Supplementary Information

$AlEt_3$-Catalyzed Synthesis of Circularly Polarized Luminescence Active Aggregation-Induced Emission Helical Polyisocyandies

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Experimental Procedures

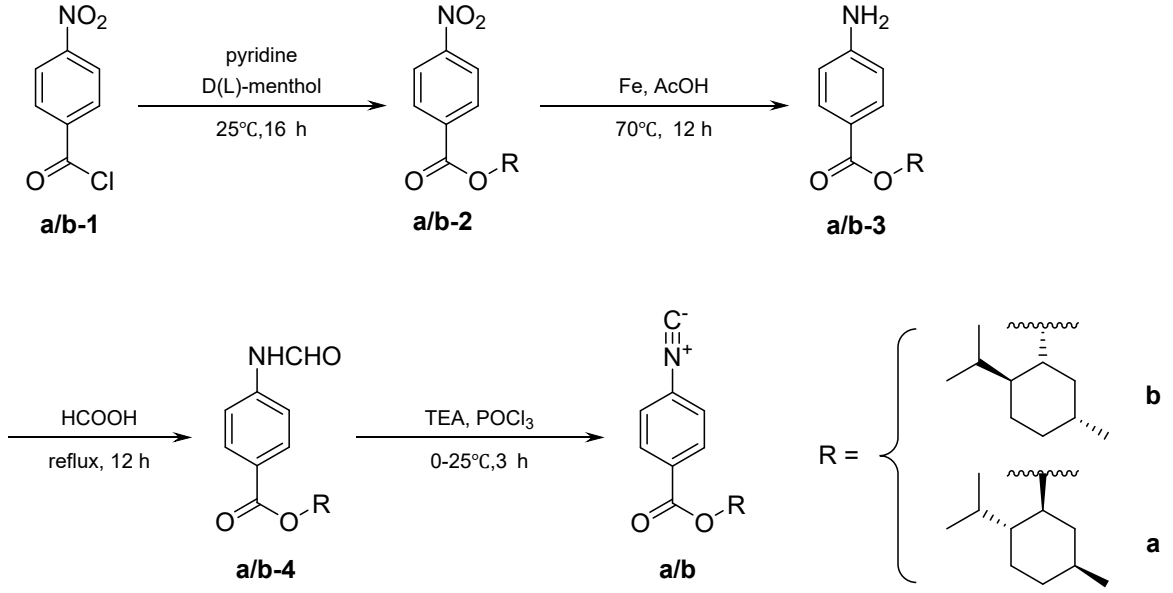
Materials.

All manipulations of air and moisture-sensitive compounds were performed under a dry and oxygen-free nitrogen atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glove box. Nitrogen (Beijing AP Beifen Gases Industrial Co., Ltd.) was purified by passing through a Dryclean column (4A molecular sieves, Dalian Replete Science And Technology Co., Ltd.) and a Gasclean column (Dalian Replete Science And Technology Co., Ltd.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Anhydrous THF, hexane and toluene were were purified by a solvent purification system (SPS-800, Mbraun), and dried over fresh Na chips in the glovebox. $AlEt_3$, $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation and used without purification. The catalyst and the isocyanide monomers were synthesized according to literatures.[1-2] The deuterated solvents benzene-d_6 (99.6 atom% D), chloroform-d_1 (99.8 atom% D) and tetrahydrofuran-d_8 were obtained from Energy Chemical.

General Methods.

^1H NMR spectra were recorded on a Bruker Avance (III-HD 400 MHz) spectrometer. The molecular weights and the molecular weight distributions of the EPI polymers were determined against polystyrene standard at 25 °C by GPC on a Waters HPLC-515 apparatus, $CHCl_3$ was employed as the eluent at a flow rate of 1 mL/min. The molecular weights and the molecular weight distributions of copolymers were determined against polystyrene standard at 25 °C by GPC on a Waters HLC-8320GPC apparatus, THF was used as the eluent at a flow rate of 1 mL/min. FT-IR spectra were recorded on a Thermo IS5 FT-IR system using KBr pellets at room temperature. The UV-Vis spectra were recorded on a TU-1901 double beam UV-vis spectrophotometer, and the fluorescence spectra were recorded on a HITACHI F-7000 fluorescence spectrophotometer. Quartz cells with 10 mm length were used in UV-Vis and fluorescence measurement, and the slit widths were set at 15 (or 10) nm for both excitation and emission during the fluorescence measurement. Circular dichroism spectra were collected on a Jasco J-1500 and the quartz cell length is 1.0 mm. High resolution mass spectra were collected on Bruker Apex IV FTMS. The circularly polarized luminescence (CPL) spectra were performed on JASCO CPL-300 spectrometer at room temperature using a 1.0 cm quartz cuvette. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research). The optical rotations were performed at 25 °C using a 10.0 cm quartz cell on a WZZ-2B polarimeter.

Scheme S1. General protocol for the synthesis of isocyanides (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoat/(*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoat (D/L-IMIT)



Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-nitrobenzoate: Under nitrogen atmosphere, compound **b-1** (1.8 g, 9.7 mmol) was dissolved in dry pyridine (20 mL), then D-menthol (1.5 g, 9.7 mmol) was added in one portion and the resulting mixture was stirred at room temperature for 16 h, after removal of pyridine under reduced pressure, the residue was dissolved in CH_2Cl_2 (30 mL) and washed with 1 N HCl, saturated $NaHCO_3$ aqueous solution and brine, the separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 10 : 1 hexane to ethyl acetate, v/v) to afford the desired compound **b-2** as a yellow solid (2.40 g, 81% yield) ^{1}H NMR (CDCl3, 400 MHz): δ 0.79 (d, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 6.4 Hz, 6H), 0.88-0.98 (m, 1H), 1.08-1.17 (m, 2H), 1.54-1.62 (m, 2H), 1.74 (d, *J* = 12.4 Hz, 2H), 1.88-1.95 (m, 1H), 2.12 (d, *J* = 11.6 Hz, 1H), 4.97 (dt, *J* = 4.4, 11.2 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H).

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-aminobenzoate: Under nitrogen atmosphere, compound **b-2** (2.40 g, 7.86 mmol) was dissolved in 30 mL of acetic acid, then iron powder (4.4 g, 78.6 mmol) was added in one portion, the resulting mixture was stirred at 70 ℃ overnight. Then the mixture was filtered and the filter cake was washed with ethyl acetate (20 mL), the filtrate was concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 4 : 1 hexane to ethyl acetate, v/v) to afford the desired compound **b-3** as yellow oil (1.61 g, 75% yield) ^{1}H NMR (CDCl3, 400 MHz): δ 0.78 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.85-0.96 (m, 1H), 1.02-1.14 (m, 2H), 1.48-1.54 (m, 2H), 1.69-1.72 (m, 2H), 1.94-1.98 (m, 1H), 2.09-2.12 (m, 1H), 4.04 (s, 2H), 4.87 (dt, *J* = 4.4, 10.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.8 Hz,

2H).

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-formamidobenzoate:

Compound **b-3** (1.61 g, 5.85 mmol) was dissolved in a mixture of formic acid (16 mL) and acetic acid (3 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed under reduced pressure, the residue was washed with saturated aqueous Na_2CO_3 (10 mL) and filtered, the filter cake was washed twice with water and dried in vacuum to afford crude compound as a white solid (1.70 g, crude), this compound **b-4** was used directly for the next step without purification.

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoat: Compound **b-4** (1.70 g, crude) and triethylamine (5.2 mL, 37.5 mmol) were dissolved in dry THF (15 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 ℃, $POCl_3$ (0.9 mL, 9.5 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 1 h, then the reaction mixture was slowly poured into 20 mL saturated aqueous Na_2CO_3 and stirred at room temperature for 0.5 h, the mixture was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al_2O_3, 12:1 hexane to ethyl acetate, v/v) to afford the desired compound **b** as a black syrup (1.35 g, 81% yield for two steps) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 (d, *J* = 6.8 Hz, 3H), 0.91 (dd, *J* = 5.6, 6.8 Hz, 6H), 0.86-0.96 (m, 1H), 1.05-1.17 (m, 2H), 1.50-1.59 (m, 2H), 1.70-1.74 (m, 2H), 1.86-1.94 (m, 1H), 2.07-2.12 (m, 1H), 4.93 (dt, *J* = 4.4, 10.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 8.07 (dt, *J* = 2.0, 8.8 Hz, 2H).

The synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate was the same with that of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate.

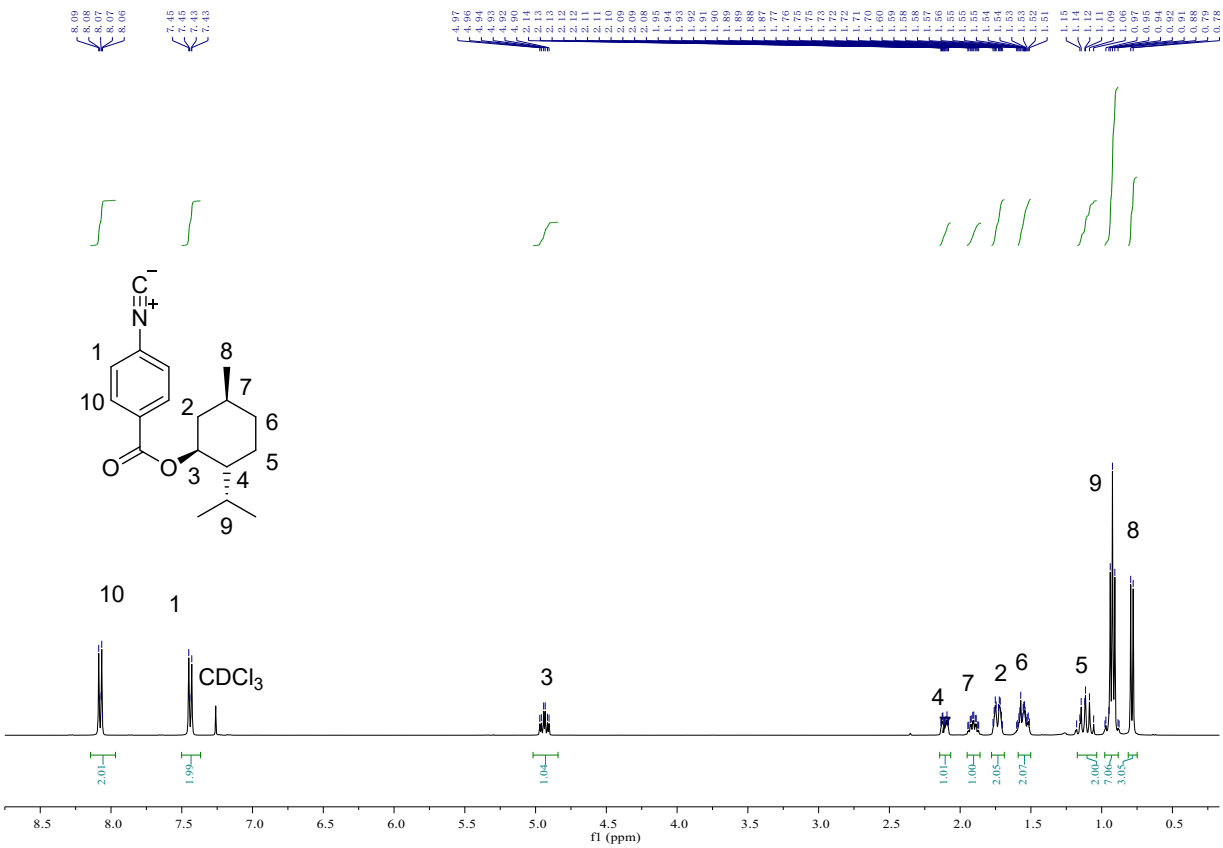


Figure S1. ^{1}H NMR spectrum of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoat (**a**).

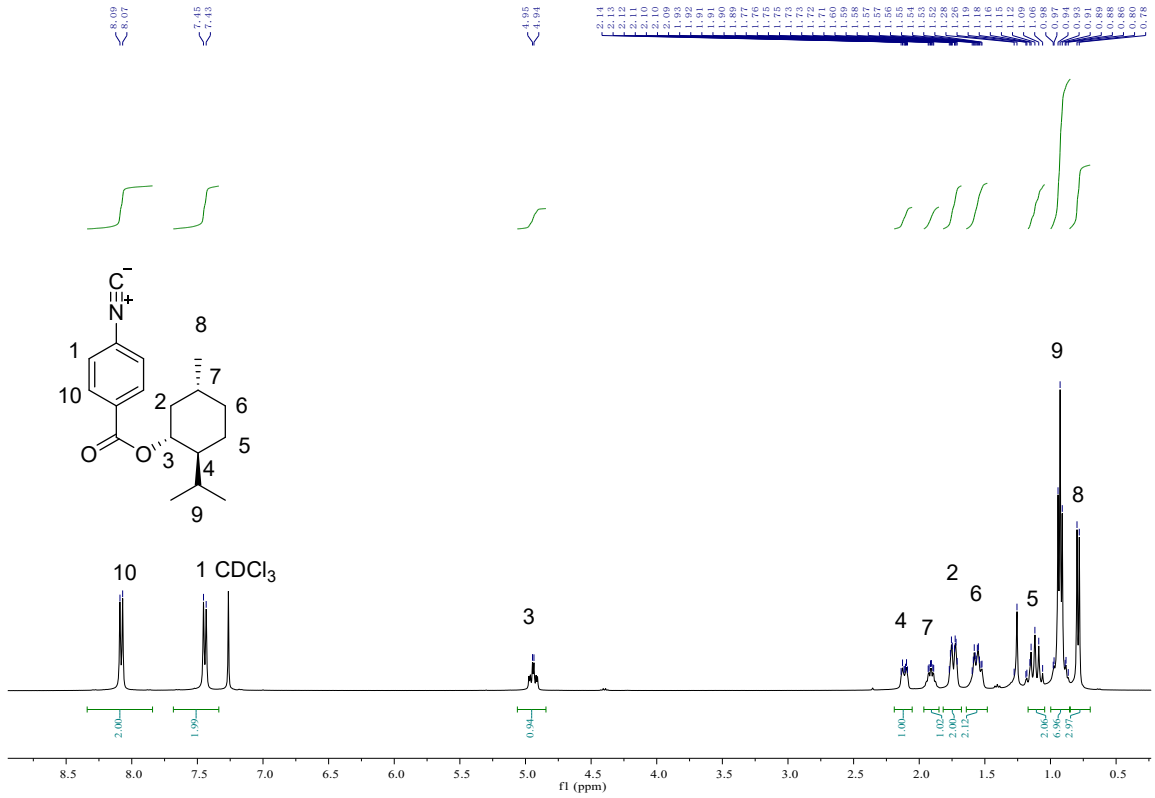


Figure S2. ^{1}H NMR spectrum of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoat (**b**).

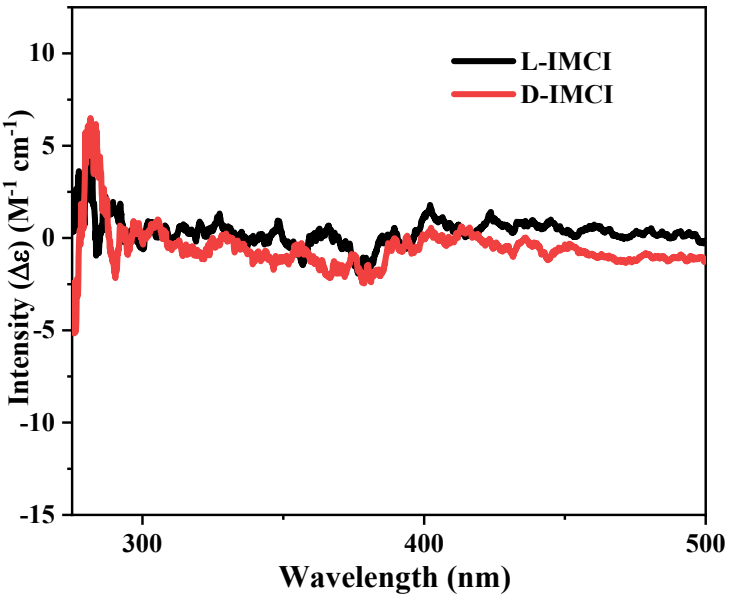
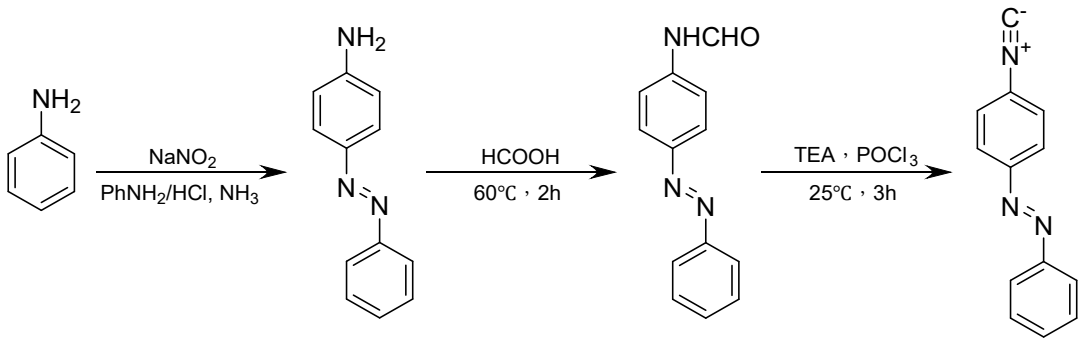


Figure S3. CD spectra of D/L-IMC in THF (c = 0.2 mg mL^{-1}) at 25 °C.

Scheme S2. Synthesis of (*E*)-1-(4-isocyanophenyl)-2-phenyldiazene (IPPD)



c-1 **c-2** **c**

Synthesis of (*E*)-4-(phenyldiazenyl)aniline:

To a solution of 37 % conc. HCl (6.5 mL), aniline (2 g, 21.7 mmol) and an aqueous solution of sodium nitrite (1.51 g, 21.7 mmol) was added dropwise in 0 ℃, and the mixture was stirred for 1 h to an yellow transparent diazonium salt solution. The coupling solution was prepared by using aniline (2 g, 21.7 mmol) and hydrochloric acid (1 N, 22 mL) with vigorous stirring at 0 ℃. The diazonium salt solution was added dropwise to the coupling solution at 0 ℃ and the solution was stirred for 3 h. The final solution was slowly added to ammonia solution (1 N, 30 mL) and an orange crude product was obtained. The crude product was then recrystallized from ethanol, finally dried in vacuum to afford compound **c-1** as an orange solid (2.6 g, 60 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (tt, *J* = 9.7, 2.1 Hz, 4H), 7.52 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 6.82 – 6.69 (m, 2H), 4.03 (s, 2H).

Synthesis of (*E*)-*N*-(4-(phenyldiazenyl)phenyl)formamide:

Compound **c-1** (5.0 g, 30.3 mmol) was dissolved in formic acid (60 mL), the resulting mixture was heated to 60 ℃ overnight. After the reaction mixture was cooled to room temperature, the solvents were removed under reduced pressure. The residue was dissolved in DCM (50 mL) and washed with saturated aqueous Na_2CO_3 (3 × 30 mL). The separated organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure to afford compound **c-2** as a white solid (crude product), this compound was used directly for the next step without purification.

Synthesis of (*E*)-1-(4-isocyanophenyl)-2-phenyldiazene:

Compound **c-2** (6.0 g, 31.1 mmol) and triethylamine (43 mL, 311 mmol) were dissolved in dry DCM (60 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 ℃, $POCl_3$ (5.8 mL, 62.2 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 3 h, then the reaction mixture was slowly poured into 50 mL saturated aqueous Na_2CO_3 and stirred at room temperature for 0.5 h, the mixture was extracted with DCM (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (10:1 hexane to ethyl acetate, v/v) to afford compound **c** (a red solid, 66 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 4H), 7.52 (t, *J* = 8.7 Hz, 5H).

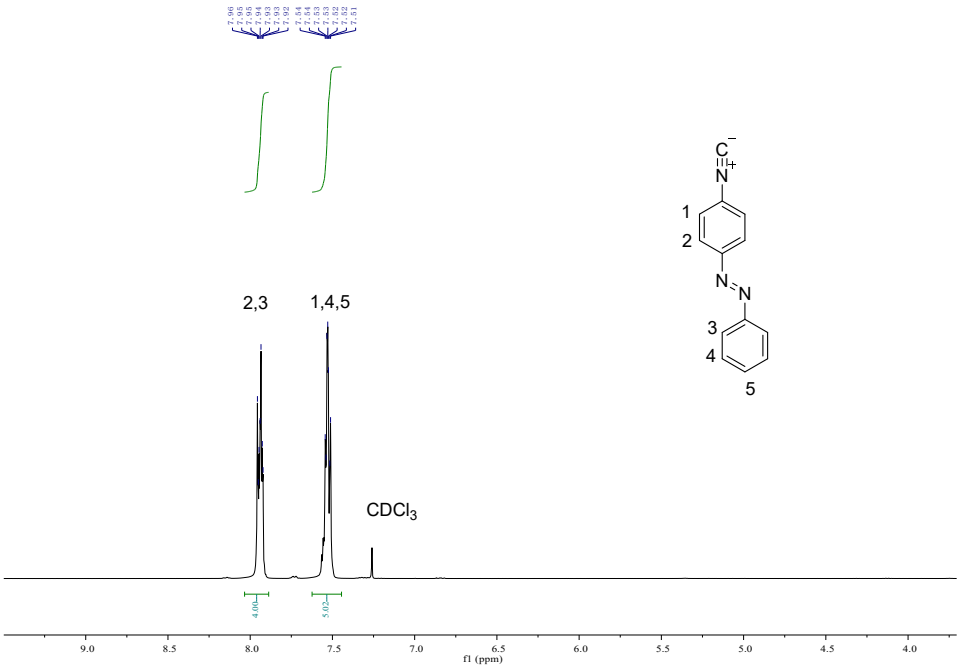


Figure S4. ^{1}H NMR spectrum of (*E*)-1-(4-isocyanophenyl)-2-phenyldiazene (**c**).

A typical procedure for the copolymerization of D-IMCI with IPPD (Table 3, entry 1)

In the glove box, $AlEt_3$ (100 μmol) in chlorobenzene (2 mL) was added to a 25 mL round bottom flask, then $[Ph_3C][B(C_6F_5)_4]$ (10 μmol) was added, the resulting mixture was stirred at 25 ℃ for 20 min. Then added to a solution of D-IMCI (0.9 mmol) and IPPD (0.1 mmol) in chlorobenzene (3 mL) and the reaction mixture was stirred at 25 ℃ for 20 min. The flask with reaction mixture was taken out of the glove box

and poured into methanol (100 mL) to precipitate the copolymer product. The orange polymer solid was collected by filtration and dried in vacuum at 40 ℃ to a constant weight. The product obtained is soluble thoroughly in THF at 25 ℃.

Calculation the activity of catalyst

$A = m_{polymer} / (n_{activator.} \cdot t)$

A: the activity of (co)polymerization (g of polymer/($mol_{activator.} \cdot h$)), $m_{polymer}$: the mass of (co)polymer (g), $n_{act.}$: molar amount of catalyst (mol), t: the reaction time of (co)polymerization (h).

$n_{act.} = m_{activatort} / M_{activator}$

$m_{activator}$: the mass of catalysts (g), $M_{activator}$: the relative molecular weight of catalyst.

Calculation of the IMCI contents of the copolymers

The IMCI contents of the copolymers were calculated from the ^{1}H NMR spectra according to the following formula:

$$\omega(\text{mol\%})\text{IMCI} = (2I_{H2}/18I_{H1} + I_{H2}) \times 100$$

In which I_{H1} is the integration of the peak at 4.13 to 4.99 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen and the proton of the ethyl carbon connected with the oxygen. I_{H2} is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted methyl and the isopropy.

The IMCI contents of poly(D-IMCI-*ran*-IPPD)s and poly(L-IMCI-*ran*-IPPD)s were calculated from the ^{1}H NMR spectra according to the following formula:

$$\omega(\text{mol\%})\text{IMCI} = \{[9(I_{H3}+I_{H4})]/[19(I_{H2}+I_{H1})+5(I_{H3}+I_{H4})]\} \times 100$$

In which I_{H1} is the integration of the peak at 7.08 ppm which assigned to the aryl protons of IPPD units and the β-H of the aryl ring of IMCI units. I_{H2} is the integration of the peak at 5.82 ppm which assigned to the α-H of the aryl ring of IMCI units. I_{H3} is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen. I_{H4} is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted methyl and the isopropyl.

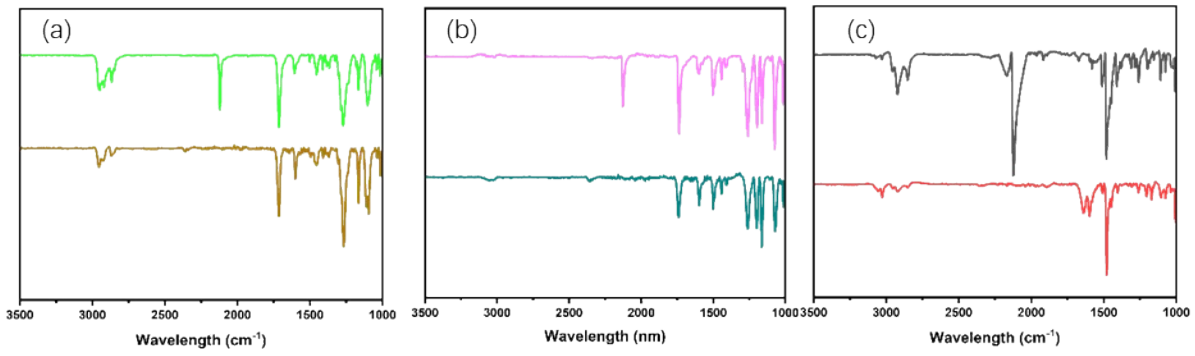


Figure S5. FT-IR spectra of isocyanide monomers and polymers (a) D-IMCI and poly(D-IMCI), (b) L-IMCI and poly(L-IMCI), (c) IPPD and poly(IPPD).

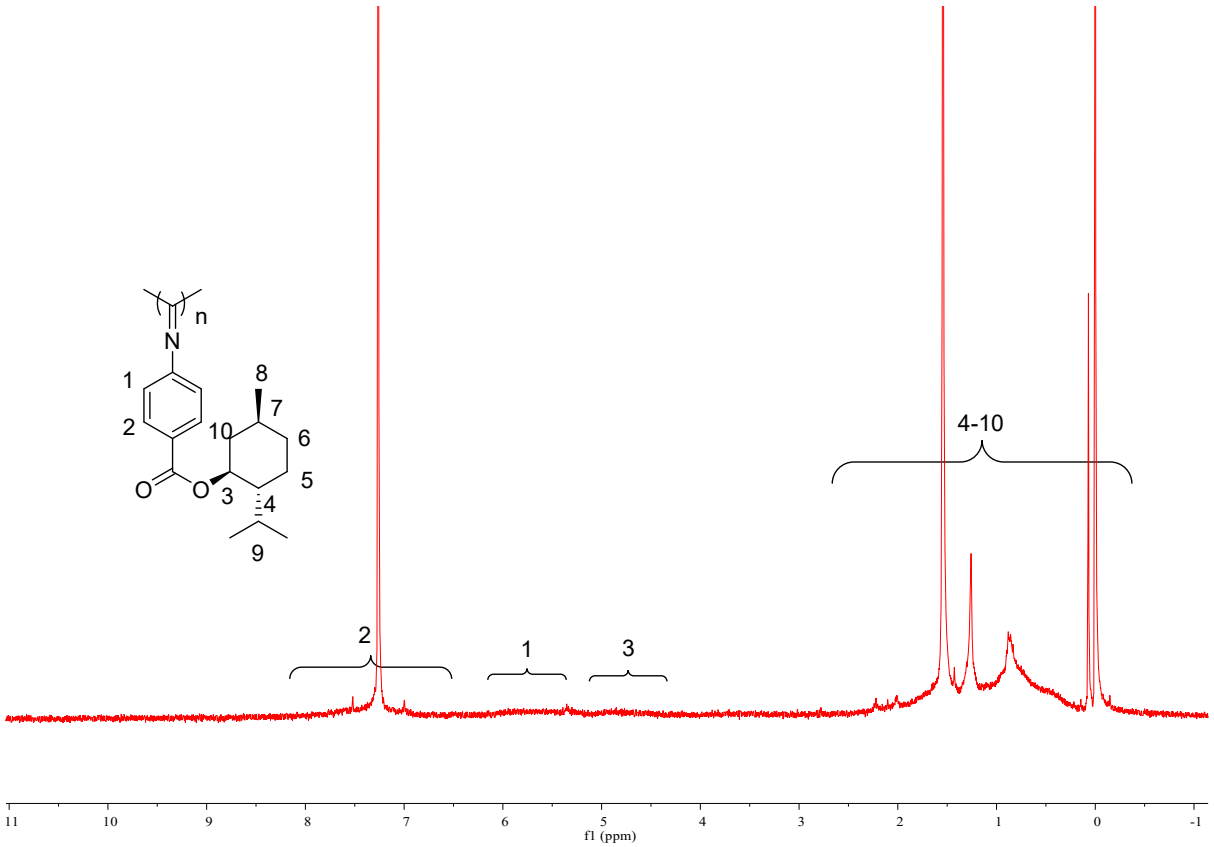


Figure S6. ^{1}H NMR spectrum of poly(D-IMCI) in Table 1, entry 1.

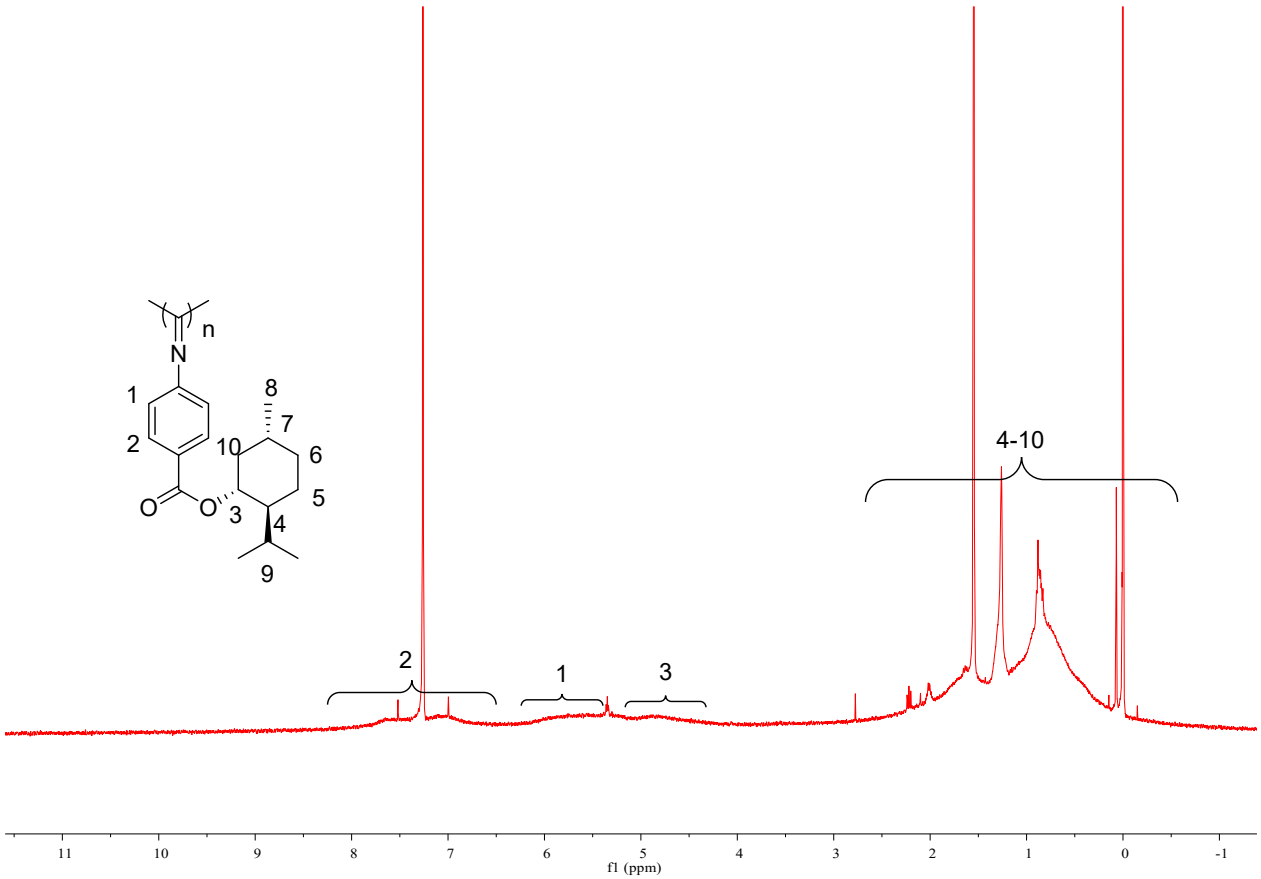


Figure S7. ^{1}H NMR spectrum of poly(L-IMCI) in Table 1, entry 2.

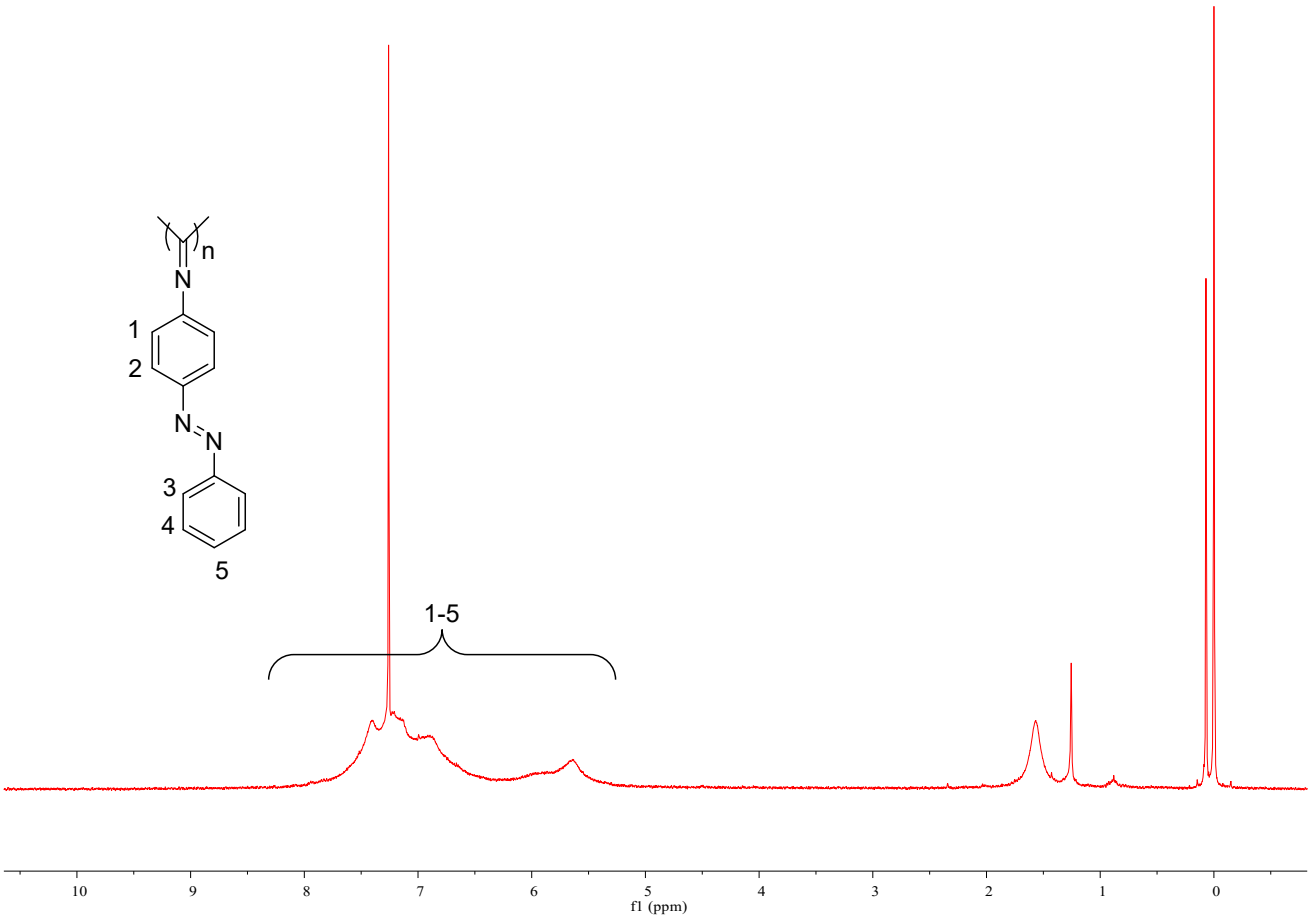


Figure S8. ^{1}H NMR spectrum of poly(IPPD).

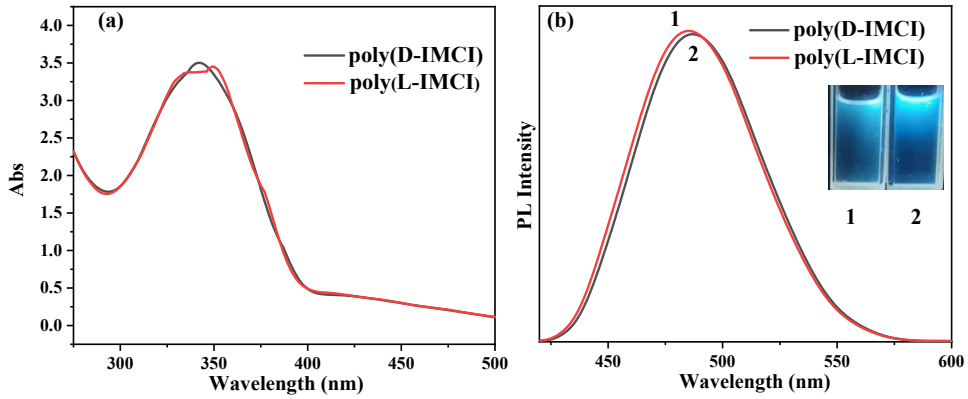


Figure S9. (a) UV-vis spectra of poly(D/L-IMCI)s in THF (c = 0.2 mg mL^{-1}) at 25 ℃. (b) Fluorescence spectra of poly(D/L-IMCI)s in THF (c = 0.2 mg mL^{-1}) at 25 ℃.

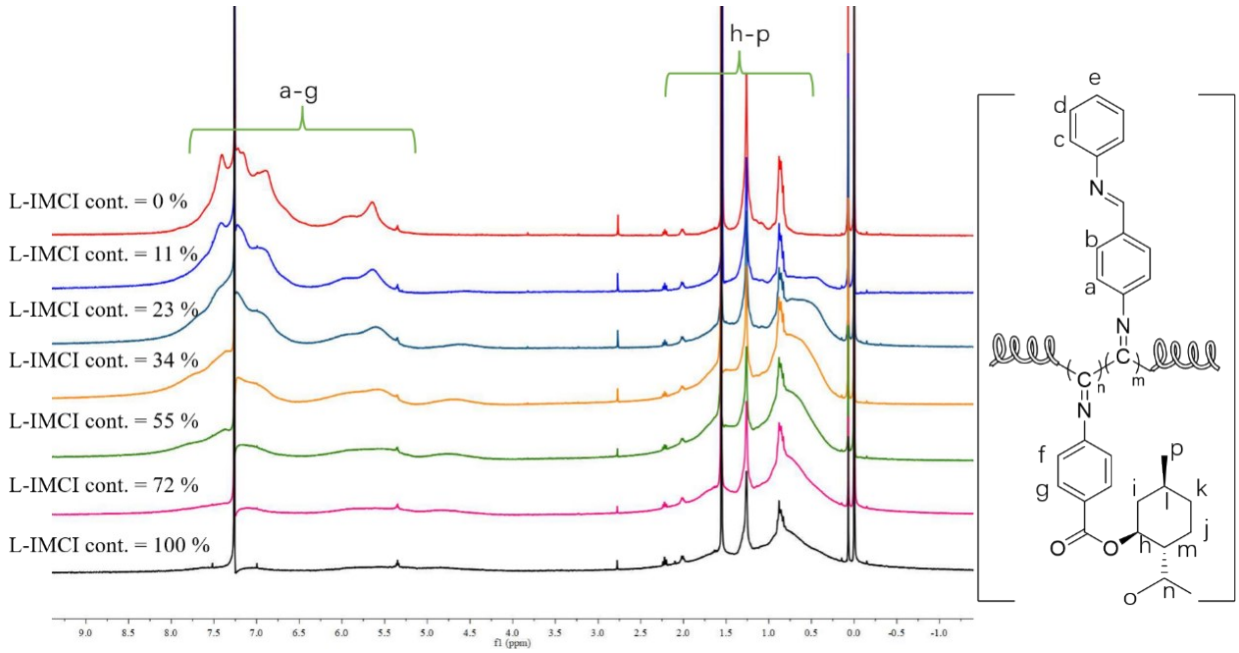


Figure S10. ^{1}H NMR spectra of poly(IPPD), poly(D-IMCI-*ran*-IPPD)s and poly(D-IMCI).

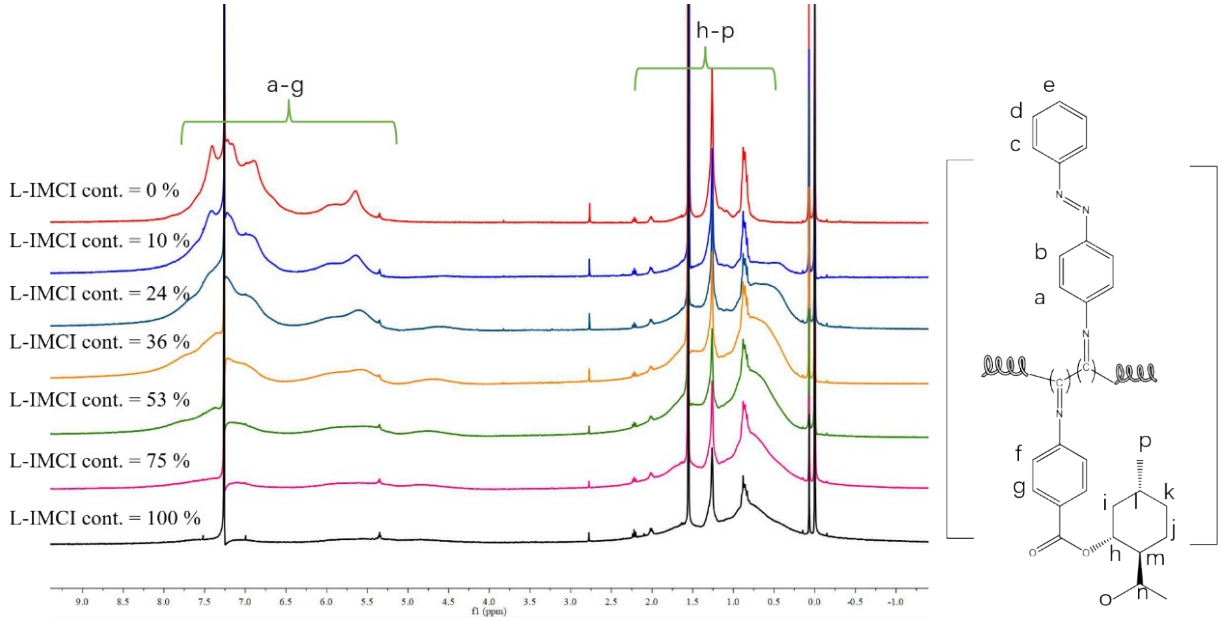


Figure S11. ^{1}H NMR spectra of poly(IPPD), poly(L-IMCI-*ran*-IPPD)s and poly(L-IMCI).

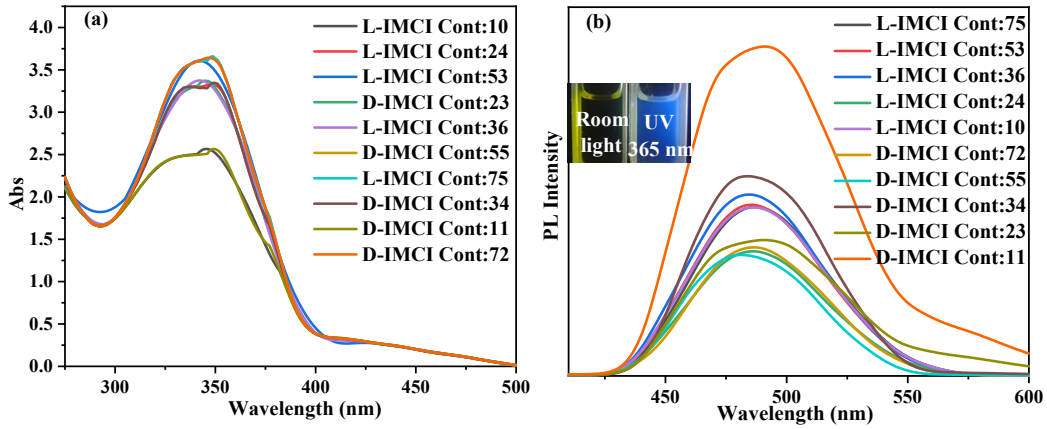


Figure S12. (a) UV-vis spectra of poly(D/L-IMCI-*ran*-IPPD)s in THF (c = 0.2 mg mL^{-1}) at 25 ℃. (b) Fluorescence spectra of poly(D/L-IMCI-*ran*-IPPD)s in THF (c = 0.2 mg mL^{-1}) at 25 ℃.

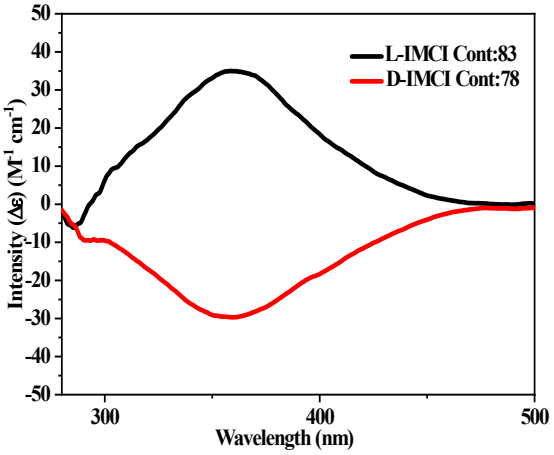


Figure S13. CD spectra of poly(L-IMCI-*ran*-IPPD) with 83 mol% L-IMCI content and poly(D-IMCI-*ran*-IPPD) with 78 mol% D-IMCI content in THF (c = 0.2 mg mL^{-1}) at 25 ℃.

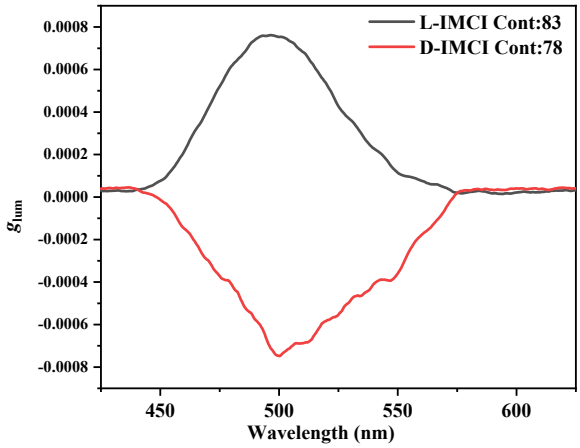
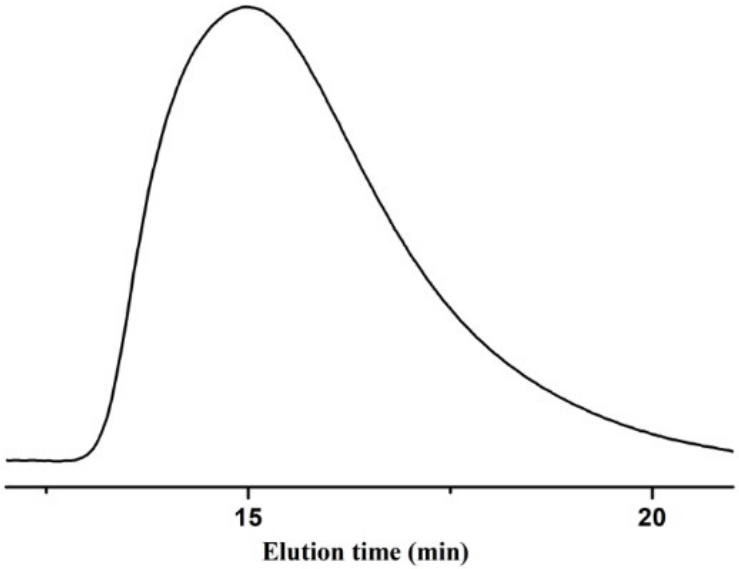


Figure S14. g_{lum} spectra of poly(L-IMCI-*ran*-IPPD) with 83 mol% L-IMCI content and poly(D-IMCI-*ran*-IPPD) with 78 mol% D-IMCI content in THF (c = 0.2 mg mL^{-1}) at 25 ℃.

Table S1 Characterization data for poly(L-IMCI-*ran*-IPPD) with 83 mol% L-IMCI content and poly(D-IMCI-*ran*-IPPD) with 78 mol% D-IMCI content.

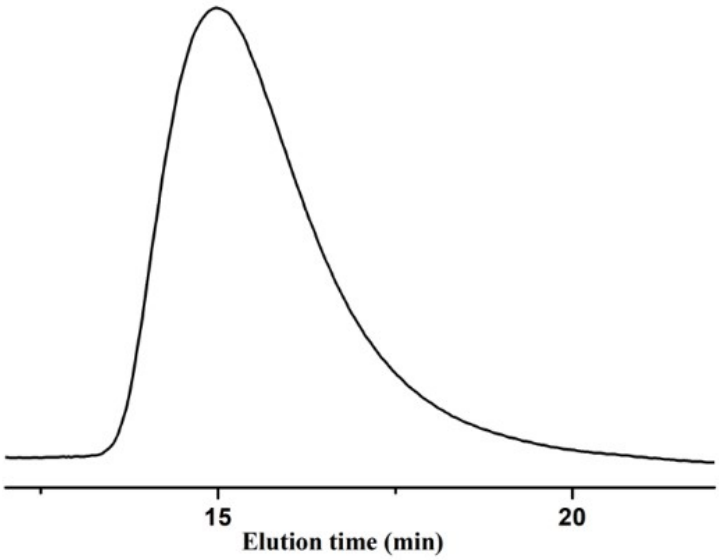
Entry	Mon.	$\Delta\varepsilon_{365}$[a] (M^{-1} cm^{-1})	$[\alpha]_D$[b]	g_{abs}[c] (10^{-4})	Φ_{FL}[d] (%)	g_{lume}[e] (10^{-4})
1	**a**	-33.52	-3533	-10.1	24.9	-7.7
2	**b**	+34.51	+3697	10.3	25.3	7.8

[a]Determined by CD spectroscopy in THF (c = 0.2 mg mL^{-1}, 0.1 cm path length). [b]$[\alpha]_D$ values of the polymers were measured in $CHCl_3$. [c]Determined by the CD and UV-vis spectroscopies. [d]Absolute fluorescence quantum yields were obtained using a calibrated integrating sphere system. [e]Determined by the CPL spectroscopy.



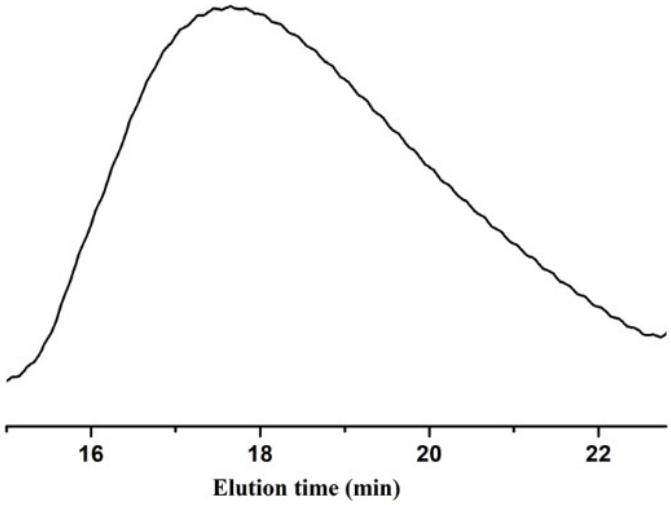
Peak No	M_n (Da)	M_w (Da)	PDI
1	90462	301886	3.337

Figure S15. GPC curve of poly(D-IMCI) in Table 1, entry 1.



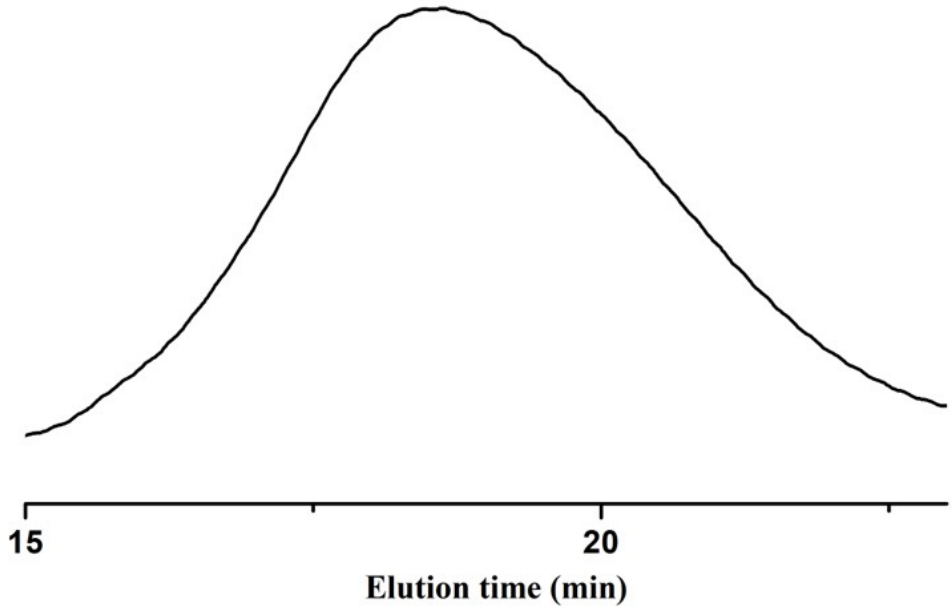
Peak No	M_n (Da)	M_w (Da)	PDI
1	133014	247622	1.862

Figure S16. GPC curve of poly(L-IMCI) in Table 1, entry 2.



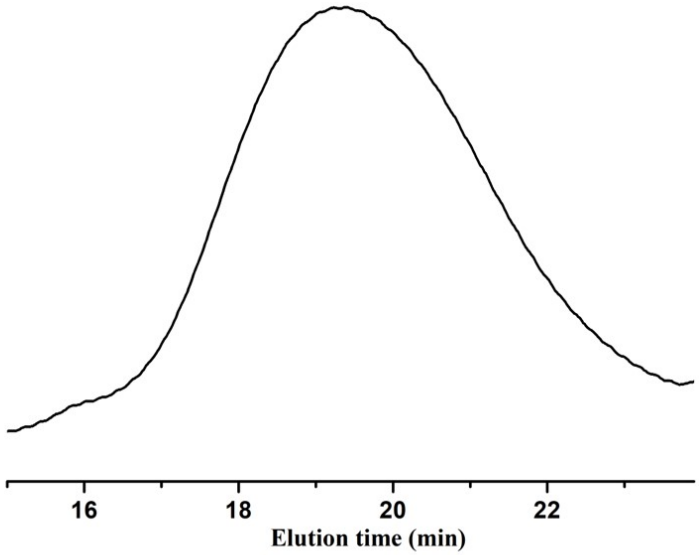
Peak No	M_n (Da)	M_w (Da)	PDI
1	14242	29580	2.077

Figure S17. GPC curve of poly(D-IMCI-*ran*-IPPD) in Table 3, entry 1.



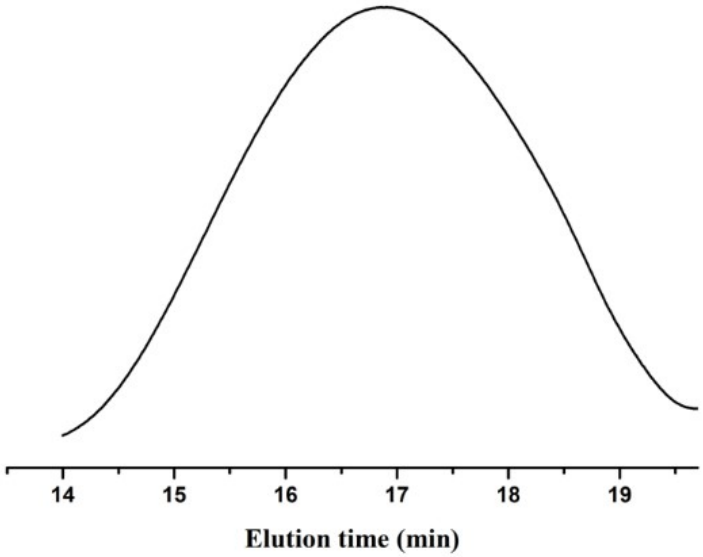
Peak No	M_n (Da)	M_w (Da)	PDI
1	10049	19684	1.959

Figure S18. GPC curve of poly(D-IMCI-*ran*-IPPD) in Table 3, entry 2.



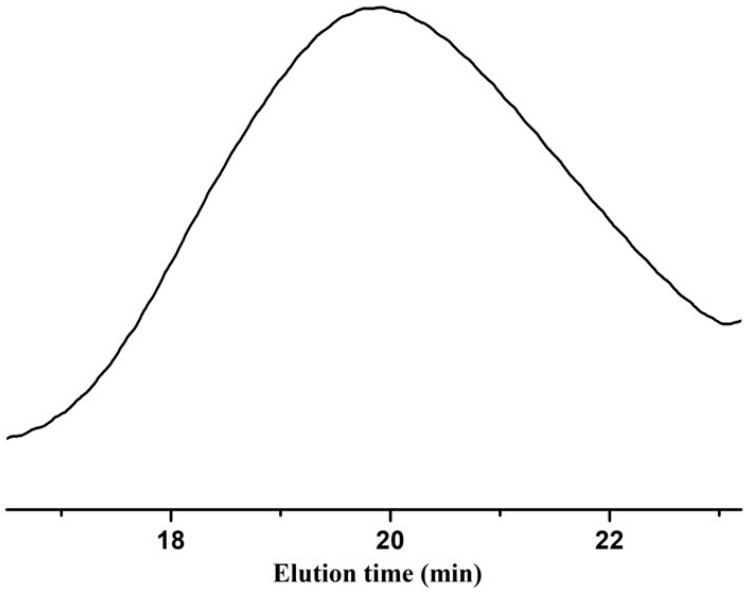
Peak No	M_n (Da)	M_w (Da)	PDI
1	7603	12901	1.691

Figure S19. GPC curve of poly(D-IMCI-*ran*-IPPD) in Table 3, entry 3.



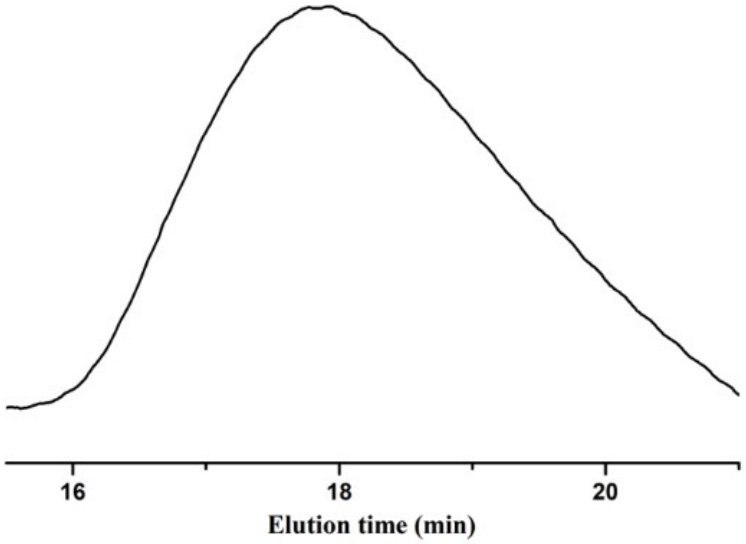
Peak No	M_n (Da)	M_w (Da)	PDI
1	8765	14598	1.665

Figure S20. GPC curve of poly(D-IMCI-*ran*-IPPD) in Table 3, entry 4.



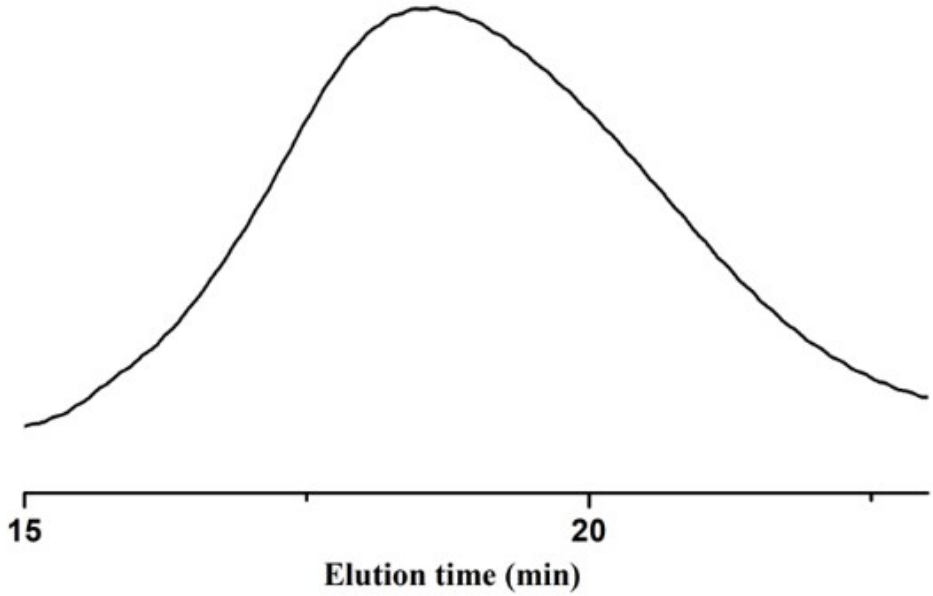
Peak No	M_n (Da)	M_w (Da)	PDI
1	6577	10448	1.589

Figure S21. GPC curve of poly(D-IMCI-*ran*-IPPD) in Table 3, entry 5.



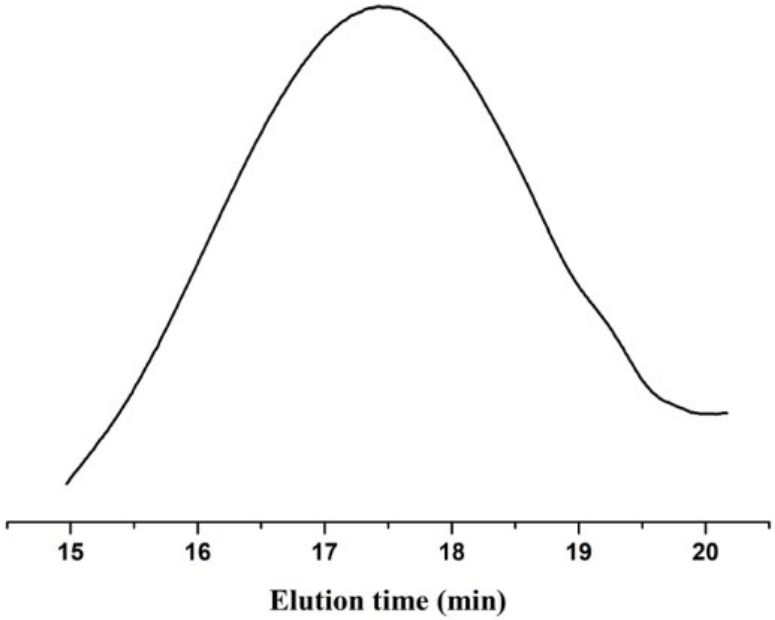
Peak No	M_n (Da)	M_w (Da)	PDI
1	14409	24123	1.674

Figure S22. GPC curve of poly(L-IMCI-*ran*-IPPD) in Table 3, entry 6.



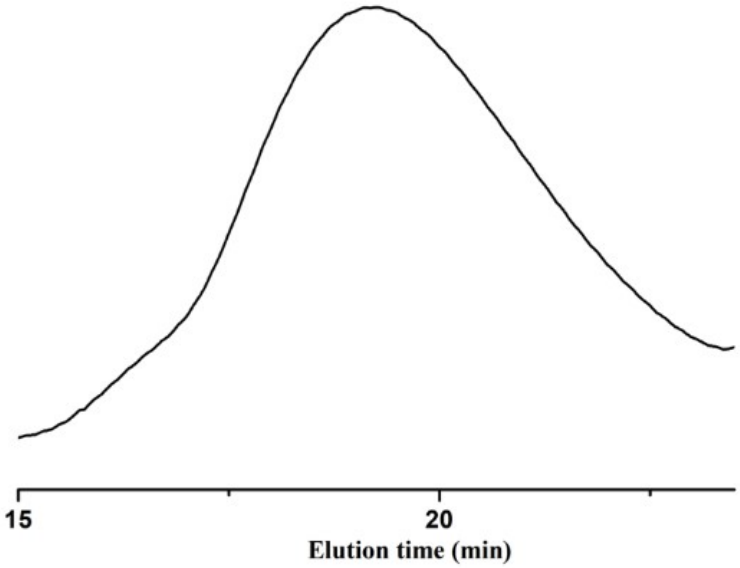
Peak No	M_n (Da)	M_w (Da)	PDI
1	10982	20634	1.879

Figure S23. GPC curve of poly(L-IMCI-*ran*-IPPD) in Table 3, entry 7.



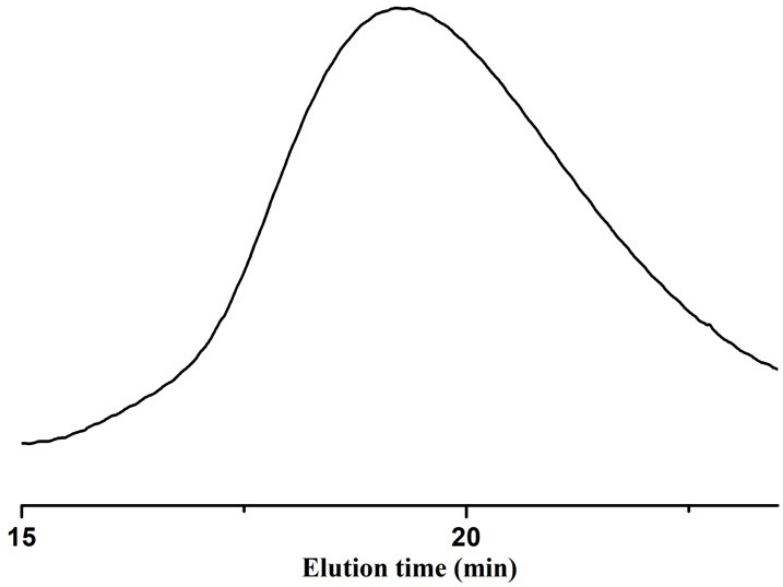
Peak No	M_n (Da)	M_w (Da)	PDI
1	6900	11259	1.632

Figure S24. GPC curve of poly(L-IMCI-*ran*-IPPD) in Table 3, entry 8.



Peak No	M_n (Da)	M_w (Da)	PDI
1	7451	14814	1.988

Figure S25. GPC curve of poly(L-IMCI-*ran*-IPPD) in Table 3, entry 9.



Peak No	M_n (Da)	M_w (Da)	PDI
1	6304	12630	2.003

Figure S26. GPC curve of poly(L-IMCI-*ran*-IPPD) in Table 3, entry 10.

References

(1) Gao, F.; Chen, J.; Cao, Q. Three Different Types of Asymmetric Polymerization of Aryl Isocyanides by Using Simple Rare-Earth Metal Trialkyl Precursors. *Macromolecules* **2022**, *55*(17), 7488-7497.

(2) Wu, X.; Yan, X.; Yang, Z. Al^{i}Bu$_3$: Unprecedented Main-Group Metal Catalyst for Helical Sense-Selective Polymerization of Chiral Aryl Isocyanides and Copolymerization with Achiral Aryl Isocyanides. *Materials Chemistry Frontiers* **2019**, *3*(6), 1192-1198.