

Tunable cyano substituents in D-A conjugated polymers accessed *via* direct arylation for photocatalytic hydrogen production

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Experimental

Materials

All the starting reagents were purchased from commercial suppliers and used directly without further purification. Anhydrous toluene employed in the syntheses were distilled freshly with calcium hydride (CaH₂). All the polymerizations were carried out by using standard Schlenk techniques.

Synthesis of M1-M4

(*E*)-2-(4-bromostyryl) thiophene (**M1**): thiophene (82.0 mg, 1.0 mmol), 4-bromostyrene (91.6 mg, 0.5 mmol), Pd (OAc)₂ (22.4 mg, 5% mmol), benzoquinone (108.0 mg, 1.0 mmol), 2 mL HOAc, and 2 mL DMSO were placed into a 10 mL Schlenk tube.^{S1} The reaction mixture was kept stirring at 30 °C for 36 h. Then, the reaction mixture was washed with deionized water. The crude product was dried by anhydrous Na₂SO₄, purified by column chromatography (CC) on silica gel using petroleum ether as an eluent to get a beige solid in 78.6 % yield. ¹H NMR (400 MHz, CDCl₃) δ: 7.46 (m, 2H), 7.32 (m, 2H), 7.20 (m, 2H), 7.08 (d, *J* = 3.2 Hz, 1H), 7.02 (m, 1H), 6.85 (d, *J* = 16.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 142.4, 135.9, 131.8, 127.8, 127.7, 127.0, 126.5, 124.8, 122.5, 121.2.

(*Z*)-2-(4-Bromophenyl)-3-(thiophen-2-yl) acrylonitrile (**M2**): Thiophene-2-carbaldehyde (560 mg, 5 mmol) and 2-(4-bromophenyl) acetonitrile (980 mg, 5 mmol) were added to a round-bottom flask containing 20 mL methanol solution of sodium tert-butoxide (24 mg, 0.25 mmol).^{S2} The reaction mixture was stirred for 24 h at room temperature, the resulting solid was filtered and purified by recrystallization from water/methanol to give the title compound as a green yellow solid (1205 mg, 83.1%). ¹H NMR (400 MHz, CDCl₃) δ: 7.67 (d, *J* = 3.6 Hz, 1H), 7.65 (s, 1H), 7.57 (d, *J* = 5.2 Hz, 1H), 7.54 (s, 1H), 7.50 (m, 2H), 7.15~7.17 (dd, *J* = 4.0, 3.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 137.7, 134.5, 132.9, 132.3, 130.6, 128.0, 127.1, 123.1, 117.8, 107.1.

(*E*)-3-(4-Bromophenyl)-2-(5-bromothiophen-2-yl) acrylonitrile (**M3**): 2-(thiophen-2-yl)acetonitrile (1.5 g, 8.12 mmol) and 4-bromobenzaldehyde (1.55 g, 8.12 mmol) were added to a round-bottom flask containing 40 mL methanol solution of sodium tert-butoxide (39 mg, 0.41 mmol).^{S3} The reaction mixture was stirred at 30 °C for 24 h, the resulting solid was filtered and recrystallization from water/methanol to give the title compound as a yellow needle-like solid (2.14 g, 90.7%). ¹H NMR (400 MHz, CDCl₃) δ: 7.70 (d, *J* = 4.8 Hz, 2H), 7.58(m, 2H), 7.39 (dd, *J* = 1.2, 0.8 Hz, 1H), 7.32 (dd, *J* = 0.8, 1.2 Hz, 1H), 7.29 (s, 1H)7.06~7.09 (dd, *J* = 3.6, 3.6 Hz,1H). ¹³C NMR (100 MHz, CDCl₃) δ: 138.9, 138.0, 132.3, 132.2, 130.5, 128.3, 127.7, 116.6, 106.8.

2-(4-bromophenyl)-3-(thiophen-2-yl) fumaronitrile (**M4**): The following procedure was applied to the reaction with **M3** (58 mg, 0.2 mmol) and $K_3Fe(CN)_6$ (13.2 mg 20 mol %) in DMSO (1.0 mL) at 140 °C for 12 h under an oxygen atmosphere.^{S4} The solution was filtered to isolate the solid, which was rinsed with cold methanol-water solution to wash away ionic substances. A second crop of the pure product could often be isolated by filtration of the original filtrate after further concentration. The crude residue was dried with Na_2SO_4 , purified by column chromatography on silica gel using a mixture of CH_2Cl_2 /petroleum ether as an eluent to get yellow solid with the yield of 60.8 %. 1H NMR (400 MHz, DMSO-*d6*): δ : 7.85(d, J = 5.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.55 (t, J = 7.0 Hz, 3H), 7.20~7.14 (m, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 135.5, 135.2, 133.2, 133.0, 131.3, 129.5, 127.9, 125.3, 121.7, 118.7, 117.3, 115.7.

Synthesis of CP1-CP4 via DArP

Monomers **M1-M4** (100 mg), $Pd_2(dba)_3$ (1.5 mol %), $P(o-MeOPh)_3$ (3 mol %), anhydrous Cs_2CO_3 (2 equiv.), PivOH (30 mol %), toluene (5 mL) were added into a Schlenk tubes.^{S5} The mixture in the tubes was purged by repetitions of vacuum and argon filling. The mixture was put through freeze-vacuum-thaw cycles two times to remove dissolved air, and then rigorously stirred at 110 °C for 48 h under argon atmosphere. After cooling to room temperature, the reaction mixture was washed by CH_2Cl_2 and filtered to remove the solvent. The undissolved crude CPs product on the filter paper was washed successively by CH_2Cl_2 , methanol, water to remove the soluble impurities and inorganic salts. Then the product was dried in vacuum for 24 h at 70 °C and obtained the polymeric powders **CP1**, **CP2**, **CP3** and **CP4** in yields of 90.1%, 93.5%, 77.1% and 77.2%, respectively.

Characterizations

The Bruker Advance III 400 model 400 MHz NMR spectrometer was used for NMR measurements. The Bruker SMART APEX II CCD instrument diffractometer was used for collecting the single crystals structural data of **M2** and **M3** at 293 K with Mo $K\alpha$ radiation upon graphite mono-chromization ($\lambda=0.71073$). The Siemens SHELXTL version 5 crystallographic software package^{S6} was used to solve the structures and the full-matrix least-squares techniques were used to refine. Fourier transformed infrared (FTIR) spectra were carried out on an FT-IR spectrometer (Bruker, ALPHA) in the frequency range of 4000–500 cm^{-1} . The scanning electron microscope (SEM, MLA650F, American) was used to characterize the morphology of the photocatalysts. The UV-2600 scanning UV-vis spectrophotometer was used to record the UV-vis diffuse reflectance (DRS) spectra of the photocatalysts. Photoluminescence (PL) spectra was measured using the HORIBA Instruments FL-1000 fluorescence

spectrometer. The CHI660E (Chenhua, Shanghai) electrochemical workstation was used to the Cyclic voltammetry (CV) measurement which was carried out in a normal three electrode-cell system. It is using Ag/AgCl electrode as the reference electrode, glassy carbon electrode as the working electrode, platinum wire as the counter electrode. 5 ml acetonitrile was used to dissolve the tetra-n-butylammonium hexafluorophosphate (TBAPF₆, 1.5 g) as a supporting electrolyte. According to the equation: The LUMO levels were calculated $E_{\text{LUMO}} = -4.80 - (E_{\text{red}} - E_{\text{Fc}/\text{Fc}^+})$, and the HOMO levels were calculated based on Eg and LUMOs: $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}$. Transient photocurrent response (TPR) was carried out on an electrochemical workstation (CHI650E/700E, Shanghai), which is equipped with a conventional three-electrode. The configuration Ag/AgCl (saturated with KCl) as the reference electrode and the platinum plate as the counter electrode for the electrochemical workstation. Water contact angles were recorded on the JCY type measurement instrument (Shanghai Fang Rui Instrument Co. Ltd.). All theoretical calculation were carried in Gaussian 09 program^{S7} by using M062X^{S8,S9}-D3^{S10,S11} density functional with the 6-31+G(d,p) basis set. At 298 K, the chemical structure was optimized and characterized by frequency analysis.

PHP tests

The photocatalytic online analysis system (LabSolar-III AG, Beijing Perfect Light) was linked with a gas chromatograph (GC9790, FuLi) for the typical PHP test. The photocatalyst **CP1-CP4** (10 mg) was ultrasonically dispersed in a mixed aqueous solution containing 30 ml H₂O, 5 g AA as the sacrificial agent. The pH was adjusted to 4.0 by adding KOH solution. To remove the dissolved air in the mixture and keep in vacuum, oil pump was used. A 300 W Xe lamp (Beijing Perfect Light, PLS-SXE300) under full-arc light irradiation was used to irradiate the reaction vessel. A flow of cooling water was used for fixed the reaction temperature at 25 °C. The thermal conductive detector (TCD) was equipped in gas chromatograph which using argon as the carrier gas to analyse the amount of hydrogen produced.

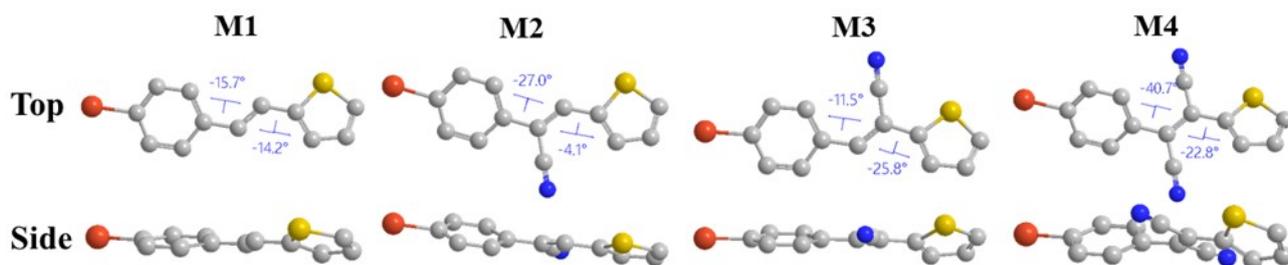


Fig. S1 Optimized geometries of M1~M4 predicted by DFT calculation.

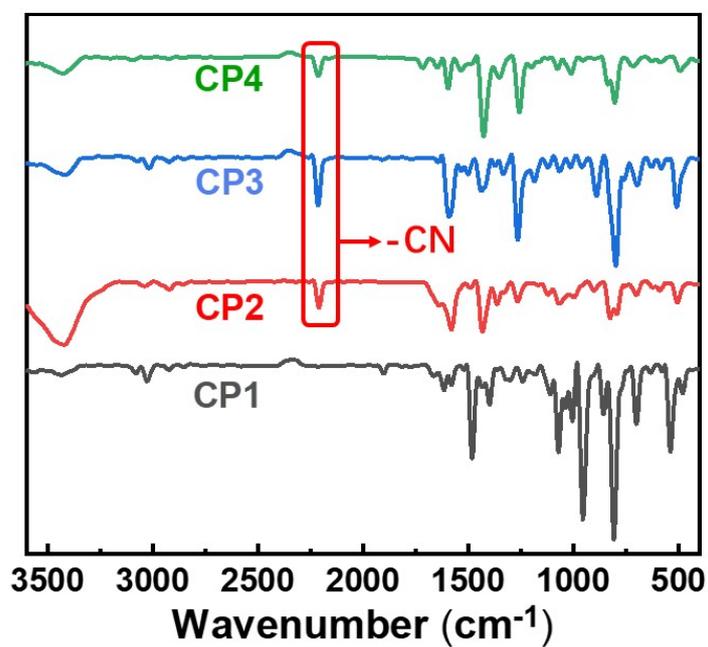


Fig. S2 FT-IR spectra of CP1-CP4

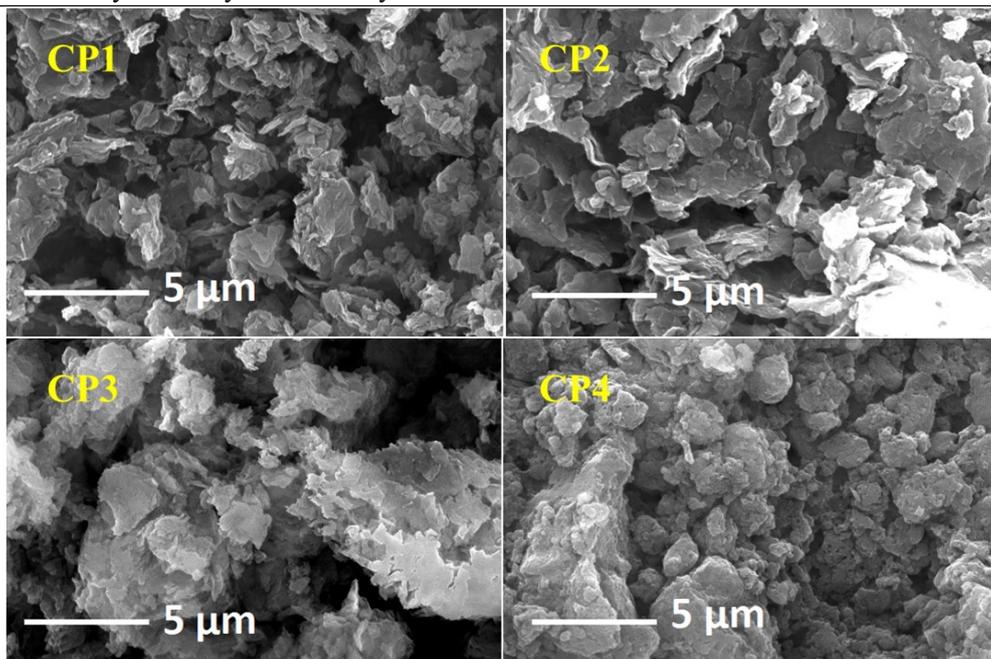


Fig. S3 SEM morphologies of CP1-CP4

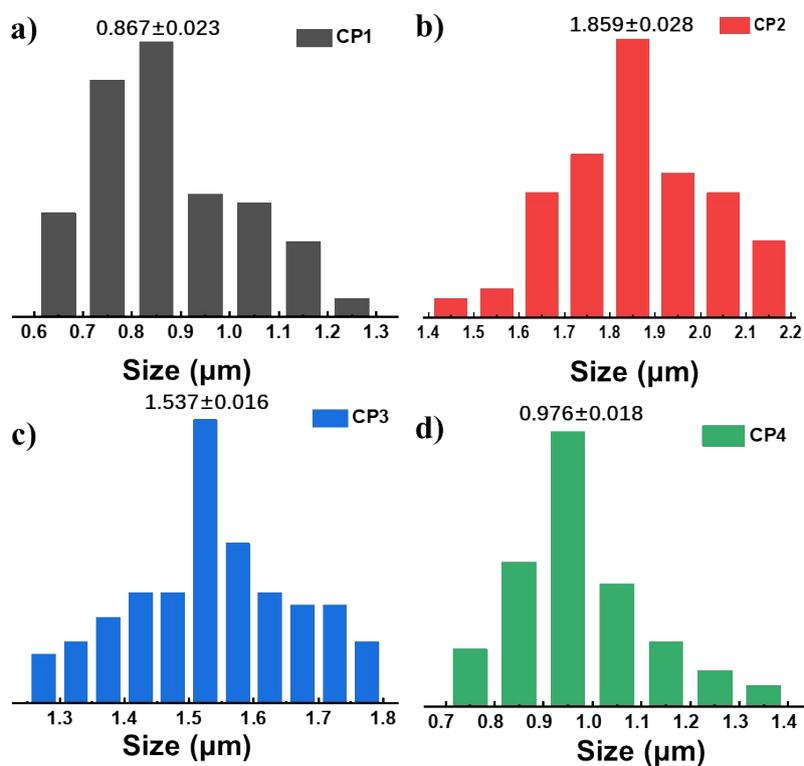


Fig. S4 Average particle sizes of CP1-CP4

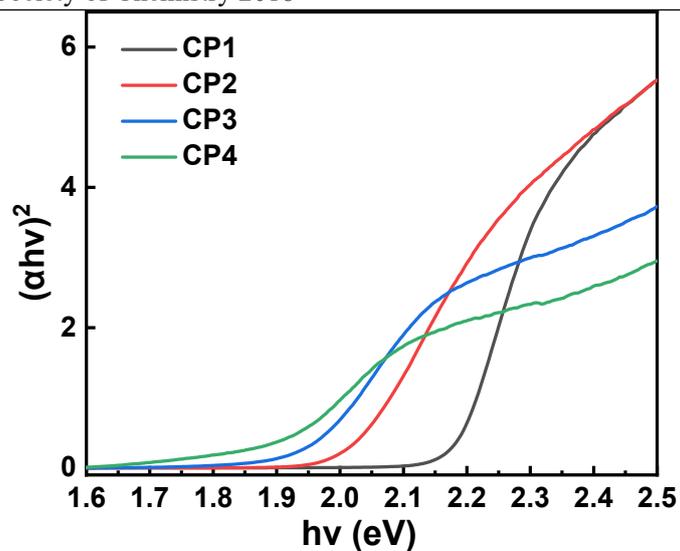


Fig. S5 Tauc plots of the transformed Kubelka–Munk function vs energy of CP1-CP4.

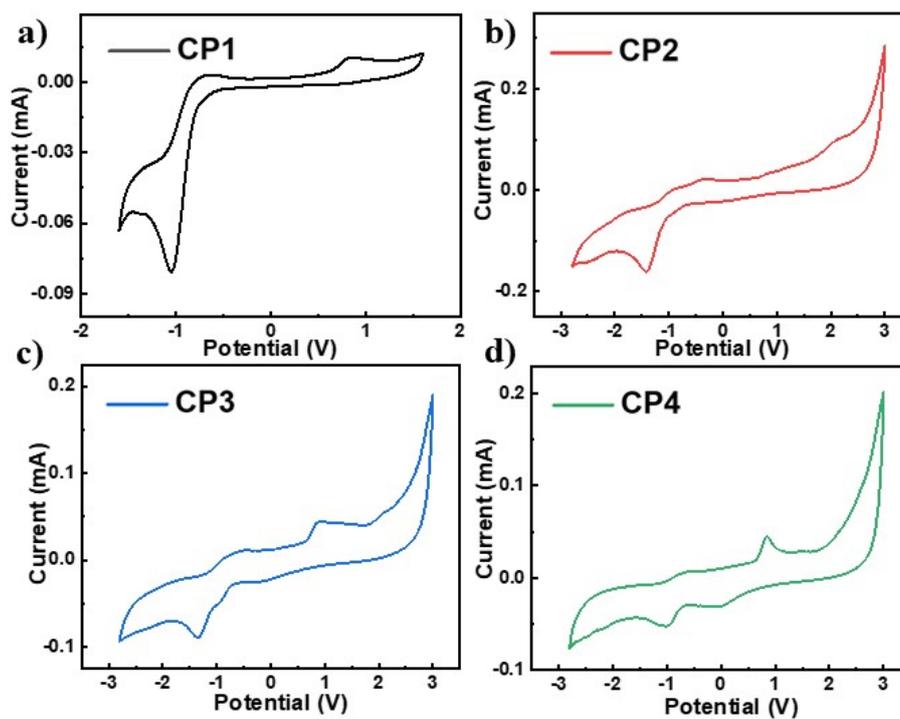


Fig. S6 CV curves of the as-prepared CP1-CP4.

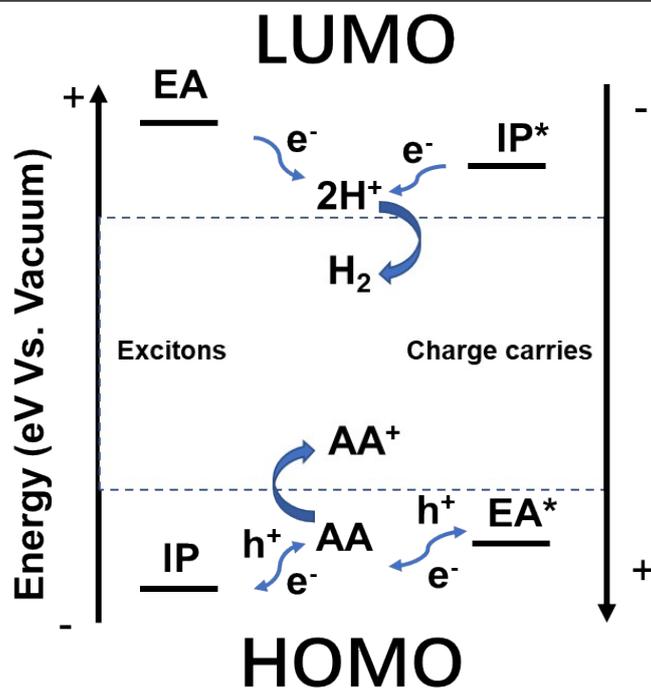


Fig. S7 Proposed mechanism of the photocatalytic reduction of proton using AA as SED

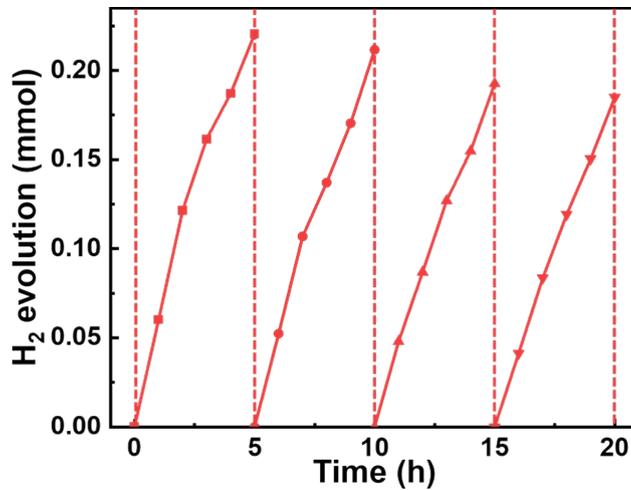


Fig. S8 PHP cycle test of CP2.

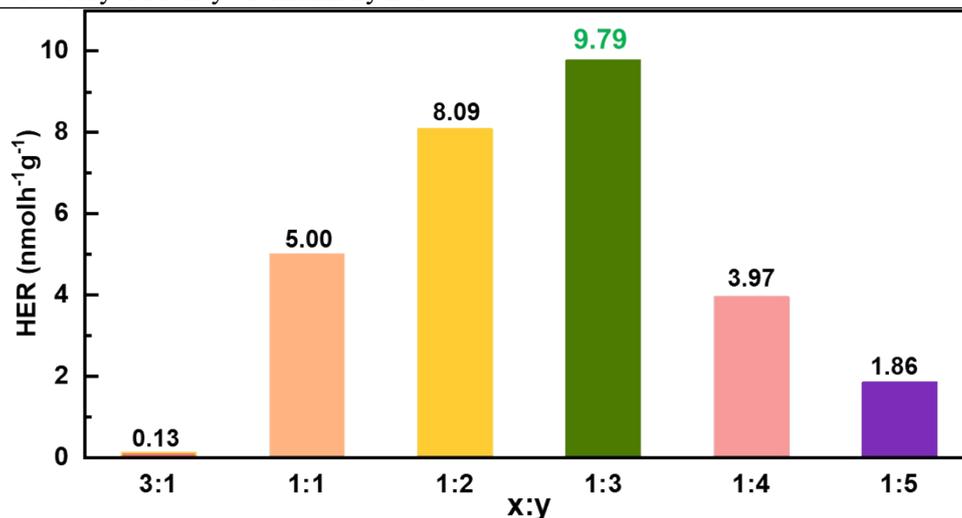


Fig. S9 HERs of the polymers obtained *via* co-polymerization between **M2** and **M4** at varied feed ratios.

Table S1 Summary of the PHP performances of the linear CPs.

Photocatalyst	Synthetic methods	Co-catalyst	SED	λ (nm) ^a	HER (mmol h ⁻¹ g ⁻¹)	Refs.
Co-polymerized CP	DArP	--	AA	>420	9.79	This work
P3HT	Yamamoto	Pt	Na ₂ S/ Na ₂ SO ₃	>400	0.005	S12
PFBT/CN	Suzuki	Pt	TEOA	>420	0.72	S13
P7-E	Sonogashira	--	TEOA	>420	6.02	S14
L-PDBT-O	Sonogashira	--	TEOA	>420	4.43	S15
Flu-SO	Suzuki	Pt	TEA	>420	5.04	S16
P10	Suzuki	--	TEA	>420	3.26	S17
CP4	DArP	--	AA	>420	0.17	S18
FSO-FS	Suzuki	--	TEOA	>420	3.40	S19
PyPm	Suzuki	Pt	TEOA	>300	0.37	S20
p-FuS	Suzuki	--	TEA	>420	5.88	S21
FSO-TPdT	Suzuki	Pt	TEOA	>420	7.39	S22
PEB-DBT-0.1PY	Sonogashira	--	TEOA	>420	0.54	S23

AA: ascorbic acid, SA: sodium ascorbate, TEOA: triethanolamine, and TEA: trimethylamine. ^a All light sources are 300 W Xe lamp.

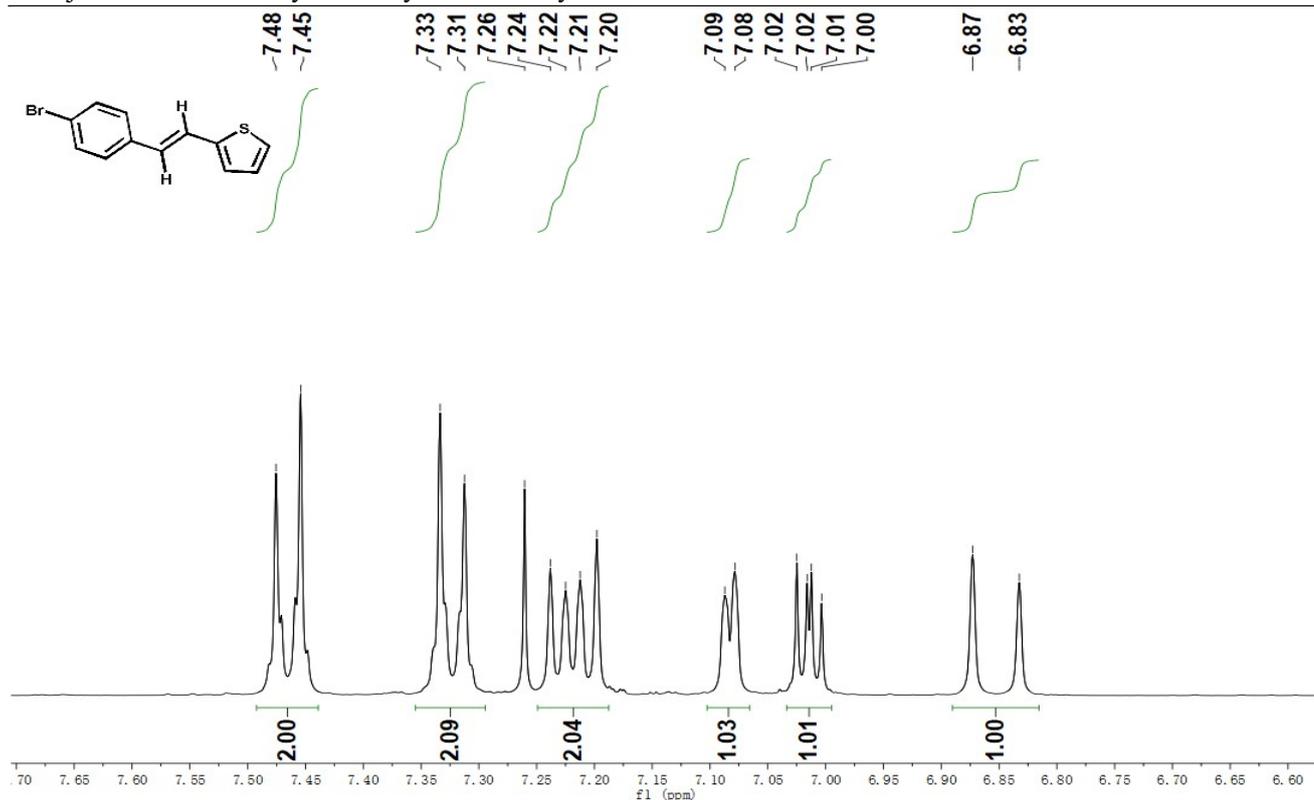


Figure S10 ^1H NMR spectrum of **M1** (400 MHz, CDCl_3)

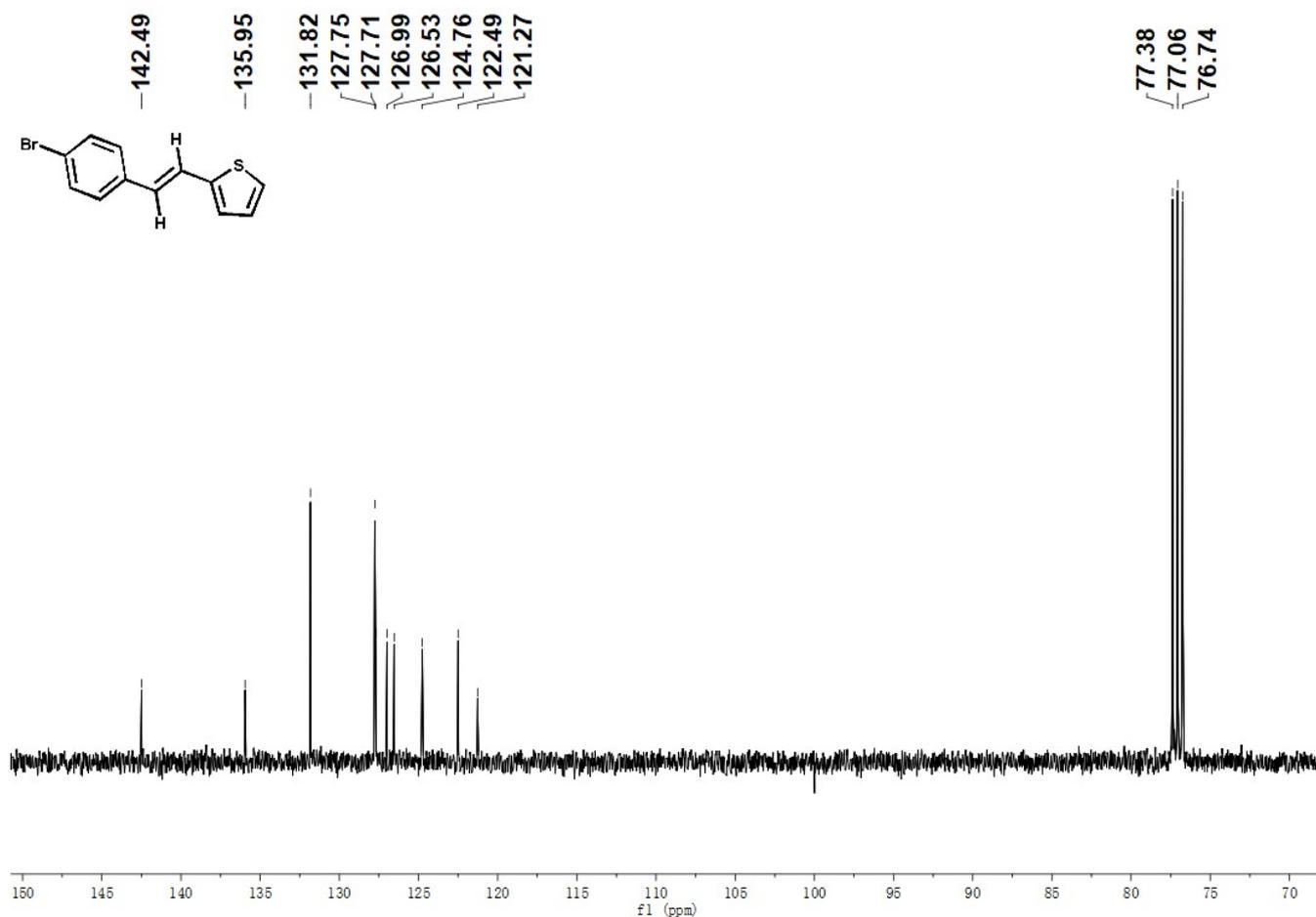


Figure S11 ^{13}C $\{^1\text{H}$ NMR $\}$ spectrum of **M1** (100 MHz, CDCl_3)

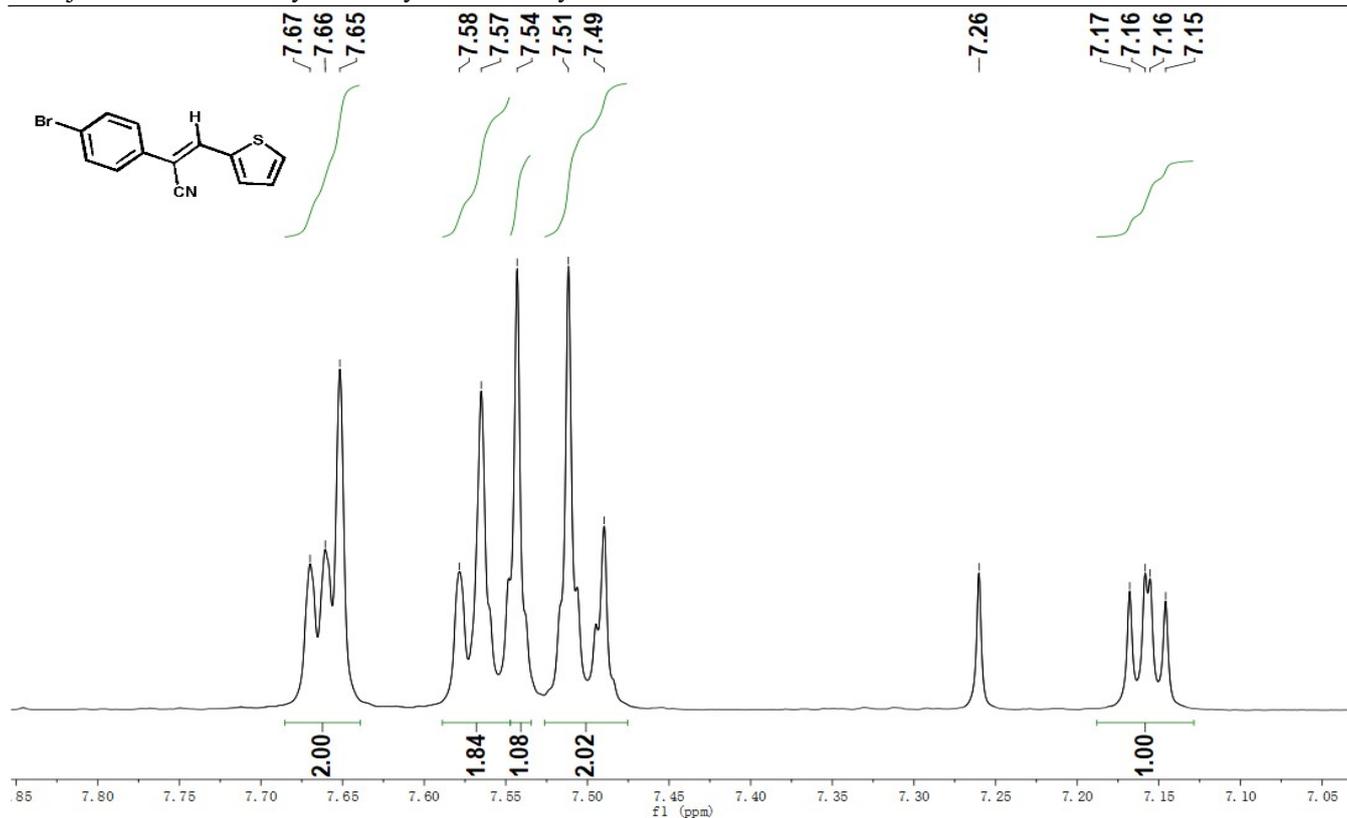


Figure S12 ¹H NMR spectrum of M2 (400 MHz, CDCl₃)

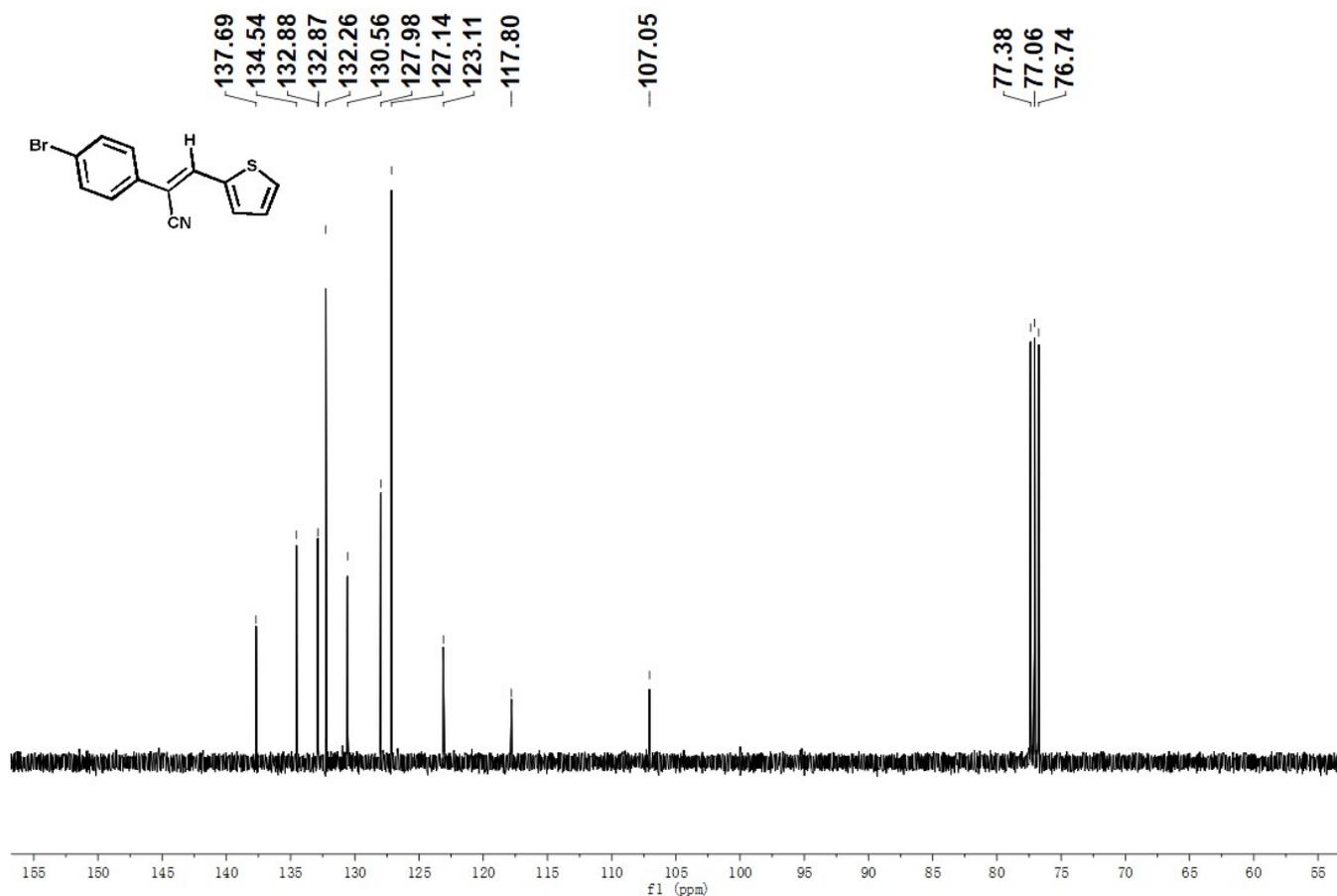
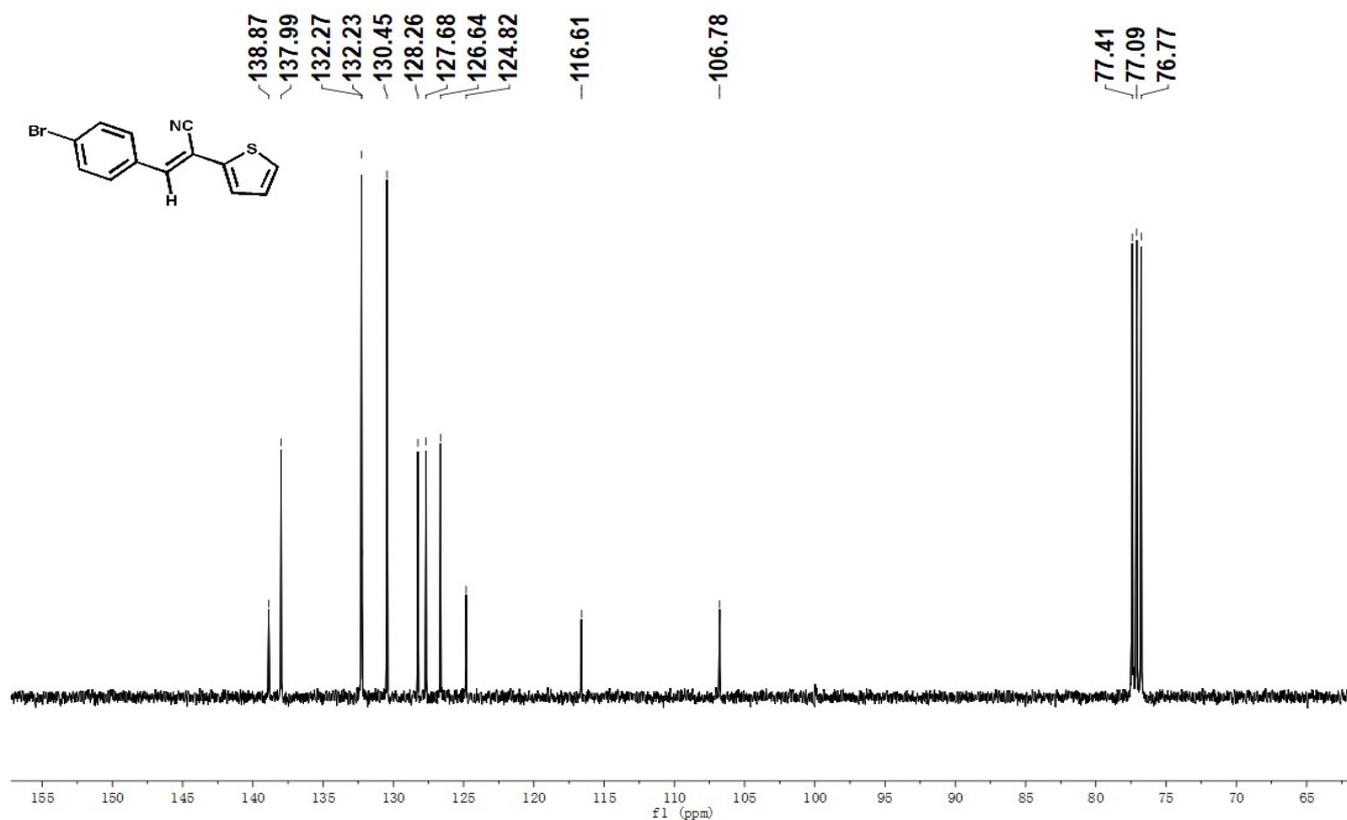
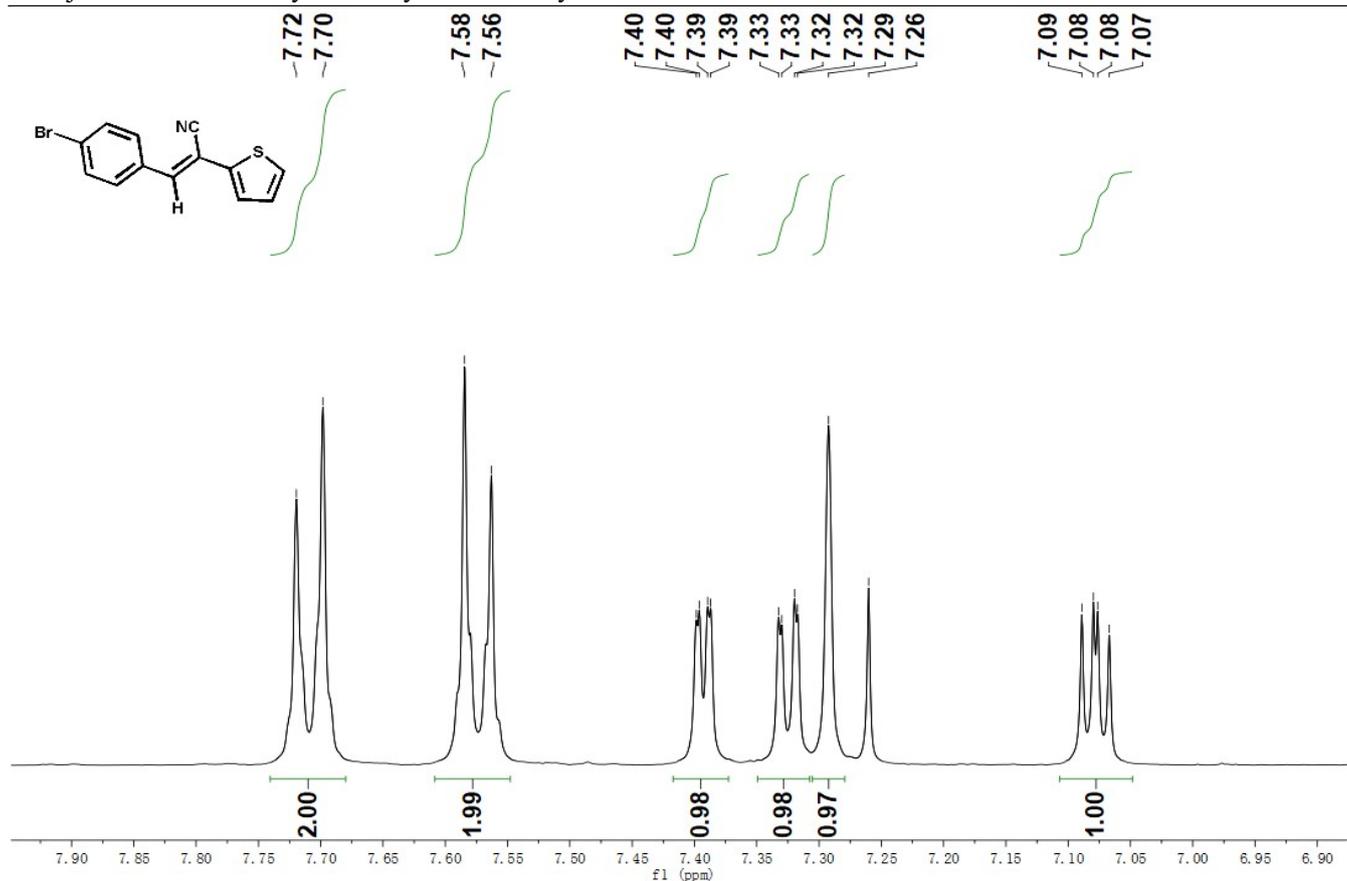


Figure S13 ¹³C {¹H NMR} spectrum of M2 (100 MHz, CDCl₃)



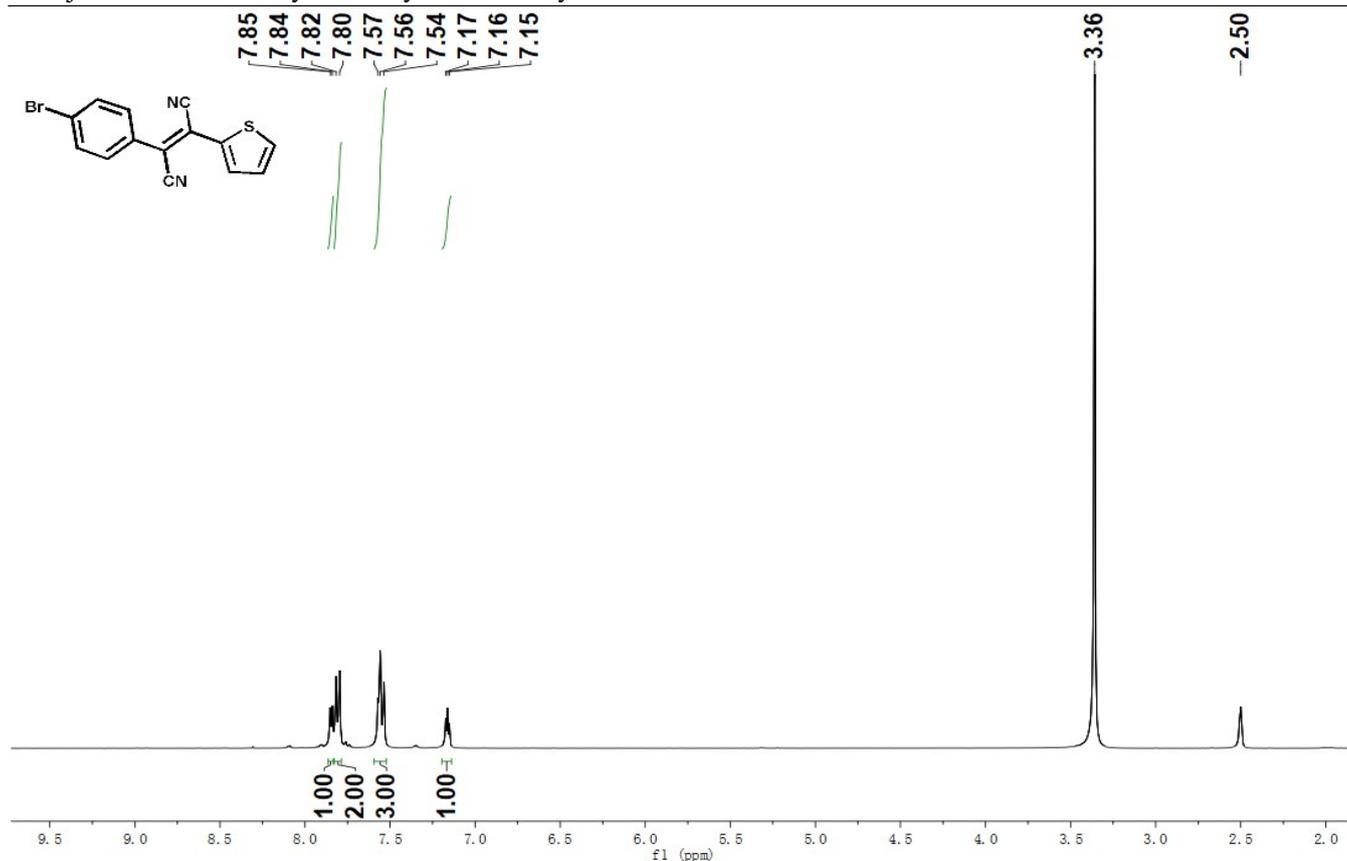


Figure S16 ^1H NMR spectrum of M4 (400 MHz, DMSO- d_6)

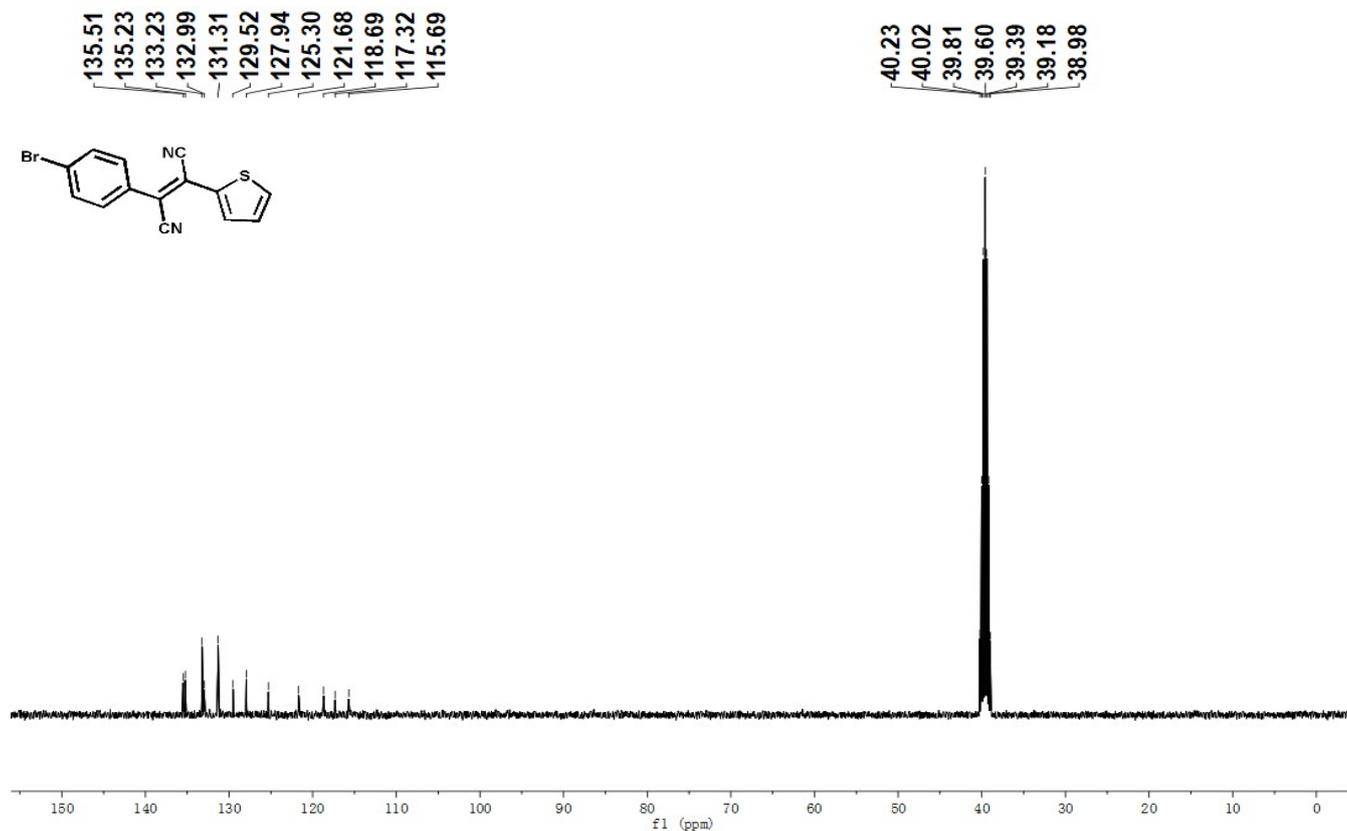


Figure S17 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of M4 (100 MHz, DMSO- d_6)

References

- S1. W. Fu, Y. Feng, Z. Fang, Q. Chen, T. Tang, Q. Yu and T. Tang, *Chem Commun*, 2016, **52**, 3115.
- S2. B. Li, B. Liu, Q. Li, H. Fang and M. Yu, *J. Chem. Res.*, 2010, **34**, 653.
- S3. Z. Lin, X. Liu, W. Zhang, J. Huang, Q. Wang, K. Shi, Z. Chen, Y. Zhou, L. Wang and G. Yu, *Macromolecules*, 2018, **51**, 966.
- S4. C. Lu, M. Ye, L. Long, Y. Zheng, J. Liu, Y. Zhang and Z. Chen, *J Org Chem*, 2022, **87**, 1545.
- S5. Z. R. Tan, Y.Q. Xing, J. Z. Cheng, G. Zhang, Z. Q. Shen, Y. J. Zhang, G. Liao, L. Chen and S. Y. Liu, *Chem. Sci.*, 2022, **13**, 1725.
- S6. SHELXTL Reference Manual, version 5, Siemens Energy & Automation Inc., Madison, WI, 1994.
- S7. M. J. Frisch, *et al.* Gaussian 09 (Revision D.01) I. Gaussian, Wallingford, CT, 2013.
- S8. Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* 2008, **41**(2), 157.
- S9. D. Jacquemin, E. A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.* 2010, **6**, 2071.
- S10. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
- S11. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* 2011, **32**, 1456.
- S12. H. J. Yan, Y. Huang, *Chem. Commun*, 2011, **47**, 4168.
- S13. J. Chen, C. L. Dong, D. Zhao, Y. C. Huang, X. X. Wang, L. Samad, L. N. Dang, M. Shearer, S. H. Shen, L. J. Guo, *Adv. Mater.* 2017, 1606198.
- S14. X. H. Zhang, X. P. Wang, J. Xiao, S. Y. Wang, D. K. Huang, X. Ding, Y. G. Xiang, H. Chen, *J. Catal*, 2017, **350**, 64.
- S15. X. P. Wang, B. Chen, W. B. Dong, X. H. Zhang, Z. B. Li, Y. G. Xiang and H. Chen, *Macromol. Rapid Commun*, 2018, 1800494.
- S16. C. H. Dai, S. D. Xu, W. Liu, X. Z. Gong, M. Panahandeh-Fard, Z. T. Liu, D. Q. Zhang, C. Xue, K. P. Loh, and B. Liu, *Small*, 2018, 1801839.
- S17. M. Sachs, R. S. Sprick, D. Pearce, S. A. J. Hillman, A. Monti, A. A. Y. Guilbert, Nick J. Brownbill, S. Dimitrov, X. Y. Shi, F. Blanc, M. A. Zwijnenburg, J. Nelson, J. R. Durrant, A. I. Cooper, *Nature Communications*, 2018, **9**, 4968.
- S18. W. Huang, Z. Shen, J. Cheng, L. Liu, K. Yang, X. Chen, H. Wen and S. Liu, *J. Mater. Chem. A*, 2019, **7**, 24222.
- S19. Z. A. Lan, G. G. Zhang, X. Chen, Y. F. Zhang, K. A. I. Zhang, X. C. Wang, *Angew. Chem. Int. Ed.*, 2019, **58**, 10236.
- S20. Z. J. Wang, N. Mao, Y. B. Zhao, T. J. Yang, F. Wang, J. X. Jiang, *Polymer Bulletin*, 2019, **76**, 3195.
- S21. Y. Bai, D. C. J. Woods, L. Wilbraham, C. M. Aitchison, M. A. Zwijnenburg, R. S. Sprick, A. I. Cooper, *J. Mater. Chem. A*, 2020, **8**, 8700.
- S22. R. K. Chen, P. W. Hu, Y. X. Xian, X. H. Hu, G. B. Zhang, *Macromol. Rapid Commun*, 2022, **43**, 2100872.
- S23. J. Xiao, Z. H. Xiao, J. H. Hu, X. F. Gao, M. Asim, L. Pan, C. X. Shi, X. W. Zhang, J. J. Zou, *Macromolecules*, 2022, **55**, 5412.