

## Electronic Supplementary Information

### Chloride-promoted self-assembly and photoluminescence of naphthalene diimides tethered to polyacetylene

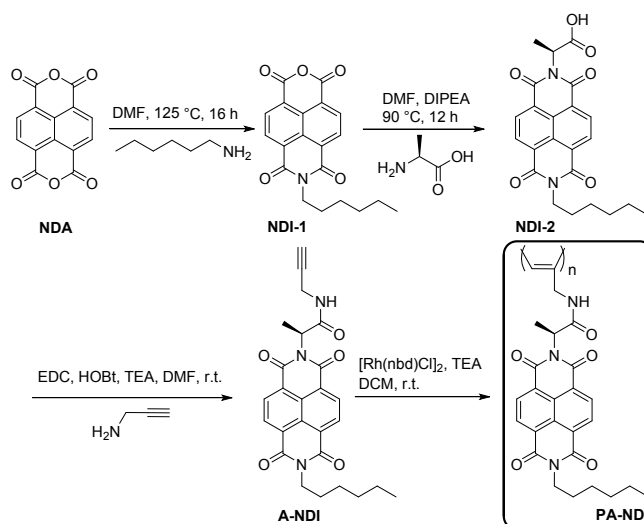
<b>1. Experimental Section.....</b>	<b>2</b>
(1) Materials and methods.....	2
(2) Synthesis and characterization .....	2
(3) Fractional precipitation of polymer and the effect of molecular weight on optical activity.....	5
<b>2. UV-Vis absorption, CD and fluorescence spectra, Sample pictures and GPC measurement.....</b>	<b>6</b>
<b>3. <sup>1</sup>H NMR titration experiment.....</b>	<b>11</b>
<b>4. SEM images of PA-NDI .....</b>	<b>12</b>
<b>5. References .....</b>	<b>12</b>

# 1. Experimental Section

## (1) Materials and methods

Chemicals and solvents were purchased from commercial resources. Unless otherwise specified, all reagents were used without further purification.  $^1\text{H}$  NMR spectra were recorded on a Bruker AV300 or AV400 spectrometer at room temperature with TMS ( $\delta=0.00$  ppm) as the internal standard.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV400 spectrometer at room temperature. All shifts are given in ppm. High resolution mass spectra (HRMS) were acquired on a Bruker Autoflex III in positive-ion mode, which was equipped with a 355-nm nitrogen laser with 5-ns duration pulse. Optical rotations were measured on a PerkinElmer 341LC polarimeter in a dm tube. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex70 Win-IR instrument. Scanning electron microscopy (SEM) images were taken using an XL 30 ESEM FEG field emission scanning electron microscope (Micrion FEI PHILIPS). Samples were prepared by drop a small amount of solution onto small glass or silicon wafer followed by natural evaporation of solvent. The number average molecular weights ( $M_n$ ) and molecular weight distributions (PDI) of polymers were measured at 30 °C by using PL-GPC 50 equipped with two tandem columns (PL gel MIXED-B LS 300x7.5mm) and a refractive index detector. The thermal properties were determined by thermogravimetric analysis (TGA, PerkinElmer) with the heating rate of 10 °C/min under  $\text{N}_2$ . UV/Vis spectra were recorded on a Shimadzu UV-2500 UV/Vis spectrophotometer at room temperature using a 1 mm cuvette. Circular dichroism (CD) spectra were recorded on a BioLogic MOS-450 spectropolarimeter using a 1 mm demountable quartz cuvette at room temperature. Fluorescence experiment was performed using PERKIN-ELMER FL 6500 spectrophotometer using a fluorescence cell with 1 mm path. All measurements were performed at room temperature and with air. Time-dependent, UV/Vis, CD and fluorescence spectra were recorded at selected or random intervals. Unless otherwise specified, the concentration of the polymer used for all spectroscopic measurements was 0.25 mg/mL (0.5 mM) based on repeat unit.

## (2) Synthesis and characterization



Scheme S1 Synthetic route of PA-NDI

### Synthesis of NDI-1:

Naphthalene dianhydride (7.57 g, 28.2 mmol) was suspended in anhydrous DMF (75 mL) and heated to 125 °C under a  $\text{N}_2$  atmosphere in a 250 mL three-necked round-bottomed flask equipped with a stir bar and reflux condenser to afford a brown slurry. 1-Hexylamine (3.4 mL, 25.7 mmol) was added dropwise over 30 min to aid the preferential formation of the monoimide, at which point a homogenous solution was obtained. The reaction

mixture was then heated under reflux in an N<sub>2</sub> atmosphere overnight. Afterwards, the solution was cooled to room temperature and the solvent removed by vacuum evaporation. The resulting residue was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, followed by washing with H<sub>2</sub>O (3 x 50 mL). The organic layer was dried (MgSO<sub>4</sub>), filtered, and the solvent removed. The brown crude product was then subjected to flash chromatography (SiO<sub>2</sub> / CH<sub>2</sub>Cl<sub>2</sub>) to afford the pure NDI-1 (3.5 g, 35%) as a colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 8.82 (s, 4H), 4.25-4.14 (m, 2H), 1.79-1.68 (m, 2H), 1.48-1.38 (m, 2H), 1.38-1.26 (m, 4H), 0.90 (t, J = 7.26 Hz, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 162.2, 158.8, 133.1, 131.2, 128.9, 128.0, 126.9, 122.8, 41.2, 31.5, 28.0, 26.7, 22.5, 14.0. HRMS m/z: [M + Na + MeOH]<sup>+</sup> calcd for C<sub>21</sub>H<sub>21</sub>NO<sub>6</sub>Na<sup>+</sup>: 406.12666; found 406.12685.

#### Synthesis of NDI-2:

NDI-1 (1 g, 2.85 mmol) was first dissolved in dimethylformamide (DMF, 15 mL), by heating at 60°C followed by the sequential addition of Alanine (0.51 g, 5.87 mmol) and DIPEA (0.98 ml, 5.87 mmol). The reaction mixture was heated at 90°C with stirring for 12 h. The solvent was evaporated under vacuum and the crude residue was suspended in 2:1 water/methanol (100 mL) and the pH of the solution was adjusted to 3 by adding hydrochloric acid (6 N). The obtained solid was thoroughly washed with water to afford 1.2 g crude product (99% yield) of NDI-2. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 8.74 (s, 4H), 5.71-5.76 (m, 1H), 4.17-4.20 (t, 2H), 1.72-1.77 (m, 2H), 1.66-1.67 (d, 2H), 1.39-1.47 (m, 2H), 1.30-1.37 (m, 4H), 0.87-0.91 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 174.5, 162.7, 162.2, 131.4, 130.9, 126.9, 126.8, 126.7, 126.2, 49.4, 41.1, 31.5, 28.0, 26.7, 22.5, 14.6, 14.0. HRMS m/z: [M + Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup>: 445.13756; found 445.13669.

#### Synthesis of A-NDI:

A mixture of NDI-2 (1.1 g, 2.00 mmol) and N-hydroxybenzotriazole (0.13 g, 1 mmol) were dissolved in DMF (25 mL). Propargylamine (0.27 ml, 2 mmol) and triethylamine (0.20 g, 2 mmol) were added to the reaction and stirred at room temperature for 5 min. Then 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide-HCl (EDAC, 0.46 mg, 2.4 mmol) was added to the reaction. After 18 h, water (20 mL) was added to stop the reaction. The aqueous solution was extracted with ethyl acetate (10 ml x 3). The resulting solution was washed with 1 M HCl, saturated NaHCO<sub>3</sub>, brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford 0.77 g crude product (84% yield) of A-NDI. The crude product was purified by silica gel chromatography eluted with dichloromethane and ethyl acetate (DCM : EA = 40:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 8.75 (s, 4H), 5.99-6.01 (t, 1H), 5.72-5.77 (m, 1H), 4.17-4.20 (t, 2H), 4.10-4.17 (m, 2H), 2.27-2.28 (t, 1H), 1.74-1.76 (d, 3H), 1.71-1.73 (m, 2H), 1.39-1.45 (m, 2H), 1.32-1.39 (m, 4H), 0.88-0.91 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 168.9, 162.6, 162.5, 131.3, 130.9, 126.8, 126.6, 126.4, 79.2, 72.0, 50.6, 41.0, 31.5, 29.8, 28.0, 26.7, 22.5, 14.6, 14.0. HRMS m/z: [M + Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>O<sub>5</sub>Na<sup>+</sup>: 482.16919; found 482.16879.

#### Synthesis of PA-NDI:

The reaction flask (sealed ampoule) was dried under vacuum and argon flushed for three times. Then, monomer (A-NDI, 500 mg, 1.08 mM) was added to a flask that was evacuated on a vacuum line and flushed with dry argon (three times). Dry DCM (10 ml) was added with a syringe and then triethylamine dropwise. The catalyst solution was prepared in another flask by dissolving [Rh(nbd)Cl]<sub>2</sub> (10 mg, 0.02 mM) in 2 ml of anhydrous DCM with 0.1 ml TEA added. After aging for 15 min, it was transferred to the monomer solution using a hypodermic syringe. The reaction mixture was stirring at room temperature for 48 h. Then, the resulting polymer was diluted in DCM and it was precipitated in a large amount of methanol to afford 450 mg crude product (90% yield). Next, polymers of different molecular weights ranging from 3,000 to 23,000 was obtained by fractional precipitation (The crude product PA-NDI was soluble in THF, and then methanol was slowly added dropwise to precipitate the product).

GYP-A-CNDI #3 RT: 0.14 AV: 1 NL: 7.33E6  
T: FTMS + p ESI Full ms [100.00-1500.00]

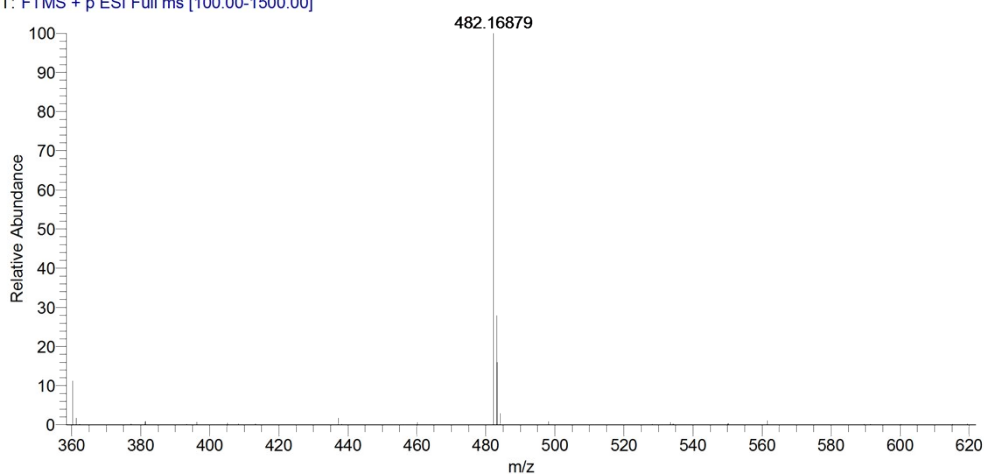


Figure S1 FTMS spectrum of A-NDI

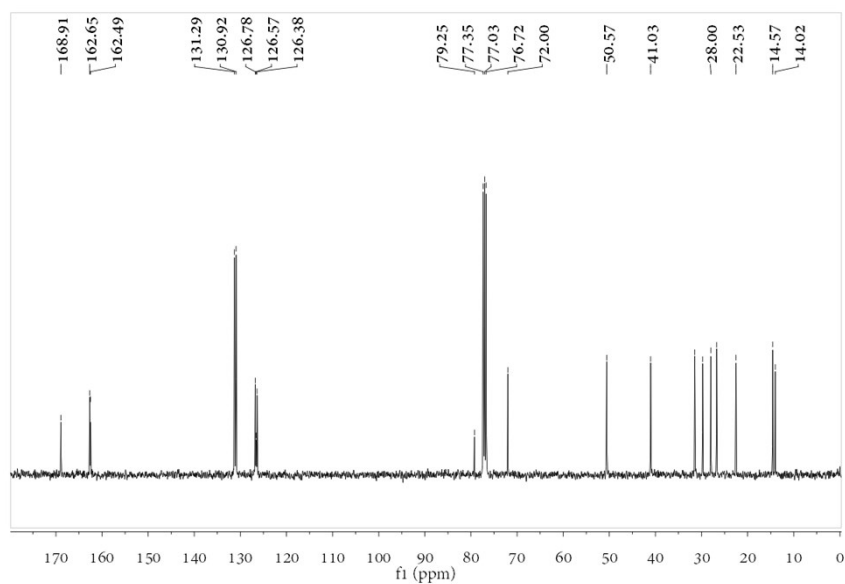


Figure S2 <sup>13</sup>C NMR spectrum of PA-NDI measured in CDCl<sub>3</sub> at room temperature.

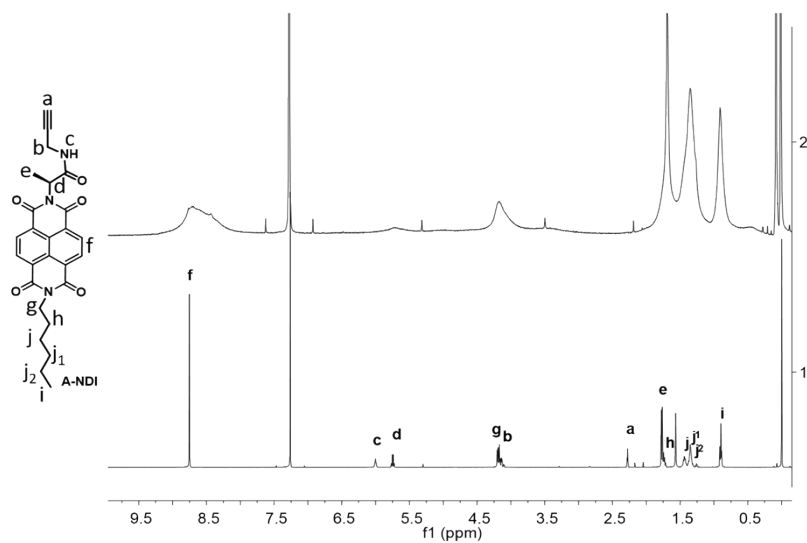
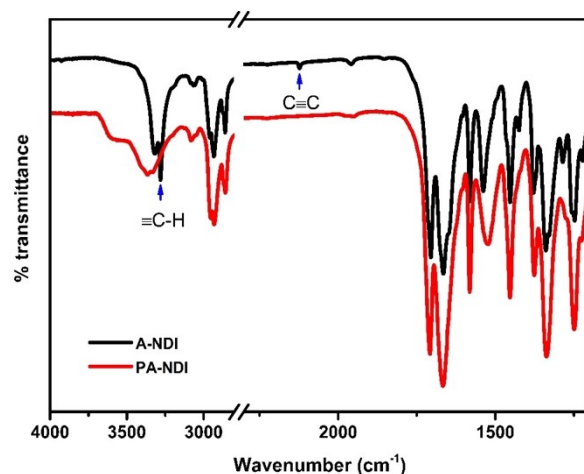
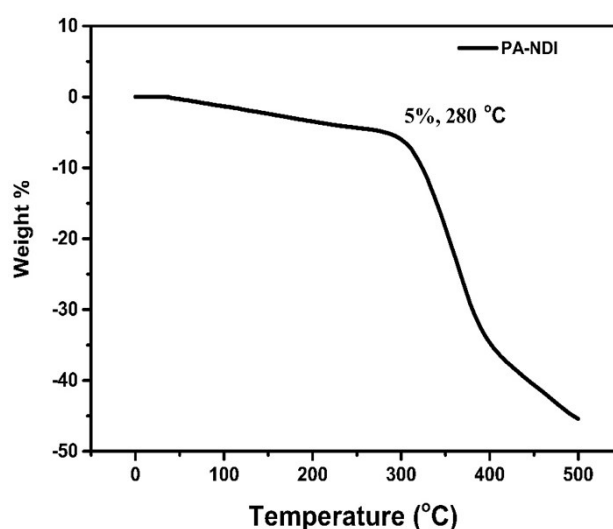


Figure S3 <sup>1</sup>H NMR spectrum of PA-NDI (2) and A-NDI (1) measured in CDCl<sub>3</sub> at room temperature.



**Figure S4** Solid-state IR spectra of A-NDI and PA-NDI



**Figure S5** TGA curves of PA-NDI recorded under nitrogen at a heating rate of 10 °C/min.

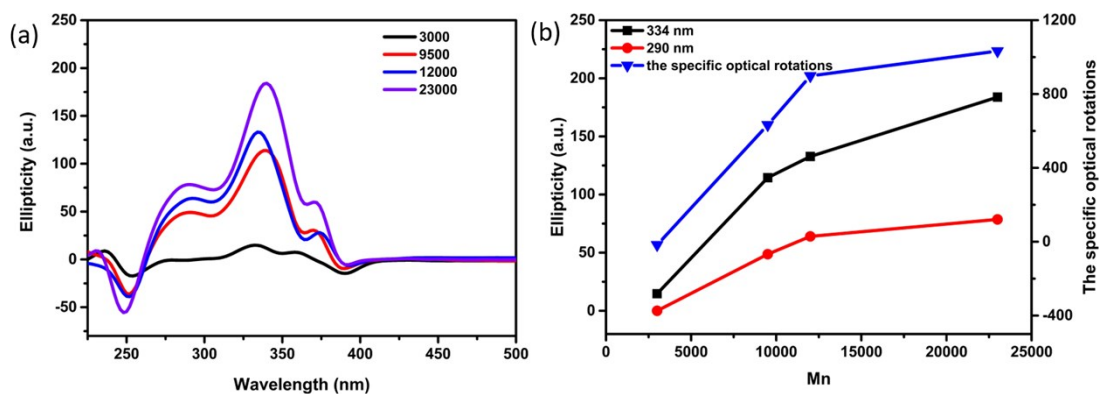
### (3) Fractional precipitation of polymer and the effect of molecular weight on optical activity

We used fractional precipitation (The crude product PA-NDI was soluble in THF, and then methanol was slowly added dropwise to precipitate the product.) to get polymers of different molecular weights ranging from 23,000 to 3,000 and we found that higher molecular weight polymer possessed stronger optical activity.

**Table S1** The results of fractional precipitation and their specific optical rotations

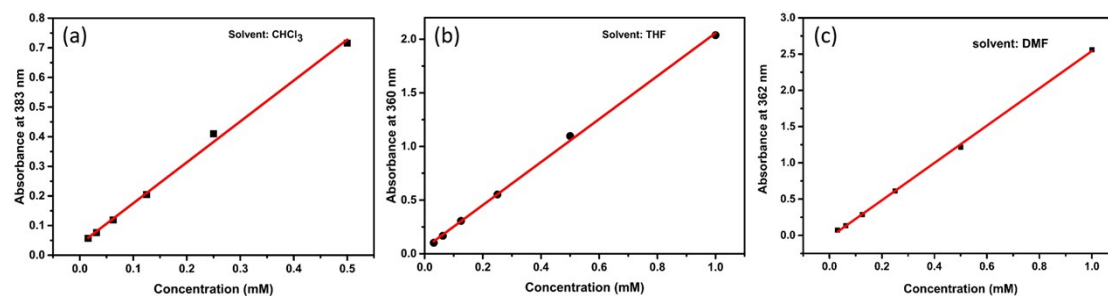
$M_n^a$	PDI <sup>a</sup>	$[\alpha]_D^{20b}$
23,000	1.37	+1033
12,000	1.63	+898
9,500	1.56	+633
3,000	1.28	-17

<sup>a</sup>Estimated by GPC in THF on the basis of a polystyrene calibration. <sup>b</sup>Specific optical rotation of PA-NDI measured in DCM

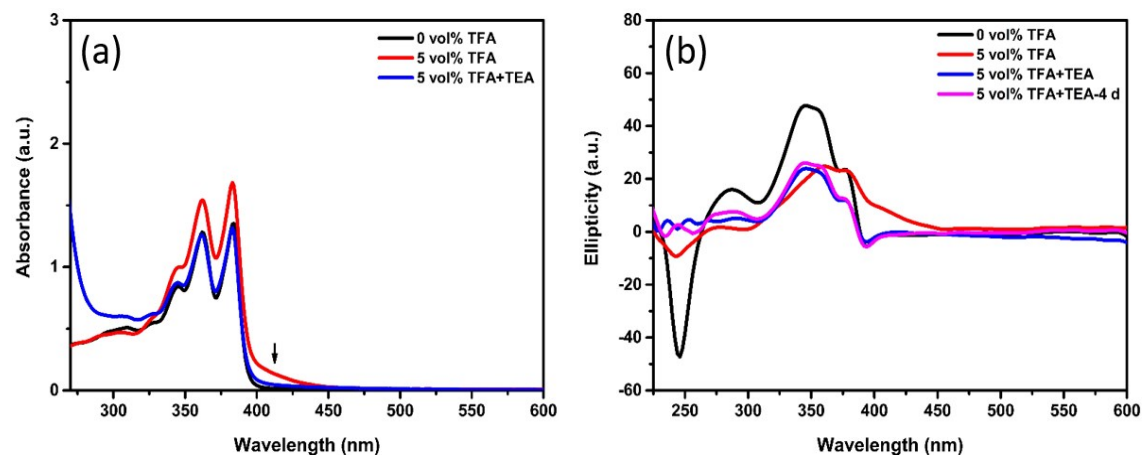


**Figure S6** (a) CD spectra of **PA-NDI** with different number-average molecular weight in DCM ([monomer units of **PA-NDI**] = 1.0 mM) and (b) the relationship between the optical activities and  $M_n$ .

## 2. UV-Vis absorption, CD and fluorescence spectra and Sample pictures



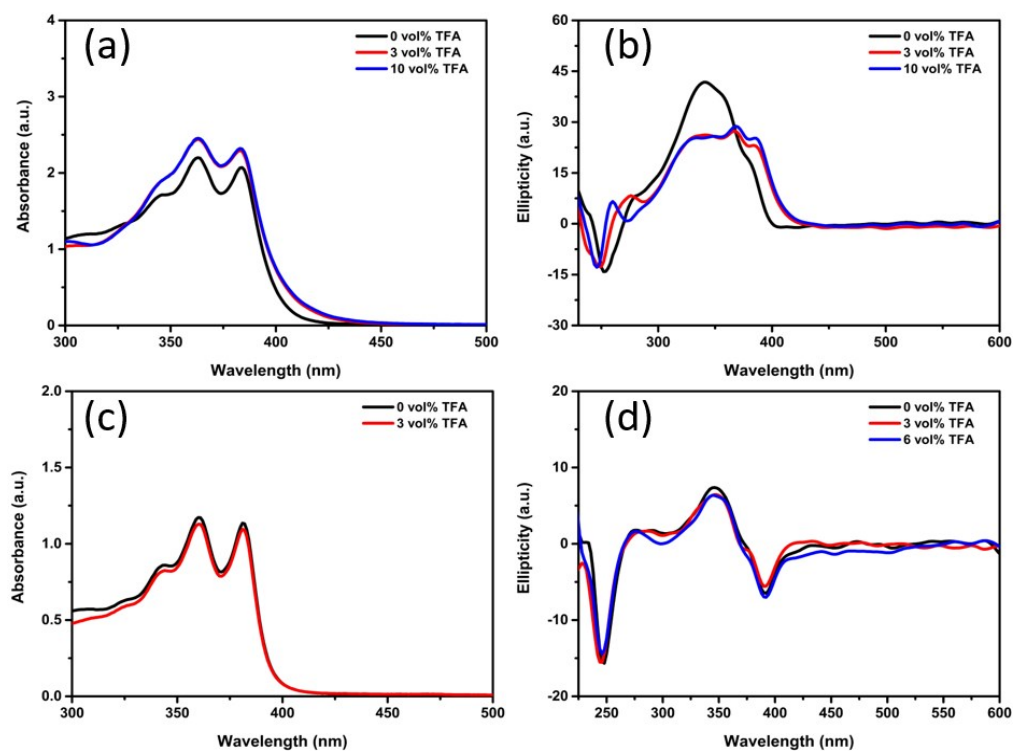
**Figure S7** Variation of absorption intensity of **PA-NDI** as a function of concentration.



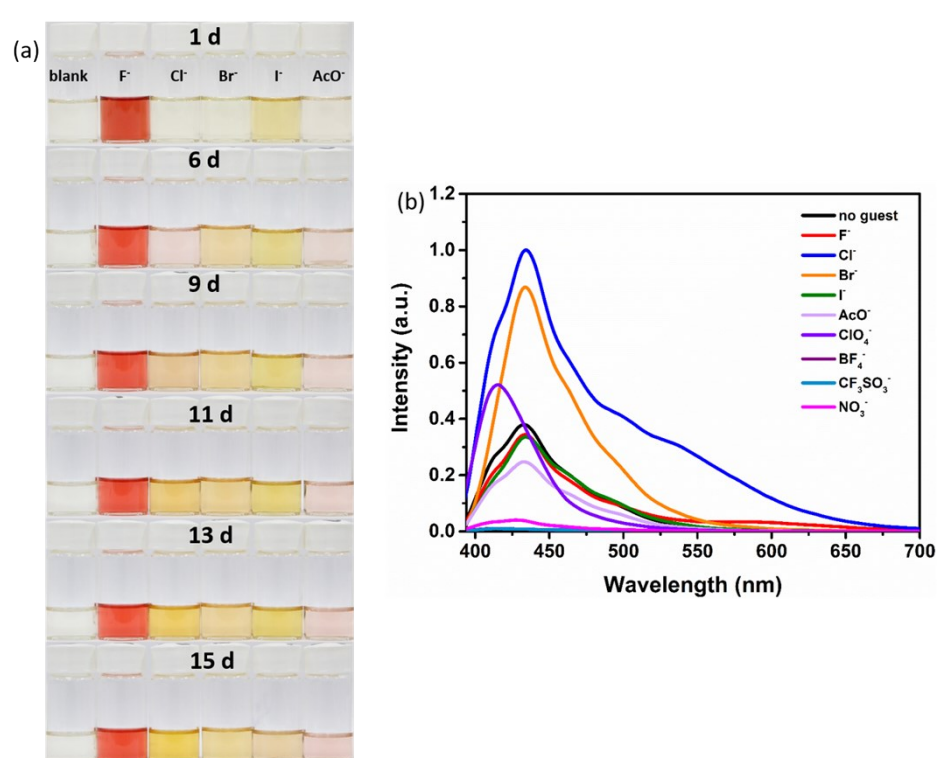
**Figure S8** (a) UV-vis and (b) CD spectra of **PA-NDI** in  $\text{CHCl}_3$  with the addition of TFA and TEA

UV-vis and CD spectra recovered by adding triethylamine (TEA) into the solution showing a reversible structure transition. The results were consistent with previous studies and it can confirm that the absorption peaks of **PA-NDI** helical backbone are located at around 290 nm and 405 nm corresponded to contracted *cis-cisoid* helical structure and the loose *cis-transoid* helical structure respectively. It is noteworthy that the CD peak at 290 nm or 405 nm of **PA-NDI** was significantly weakened or even did not appear in DMF and THF, probably because of the weak intensity.

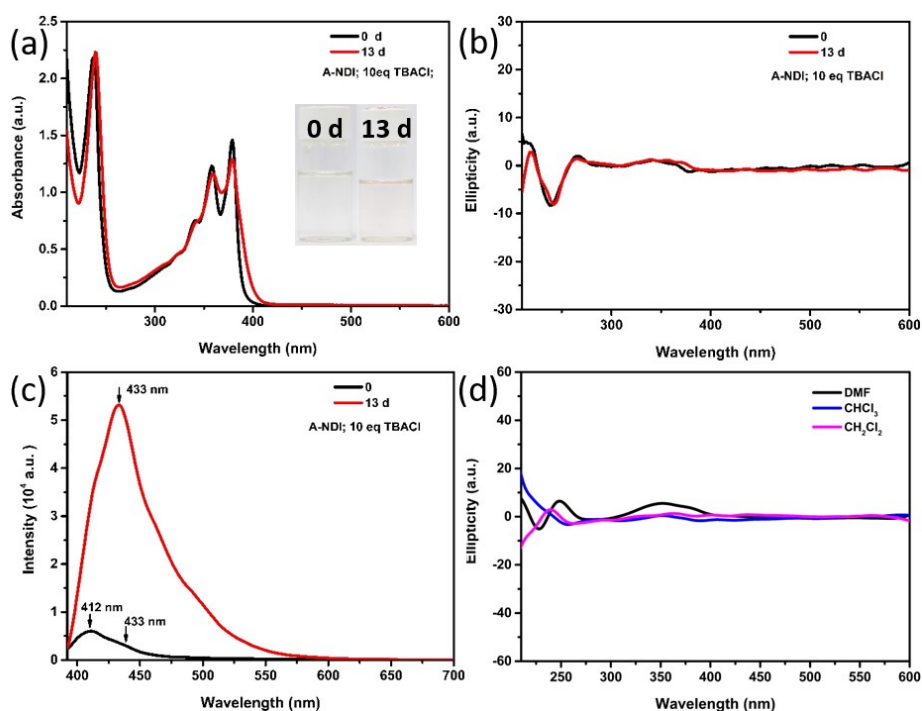
We did not observe the helical structure transition from *cis-cisoid* to *cis-transoid* of **PA-NDI** in toluene and THF with the addition of TFA. The phenomenon is similar to the behavior reported in recent studies.<sup>1, 2</sup>



**Figure S9** UV-vis spectra of **PA-NDI** in (a) toluene/TFA mixtures and (c) THF/TFA mixtures with various compositions; CD spectra of **PA-NDI** in (b) toluene/TFA mixtures and (d) THF/TFA mixtures with various compositions.

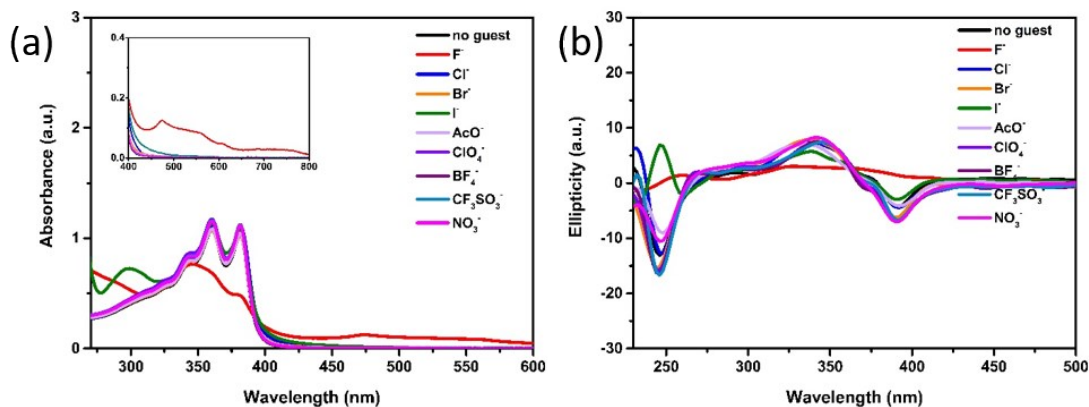


**Figure S10** (a) Time-dependent changes of color of **PA-NDI** in the presence of TBA salts of a series of anions ( $[\text{anion}] / [\text{monomer units of PA-NDI}] = 10$ ). (b) Emission spectra of **PA-NDI** in the presence of TBA salts of a series of anions in THF on day 13 ( $[\text{anion}] / [\text{monomer units of PA-NDI}] = 10$ ). There was not significant change in UV-vis and CD spectra with the addition of  $\text{I}^-$  and the color change was believed stem from the tetrahydrofuran solution of  $\text{I}^-$ .



**Figure S11** Time-dependent (a) UV-vis (inset: the corresponding sample picture), (b) CD and (c) emission spectra of **A-NDI** in THF with the addition of 10 eq  $\text{Cl}^-$  ( $c = 0.5 \text{ mM}$ ). (d) CD spectra of **A-NDI** in different solvent without the addition of  $\text{Cl}^-$  ( $c = 1.0 \text{ mM}$ ).

There were no distinct color and optical spectra changes of **A-NDI** in THF with  $\text{Cl}^-$  after 13 days indicating that the color and optical change of **PA-NDI** with anions might stem from the polymer backbone. The change in the dihedral angle of the conjugated double bonds in the backbone can cause the color change<sup>3</sup>.

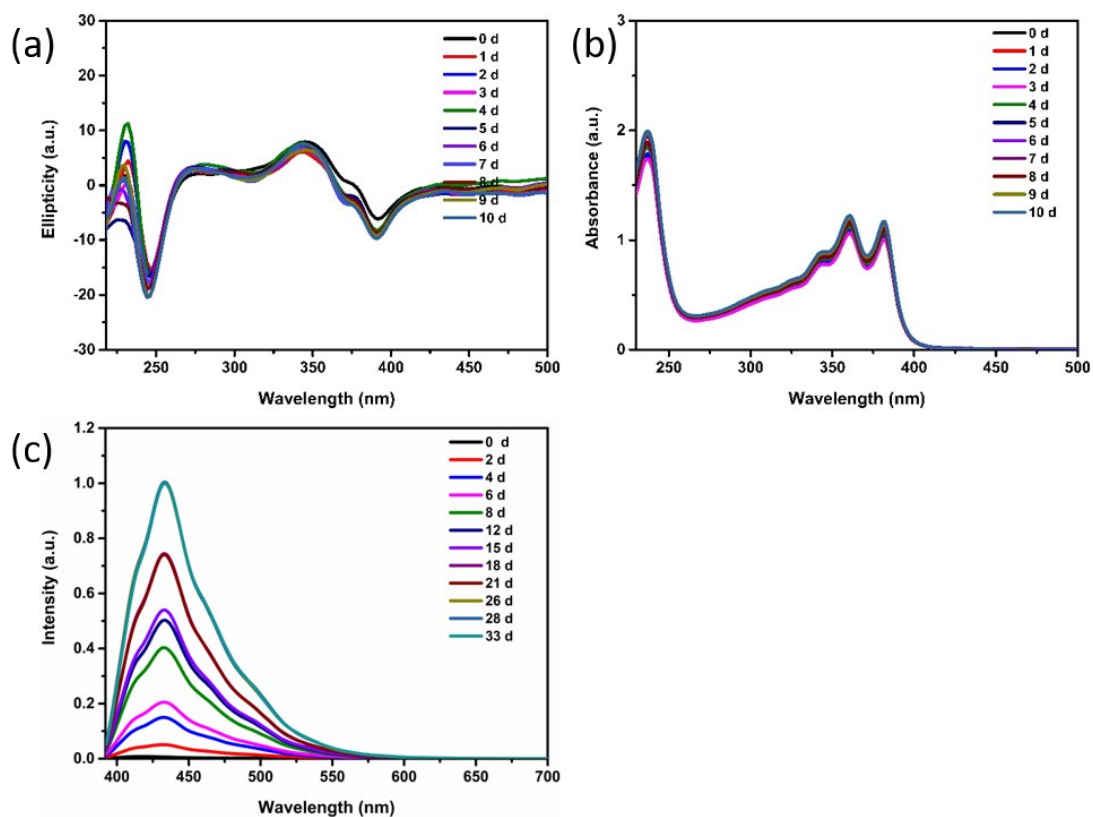


**Figure S12** (a) UV-vis and (b) CD and spectra of **PA-NDI** in the presence of TBA salts of a series of anions in THF on day 0. ( $[\text{anion}] / [\text{monomer units of PA-NDI}] = 10$ )

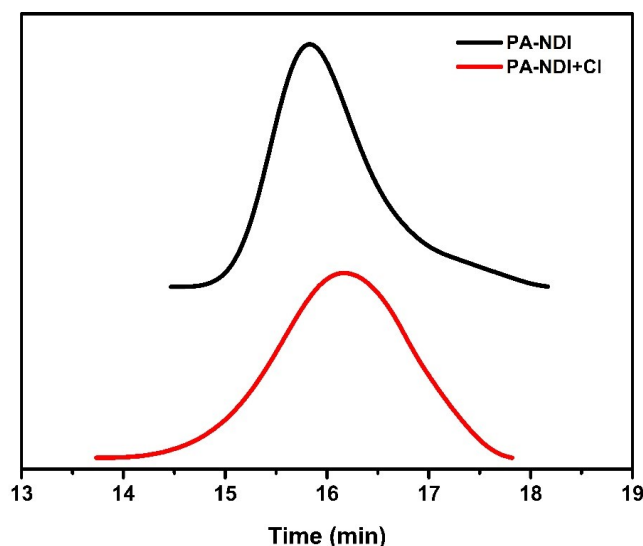
New absorption peaks at 475 nm and 560 nm corresponding to  $\text{NDI}^{\cdot-}$  and  $\text{NDI}^{2-}$  were developed in UV-vis spectra by the  $\text{F}^-$  addition, leading to a red solution (Fig. S10). The CD signal intensity of 342 nm decreased significantly from 7.4 to 2.8 (Fig. S13b). However, the polymer backbone CD peak was not observed and we were unable to judge if the backbone helical structure was destroyed. So, there might be two reasons to explain the change in CD spectra: (1) amide hydrogen bonds were destroyed by  $\text{F}^-$  resulting in helical structure disruption of helical polymer backbone or (2) repulsion between  $\text{NDI}^{2-}$  destroyed helical alignment of NDIs.



Regrettably, due to interference of the formation of  $\text{NDI}^{\cdot-}$  and  $\text{NDI}_2^{\cdot-}$ , we were unable to judge the effluence of  $\text{F}^-$  on the self-assembly of **PA-NDI**.

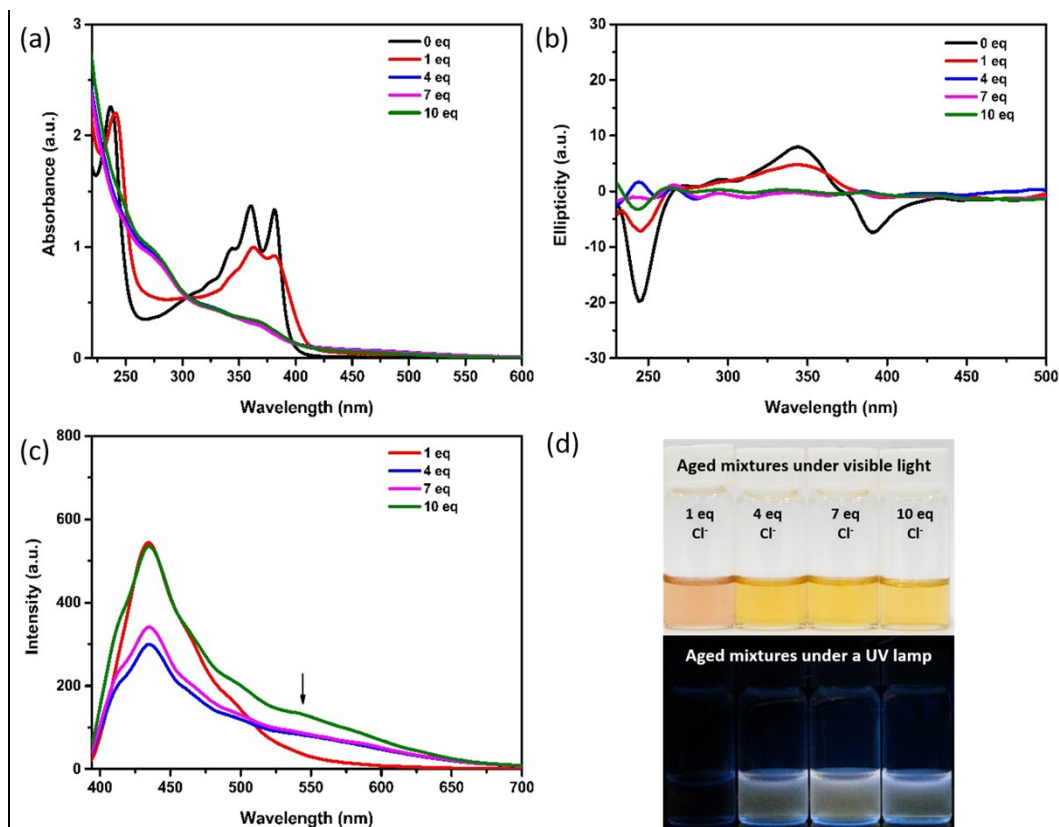


**Figure S13** Time-dependent (a) UV-vis, (b) CD and (c) emission spectra of **PA-NDI** in THF.

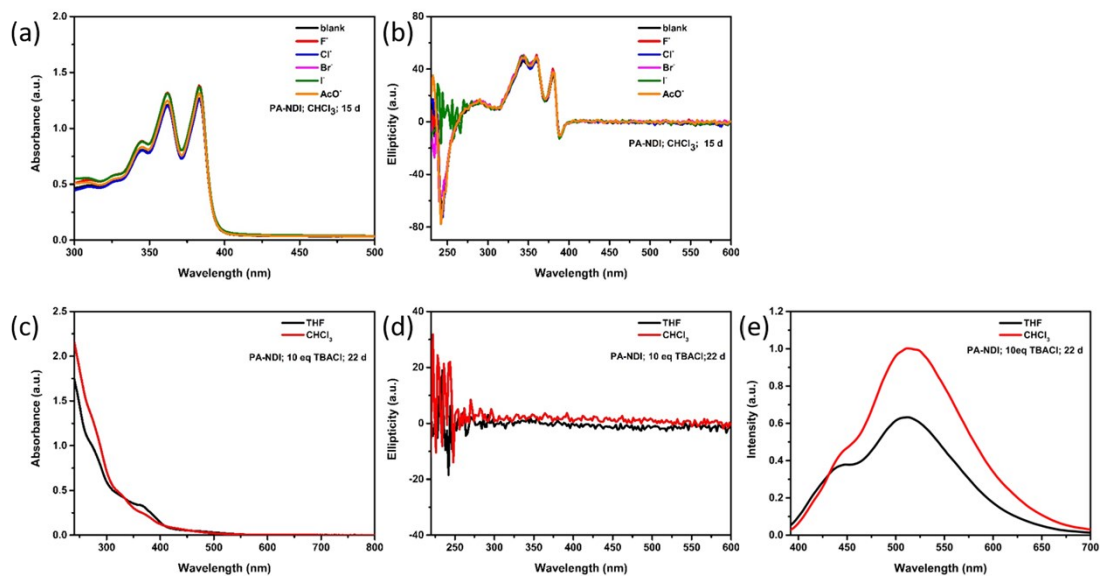


**Figure S14** GPC measurements of THF solution of **PA-NDI** that has been aged for 54 days in the presence of 10 equiv.  $\text{Cl}^-$ . No distinct difference from the original GPC trace excluded obvious cleavage and cross-linking of the polymer

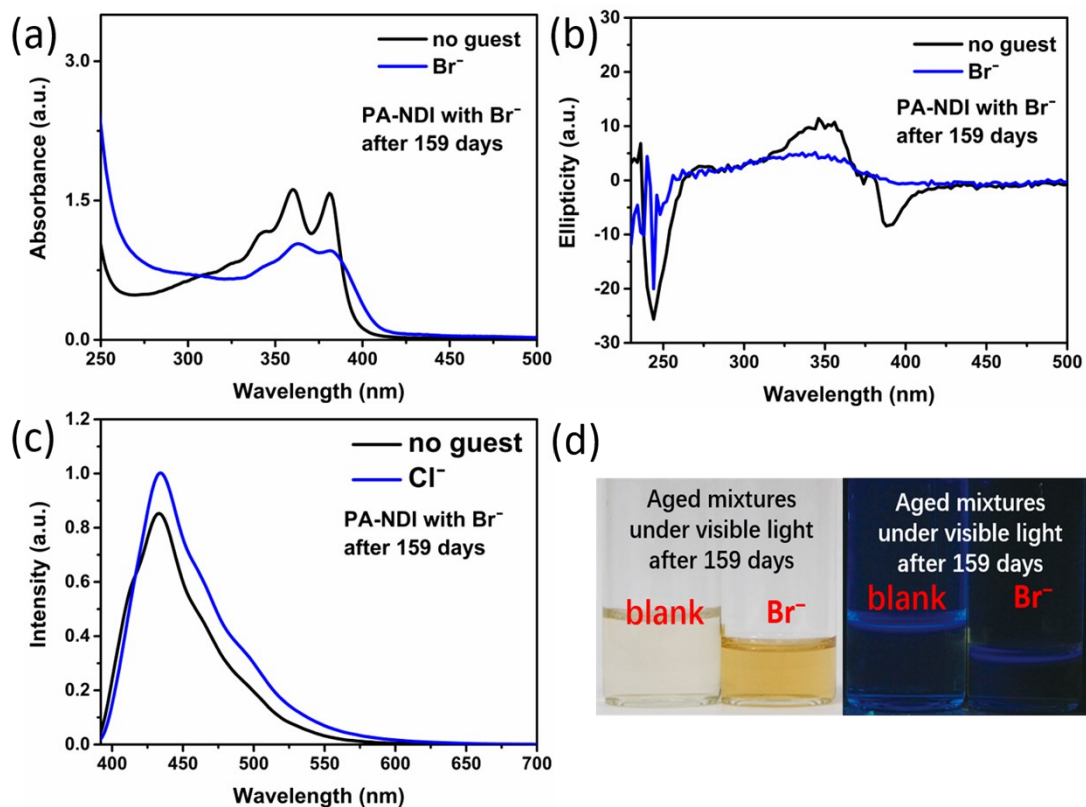
To clarify the addition of anion did not affect the chemical structure of **PA-NDI**, we carried out GPC measurements of an aged (>13 days) solution of the polymer in the presence of  $\text{Cl}^-$ , and no distinct difference from the original GPC trace, showing no obvious cleavage and cross-linking of the polymer.<sup>5</sup>



**Figure S15** (a) UV-vis, (b) CD, (c) emission spectra and (d) the corresponding Sample picture of **PA-NDI** in the presence of TBA salts of different amounts of  $\text{Cl}^-$  in THF on day 13.

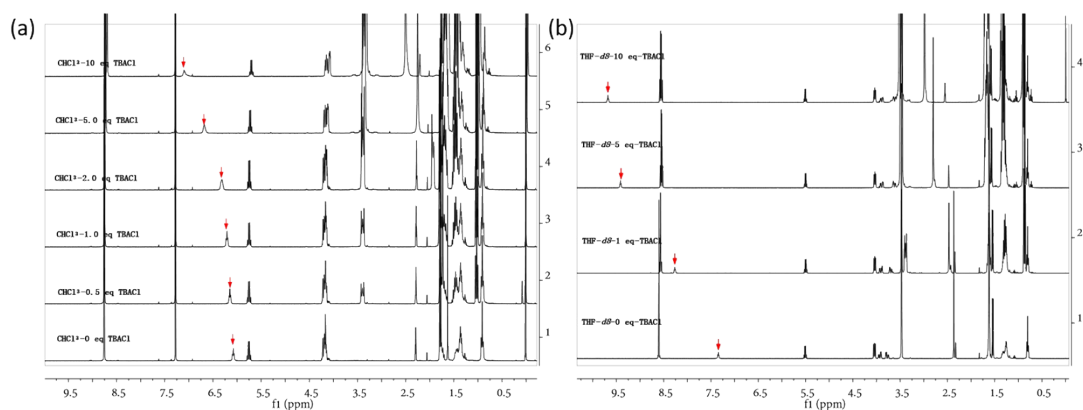


**Figure S16** (a)UV-vis and (b)CD spectra of **PA-NDI** in  $\text{CHCl}_3$  after 15 days after adding a series of anion. (c) UV-vis, (d) CD and (e) emission spectra of **PA-NDI** gathered with  $\text{Cl}^-$  on the 22th day by removing THF solvent and the solid was redissolved in  $\text{CHCl}_3$  and THF.



**Figure S17** (a) UV-vis, (b) CD, (c) emission spectra and (d) the corresponding sample picture of **PA-NDI** in the presence of  $\text{Br}^-$  on the 159th day in THF.

### 3. $^1\text{H}$ NMR titration experiment



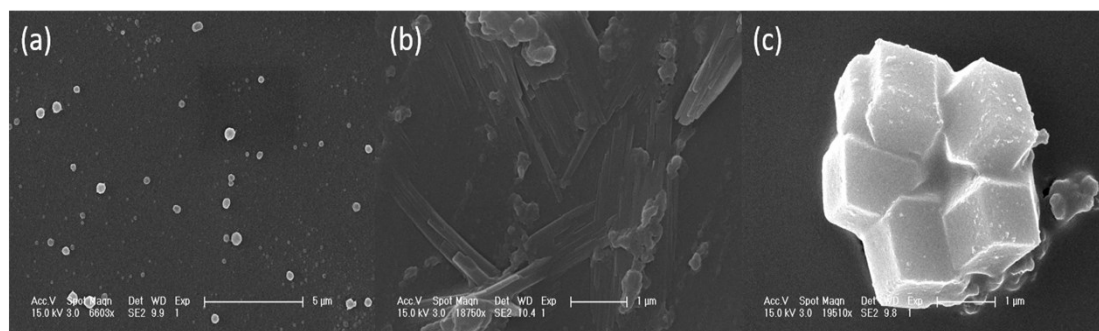
**Figure S18**  $^1\text{H}$  NMR spectra of **A-NDI** in the presence of 0-10 equiv. of TBACl in (a)  $\text{CDCl}_3$  and (b)  $\text{THF-}d_8$ . Red arrows show the signals due to the amide protons.

To further explore the mechanism of interaction between  $\text{Cl}^-$  and **PA-NDI** in THF, we performed a  $^1\text{H}$  NMR titration experiment on **A-NDI** with  $\text{Cl}^-$ , in which **A-NDI** was used as a model compound of **PA-NDI** because the broadened signals in the  $^1\text{H}$  NMR spectra of **PA-NDI** did not provide useful information.<sup>4</sup> A distinct downfield shift of amide proton was observed with the addition of  $\text{Cl}^-$  indicating the formation hydrogen bond interaction between amide group and  $\text{Cl}^-$ .<sup>4, 5</sup>

On the other hand, we found that this interaction was inhibited using  $\text{CHCl}_3$  as the solvent, and there were no

changes in CD and UV-vis spectra even after 15 days after adding  $\text{Cl}^-$  into  $\text{CHCl}_3$  solution of **PA-NDI** (Fig. S15a-b). However,  $^1\text{H}$  NMR titration experiment performed using A-NDI as a model compound of **PA-NDI** showed that hydrogen bond interaction between amide group and  $\text{Cl}^-$  could occur in  $\text{CHCl}_3$ . This might be explained by the difference in the second structures of **PA-NDI** and **A-NDI** and further confirmed our hypothesis that the compactness of the helical conformation of the PA-NDI in  $\text{CHCl}_3$  inhibited the interactions between  $\text{Cl}^-$  and the amides of the polymer.

#### 4. SEM images of PA-NDI



**Figure S19** SEM images of **PA-NDI** prepared by drop-casting a 0.25 mM solution in (a) DMF, (b) 1,4-dioxane and (c) THF on silicon wafers.

Scanning electron microscope (SEM) studies revealed the micromorphology of self-assembled **PA-NDI** regulated by solvents. In DMF, 1,4-dioxane and THF, **PA-NDI** were assembled into very regular structure, such as spherical particles in DMF, cube in THF and nanoribbons in 1,4-dioxane. However, there was no clear morphology in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ .

#### 5. References

1. L. M. Lai, J. W. Y. Lam, A. J. Qin, Y. Q. Dong and B. Z. Tang, *J Phys. Chem. B.*, **2006**, *110*, 11128-11138.
2. S. Wang, X. Feng, Z. Zhao, J. Zhang and X. Wan, *Macromolecules*, **2016**, *49*, 8407-8417.
3. R. Sakai, T. Satoh and T. Kakuchi, *Polym. Rev.*, **2016**, *57*, 159-174.
4. R. Sakai, N. Sakai, T. Satoh, W. Li, A. Zhang and T. Kakuchi, *Macromolecules*, **2011**, *44*, 4249-4257.
5. R. Kakuchi, S. Nagata, Y. Tago, R. Sakai, I. Otsuka, T. Satoh and T. Kakuchi, *Macromolecules*, **2009**, *42*, 1476-1481.