Supporting Information

Room-temperature AIE ionic liquid crystals based on diphenylacrylonitrile-imidazole salts

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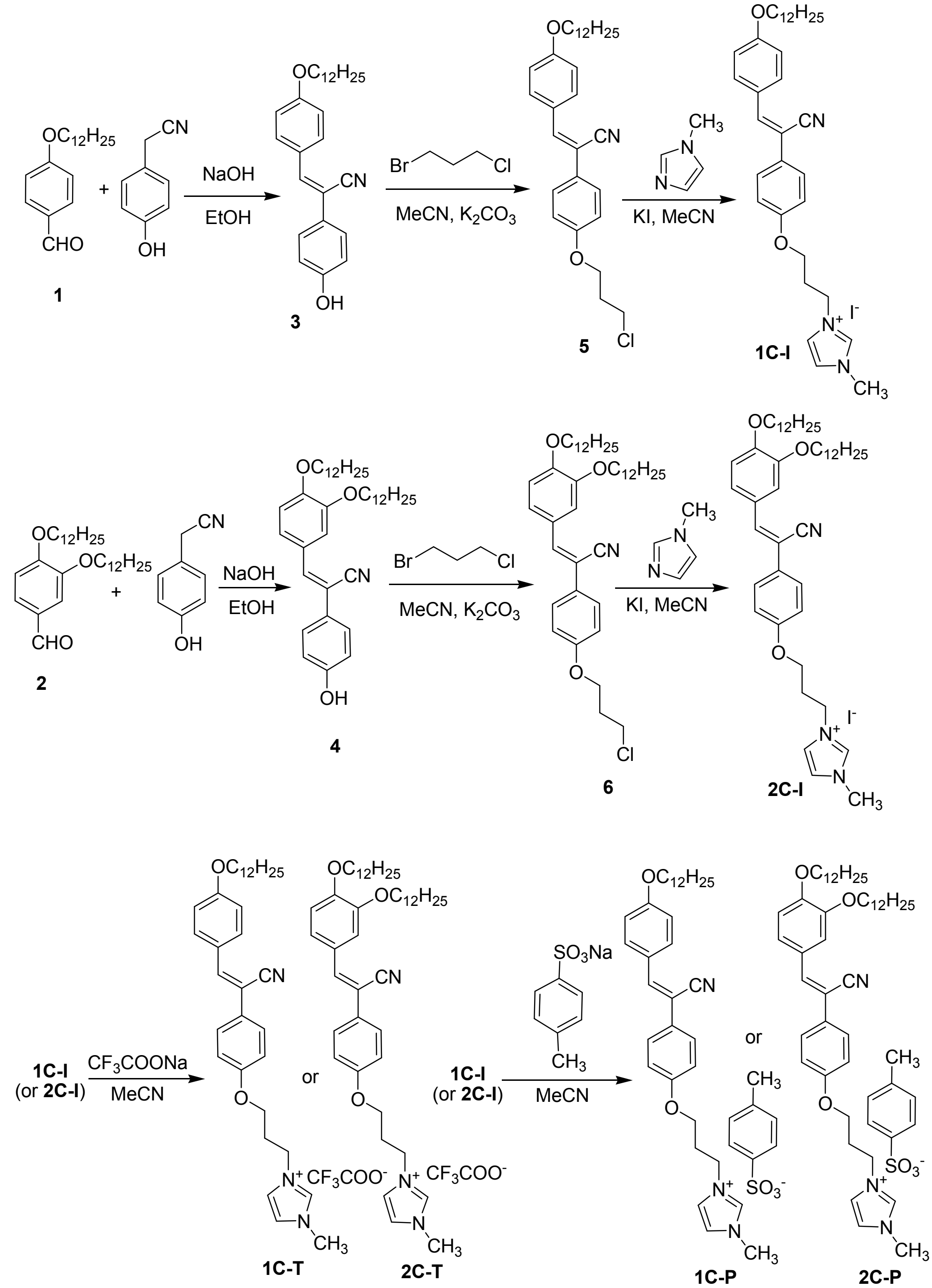
1. General

All chemical reagents including organic and inorganic compounds were obtained byAladdin Reagent Co., Ltd. and used directly. Pre-coated glass plates were used for TLC detection. Columnchromatography was performed on using silica gel (200-300 mesh). Bruker-ARX 400 instrument was used for measuring the NMR spectra with tetramethylsilane (TMS) as internal standard. Bruker mass spectrometer was applied for MS spectral analysis. UV-Vis spectra were recorded on Varian UV-Vis spectrometer. Edinburgh Instruments FS5 spectrometer was used for examining fluorescence spectra. The fluorescence absolute Φ_F values were investigated on an Edinburgh Instruments FLS920 Fluorescence Spectrometer bearing a 6-inch integrating sphere. Compounds 3 and 4 were prepared according to the published procedure (The influence of multiple alkyl chains on mesomorphic and photophysical properties of diphenylacrylonitrile liquid crystals, Liangbin Lin; Wenwei Qin; Bifeng Cheng; Hongyu Guo; Fafu Yang, Liquid Crystals, 2020,10.1080/02678292.2019.1692931).



Scheme S1 The synthetic routes for title compounds

2. The synthetic process and characteristic spectra.

2.1 Synthesis of compounds 5 and 6

A mixture of compound 3 or 4 (2.0 mmol), bromochloropropane (0.37 g, 2.0 mmol) and K_2CO_3 (1.4 g, 10 mmol) in 45 mL of dry MeCN was refluxed at 83 ^oC for 12 h. The reaction was monitored by TLC analysis. After reaction, 40 mL of HCl solution (1M) and 45 mL of CH_2Cl_2 were poured in the reaction system. Then the organic layer was separated and concentrated under reduced pressure. The residue was further purified by column chromatography with CH_2Cl_2/hexane (3:7, *V*/*V*) as eluent. Compounds 5 and 6 were obtained as yellow solid in yields of 70% and 68%, respectively.

Compound **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84(d, *J* = 8.0 Hz, 2H, ArH), 7.57(d, *J* = 8.0 Hz, 2H, ArH), 7.35(s, 1H, CH=C), 6.95(d, *J* = 8.0 Hz, 4H, ArH), 4.14(t, *J* = 6.0 Hz, 2H, $ClCH_2$), 4.01 (t, *J* = 6.0 Hz, 2H, OCH_2), 3.76(t, *J* = 6.0 Hz, 2H, OCH_2),2.24 (m, 2H, OCH_2CH_2), 1.78-1.82(t, 2H, OCH_2CH_2), 1.27-1.46(m, 18H, CH_2), 0.86(t, *J* = 6.0 Hz, 3H, CH_3).

Compound **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62(s, 1H, ArH), 7.57 (d, *J* = 8.0 Hz, 2H, ArH), 7.32(bs, 2H, ArH and CH=C), 6.95 (d, *J* = 8.0 Hz, 2H, ArH), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 4.16(t, *J* = 6.0 Hz, 2H, $ClCH_2$), 4.04-4.10(m, 4H, OCH_2), 3.76(t, *J* = 6.0 Hz, 2H, OCH_2), 0.86-2.29 (m, 48H, CH_2 and CH_3).

2.2 Synthesis of compounds 1C-I and 2C-I

The mixture of compound **5** or **6** (0.5 mmol), 1-methylimidazole (0.04 g, 0.5 mmol) and KI (0.17 g, 1 mmol) was refluxed in dry MeCN at 83 ^oC for 4 h. The reaction was monitored by TLC analysis. After reaction, the solvent was distilled under reduced pressure. The residue was pu**rified** by column chromatography with CH_2Cl_2/MeOH (9:1, *V*/*V*) as eluent. Compounds **1C-I** and **2C-I** were obtained as yellow viscous substance in yields of 65% and 63%, respectively.

Compound **1C-I**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.88 (s, 1H, ArH), 7.80 (d, *J* = 8.0 Hz, 2H, ArH), 7.51 (d, *J* = 8.0 Hz, 2H, ArH), 7.47 (s, 1H, ArH), 7.43(s, 1H, ArH), 7.32(s, 1H, CH=C) , 6.91(d, *J* = 8.0 Hz, 4H, ArH), 4.59(t, *J* = 6.0 Hz, 2H, NCH_2), 4.09(t, *J* = 6.0 Hz, 2H, OCH_2), 4.04 (s, 3H, NCH_3) 3.96(t, *J* = 6.0 Hz, 2H, OCH_2), 1.47-2.48(m, 22H, CH_2), 0.86 (t, *J* = 6.0 Hz,3H,CH_3).^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.78, 158.59, 140.29, 137.07, 130.85, 127.64, 127.02, 126.28, 123.67, 122.58, 118.76, 114.99, 114.74, 107.32, 68.19, 64.59, 47.19, 36.91, 31.78, 29.81, 29.63, 29.43, 29.01, 26.00, 22.67, 14.11. MALDI-TOF-MS ($C_{34}H_{46}N_3O_2$) Calcd. For *m*/*z* = 528.359, found: 528.502. Anal. Calcd for $C_{34}H_{46}N_3O_2I$: C, 62.28; H, 7.07; N, 6.41. Found: C, 62.24; H, 7.01; N, 6.35.

Compound **2C-I**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.06(s, 1H, ArH), 7.60(s, 1H,ArH), 7.55(d, *J* = 8.0 Hz, 2H, ArH), 7.32-7.38(m, 4H,ArH and CH=C), 6.93 (d, *J*= 8.0 Hz, 2H, ArH), 6.89(d, *J* = 8.0 Hz, 1H, ArH), 4.61(t, *J* = 6.0 Hz, 2H,NCH_2), 4.06-4.14(m, 9H, OCH_2 and

CH_3), 0.86-2.52(m, 48H, CH_2 and CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.52, 151.22, 148.91, 140.74, 137.08, 127.94, 127.16, 126.67, 123.99, 123.50, 122.48, 118.91, 115.02, 112.87, 107.48, 69.32, 69.10, 64.38, 47.39, 37.24, 31.91, 29.64,29.36, 29.22, 29.00, 26.07, 26.00, 22.68, 14.10. *MALDI-TOF-MS ($C_{46}H_{70}N_3O_3$) Calcd. for m/z = 712.542.* Found: 712.572. Anal. Calcd for $C_{46}H_{70}N_3O_3I$: C, 65.78; H, 8.40; N, 5.00. Found: C, 65.72; H, 8.44; N, 4.96.

2.3 Synthesis of compounds 1C-T, 2C-T, 1C-P and 2C-P

The mixture of compound **1C-I** or **2C-I** (0.5 mmol) and sodium trifluoroacetate or sodium p-toluenesulfonate (2.5 mmol) was stirred in MeOH/CH_2Cl_2 (2:8) at 65°C for 4h. After reaction, the solvent was evaporated under reduced pressure. The obtained yellow sticky product was washed by distilled water and then was dried under vacuum to afford sticky compounds **1C-T, 2C-T, 1C-P and 2C-P** in yields of 75%, 78%, 80% and 76%, respectively.

Compound **1C-T**: ^1H NMR (400 MHz, $CDCl_3$) δ: 9.64 (s, 1H, ArH), 7.76 (d, J = 8.0 Hz, 2H, ArH), 7.45 (d, J = 8.0 Hz, 2H, ArH), 7.38-7.44 (m, 3H, ArH), 6.87(d, J= 8.0 Hz, 2H, ArH), 6.83(d, J = 8.0 Hz, 2H, ArH), 4.41(bs, 2H, NCH_2), 3.86-3.96(m, 7H, OCH_2 and NCH_3), 1.25-2.33(m, 22H, CH_2), 0.84 (t, J = 6.0 Hz,3H,CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.82, 158.63, 140.31, 137.62, 131.55, 130.93, 130.18, 127.72, 126.99, 126.30, 123.53, 122.48, 118.74, 114.83, 114.47, 107.44, 68.19, 64.27, 47.00, 36.12, 31.90, 31.58, 29.58, 29.34, 29.16, 25.99, 22.59, 13.92. MALDI-TOF-MS($C_{34}H_{46}N_3O_2$) Calcd. For m/z = 528.359, Found: 528.583. Anal. Calcd for $C_{36}H_{46}N_3O_4F_3$: C, 67.37; H, 7.22; N, 6.55. Found: C, 67.32; H, 7.25; N, 6.50.

Compound **2C-T**: ^1H NMR (400 MHz, $CDCl_3$) δ**:** 9.79 (s, 1H, ArH), 7.32-7.61(**m**, 7H, ArH)**,** 6.90(m, 3H, ArH)**,** 4.53(bs, 2H, NCH_2)**,** 3.99-4.06(m, 9H , OCH_2 and NCH_3**)**, 2.42(bs, 2H, CH_2)**,** 1.84(bs, 4H, CH_2)**,** 1.27(bs, 36H, CH_2)**,** 0.89(bs, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.57, 151.19, 149.05, 140.78, 137.67, 130.48, 127.92, 127.10, 126.65, 126.07, 123.93, 123.47, 122.46, 118.83, 114.90, 113.24, 112.82, 107.45, 69.28, 69.06, 64.29, 47.18, 36.56, 31.91, 29.64, 29.36, 29.10, 25.93, 22.67, 14.10. MALDI-TOF-MS ($C_{46}H_{70}N_3O_3$) Calcd. for m/z = 712.542. Found: 712.376. Anal. Calcd for $C_{48}H_{70}N_3O_5F_3$: C, 69.79; H, 8.54; N, 5.09. Found: C, 69.73; H, 8.58; N, 5.02.

Compound **1C-P**: ^1H NMR (400 MHz, $CDCl_3$) δ**:** 9.73 (s, 1H, ArH), 7.78 (d**,** J = 8.0 Hz, 2H, ArH), 7.44-7.49 (m**,** 4H, ArH), 7.31(s, 1H, C***H***=C), 7.22 (d**,** *J*= 8.0 Hz, 2H, ArH), 7.07(d**,** *J* = 8.0 Hz, 2H, ArH), 6.87-6.90 (m**,** 4H, ArH), 4.53**(**t**,** *J* = 8.0 Hz, 2H,NCH$_2$), 4.04(t**,** *J* = 8.0 Hz, 2H, OCH$_2$), 3.99(s, 3H, NCH$_3$) 3.94(t, *J* = 8.0 Hz, 2H, OCH$_2$), 2.23-2.48(m, 5H, CH$_2$ and CH$_3$**)**, 1.21-1.78(m, 20H, CH$_2$), 0.84(t, 3H, CH$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ: 160.84, 158.56, 143.31, 140.61, 137.05, 131.58, 130.98, 130.26, 127.90, 127.12, 126.42, 125.77, 123.58, 122.71, 118.83, 115.11, 114.81, 107.49, 68.33, 64.42, 53.37, 47.49, 37.11, 32.07, 29.60, 29.34, 25.97, 22.67, 14.20. MALDI-TOF-MS ($C_{34}H_{46}N_3O_2$) Calcd. For *m*/*z* = 528.359, found: *528.257.* Anal. Calcd for $C_{41}H_{53}N_3O_5S$: C, 70.35; H, 7.63; N, 6.00. Found: C, 70.32; H, 7.68; N, 5.94.

Compound **2C-P**: ^{1}H NMR (400 MHz, CDCl$_3$) δ**:** 9.40(**s, 1H, ArH***)*, 7.74 (bs**, 2H, ArH),** 7.61(**s, 1H, ArH),** 7.47(bs**, 2H, ArH)**, 7.29 (bs, 4H, **C***H***=C and ArH**), 7.12(bs**, 2H, ArH),** 6.83(bs**, 3H, ArH),** 4.38**(bs, 2H, NCH$_2$),** 3.84-4.12**(m, 9H, OCH$_2$ and** NCH$_3$), 2.28**(bs, 5H, CH$_2$** and CH$_3$), 1.84**(bs, 4H, CH$_2$)**, 1.28**(bs, 36H, CH$_2$)**, 0.89**(t, 6H, CH$_3$).** ^{13}C NMR (101 MHz, CDCl$_3$) δ: 158.66, 151.15, 148.96, 143.24, 140.66, 139.75, 137.54, 128.83, 127.77, 127.05, 126.69, 125.81, 123.97, 123.47, 122.33, 118.83, 114.94, 112.93, 112.77, 107.52, 69.26, 68.96, 64.43, 53.47, 47.01, 36.40, 31.94, 29.67, 29.46, 29.39, 29.17, 26.10, 22.70, 21.27, 14.13. MALDI-TOF-MS ($C_{46}H_{70}N_3O_3$) Calcd. for m/z = 712.542. Found: 712.430. Anal. Calcd for $C_{53}H_{77}N_3O_6S$: C, 71.99; H, 8.78; N, 4.75. Found: C, 71.94; H, 8.76; N, 4.70.

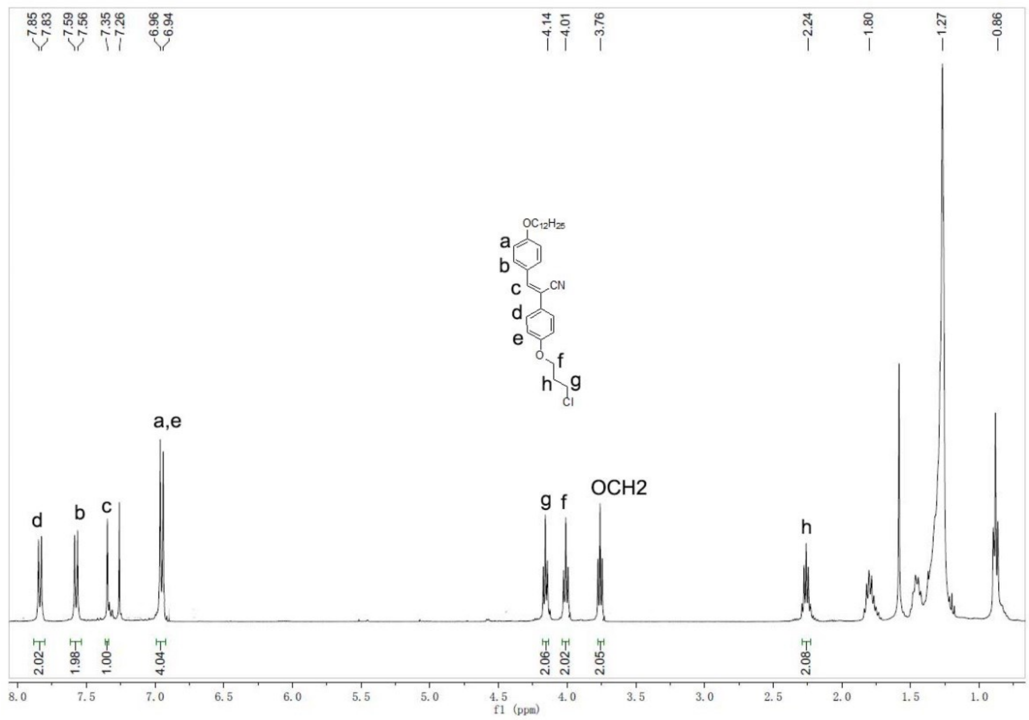


Figure S1. The ^{1}H NMR spectrum of compound **5**

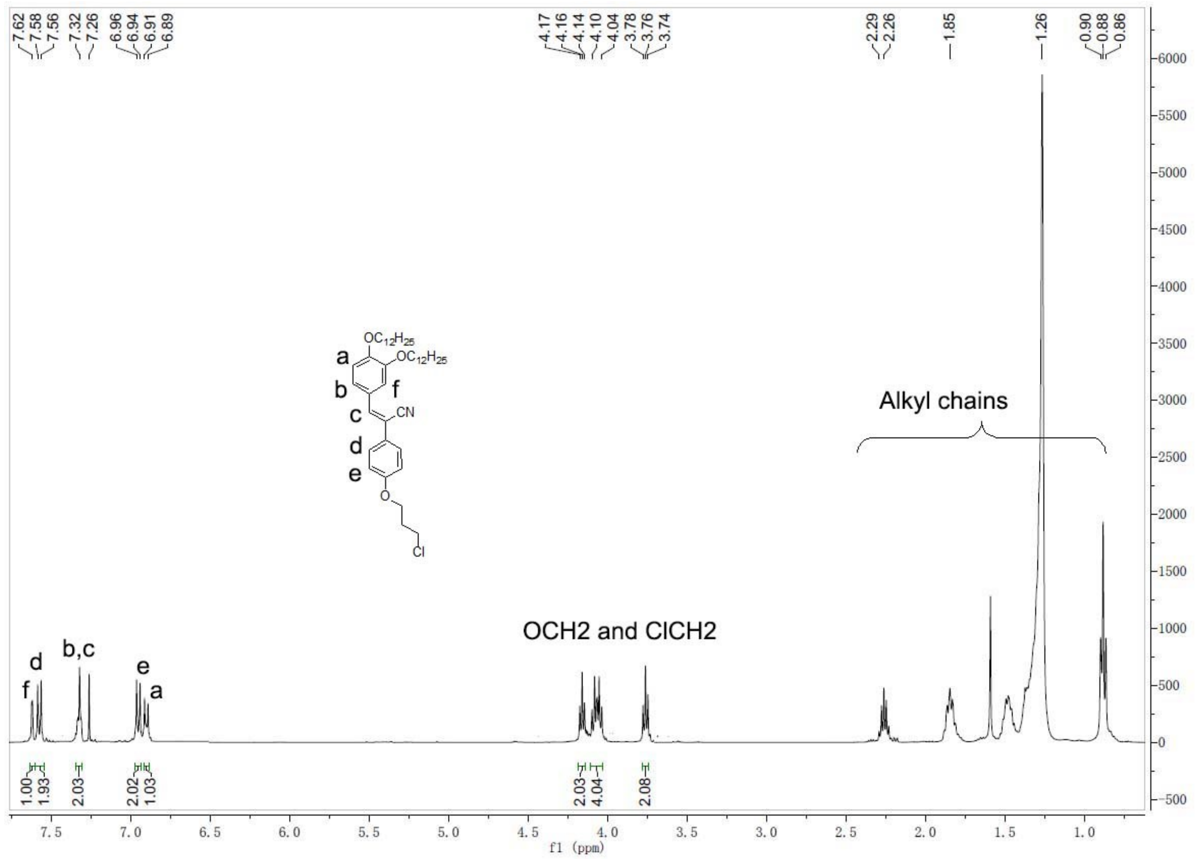


Figure S2. The ^{1}H NMR spectrum of compound **6**

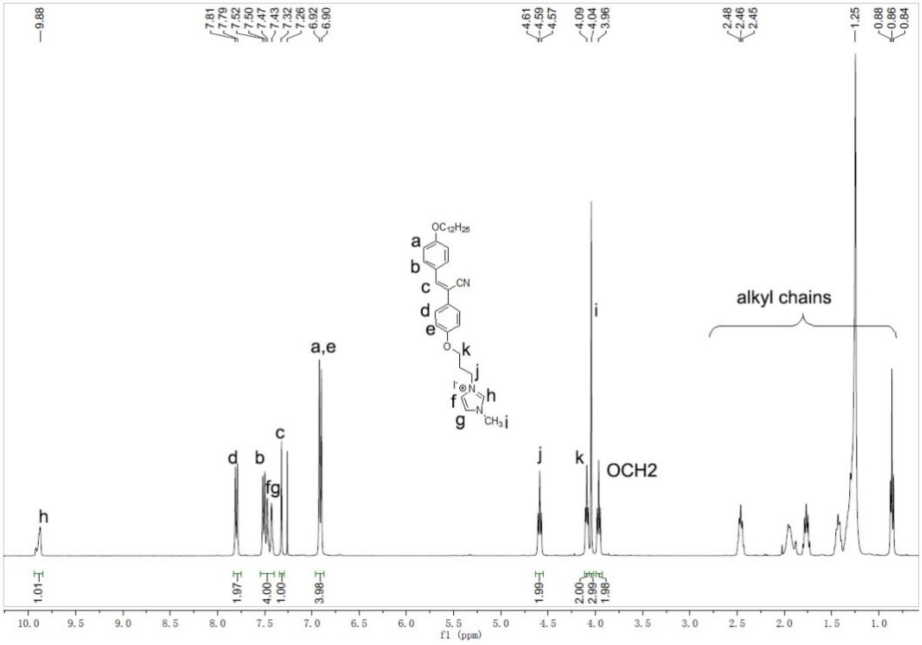


Figure S3. The ^{1}H NMR spectrum of compound **1C-I**

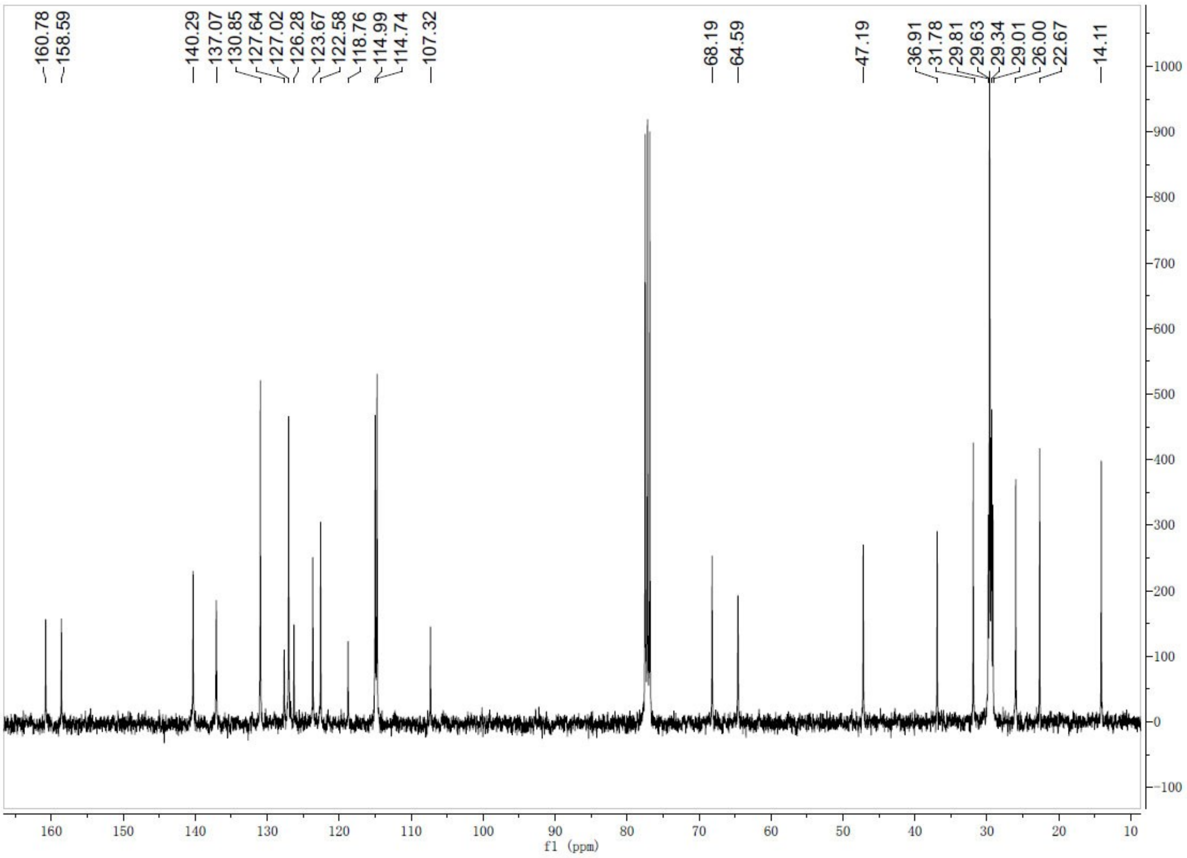


Figure S4. The ^{13}C NMR spectrum of compound **1C-I**

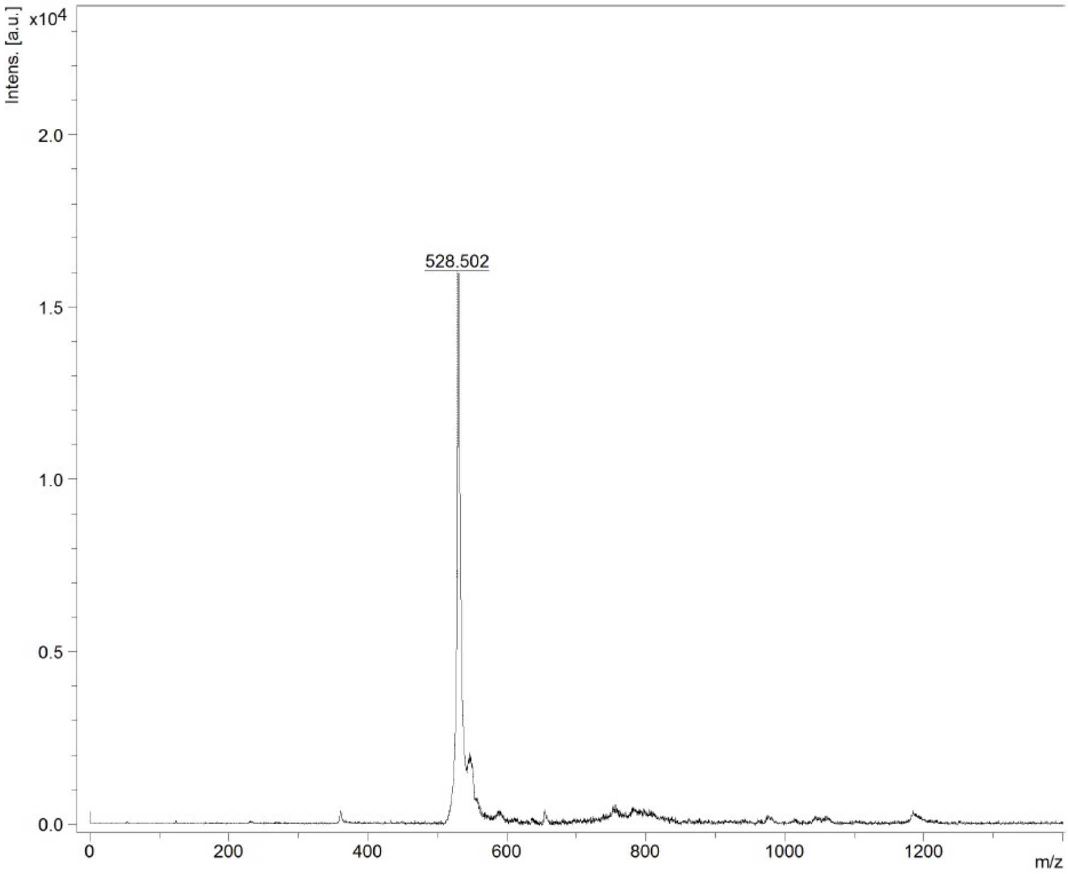


Figure S5. The MALDI-TOF-MS spectrum of compound 1**C-I**

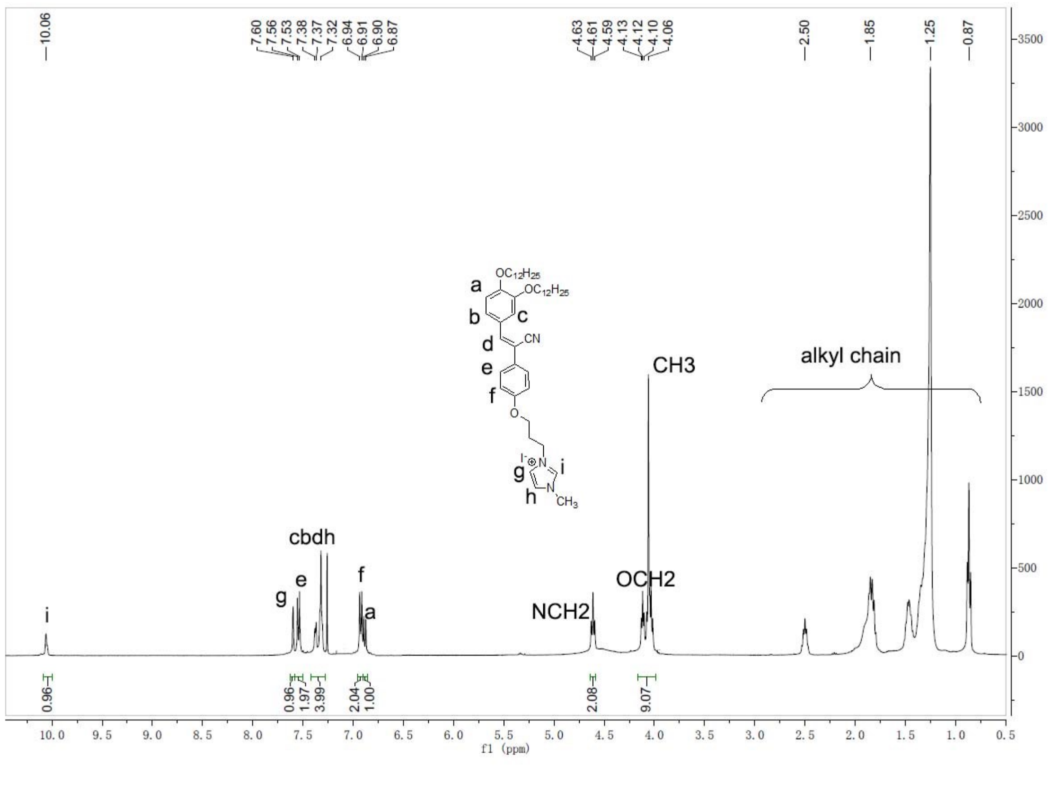


Figure S6. The ^{1}H NMR spectrum of compound **2C-I**

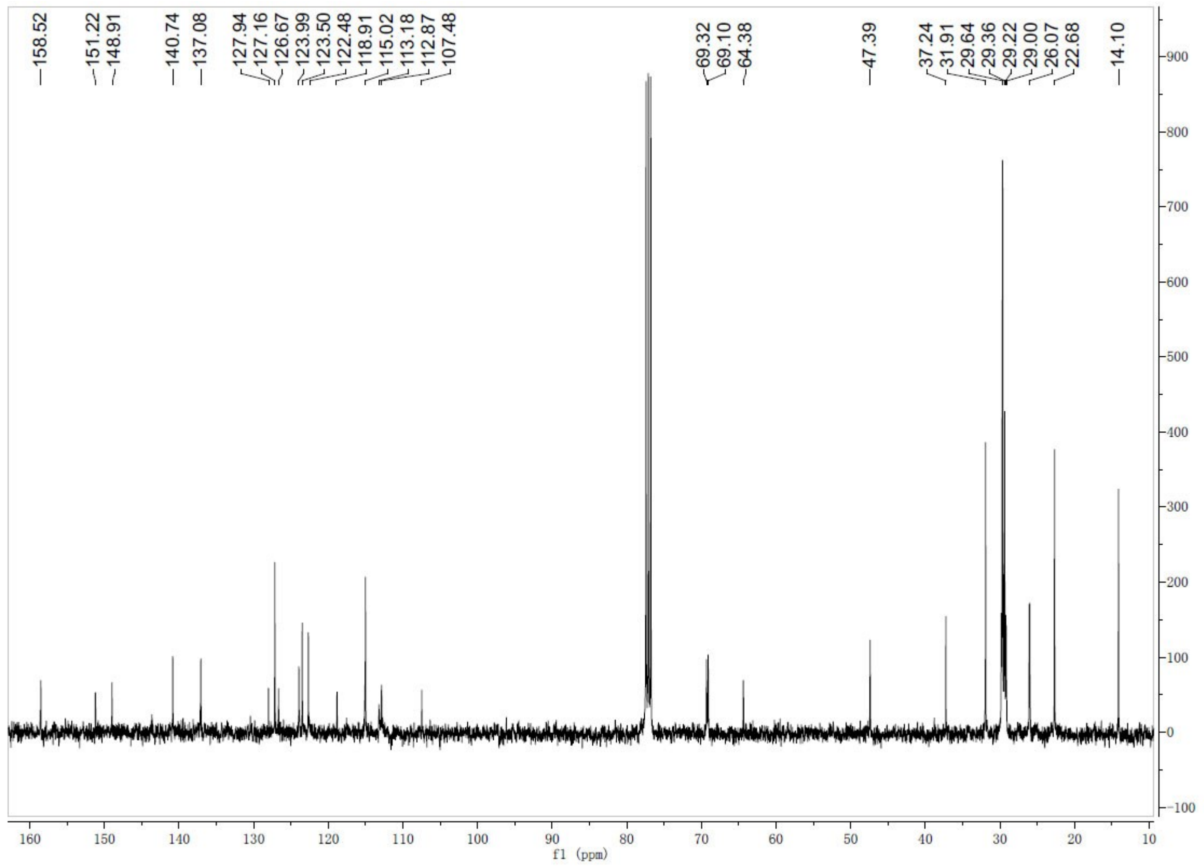


Figure S7. The ^{13}C NMR spectrum of compound **2C-I**

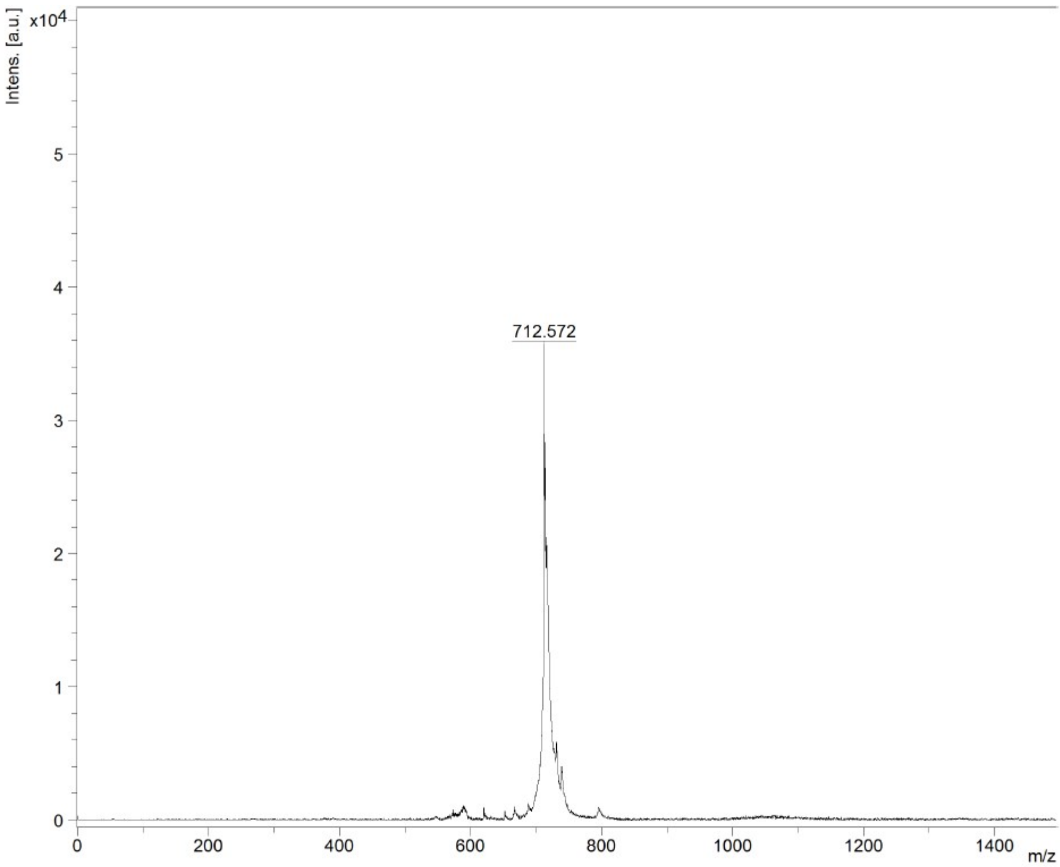


Figure S8. The MALDI-TOF-MS spectrum of compound **2C-I**

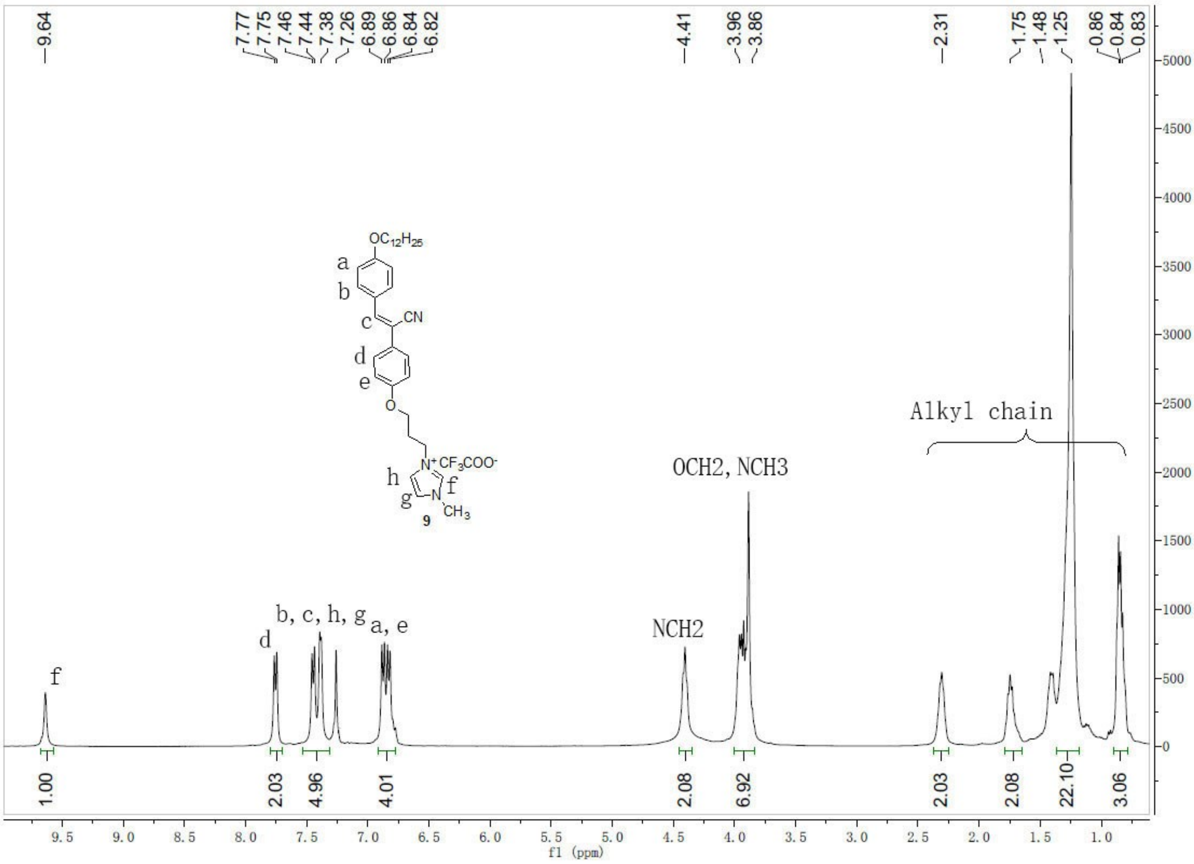


Figure S9. The ^{1}H NMR spectrum of compound **1C-T**

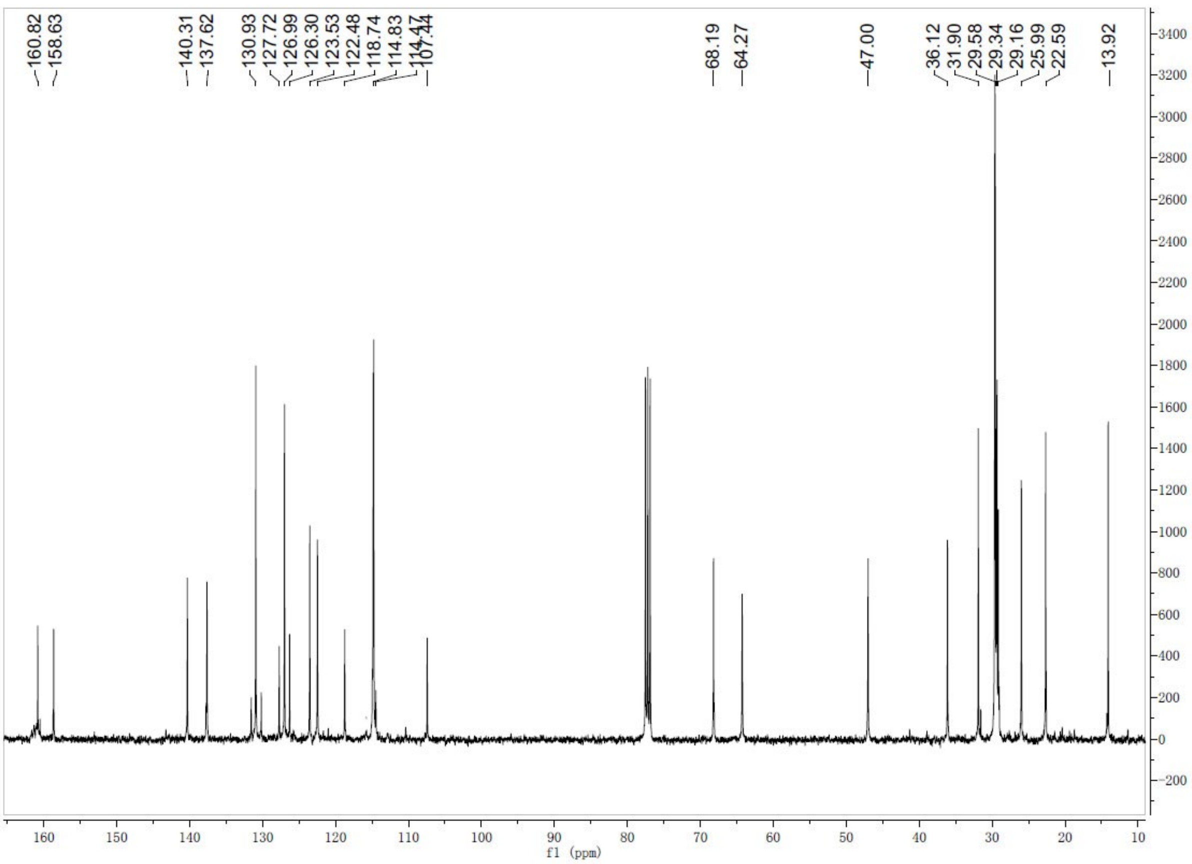


Figure S10. The ^{13}C NMR spectrum of compound **1C-T**

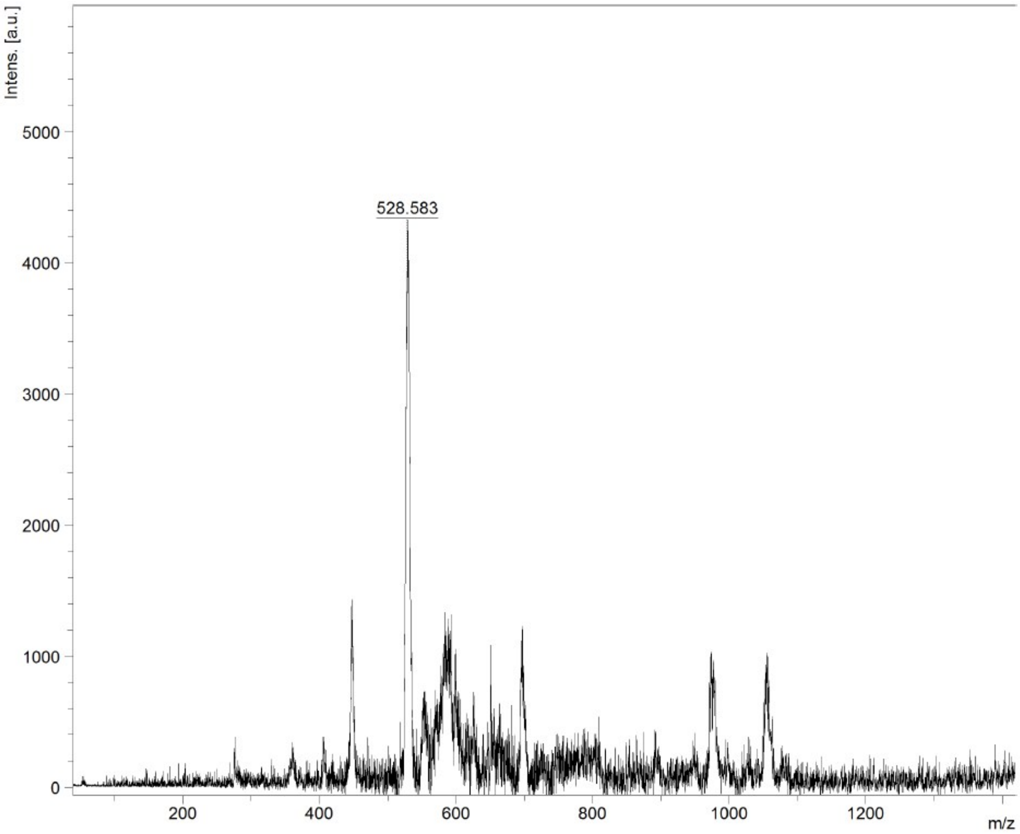


Figure S11. The MALDI-TOF-MS spectrum of compound **1C-T**

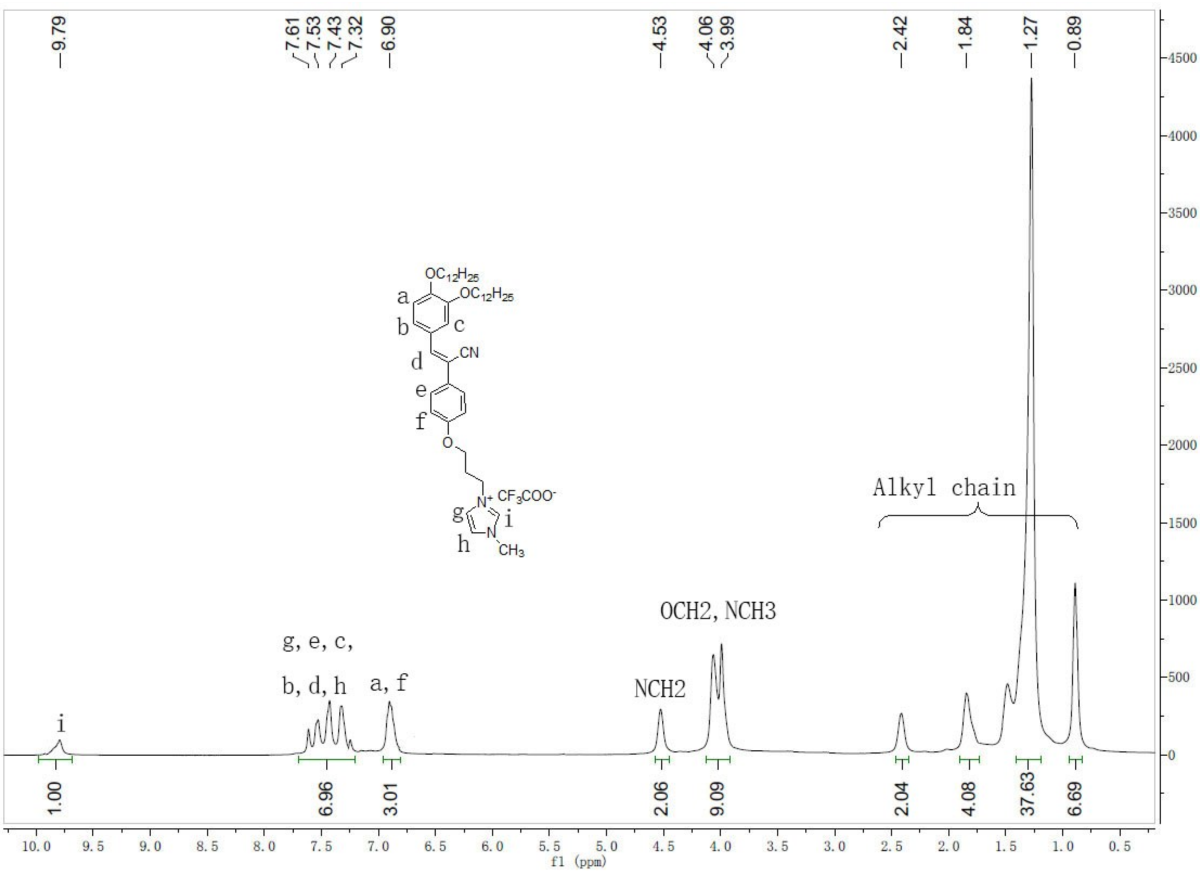


Figure S12. The ^{1}H NMR spectrum of compound **2C-T**

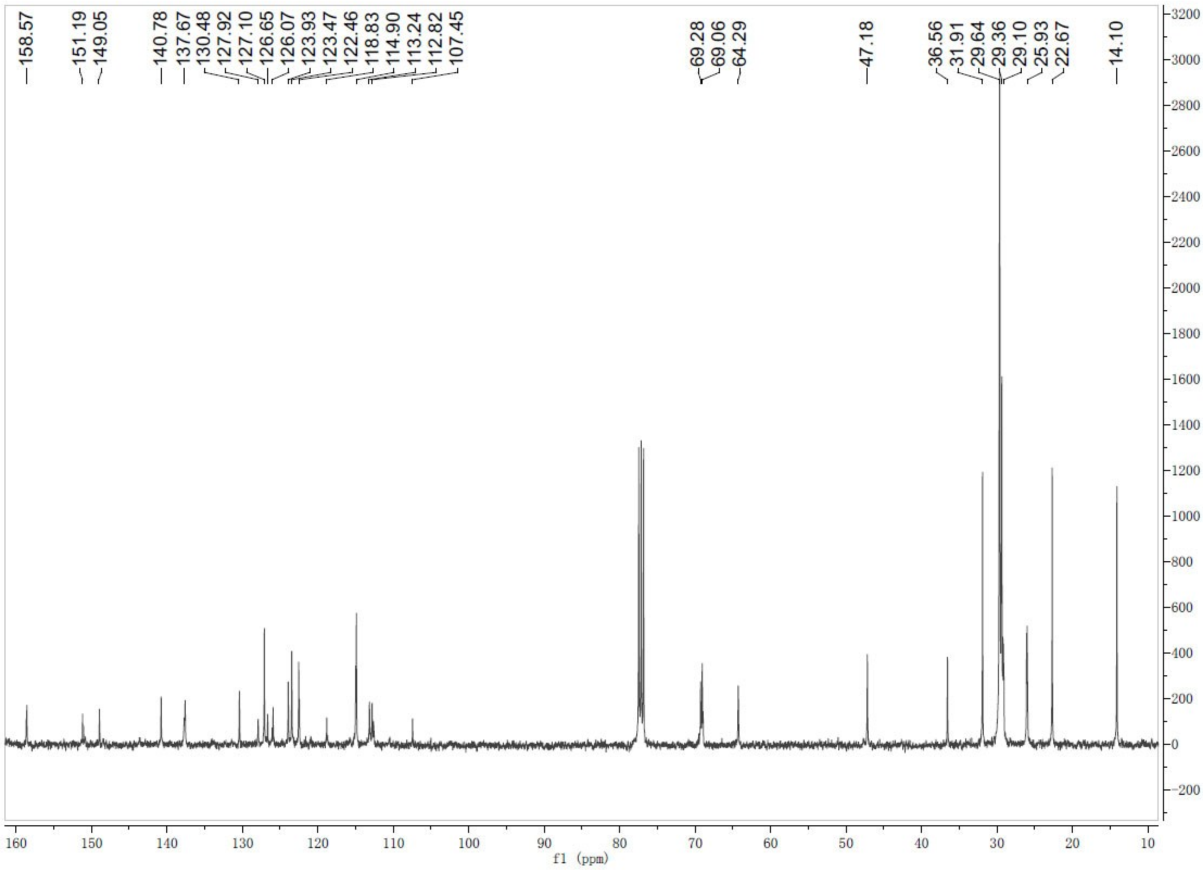


Figure S13. The ^{13}C NMR spectrum of compound **2C-T**

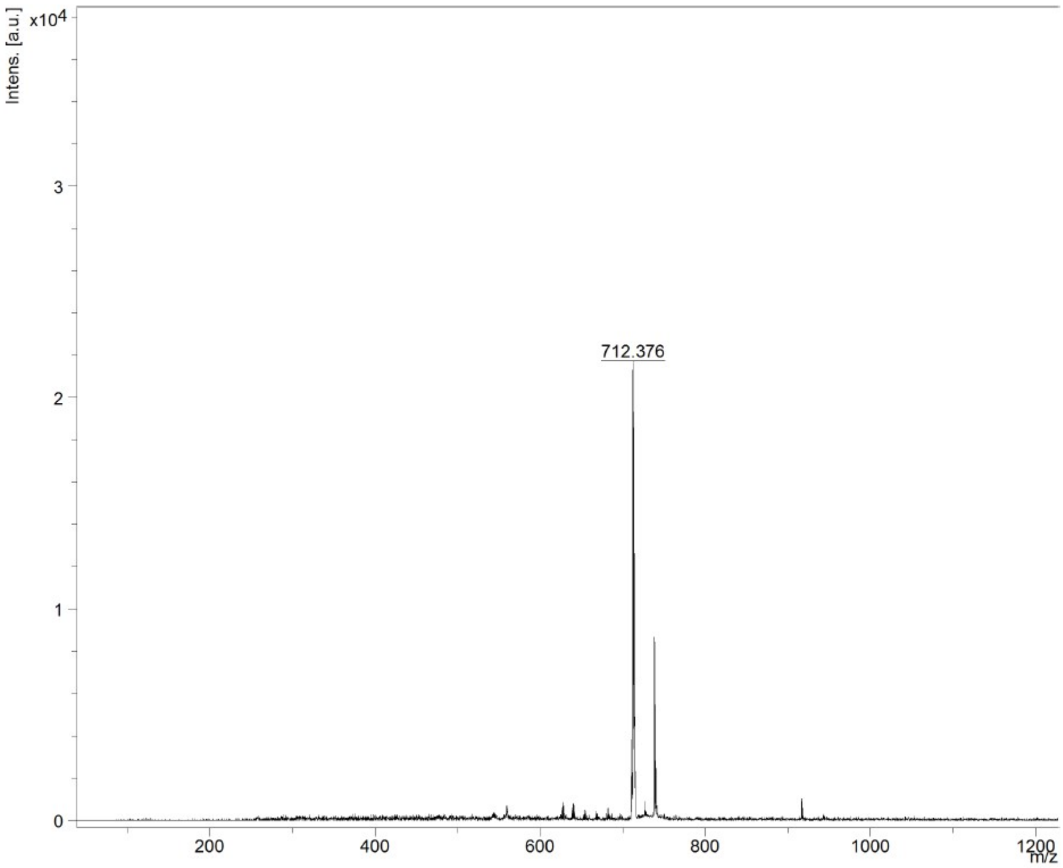


Figure S14. The MALDI-TOF-MS spectrum of compound **2C-T**

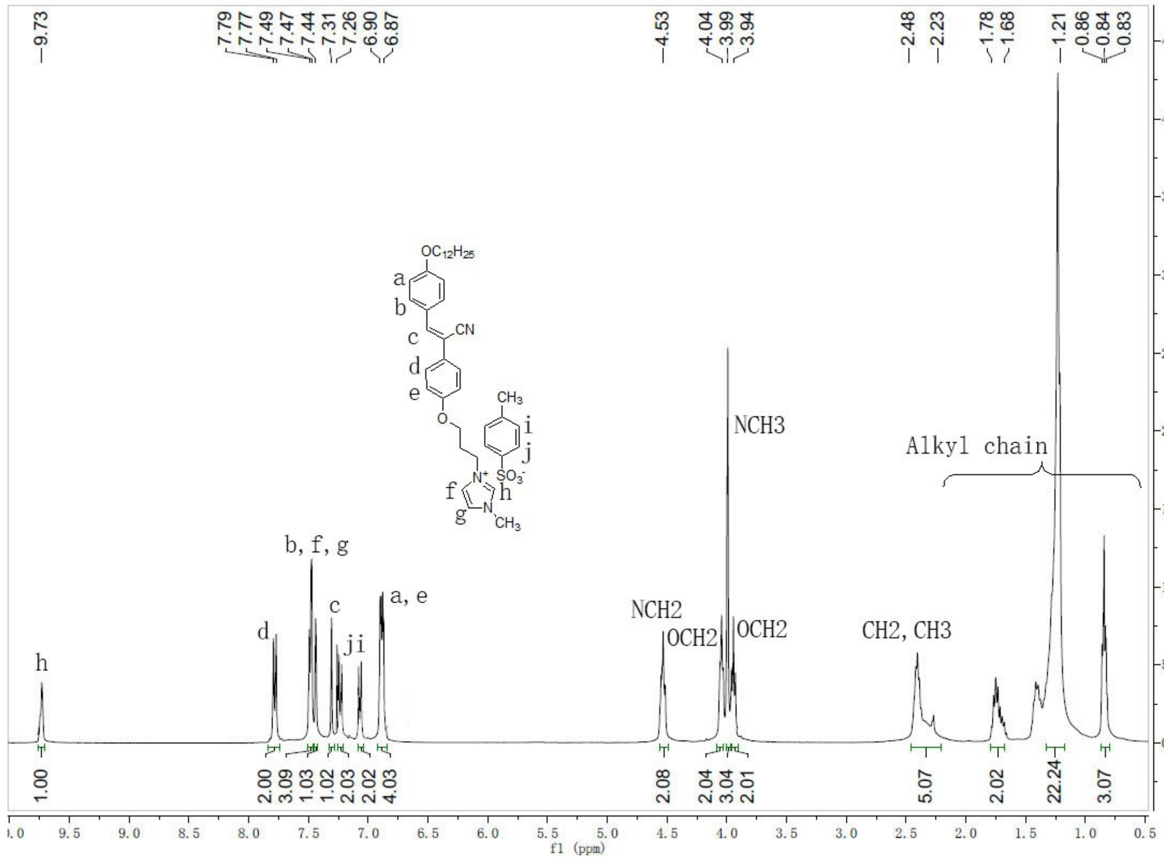


Figure S15. The ^{1}H NMR spectrum of compound **1C-P**

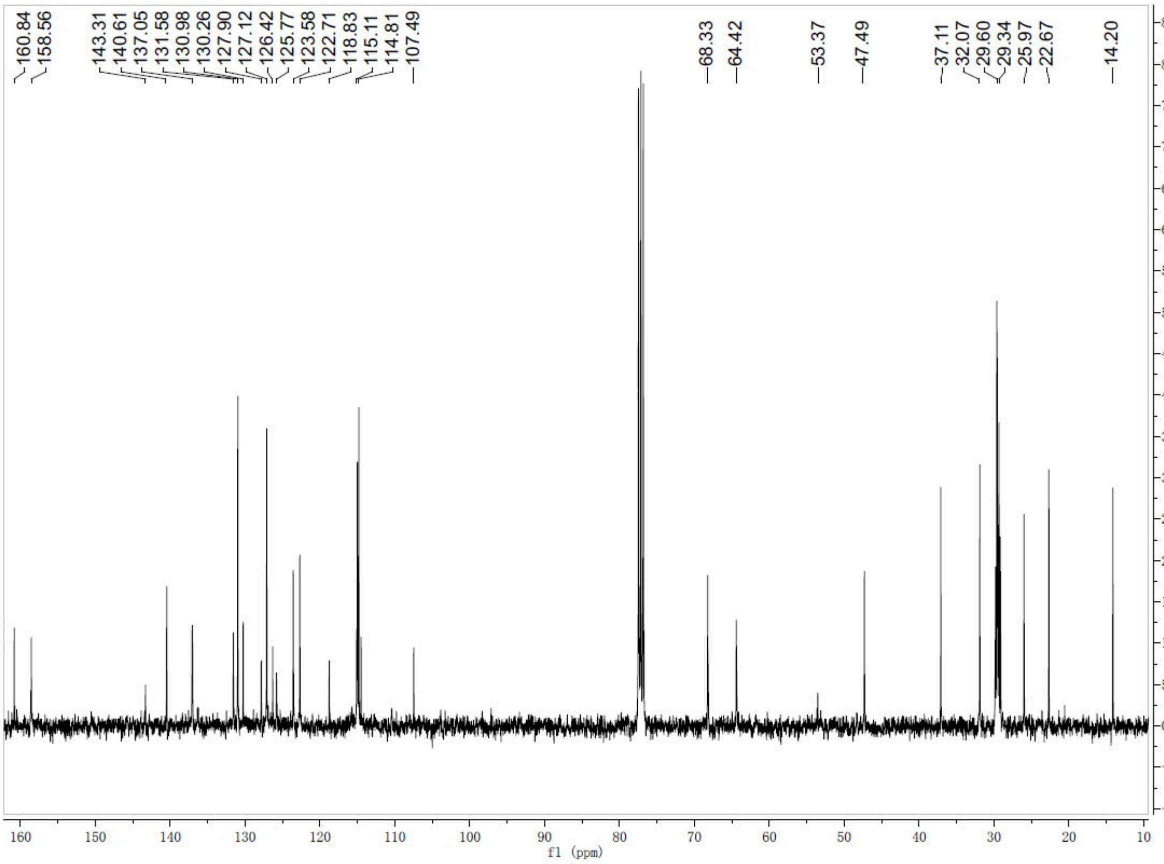


Figure S16. The ^{13}C NMR spectrum of compound **1C-P**

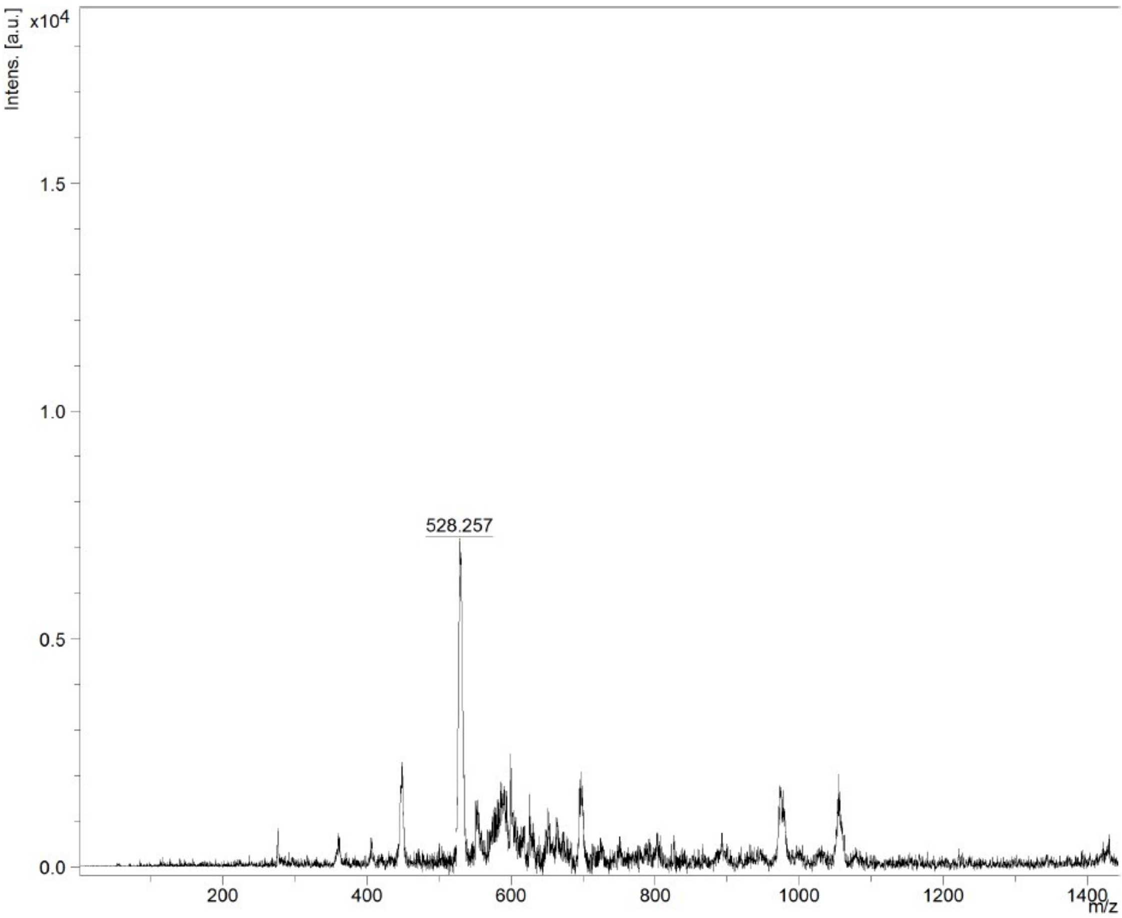


Figure S17. The MALDI-TOF-MS spectrum of compound **1C-P**

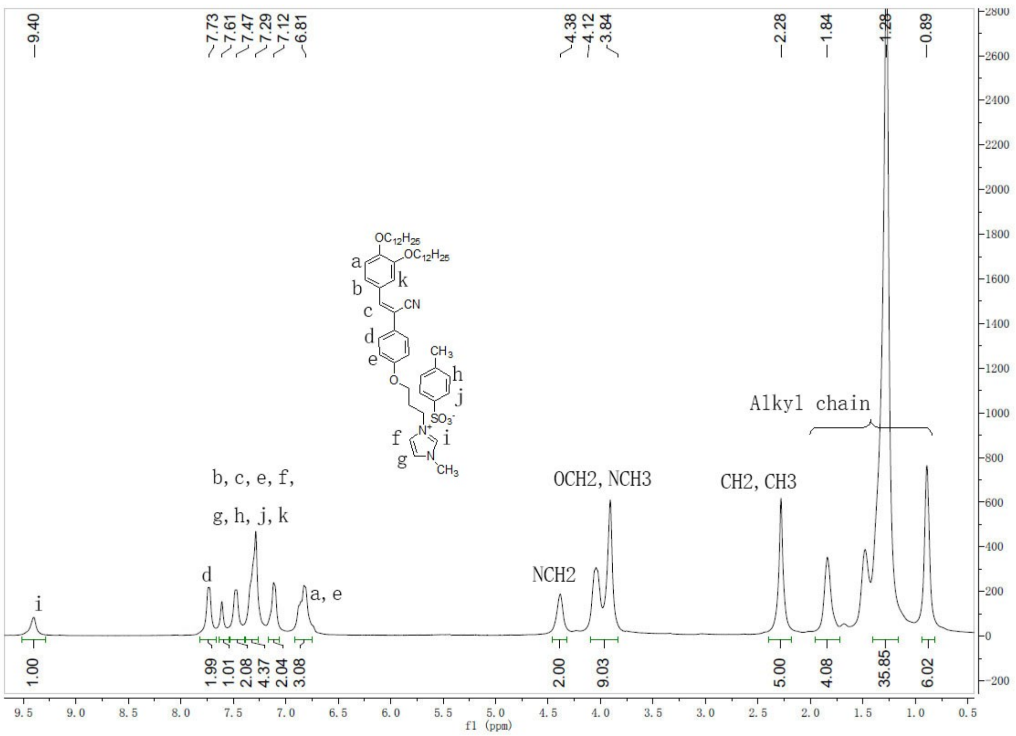


Figure S18. The ^{1}H NMR spectrum of compound **2C-P**

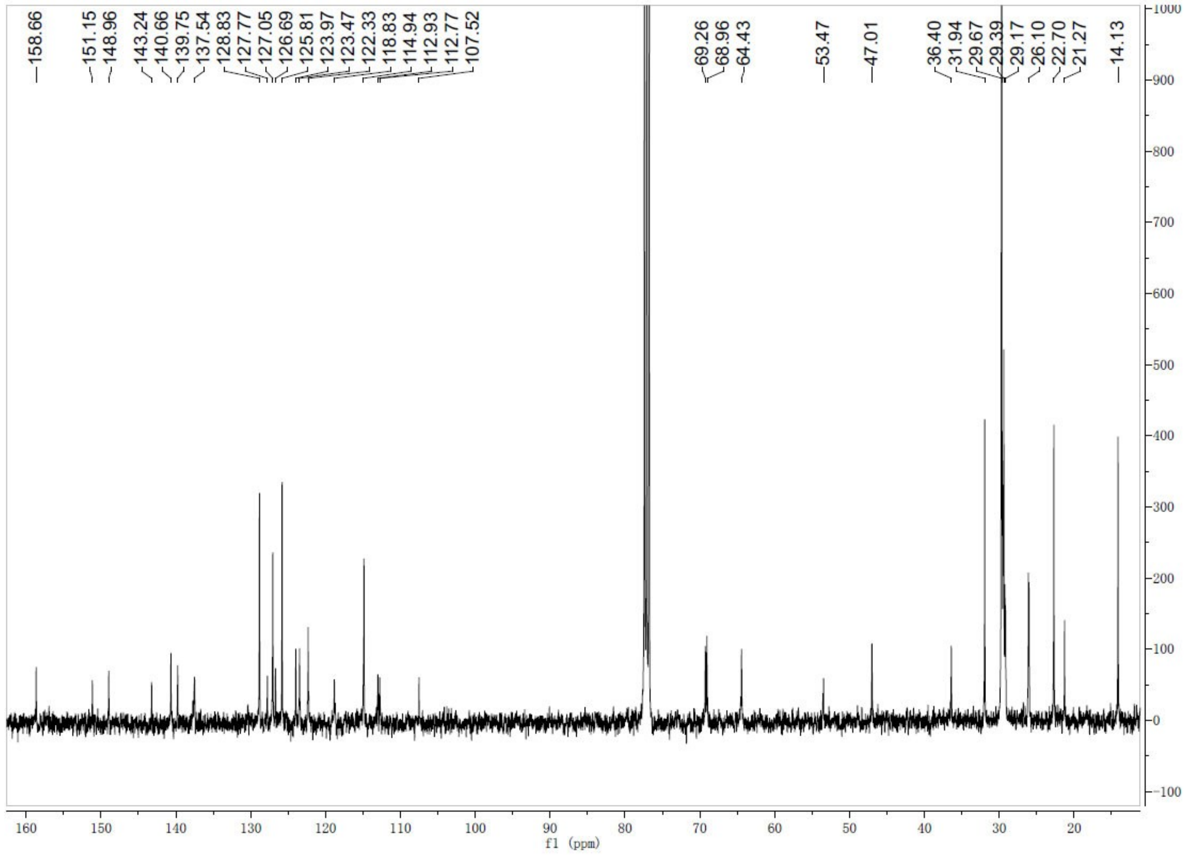


Figure S19. The ^{13}C NMR spectrum of compound **2C-P**

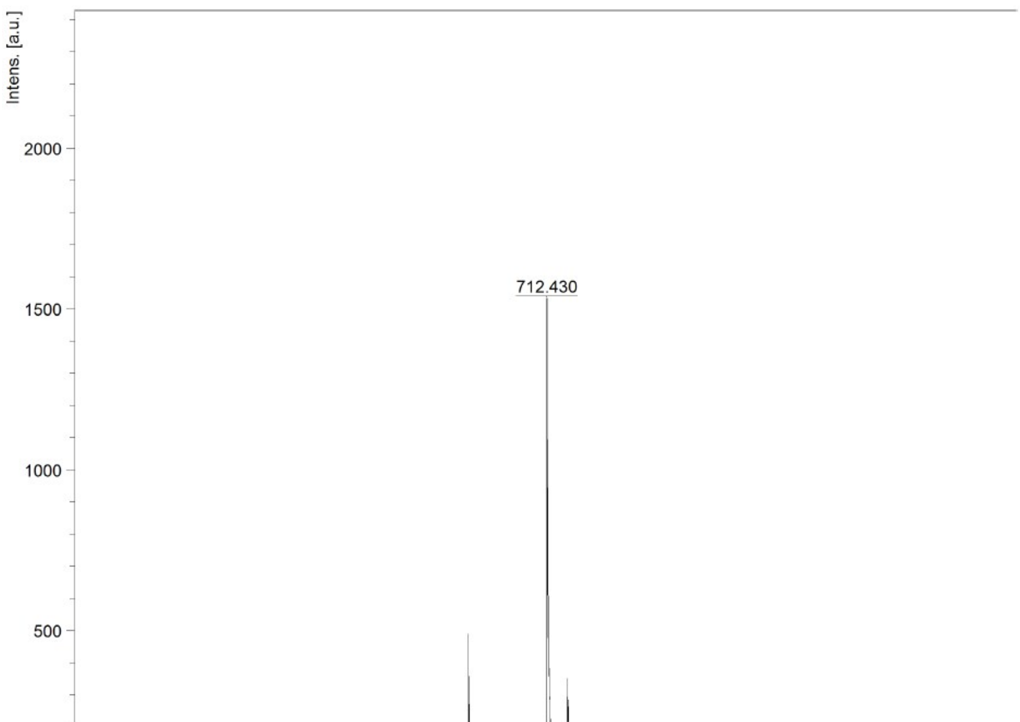


Figure S20. The MALDI-TOF-MS spectrum of compound **2C-P**

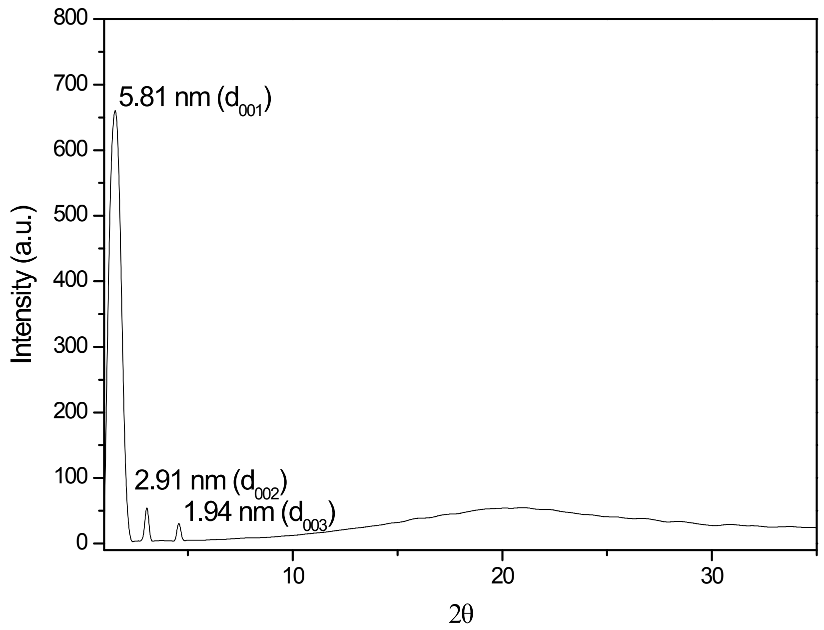


Figure S21 The XRD pattern of **1C-I**

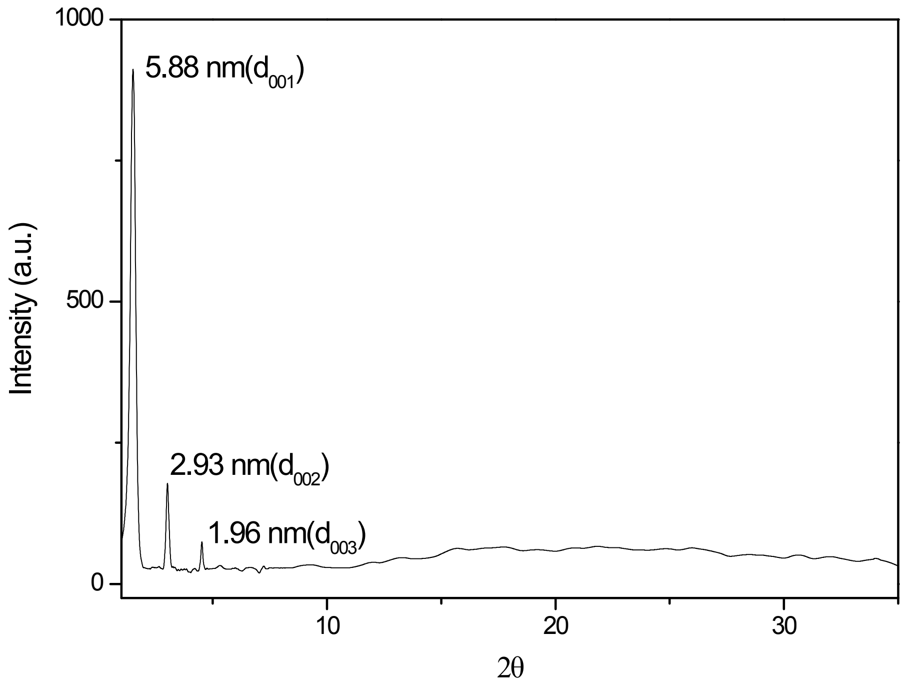


Figure S22 The XRD pattern of **1C-T**

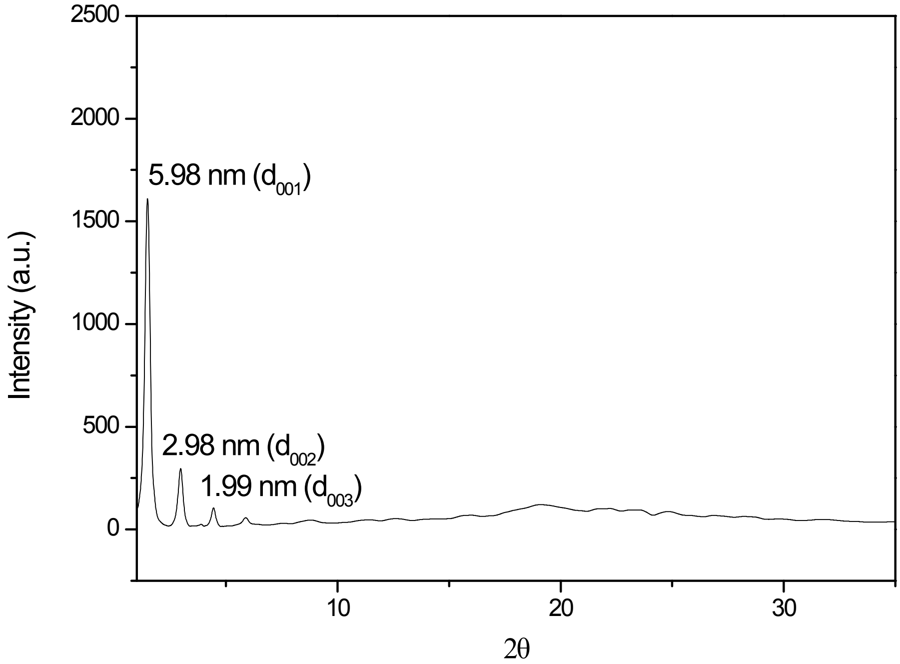


Figure S23 The XRD pattern of **1C-P**

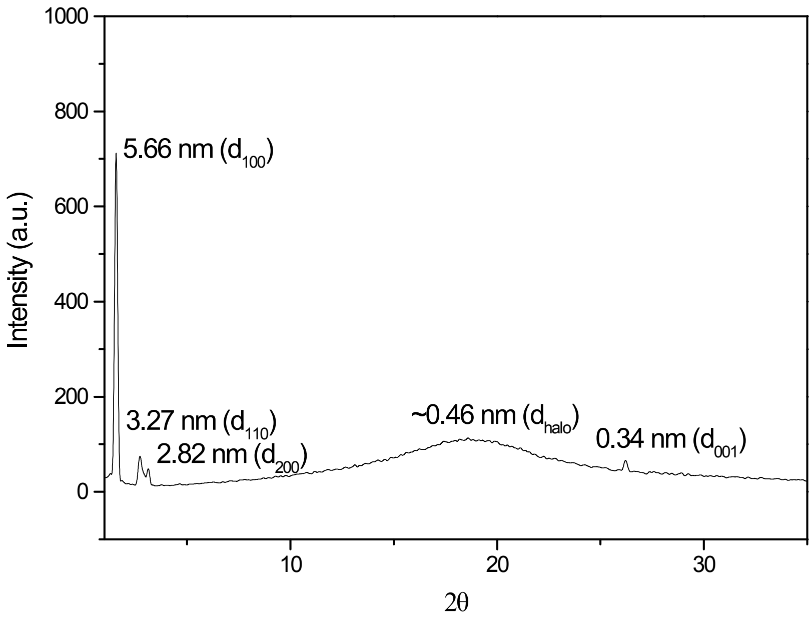


Figure S24 The XRD pattern of **2C-I**

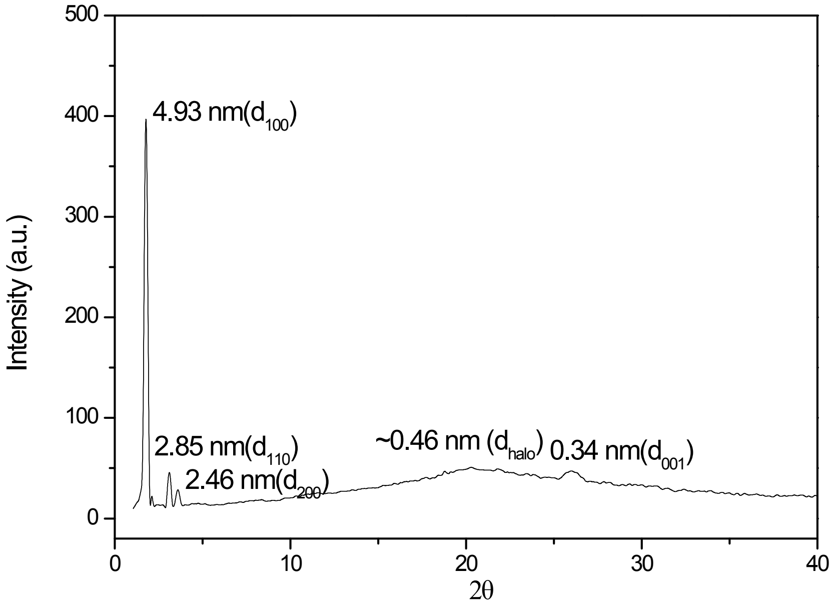


Figure S25 The XRD pattern of **2C-T**

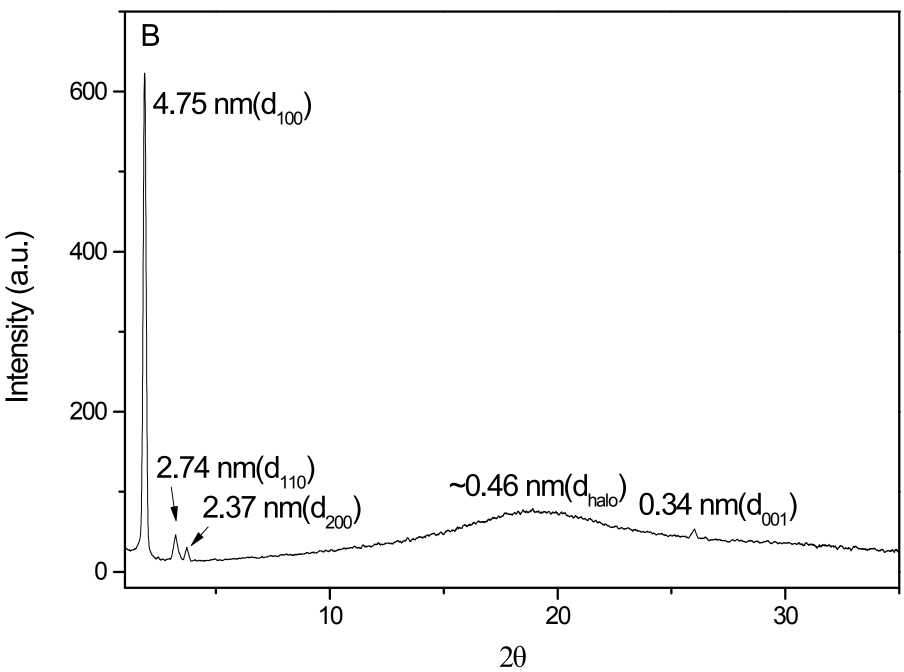


Figure S26 The XRD pattern of **2C-P**

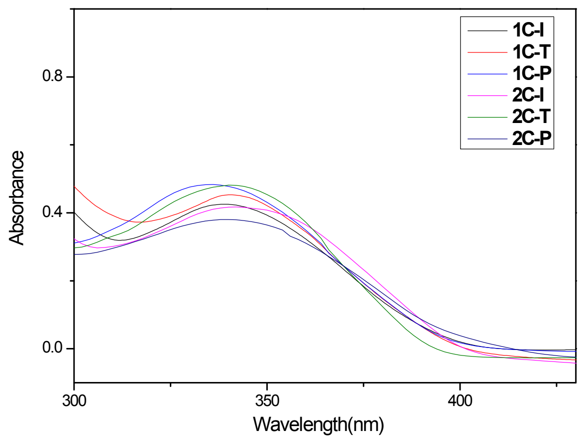


Figure **S27** The UV-vis absorption spectra of **1C-I**, **1C-T**, **1C-P**, **2C-I**, **2C-T** and **2C-P** (1.0×10^{-5} M in THF solution, each)

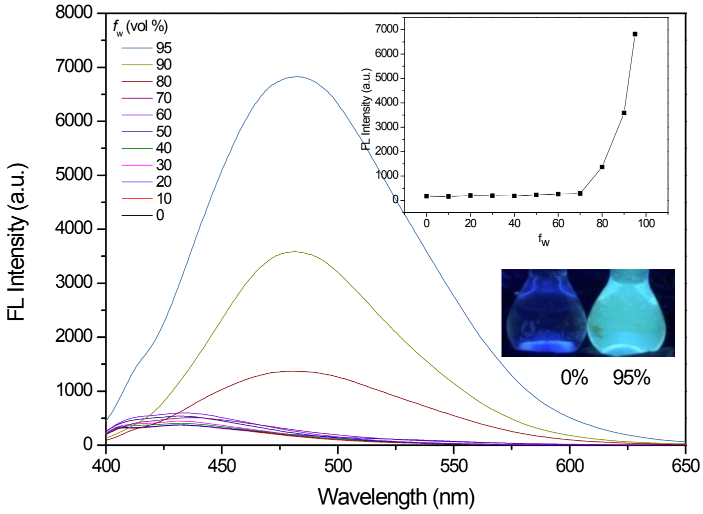


Figure S28 Fluorescence emission spectra of **1C-I** in THF-H_2O solution (1×10^{-5} M, λ_{ex} = 350 nm). Inset: Fluorescence photos of **1C-I** at 0% and 95% H_2O fractions.

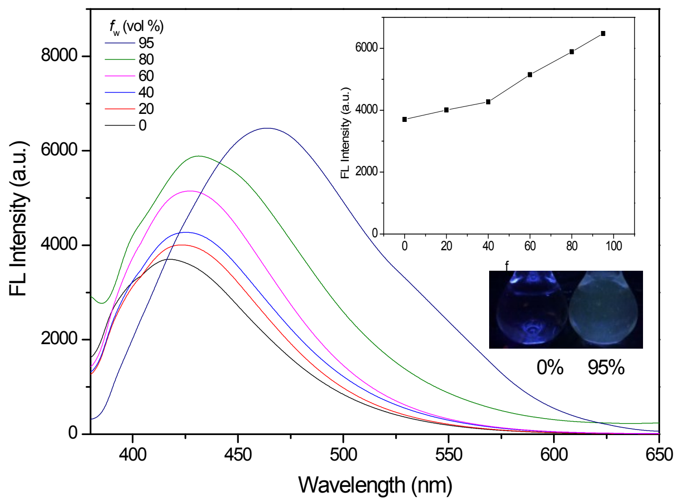


Figure S29 Fluorescence emission spectra of **1C-T** in THF-H_2O solution (1×10^{-5} M, λ_{ex} = 350 nm). Inset: Fluorescence photos of **1C-T** at 0% and 95% H_2O fractions.

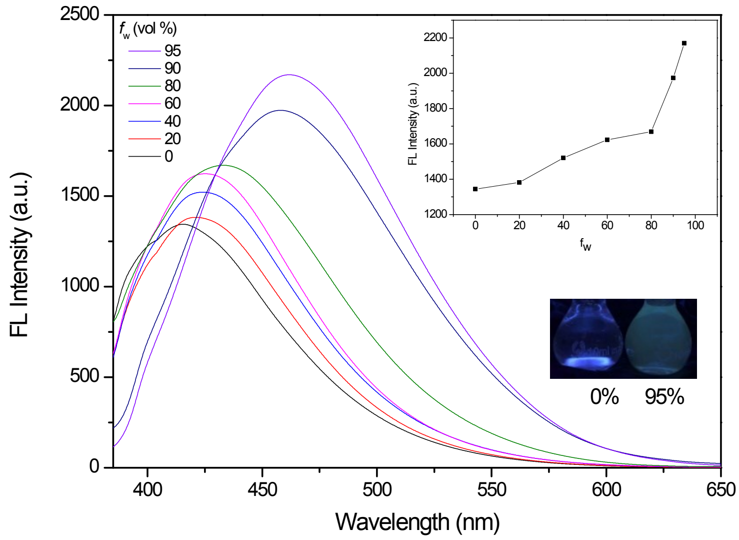


Figure S30 Fluorescence emission spectra of **1C-P** in THF-H_2O solution (1×10^{-5} M, λ_{ex} = 350 nm). Inset: Fluorescence photos of **1C-P** at 0% and 95% H_2O fractions.

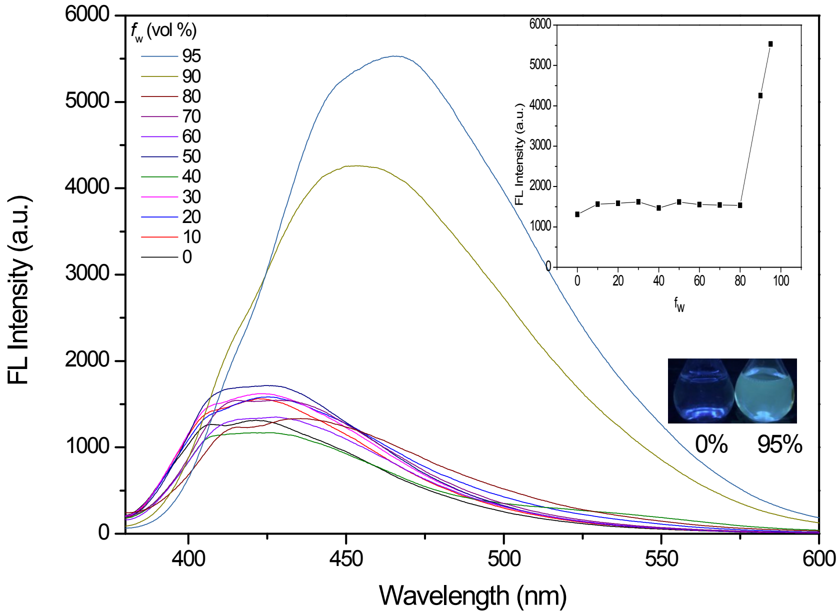


Figure S31 Fluorescence emission spectra of **2C-I** in THF-H_2O solution ($1{\times}10^{-5}$ M, λ_{ex} = 350 nm). Inset: Fluorescence photos of **1C-I** at 0% and 95% H_2O fractions.

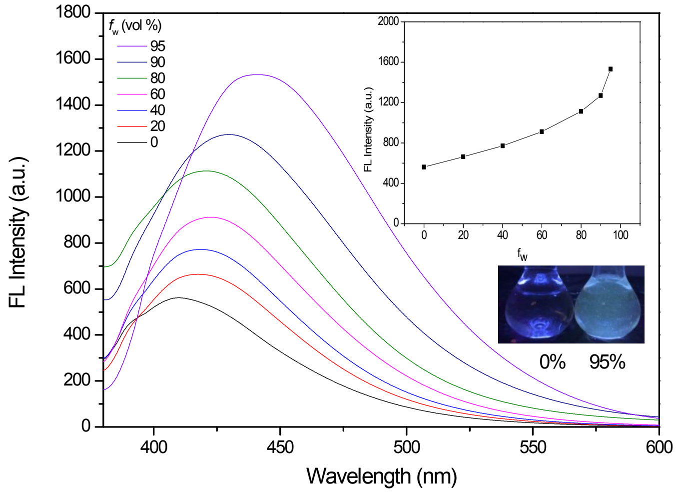


Figure S32 Fluorescence emission spectra of **2C-T** in THF-H_2O solution ($1{\times}10^{-5}$ M, λ_{ex} = 350 nm). Inset: Fluorescence photos of **1C-T** at 0% and 95% H_2O fractions.

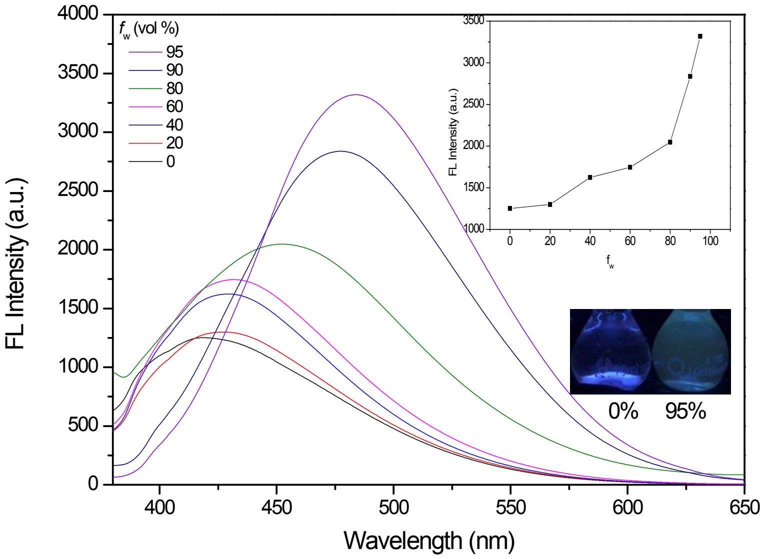


Figure S33 Fluorescence emission spectra of **2C-P** in THF-H_2O solution (1×10^{-5} M, λ_{ex} = 350 nm). Inset: Fluorescence photos of **1C-P** at 0% and 95% H_2O fractions.

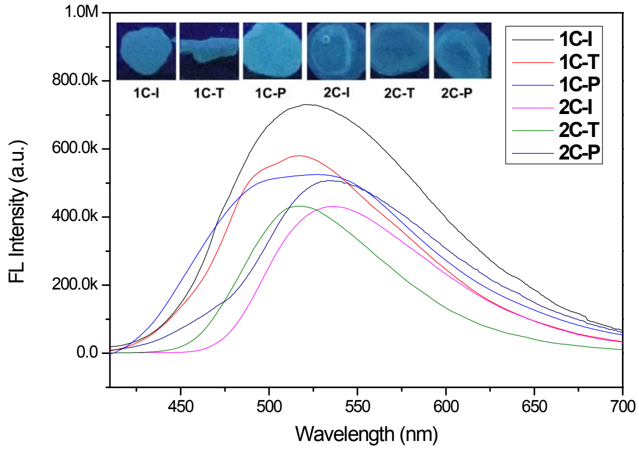


Figure S34 Fluorescence spectra of **1C-I**, **1C-T**, **1C-P**, **2C-I**, **2C-T** and **2C-P** in solid films (λ_{ex} = 350 nm).

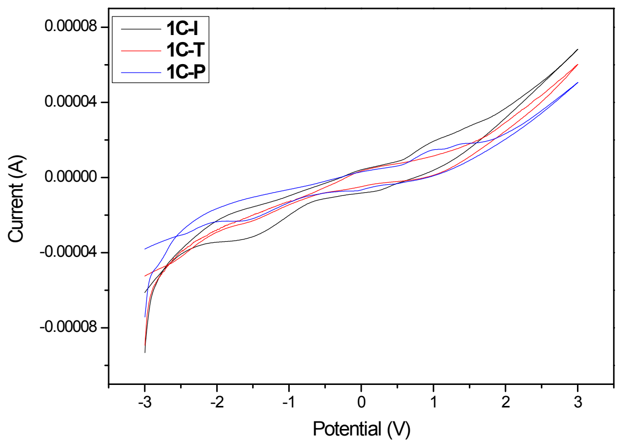


Figure S35 CVs of **1C-I**, **1C-T** and **1C-P** (1 mM) in 5% ethanol（at a scan rate of 50 mV s^{-1}）

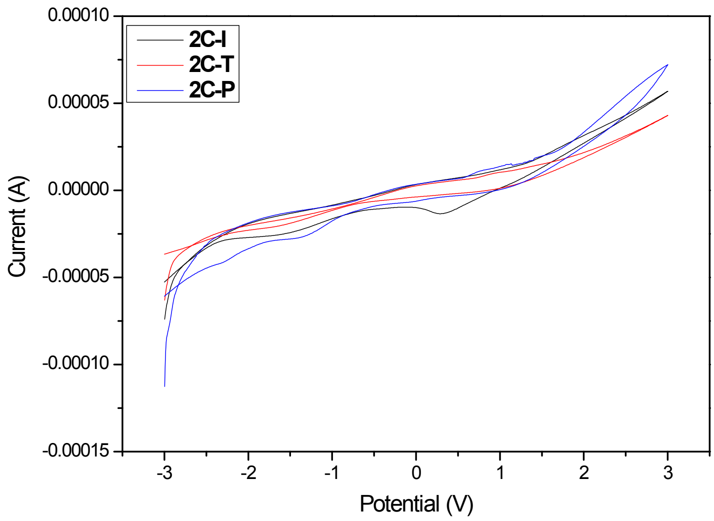


Figure S36 CVs of **2C-I**, **2C-T** and **2C-P** (1 mM) in 5% ethanol（at a scan rate of 50 mV s^{-1}）

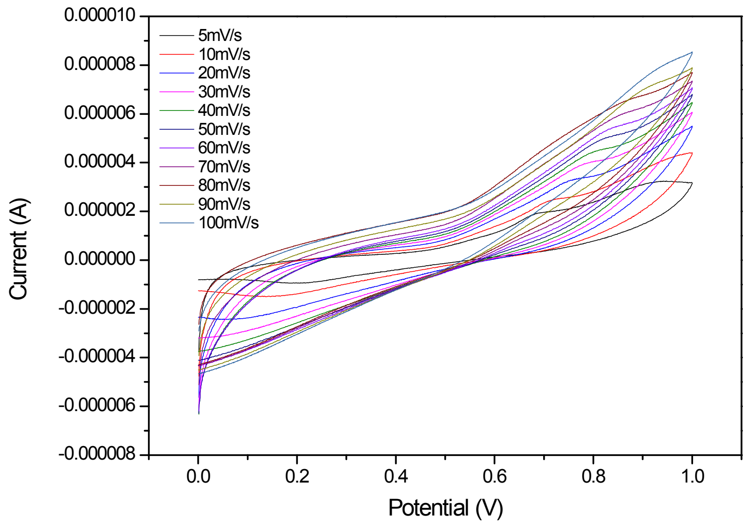


Figure S37 CVs of **1C-I** (1 mM) in 5% ethanol at different scan rates

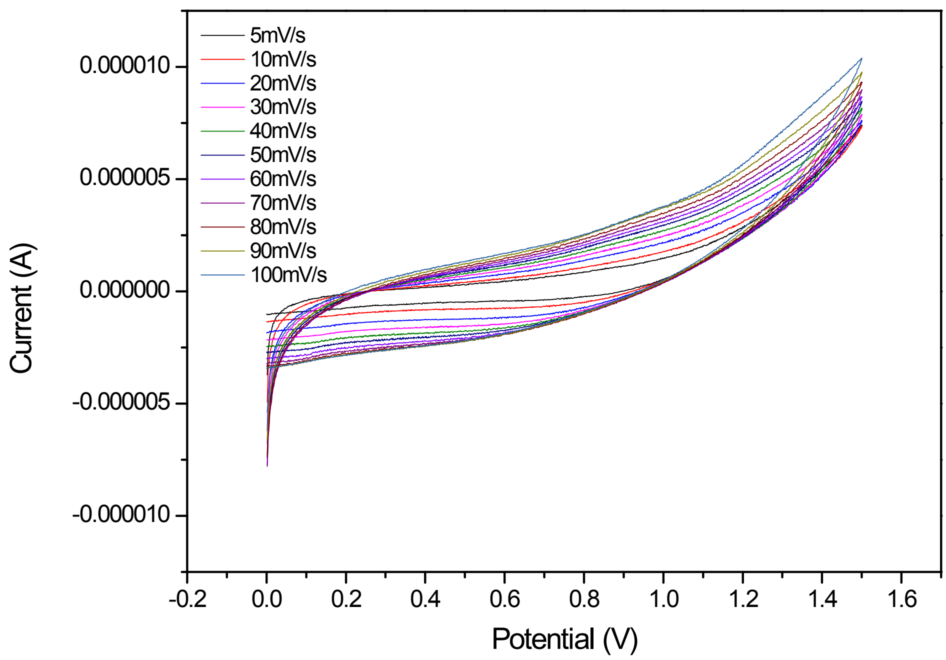


Figure S38 CVs of **1C-T** (1 mM) in 5% ethanol at different scan rates

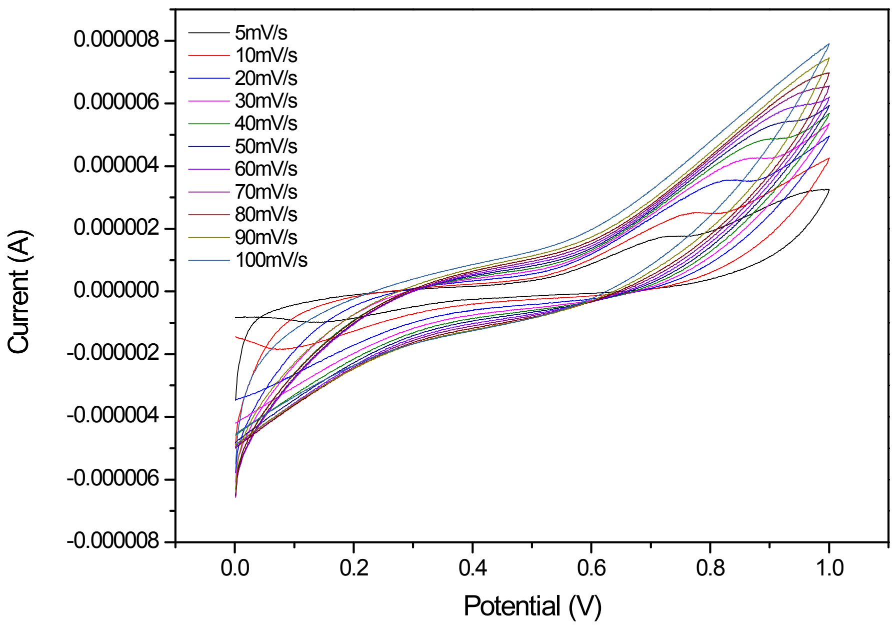


Figure S39 CVs of **1C-P** (1 mM) in 5% ethanol at different scan rates

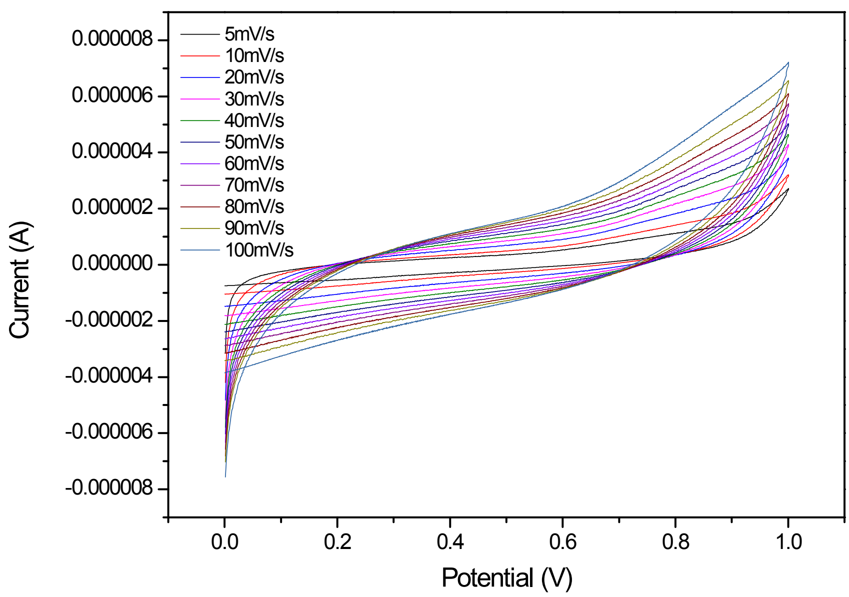


Figure S40 CVs of **2C-I** (1 mM) in 5% ethanol at different scan rates

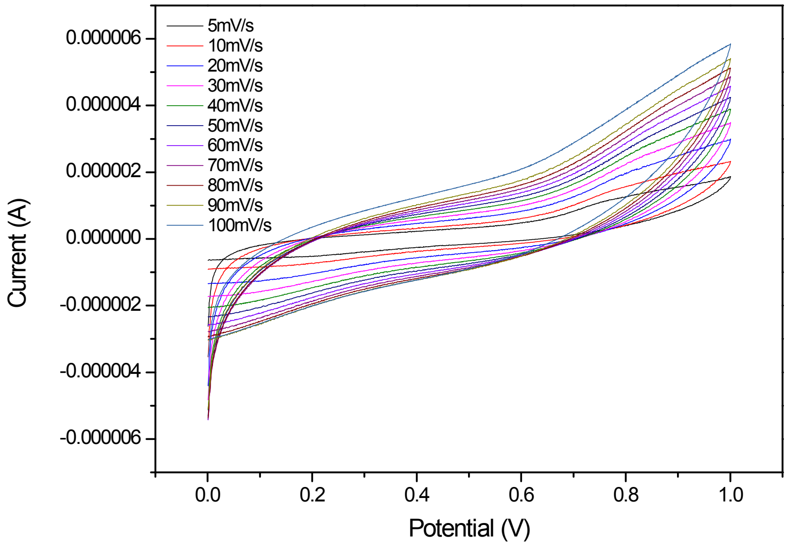


Figure S41 CVs of **2C-T** (1 mM) in 5% ethanol at different scan rates

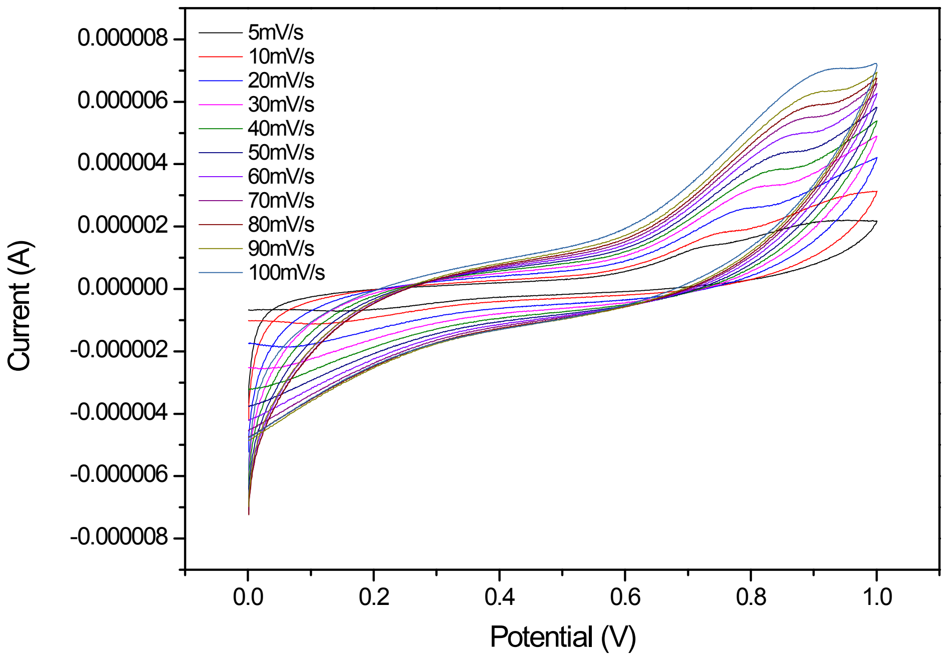


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Figure S42 CVs of **2C-P** (1 mM) in 5% ethanol at different scan rates

Table S1 Transition temperatures (°C) and enthalpies (kJ·mol^{-1}) of Novel AIE ILCs

sample	Phase transition[a]	Heating scan T(ΔH)	Cooling scan T(ΔH)
1C-I	Cr-SmA (SmA-Cr)	41.0(14.8)	146.6(4.4)
	SmA-Iso(Iso-SmA)	41.5(15.4)	135.6(4.1)
1C-T	Cr-SmA (SmA-Cr)	50.8(13.9)	162.2(3.6)
	SmA-Iso(Iso-SmA)	50.6(12.7)	160.4(4.8)
1C-P	Cr-SmA (SmA-Cr)	39.8(17.2)	147.2(4.8)
	SmA-Iso(Iso-SmA)	37.0(15.8)	139.2(4.0)
2C-I	Cr- Col_h (Col_h-Cr)	34.6(19.6)	163.1(2.8)
	Col_h-Iso(Iso-Col_h)	19.8(18.2)	147.3(2.1)
2C-T	Cr-Col_h (Col_h-Cr)	47.5(17.4)	205.6(2.6)
	Col_h-Iso(Iso-Col_h)	25.6(16.3)	195.4(2.4)
2C-P	Cr-Col_h (Col_h-Cr)	29.0(17.2)	181.6(3.4)
	Col_h-Iso(Iso-Col_h)	16.1(16.9)	175.1(2.9)

[a] Cr = crystalline, SmA = SmA mesophase,
Col_h = hexagonal columnar mesophase, Iso = isotropic

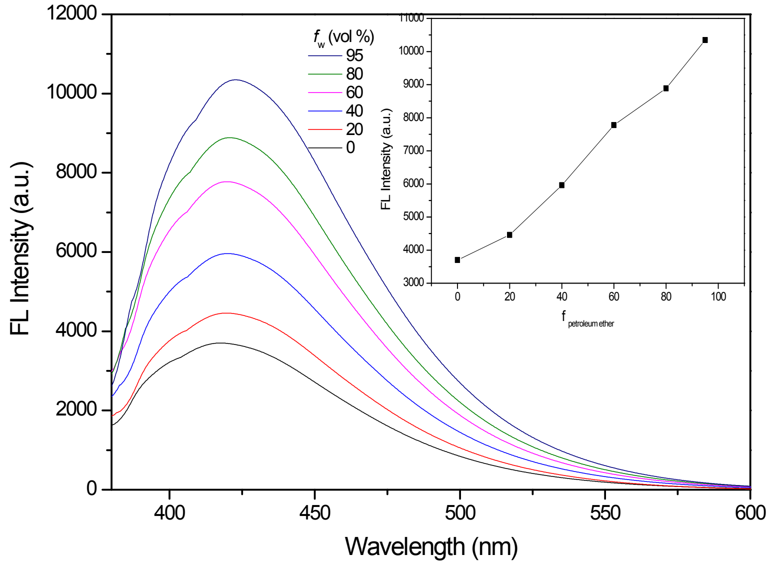

Figure S43 Fluorescence emission spectra of **1C-T** in THF-petroleum ether solution (1×10^{-5} M, λ_{ex} = 350 nm).