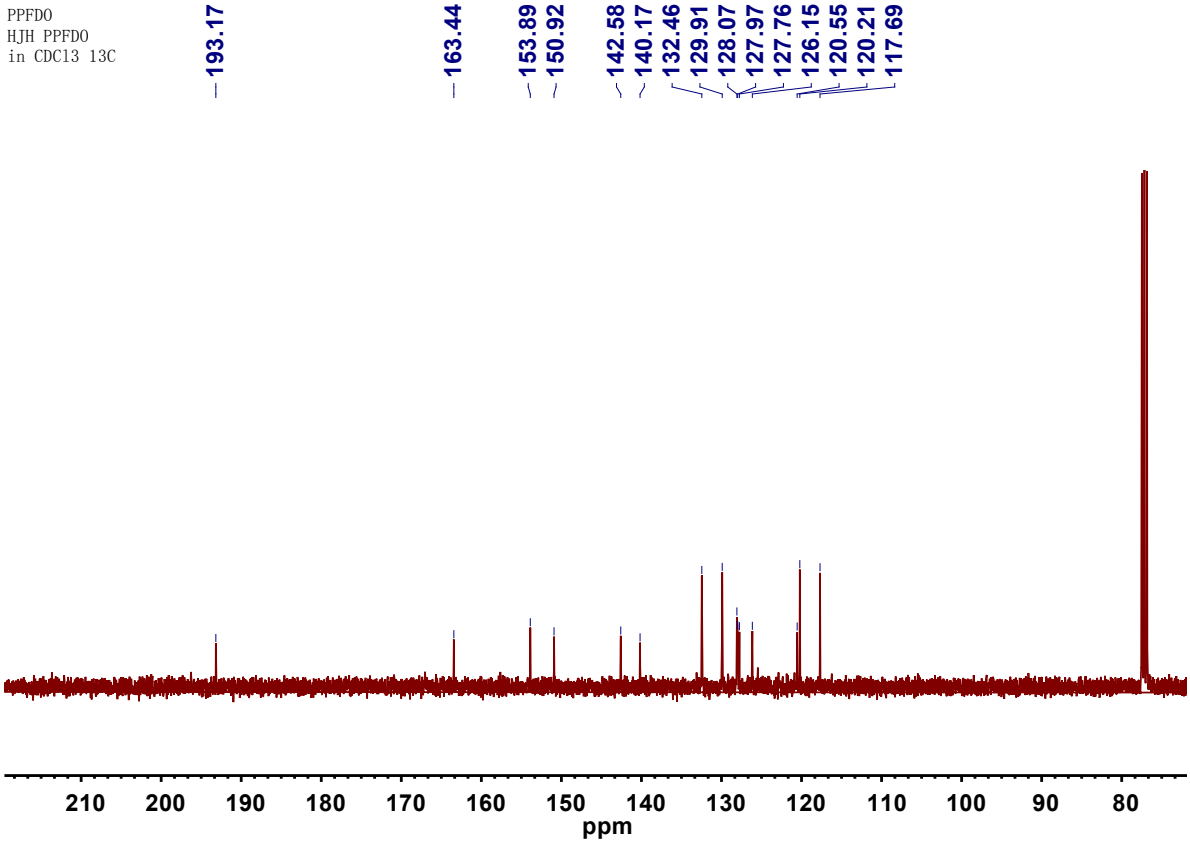


Figure S8. ^{13}C-NMR of PFO in $CDCl_3$

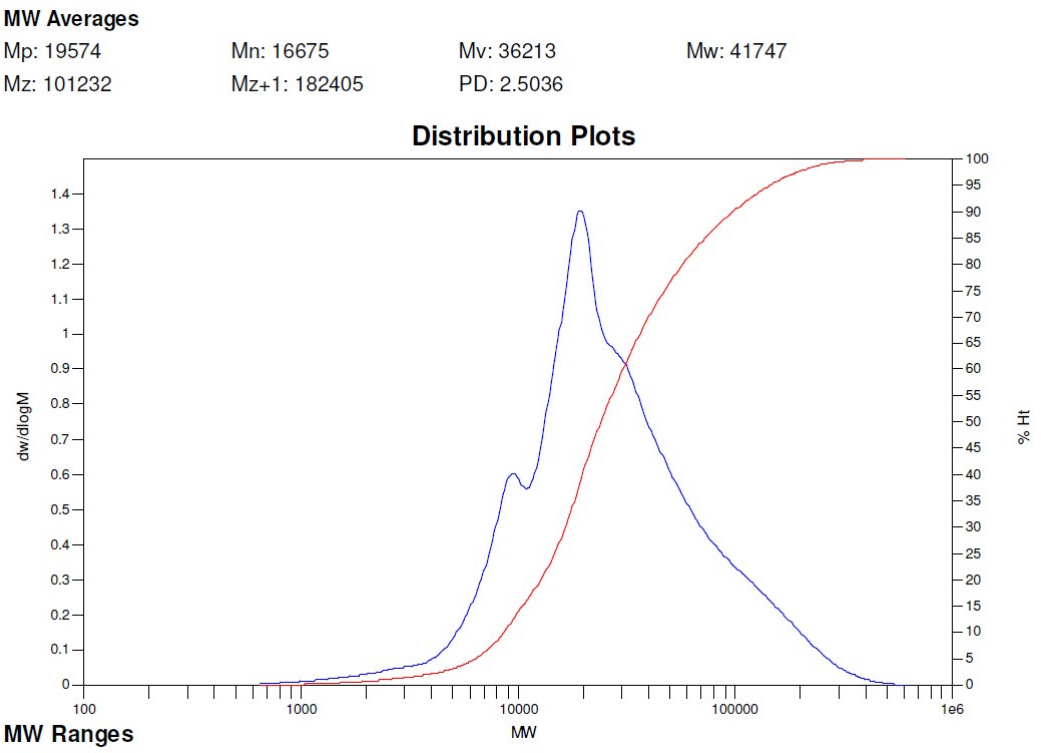


Figure S9. GPC curves of PFO

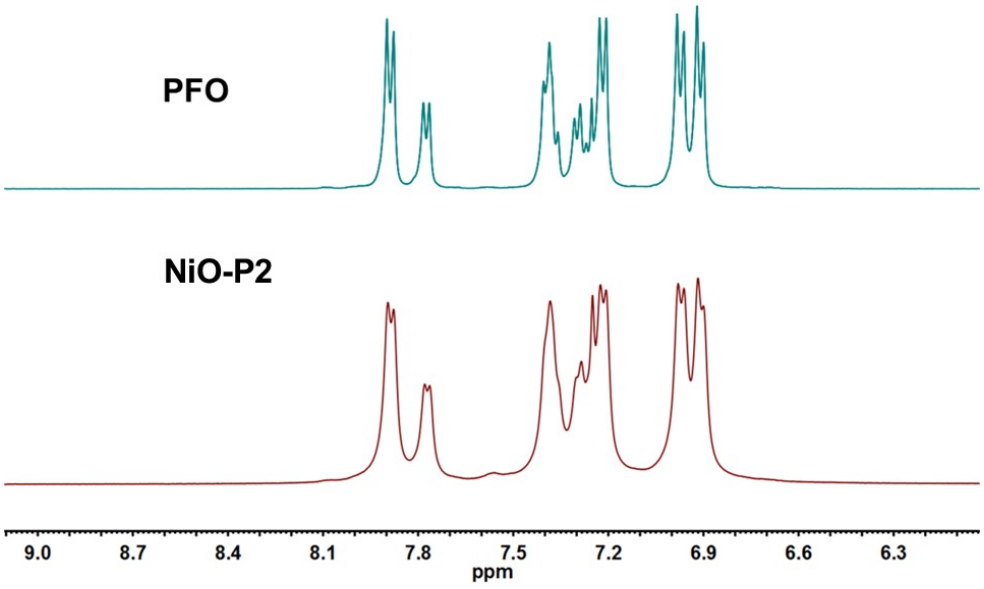


Figure S10. ^{1}H-NMR spectra of PFO and NiO-P2 in $CDCl_3$

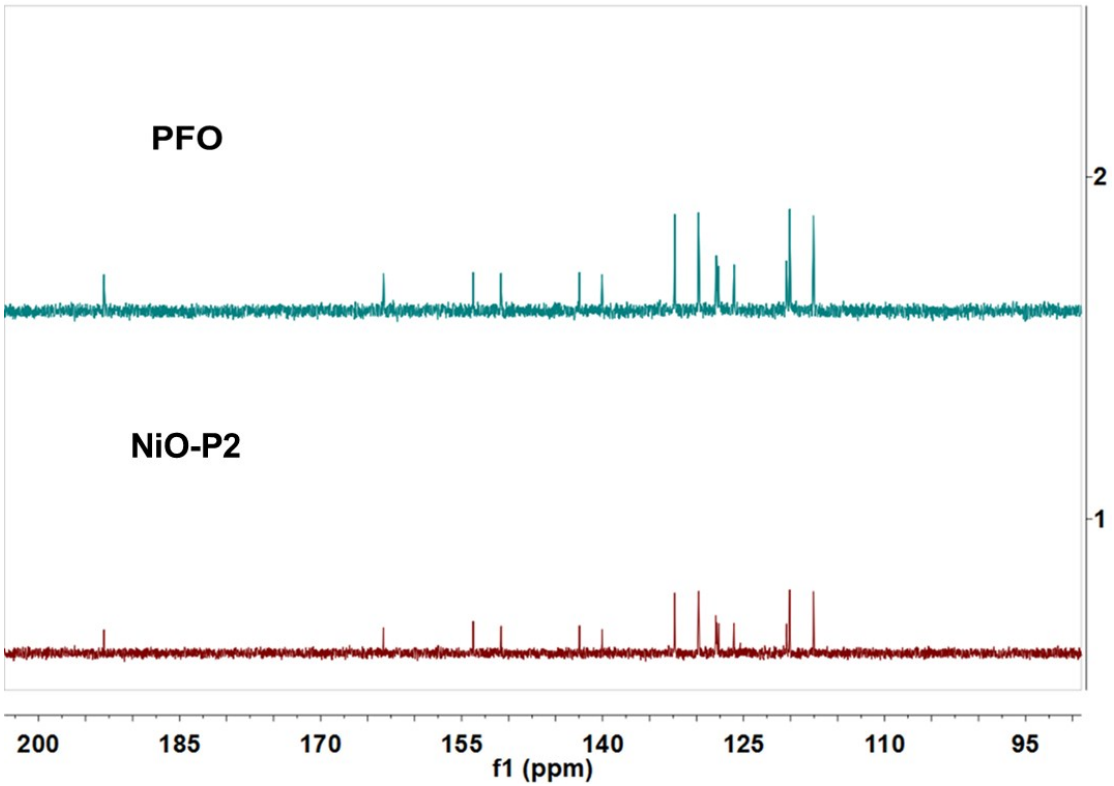


Figure S11. ^{13}C-NMR spectra of PFO and NiO-P2 in $CDCl_3$

2. NIR absorption spectra, CV and XRD curves of the complexes and polymers

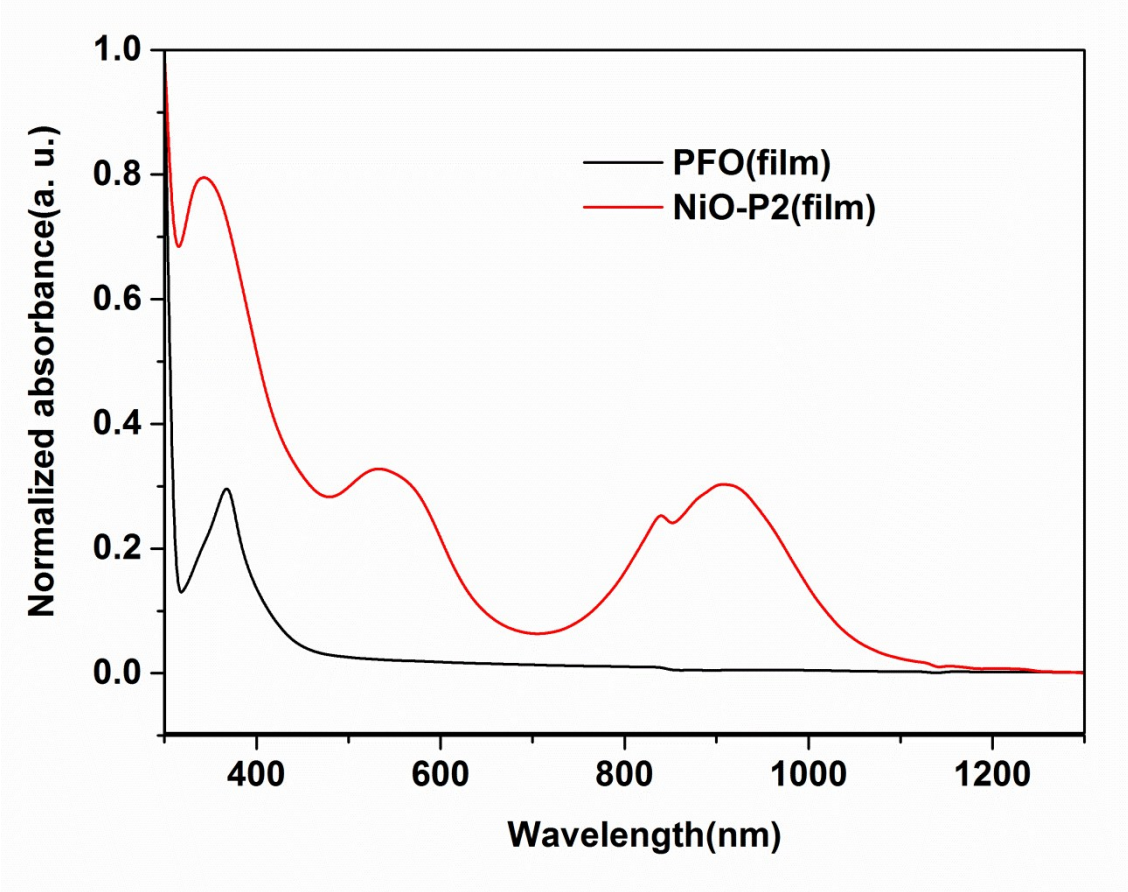


Figure S12. NIR spectra of the polymer films (PFO: thickness=40 μm; NiO-P2: thickness=25 μm) synthesized without additional ligand Ph-O.

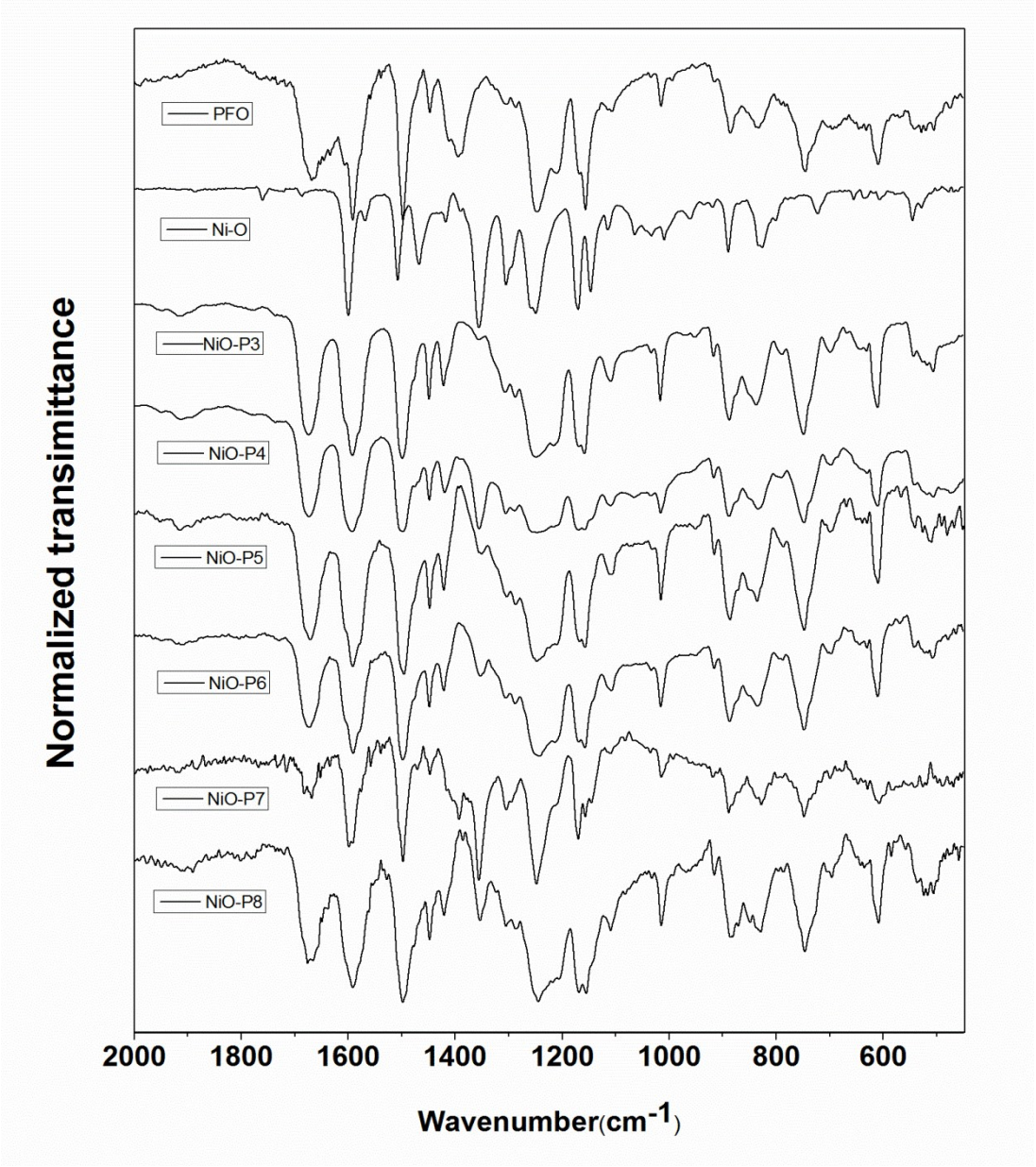


Figure S13. FT-IR spectra of NiO-P series polymers

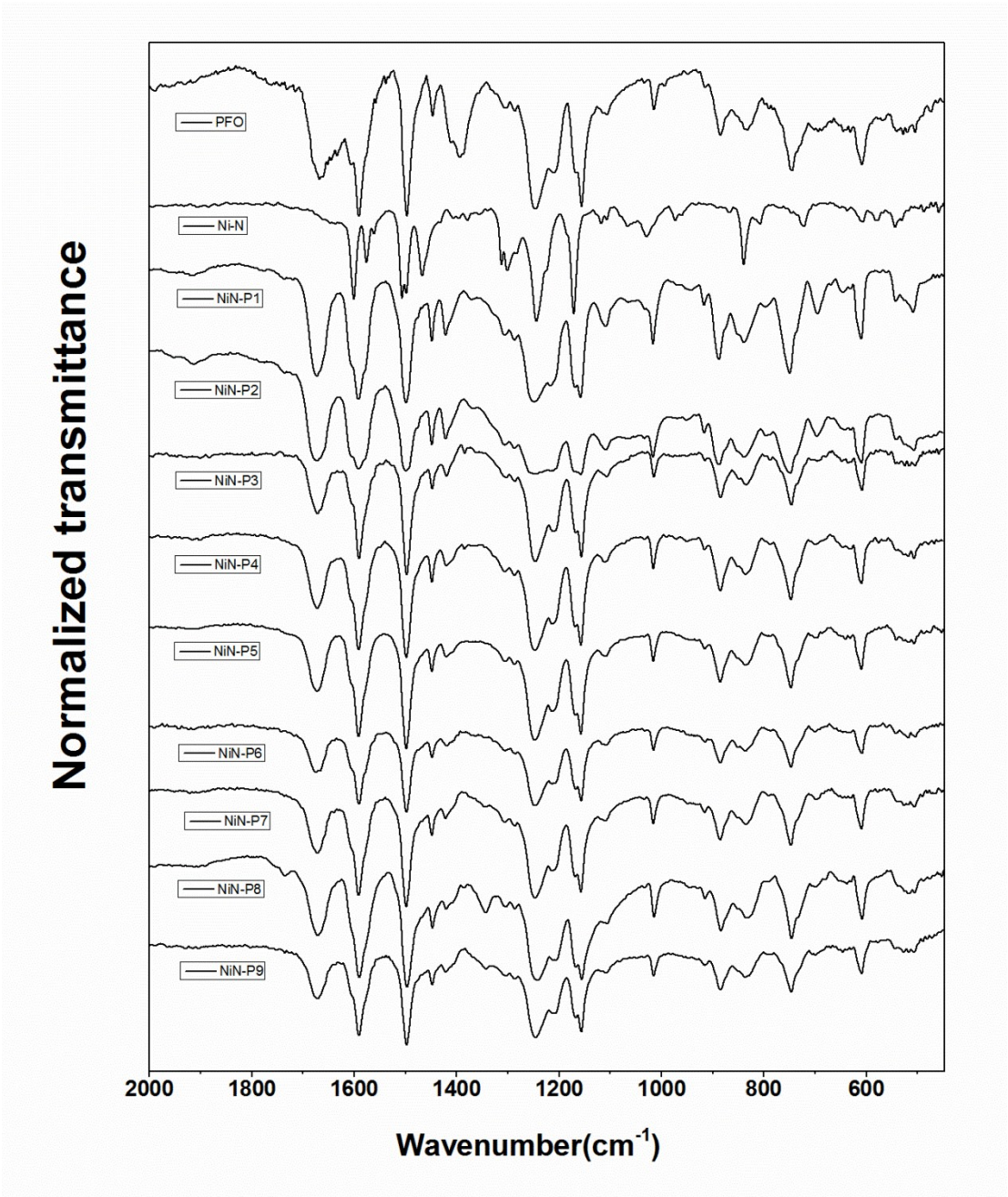
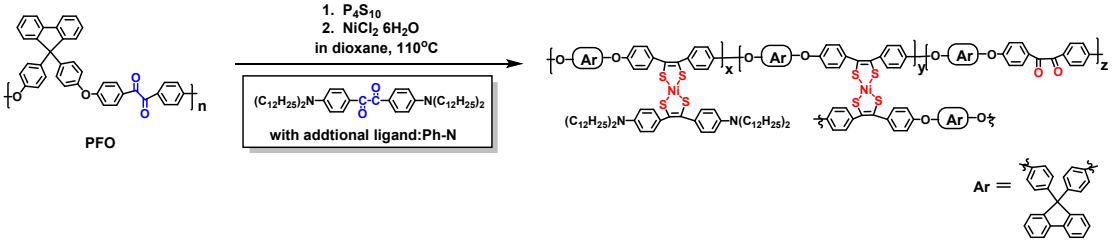
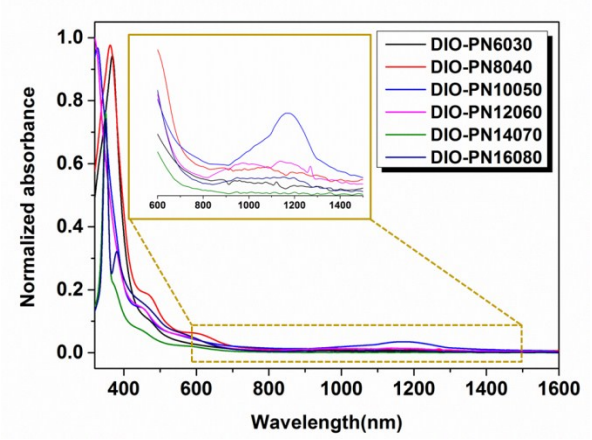


Figure S14. FT-IR spectra of NiN-P series polymers

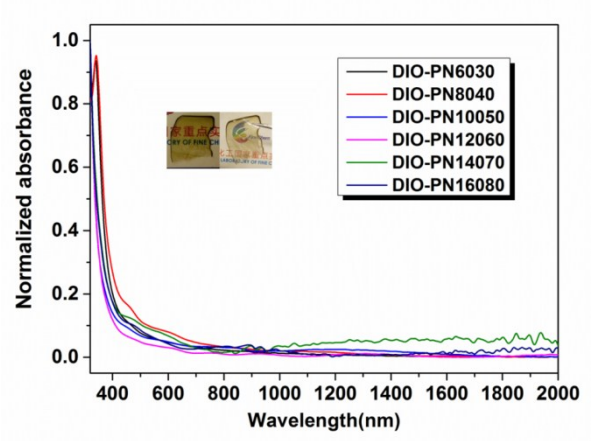
Table S1. The post-polymerization modification of PFO with Ph-N **in dioxane**



polymers	Additional ligand	$P_4S_{10}/NiCl_2.6H_2O$(mmol)
DIO-PN6030	Ph-N	0.60/0.30
DIO-PN8040	Ph-N	0.80/0.40
DIO-PN10050	Ph-N	1.00/0.50
DIO-PN12060	Ph-N	1.20/0.50
DIO-PN14070	Ph-N	1.40/0.70
DIO-PN16080	Ph-N	1.60/0.80

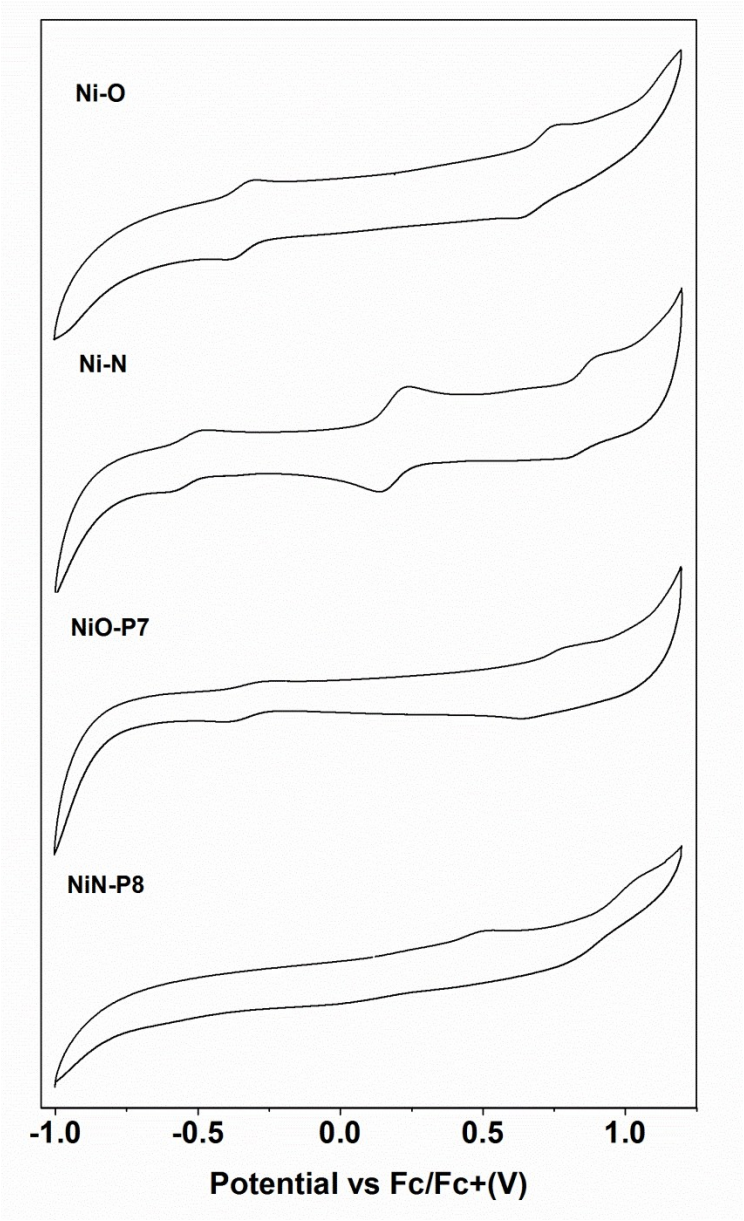


(a) in NMP solution



(b) in thin film states

Figure S15. NIR spectra of the polymers synthesized in dioxane with Ph-N



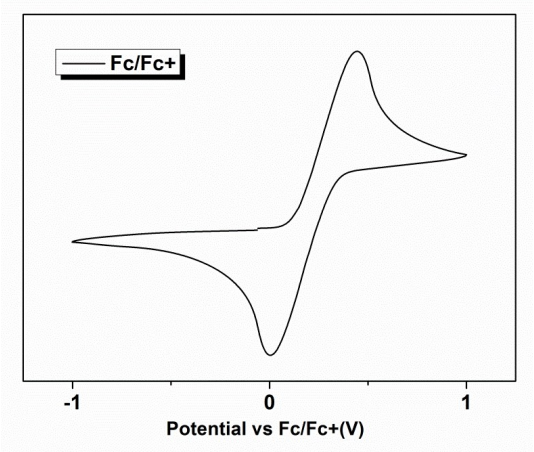


Figure S16. CV curves of the complexes and polymers

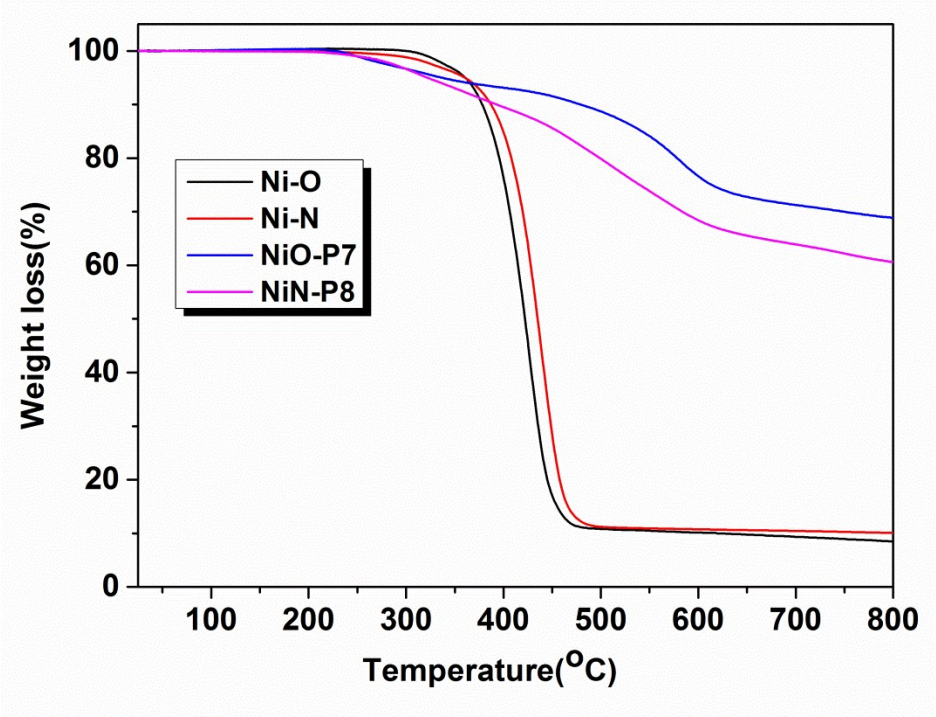


Figure S17. TGA curves of the complexes and polymers .

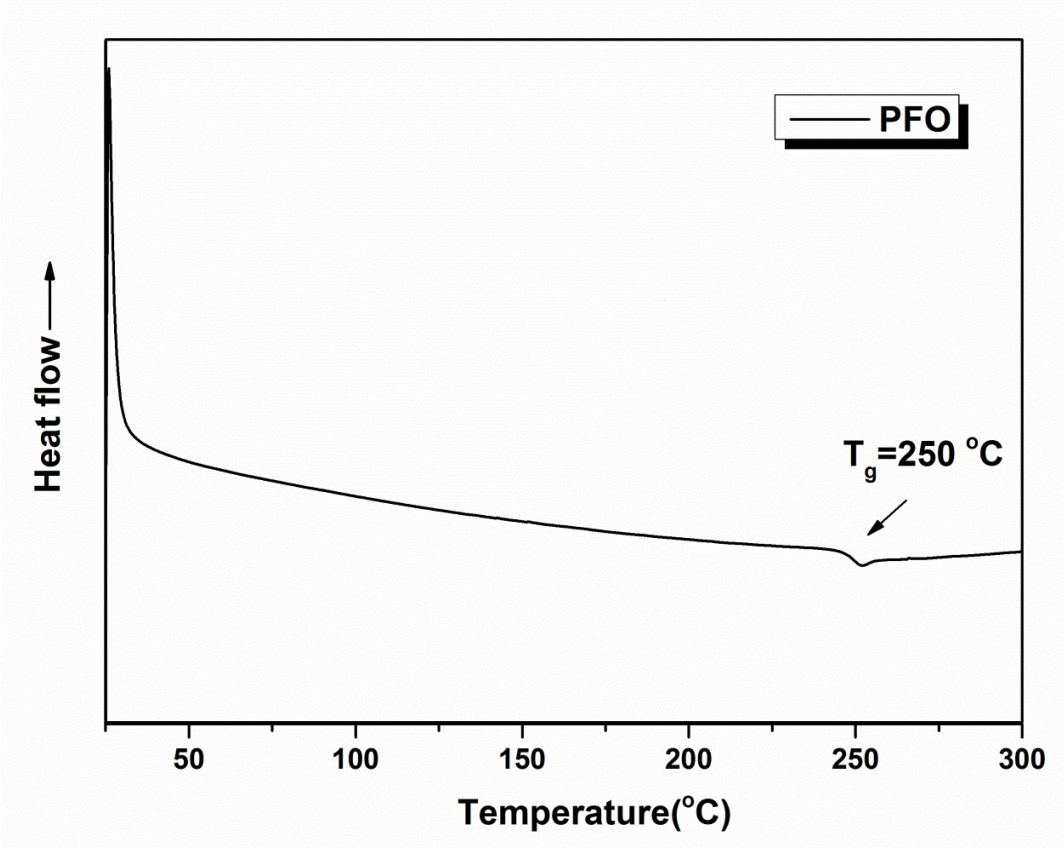


Figure S18. DSC curve of PFO.

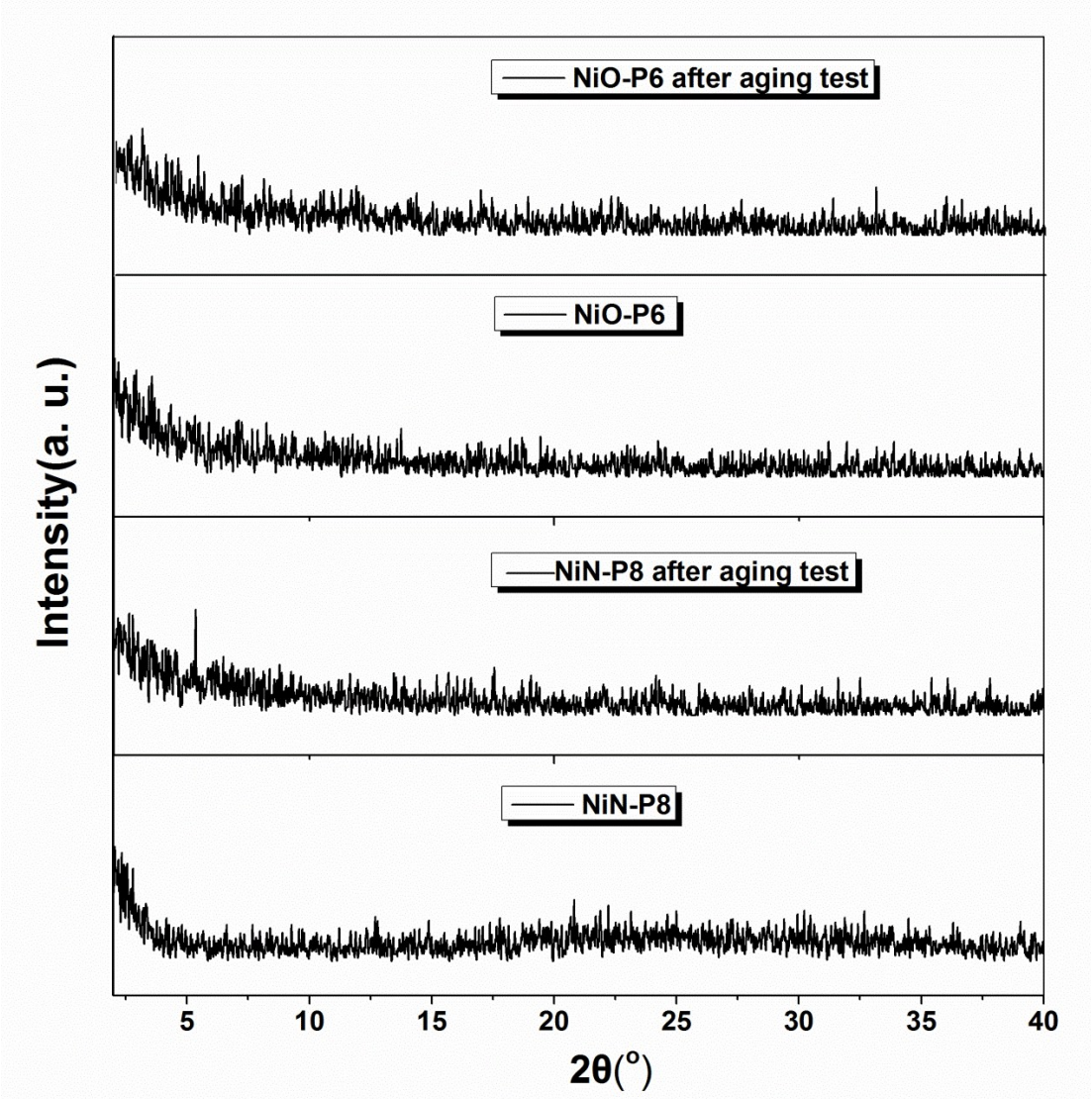


Figure S19. XRD measurements of the polymer films

3. The calculation process of coordination ratio by ^{1}H-NMR.

▲For NiO-P2, the nickel bis(dithiolene) moiety is formed from the crosslinked part. Therefore, we used this part for calculation of NiO-P2. For NiO-P3~P9 and NiN-P1~P9, the nickel bis(dithiolene) moiety is formed from two part: the additional ligand part(x) and the crosslinked part(y). We show that the crosslinked part(y) is rarely formed in NiO-P3~P9 and NiN-P1~P9. It is hard to confirm their corresponding content. However, the ratio of additional ligand part(x) can be determined by ^{1}H-NMR, as shown below. Thus, the R(x) in Table 1 referred to the ratio of crosslinked part for NiO-P2 and the ratio of additional ligand part(x) for NiO-P3~P9 and NiN-P1~P9.

(1) For NiO-P series polymers, take NiO-P6 as an example:

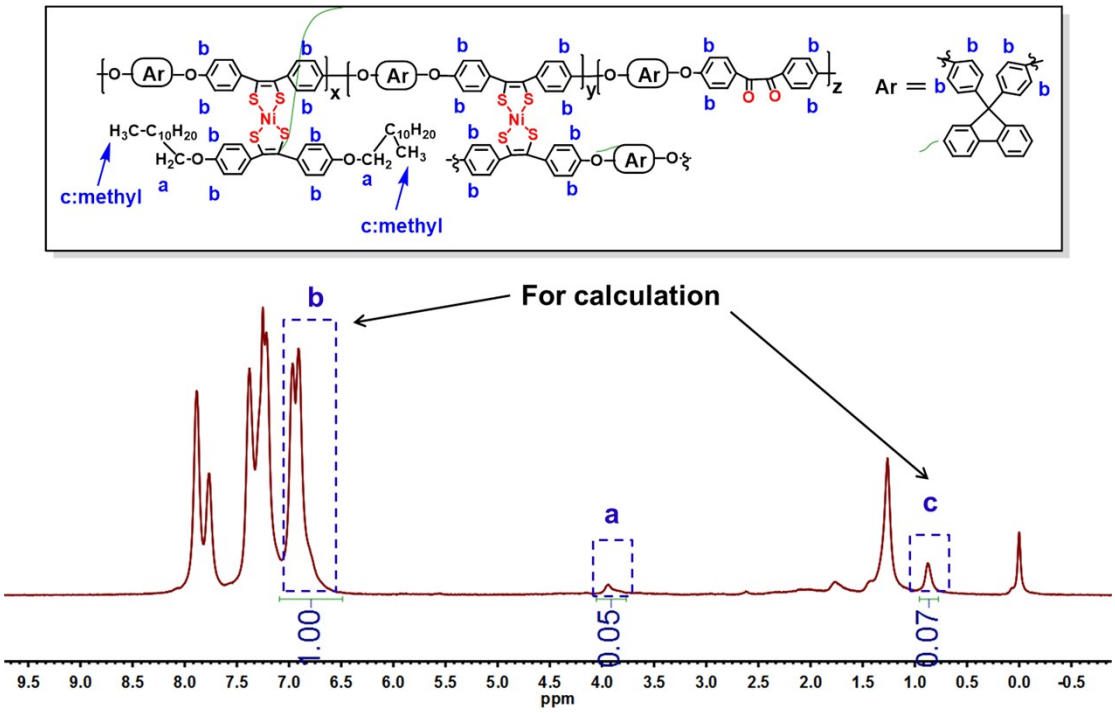


Figure S20. ^{1}H-NMR of NiO-P6

The coordination ratio corresponds to the percent of x repeat units in final polymer.

$$The\ coordination\ ratio = \frac{x}{x+y+z} = \frac{area(c) \div 6}{(area(b) - x \times 4) \div 8} = \frac{area(c) \div 6}{(area(b) - (area(c) \div 6 \times 4) \times 4) \div 8}$$

$$= \frac{0.07 \div 6}{(1.00 - 0.07 \div 6 \times 4) \div 8} = \frac{0.0117}{0.1192} \approx 0.0982 \approx 0.10$$

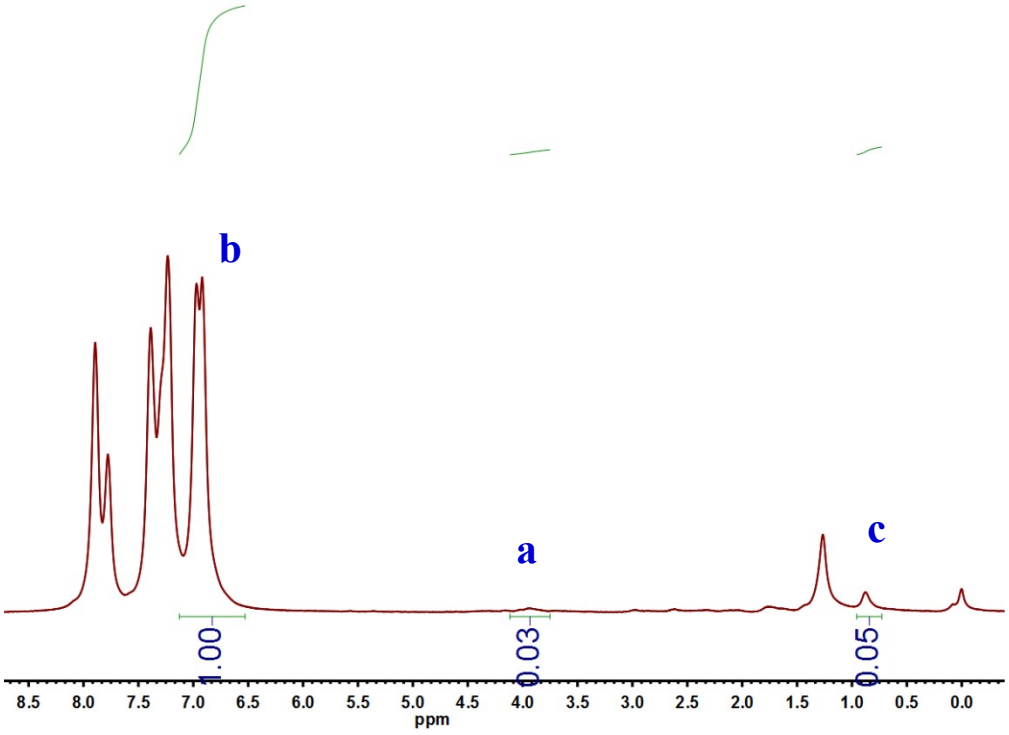


Figure S21. ^{1}H-NMR of NiO-P3.

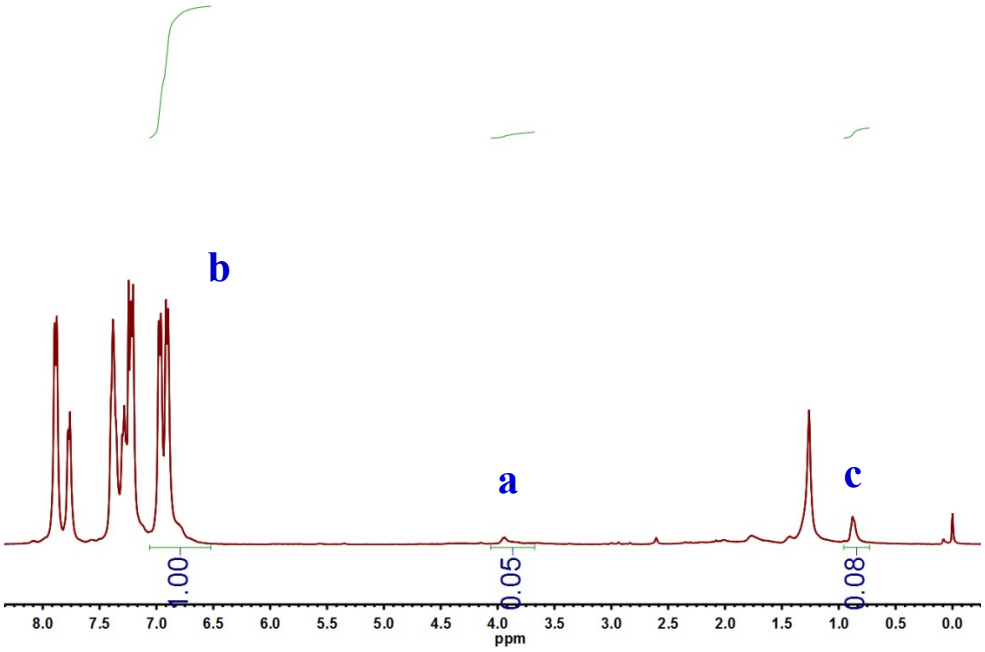


Figure S22. ^{1}H-NMR of NiO-P4.

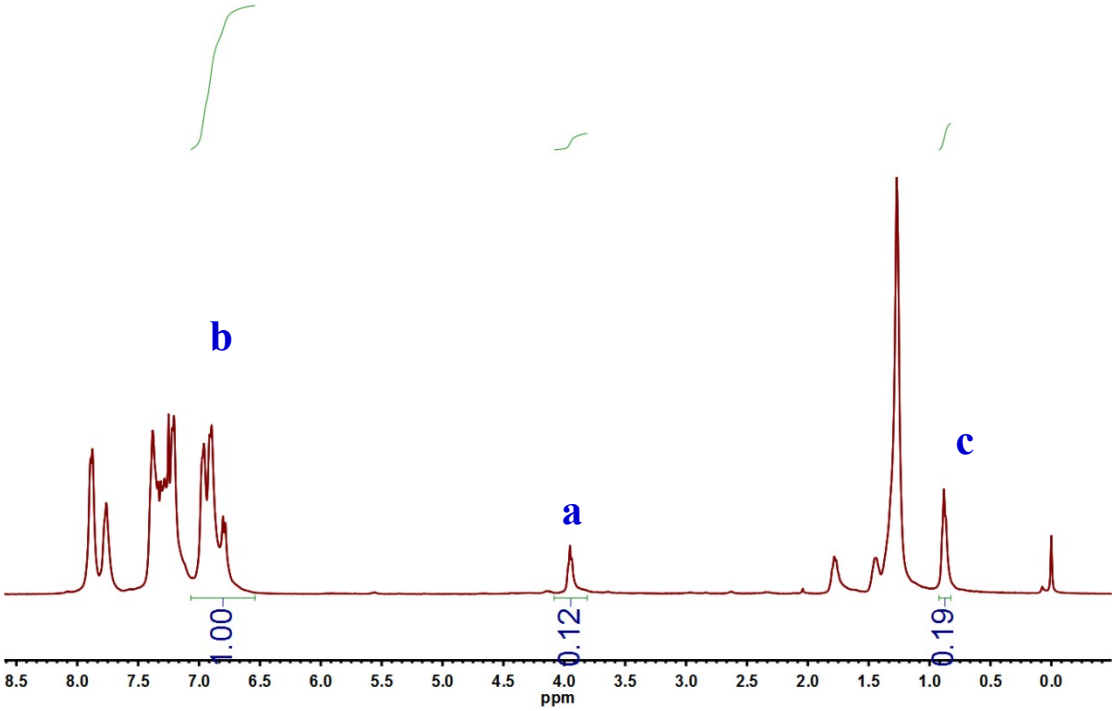


Figure S23. ^{1}H-NMR of NiO-P5

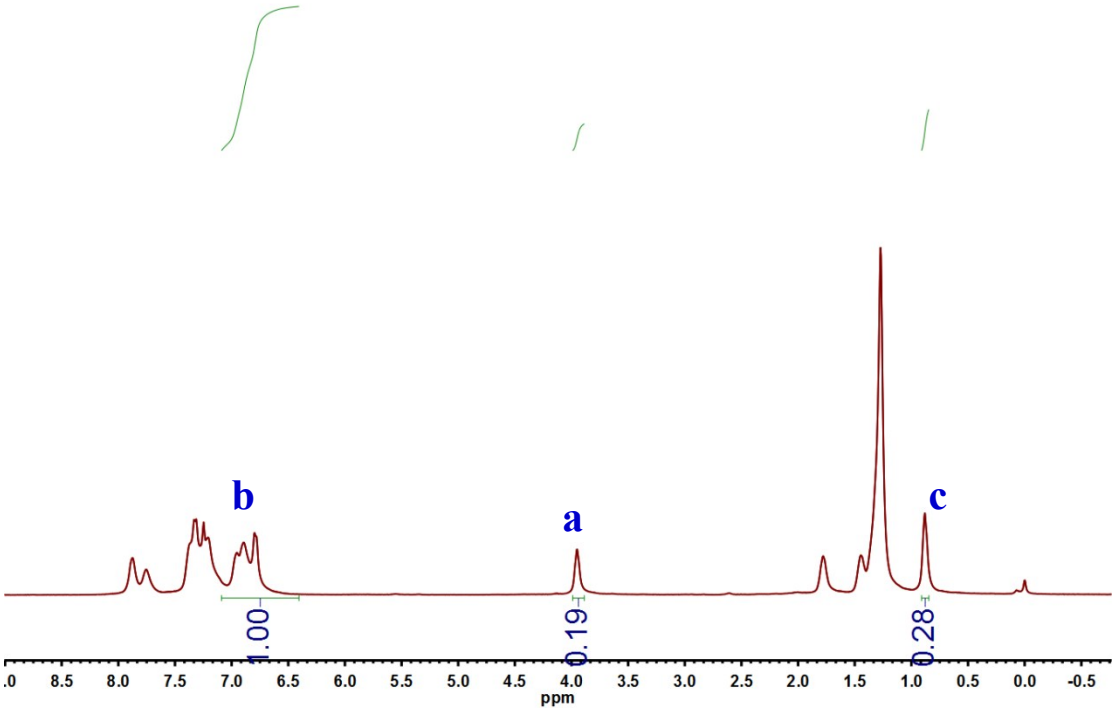


Figure S24 . ^{1}H-NMR of NiO-P7

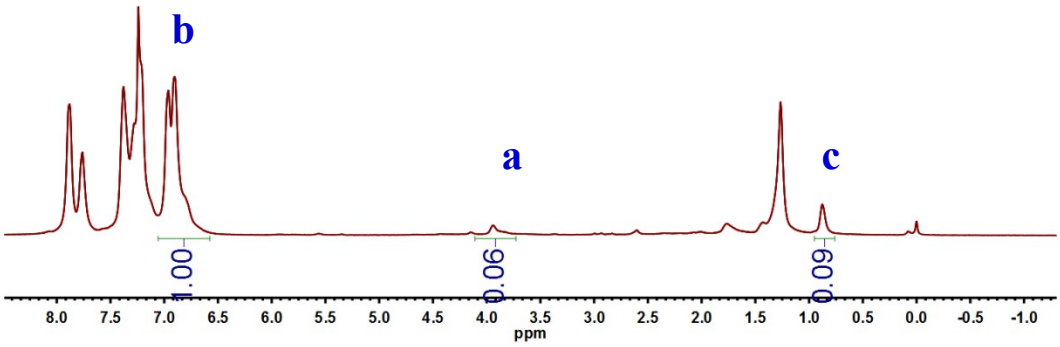


Figure S25. ^{1}H-NMR of NiO-P8

Table S2. The post-polymerization modification of PFO with Ph-O in dioxane

polymers	P_4S_{10}/$NiCl_2$.$6H_2O$ (mmol)	area of c (methyl)	the coordination ratio
NiO-P3	0.60/0.15	0.05	0.07
NiO-P4	0.80/0.20	0.19	0.29
NiO-P5	0.60/0.30	0.08	0.11
NiO-P6	0.60/0.60	0.07	0.10
NiO-P7	0.80/0.40	0.28	0.46
NiO-P8	0.80/0.80	0.09	0.13

(2) For NiN-P series polymers, take NiN-P8 as an example:

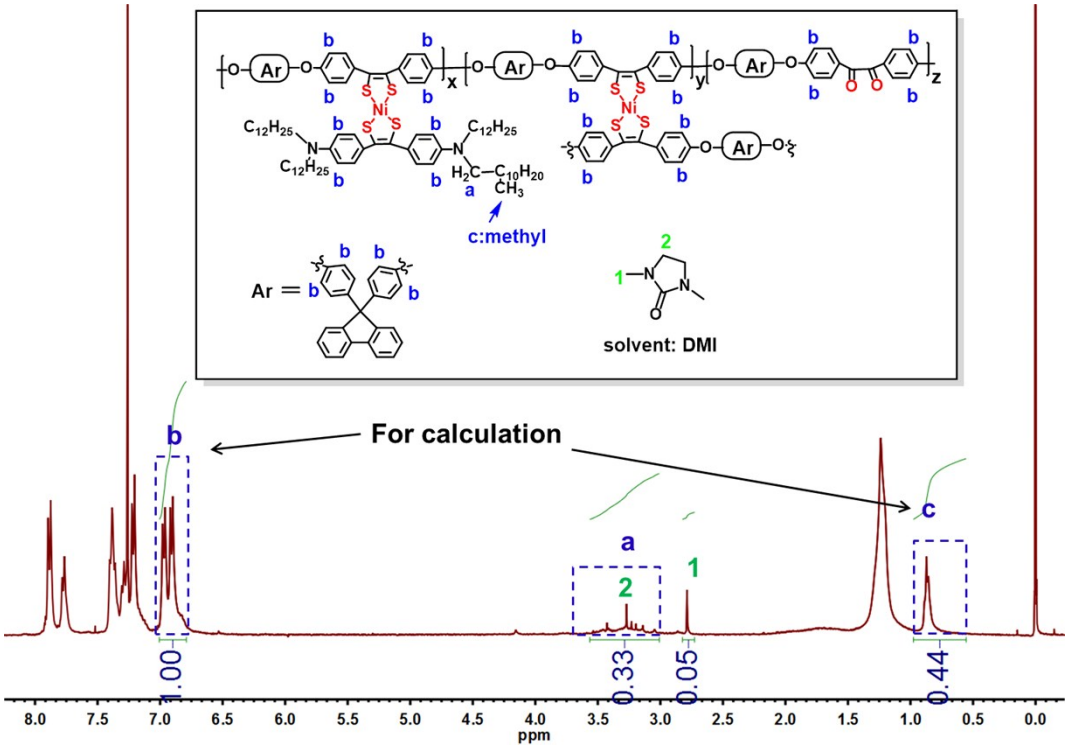


Figure S26. ^{1}H-NMR of NiN-P8

The coordination ratio corresponds to the percent of x repeat units in final polymer.

$$\textit{The coordination ratio} = \frac{x}{x+y+z} = \frac{area(c) \div 12}{(area(b) - x \times 4) \div 8} = \frac{area(c) \div 12}{(area(b) - (area(c) \div 12 \times 4) \times 4) \div 8}$$

$$= \frac{0.44 \div 12}{(1.00 - 0.44 \div 12 \times 4) \div 8} = \frac{0.03667}{0.1067} \approx 0.3437 \approx 0.34$$

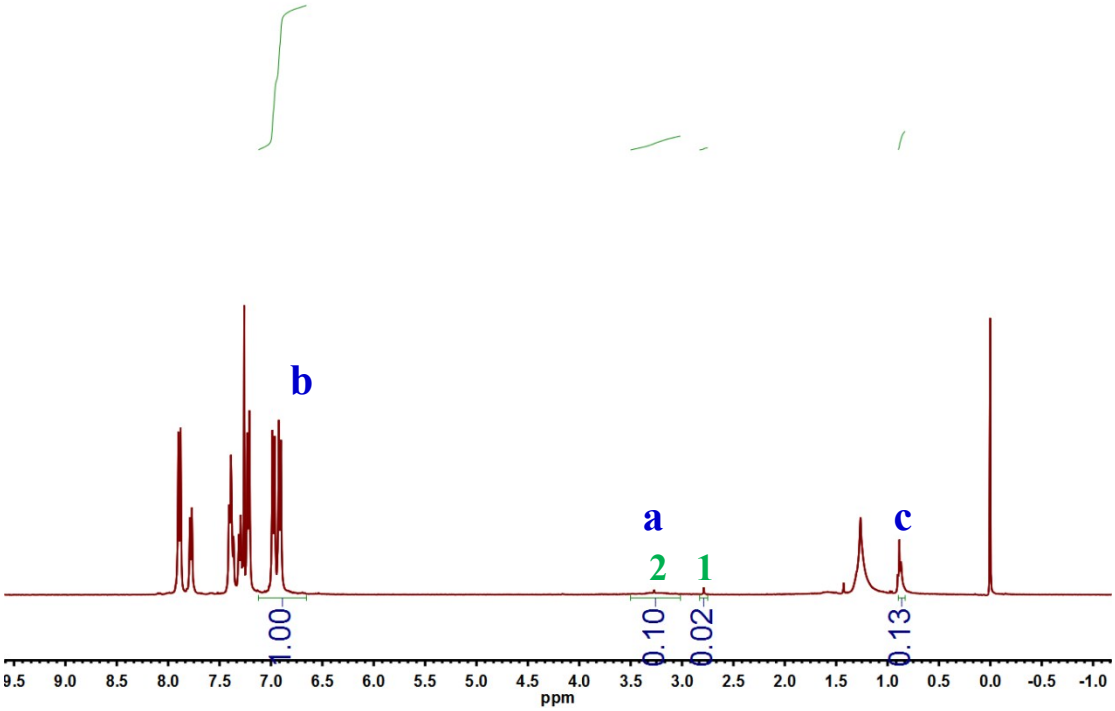


Figure S27. ^{1}H-NMR of NiN-P1

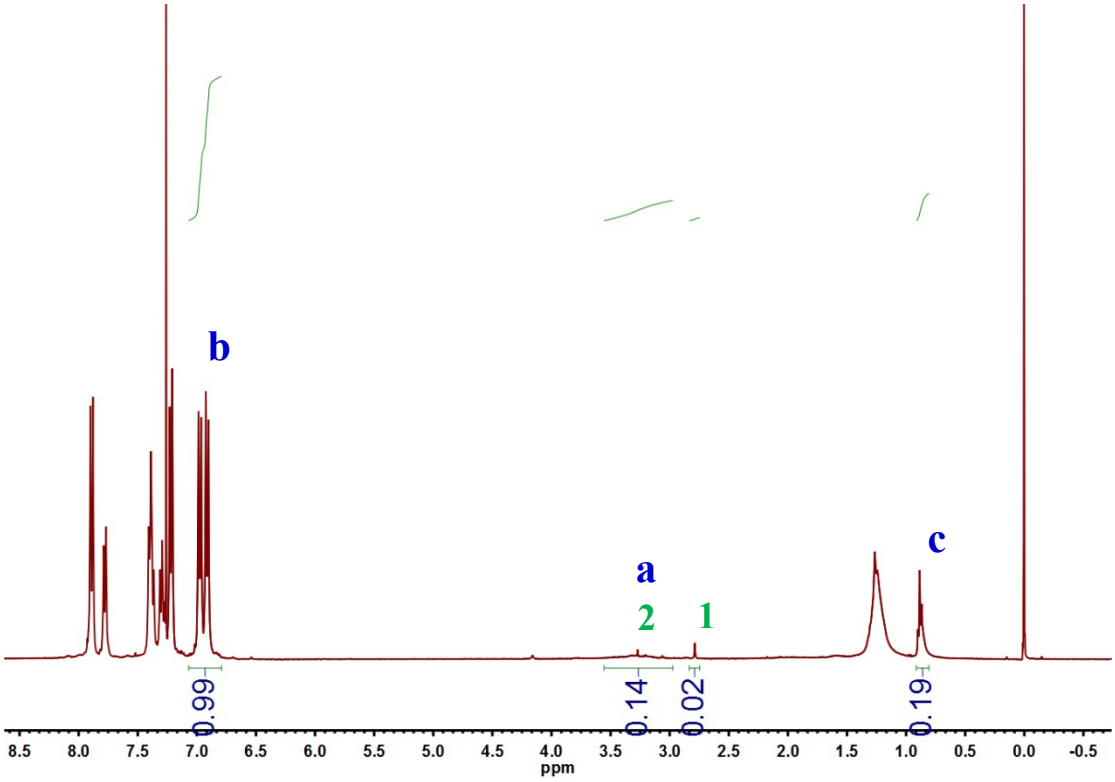


Figure S28. ^{1}H-NMR of NiN-P2

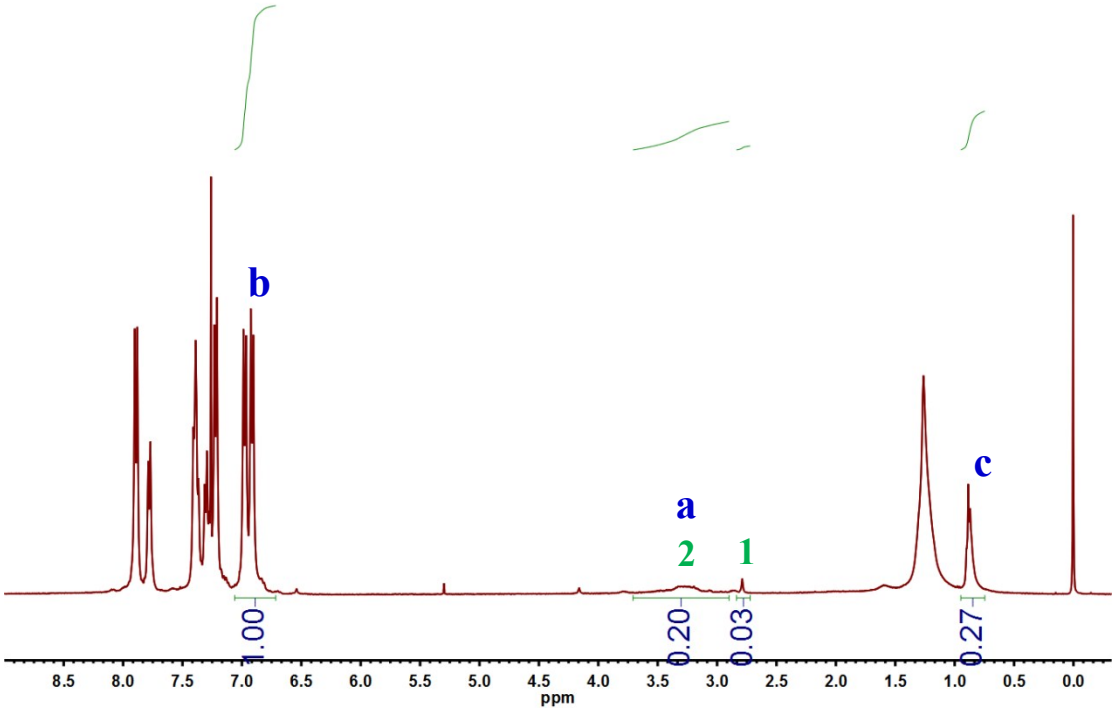


Figure S29. ^{1}H-NMR of NiN-P3

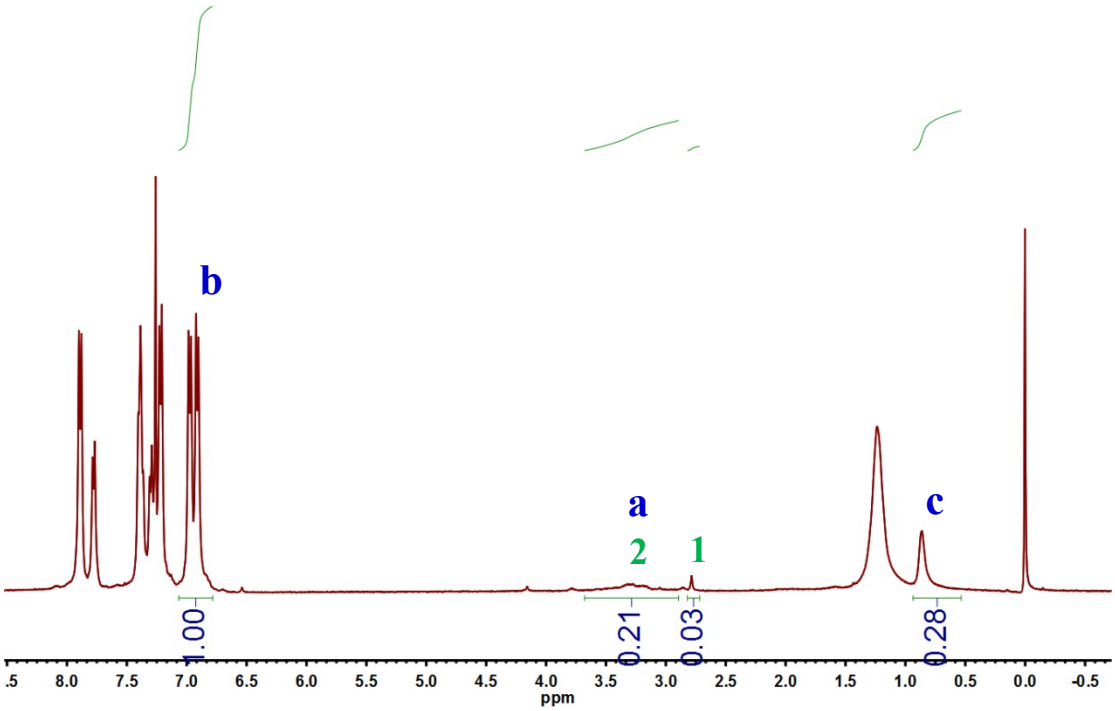


Figure S30. ^{1}H-NMR of NiN-P4

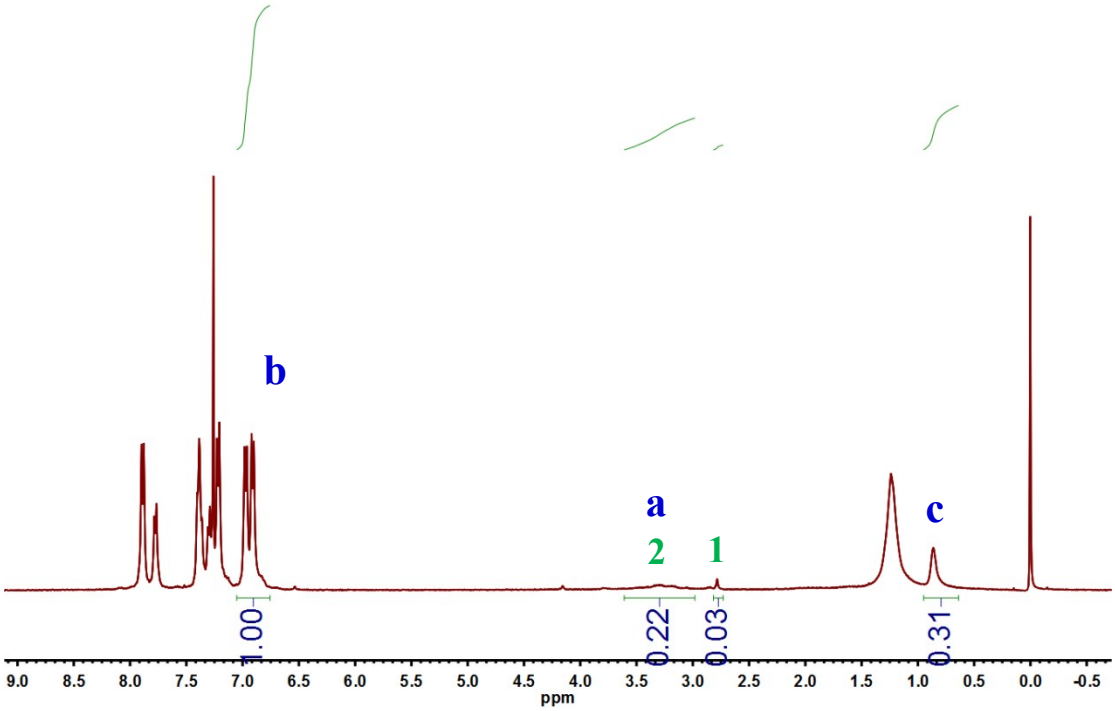


Figure S31. ^{1}H-NMR of NiN-P5

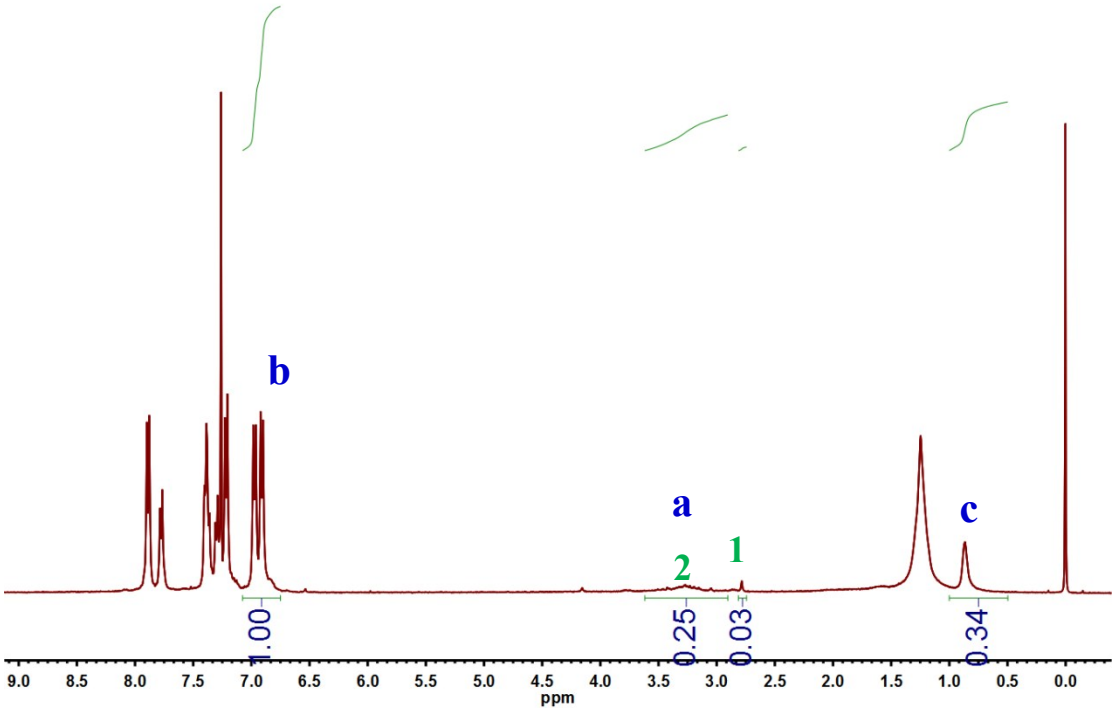


Figure S32. ^{1}H-NMR of NiN-P6

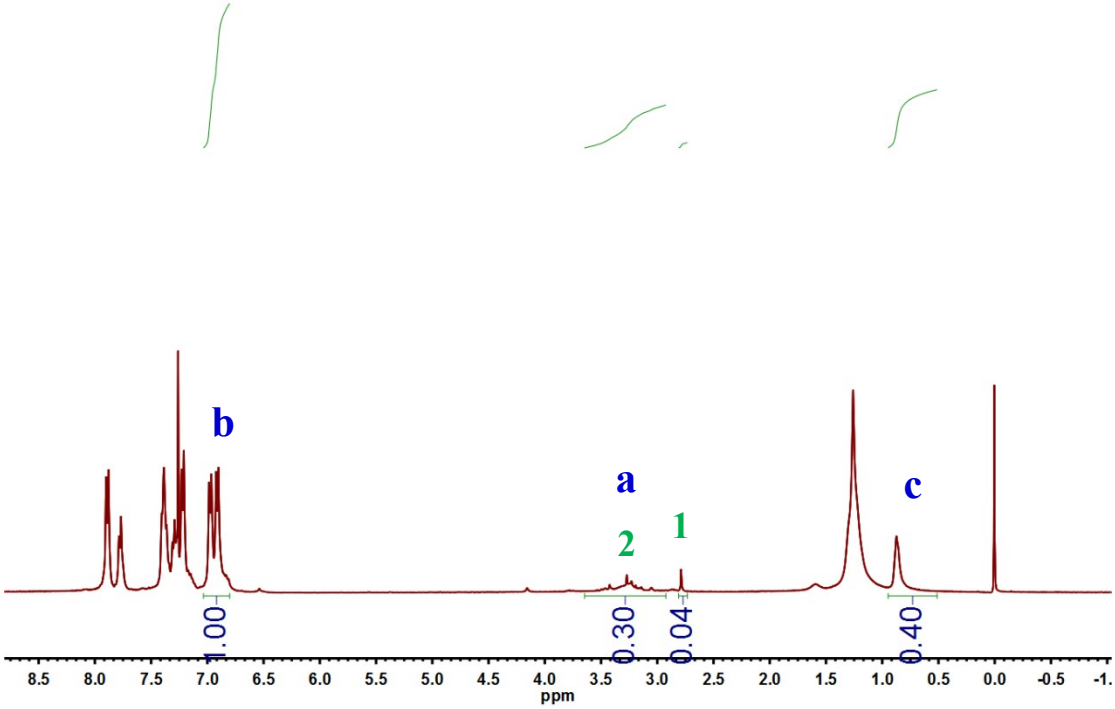


Figure S33. ^{1}H-NMR of NiN-P7

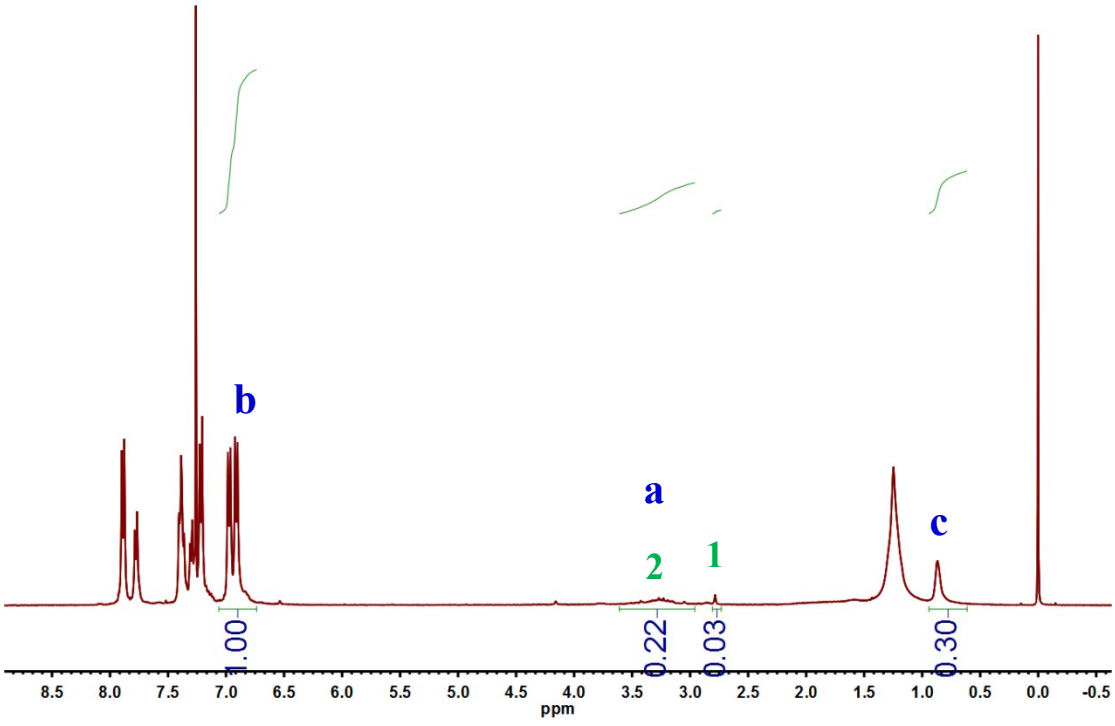


Figure S34. ^{1}H-NMR of NiN-P9

Table S3. The post-polymerization modification of PFO with Ph-N in DMI

polymers	$P_4S_{10}/NiCl_2.6H_2O$ (mmol)	area of c (methyl)	the coordination ratio
NiN-P1	0.80/0.40	0.13	0.09
NiN-P2	1.00/0.50	0.19	0.14
NiN-P3	1.20/0.50	0.27	0.20
NiN-P4	1.40/0.70	0.28	0.21
NiN-P5	1.60/0.80	0.31	0.23
NiN-P6	1.80/0.90	0.34	0.26
NiN-P7	2.00/1.00	0.40	0.31
NiN-P8	2.20/1.10	0.44	0.34
NiN-P9	2.40/1.20	0.32	0.24
NiN-P10	2.60/1.30	–	gelatin

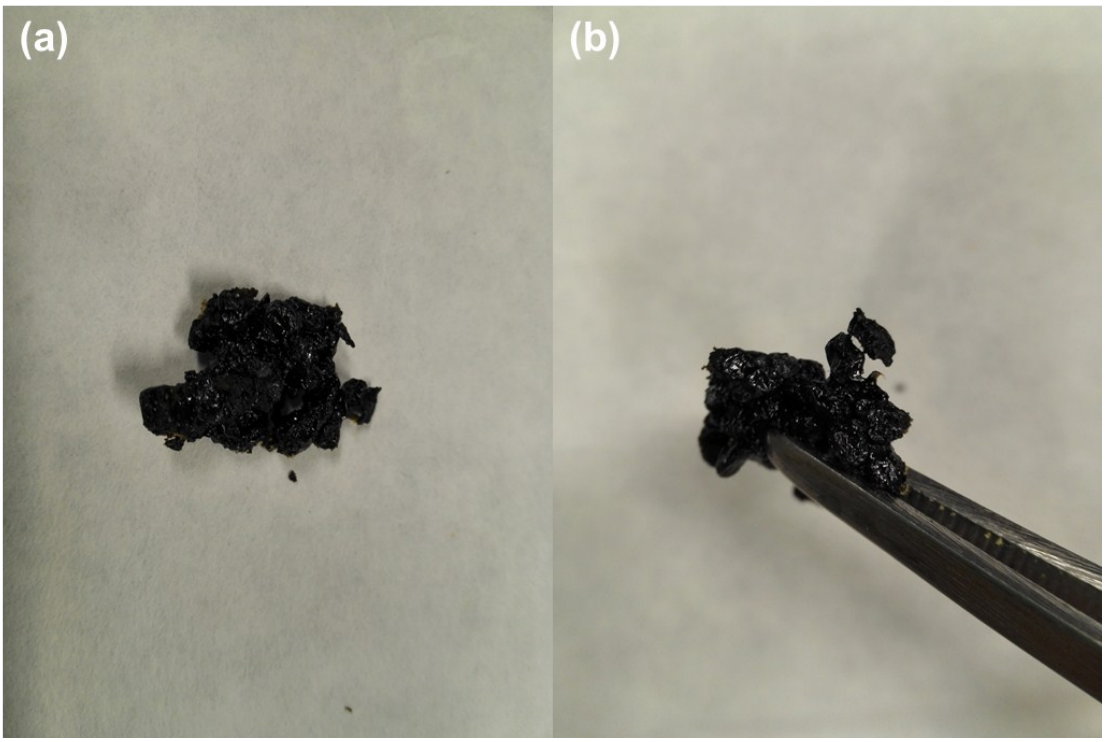
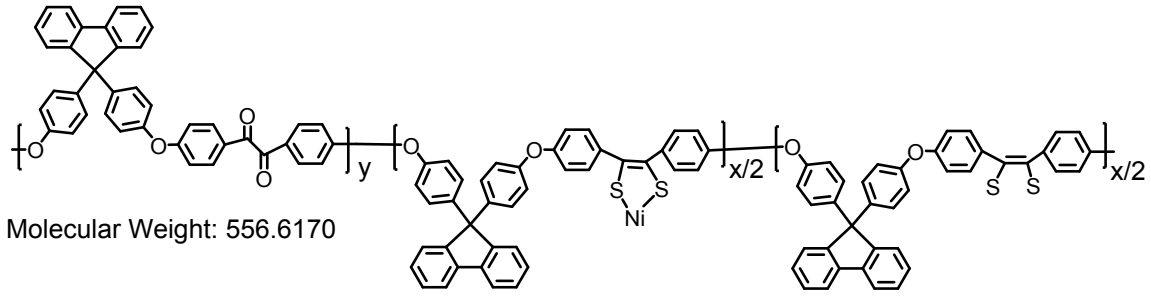


Figure S35.The gelatin state of NiN-P10.

(2) ICP measurement.

The ICP measurement of Ni-content in NiO-P2 is 0.15 wt/%. The calculated process of coordination ratio is shown below:



Molecular Weight: 556.6170

Molecular Weight: 647.4324

Molecular Weight: 588.7390

Based on idealized chain mode:

For NiO-P2:

The equation can be described as follows:

$$\frac{The\ mass\ of\ Ni\ in\ 1g\ polymer}{1g\ polymer} = \frac{\frac{x}{2} \cdot 58.6934(relative\ atomic\ weight\ \ of\ Ni)}{556.6170 \times y + 647.4324 \times \frac{x}{2} + 558.7390 \times \frac{x}{2}}$$

Then,

$$\frac{0.0015g}{1g} = \frac{\frac{x}{2} \cdot 58.6934(relative\ atomic\ weight\ \ of\ Ni)}{y \times 556.6170 + x \times 603.0857}$$

$$The\ coordination\ ratio\ R(x) = \frac{x}{x+y} \approx 0.0285 \approx 0.03$$

▲ As be noted, it is difficulties in obtaining accurate Ni content on metal tetrathiolate polymers.[1-3] We found that incomplete dissolution often ocuur in the after-processing of metal tetrathiolate polymers for ICP measurement. The same situation has been mentioned by Reynolds et al.[1]

4. The stress-strain curves of polymers

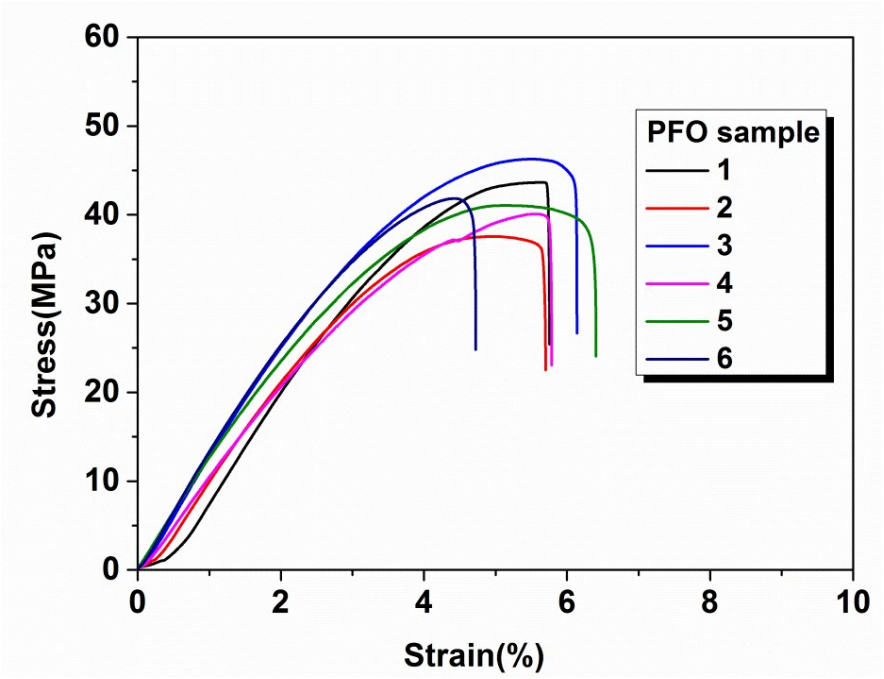


Figure S36.Stress-strain curves of PFO

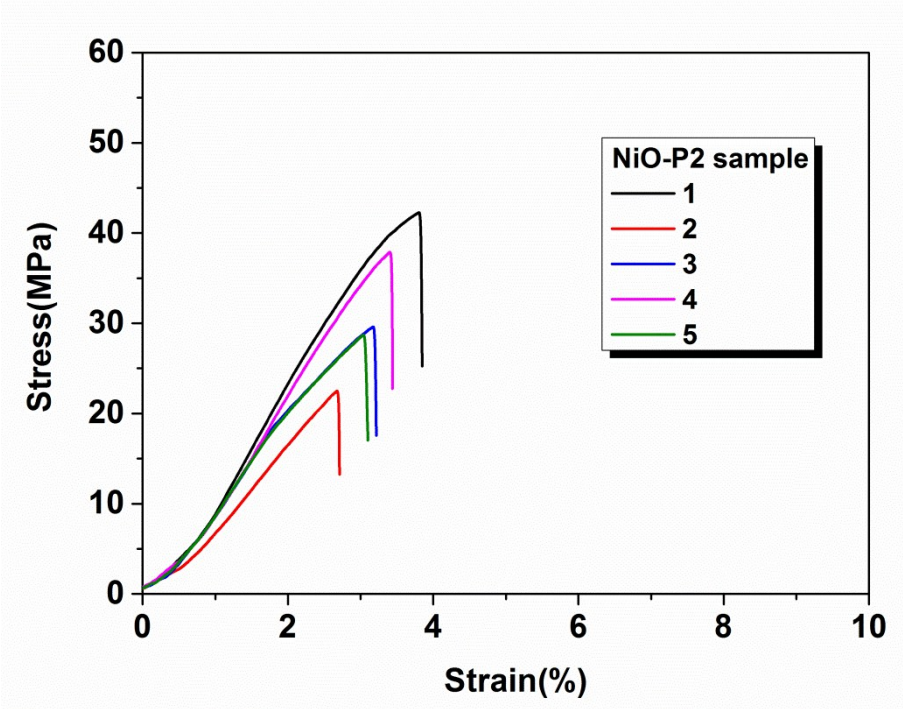


Figure S37. Stress-strain curves of NiO-P2

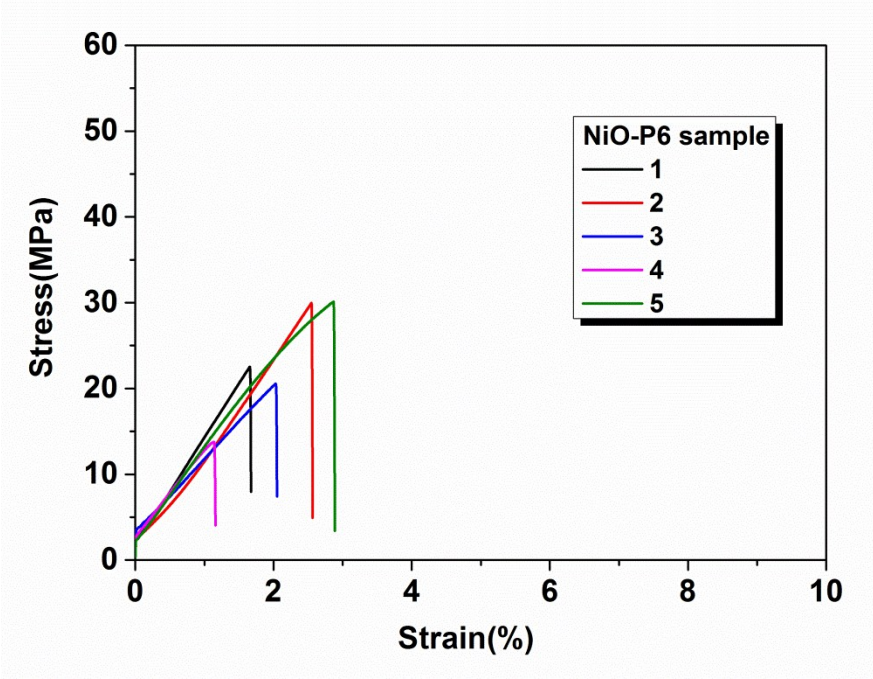


Figure S38. Stress-strain curves of NiO-P6

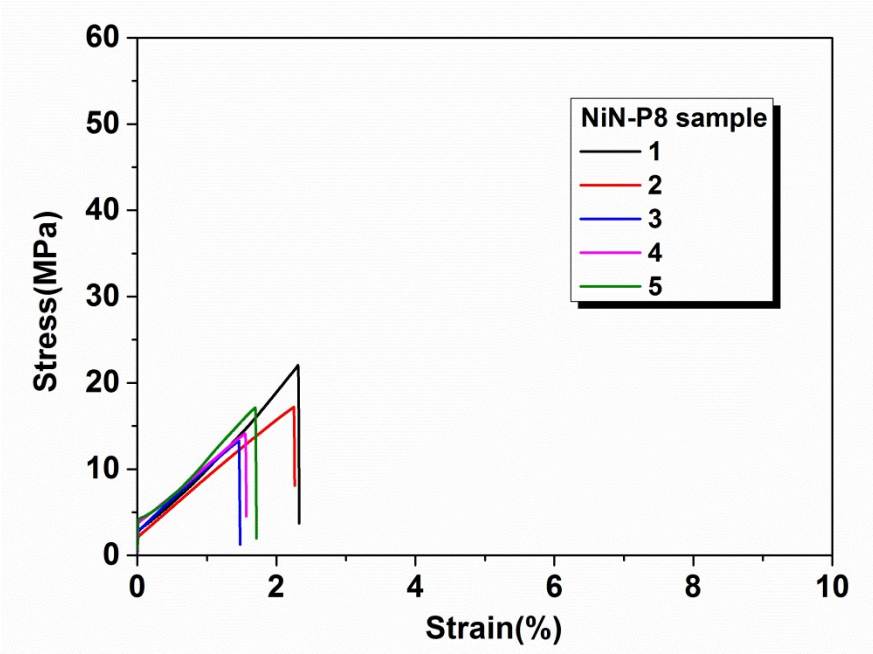


Figure S39. Strss-strain curves of NiN-P8

5. Elemental analysis

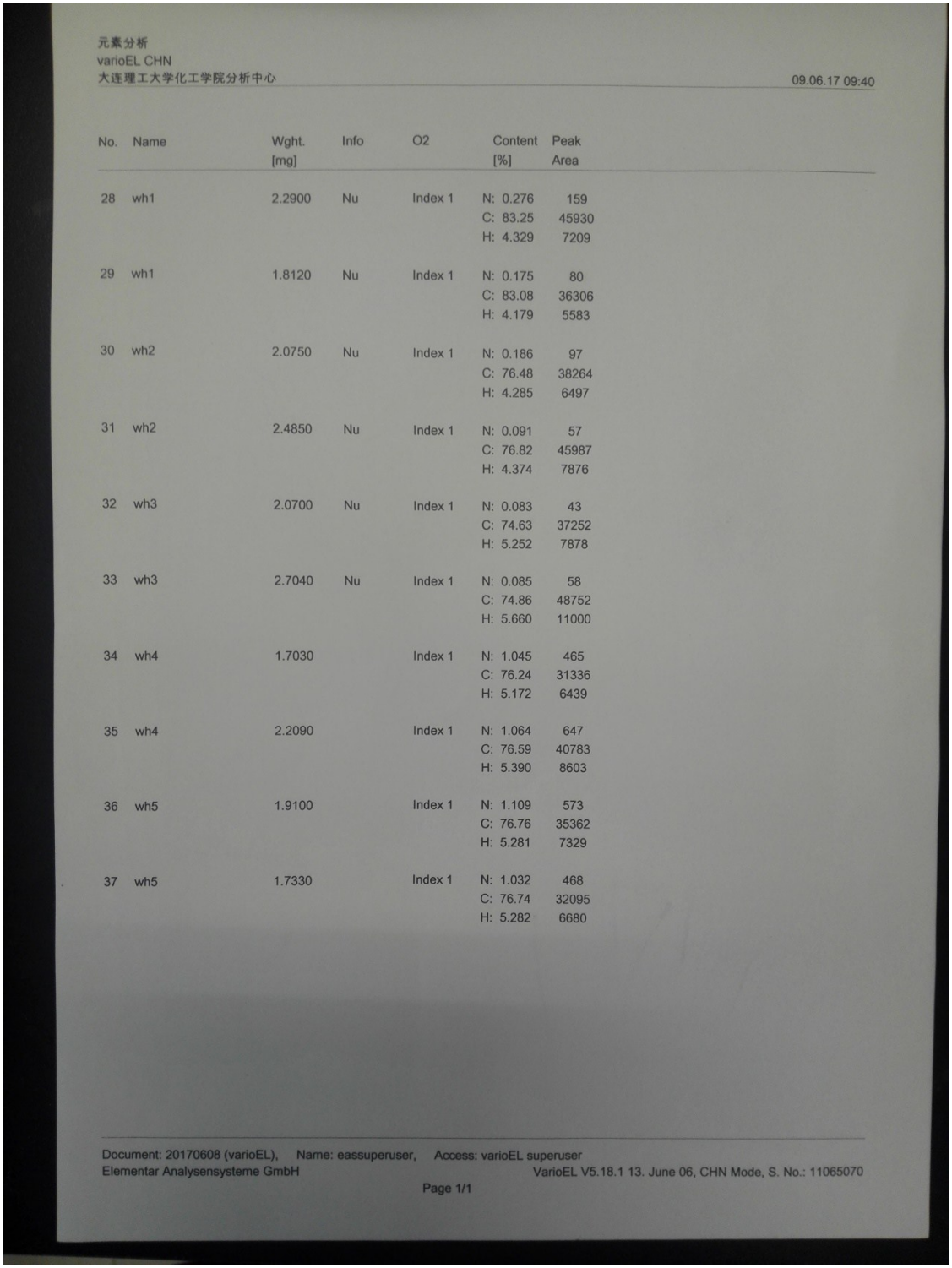
Table S4. Elemental analysis data of the polymers

Polymer	Formula	Calculated (%)			Found(%)[a]			
		C	H	N	C	H	N	C/H[b]
PFO	$C_{39}H_{24}O_4$	84.16	4.35	-	83.17	4.25	-	19.55
NiO-P6	-[c]	-	-	-	76.65	4.33	-	17.70
NiO-P7	-[c]	-	-	-	74.75	5.46	-	13.70
LPM-P6	-[c]	-	-	-	76.42	5.28	1.05	14.47
NiN-P9	-[c]	-	-	-	76.75	5.28	1.07	14.53
NiN-P8	-[c]	-	-	-	75.69	5.48	1.31	13.82

[a] The elemental analysis was measured in CHN mode. Each sample was measured twice to calculate the average value (see Figure S40 and S41). The CHNS mode was forbidden when sample contains metal. The Ni content was measured by ICP and shown in Table 2.

[b] With an increase of the nickel-bis(dithiolene) moieties with long alkyl chain in the polymer backbone, the degree of unsaturation (C/H ratio) was decreased. After modification, the C/H ratio decreased as shown in Table S4.

[c] Due to the existence of crosslinked part(y segment in Scheme 2), it is difficult to calculate the theoretical value.



元素分析
varioEL CHN
大连理工大学化工学院分析中心 09.06.17 09:40

No.	Name	Wght. [mg]	Info	O2	Content [%]	Peak Area
28	wh1	2.2900	Nu	Index 1	N: 0.276	159
					C: 83.25	45930
					H: 4.329	7209
29	wh1	1.8120	Nu	Index 1	N: 0.175	80
					C: 83.08	36306
					H: 4.179	5583
30	wh2	2.0750	Nu	Index 1	N: 0.186	97
					C: 76.48	38264
					H: 4.285	6497
31	wh2	2.4850	Nu	Index 1	N: 0.091	57
					C: 76.82	45987
					H: 4.374	7876
32	wh3	2.0700	Nu	Index 1	N: 0.083	43
					C: 74.63	37252
					H: 5.252	7878
33	wh3	2.7040	Nu	Index 1	N: 0.085	58
					C: 74.86	48752
					H: 5.660	11000
34	wh4	1.7030		Index 1	N: 1.045	465
					C: 76.24	31336
					H: 5.172	6439
35	wh4	2.2090		Index 1	N: 1.064	647
					C: 76.59	40783
					H: 5.390	8603
36	wh5	1.9100		Index 1	N: 1.109	573
					C: 76.76	35362
					H: 5.281	7329
37	wh5	1.7330		Index 1	N: 1.032	468
					C: 76.74	32095
					H: 5.282	6680

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Elementar Analysensysteme GmbH VarioEL V5.18.1 13. June 06, CHN Mode, S. No.: 11065070
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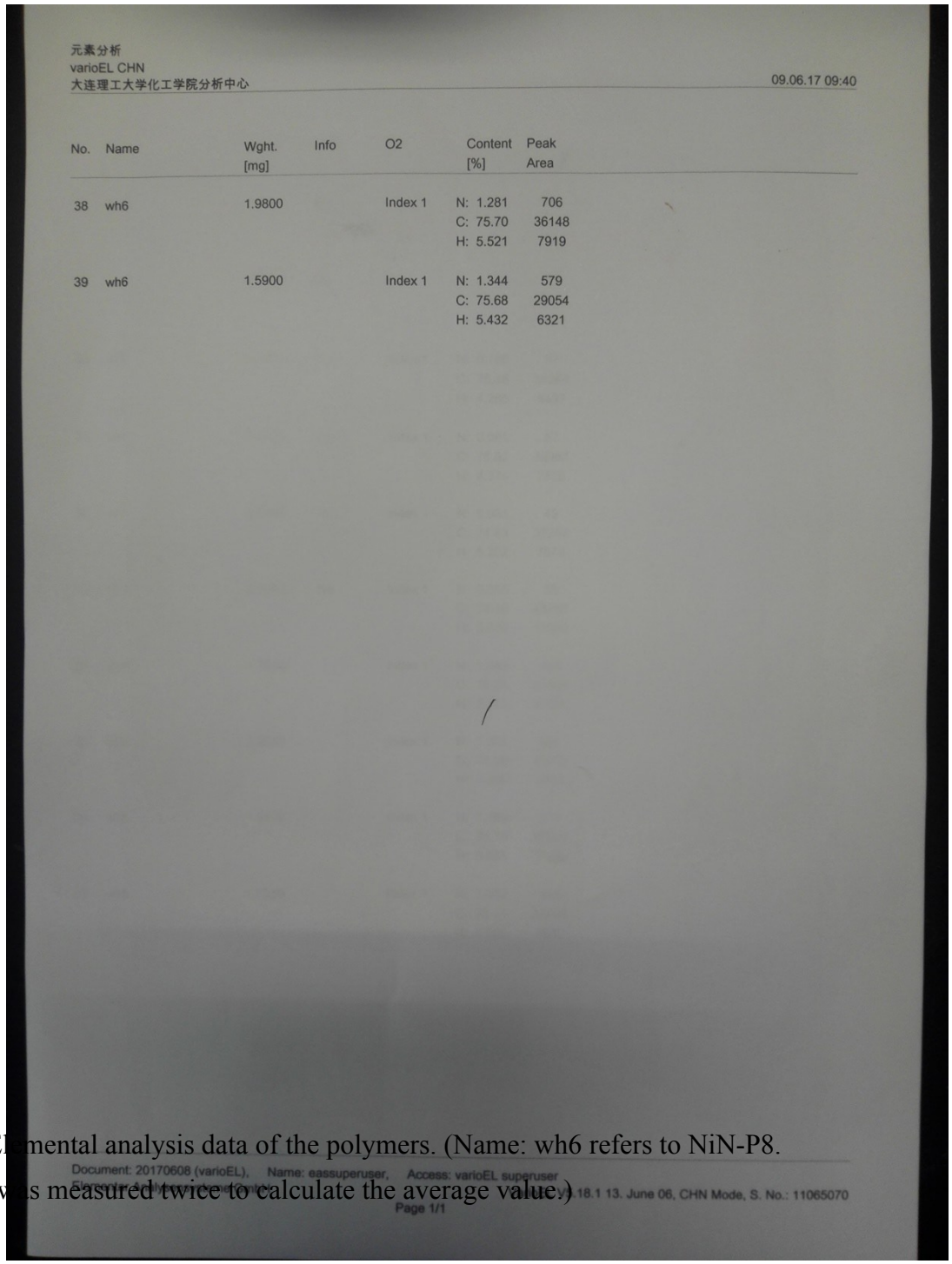
Figure S40. Elemental analysis data of the polymers. (Name: wh1 refers to PFO, wh2 refers to NiO-P6, wh3 refers to NiO-P7, wh4 refers to LPM-P6, wh5 refers to NiN-P9. “Nu” (in Info column) means that no N was detected in the corresponding sample. Each sample was measured twice to calculate the average value.)



元素分析
varioEL CHN
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No.	Name	Wght. [mg]	Info	O2	Content [%]	Peak Area
38	wh6	1.9800		Index 1	N: 1.281	706
					C: 75.70	36148
					H: 5.521	7919
39	wh6	1.5900		Index 1	N: 1.344	579
					C: 75.68	29054
					H: 5.432	6321

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Figure S41. Elemental analysis data of the polymers. (Name: wh6 refers to NiN-P8. Each sample was measured twice to calculate the average value.)

References

1. F. Wang, Y. J. Qiu and J. R. Reynolds, *Macromolecules*, 1991, **24**, 4567-4574.
2. C. W. Dirk, M. Bousseau, P. H. Barrett, F. Moraes, F. Wudl and A. J. Heeger, *Macromolecules*, 1986, **19**, 266-269.
3. R. Vicente, J. Ribas, P. Cassoux and L. Valade, *Synthetic Metals*, 1986, **13**, 265-280.