Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information for

Recyclable Mechanoluminescent Luminogen: Different Polymorphs, Different Self-Assembly Effect of Thiophene Moiety and Recovered Molecular Packing via Simple Thermal-Treatment

Can Wang[a], Yun Yu[a], Zhaofei Chai[a], Fangdi He[a], Chaozheng Wu[a], Yanbin Gong[a], Mengmeng Han[a], Qianqian Li[a], and Zhen Li*[a,b]

[a] Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University Wuhan, 430072, China.

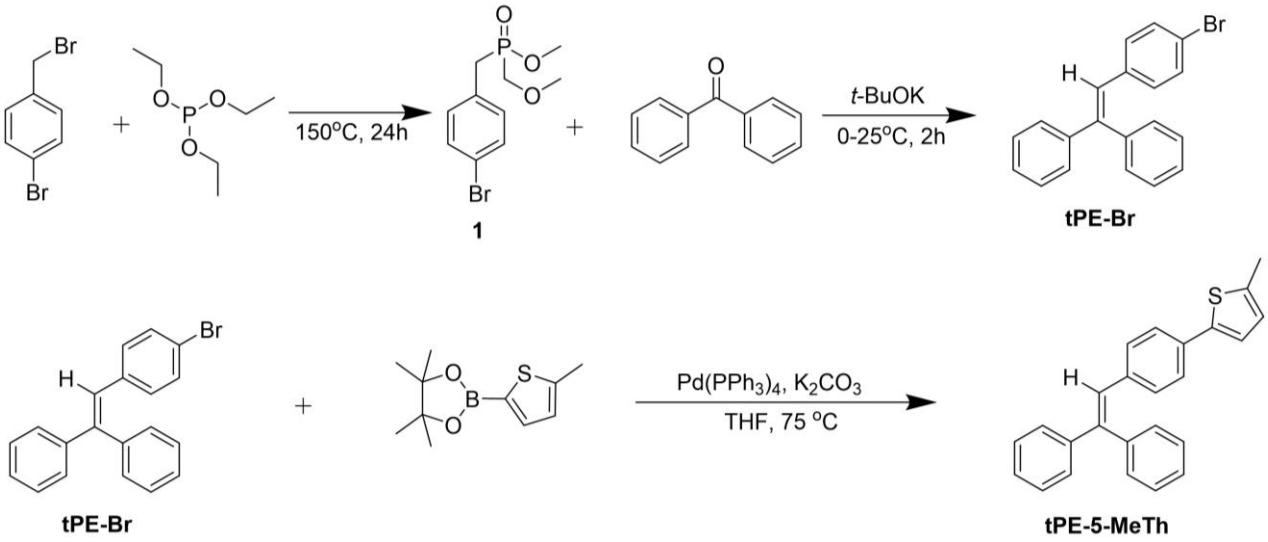
E-mail: lizhen@whu.edu.cn, lichemlab@163.com

Fax: +86-27-68755767

[b] Institute of Molecular Aggregation Science, Tianjin University, Tianjin 300072, China

Keywords： recyclability, mechanoluminescence, packing mode, self-assembly, thermal-treatment

Table of Contents



Scheme S1. The synthetic route of tPE-5-MeTh.

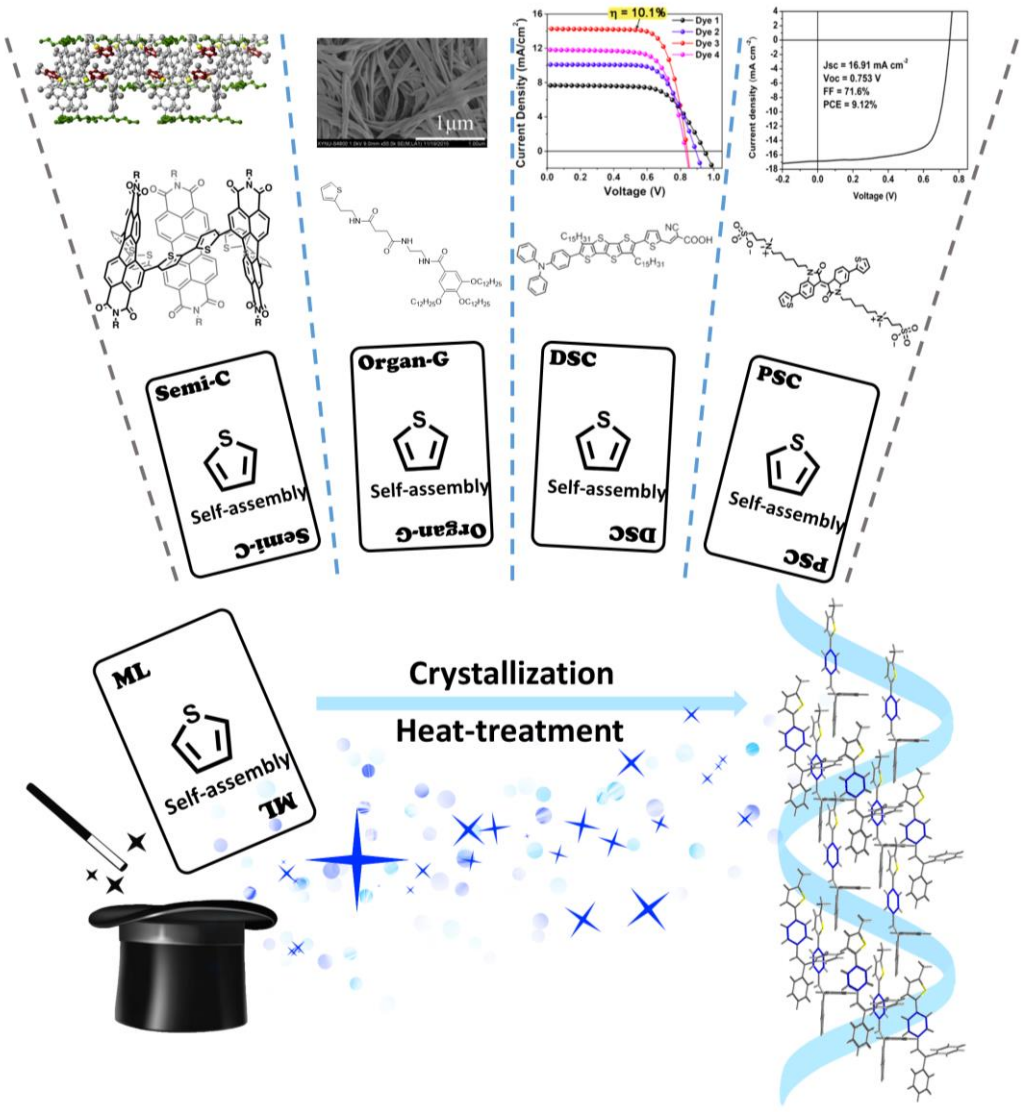


Chart S1. Different researches using the thiophene derivatives as the self-assembly unit with the ordered packing mode.

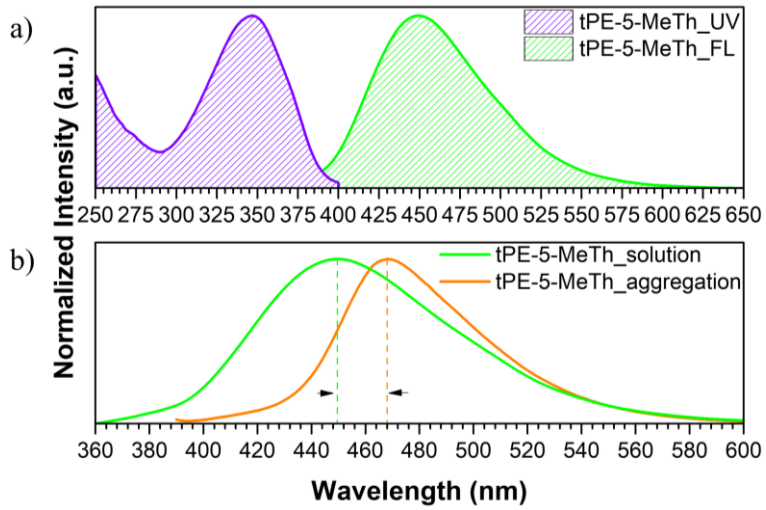


Figure S1. a) UV-vis spectrum (violet) and PL spectrum (green) of tPE-5-MeTh in dilute THF solution. b) PL spectra of tPE-5-MeTh in aggregation state (orange). Excitation wavelength: 343 nm (solution) and 376 nm (aggregation). Concentration: 10^{-5} M.

Table S1. The culturing in different solvents for the single crystal.

No.	Content (mg)	solvents	polymorphs
1	50	Recrystallization in different solvents	Crystal-P2
2	20	CH_2Cl_2/CH_3OH (rt)	Crystal-P2
3	20	$CHCl_3/CH_3OH$ (rt)	Crystal-P1/P2
4	20	acetone/CH_3OH (rt)	Crystal-P1
5	20	CH_2Cl_2/CH_3OH (30 °C)	Crystal-P1/P2
6	20	$CHCl_3/CH_3OH$ (30 °C)	Crystal-P1
7	20	acetone/CH_3OH (30 °C)	Crystal-P1

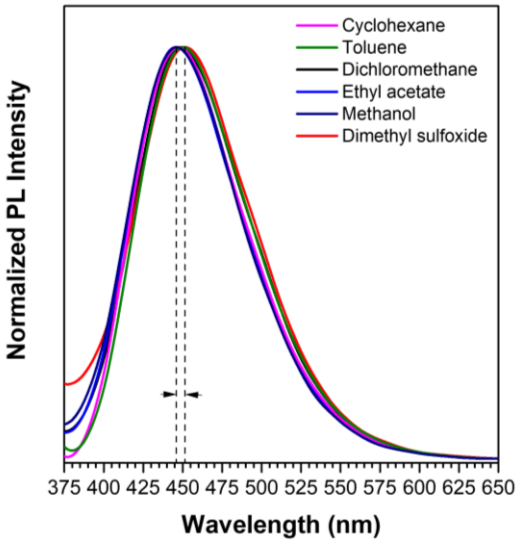


Figure S2. PL spectra of tPE-5-MeTh in organic solvents with different polarities. Excitation wavelength: 343 nm. Concentration: 10^{-5} M.

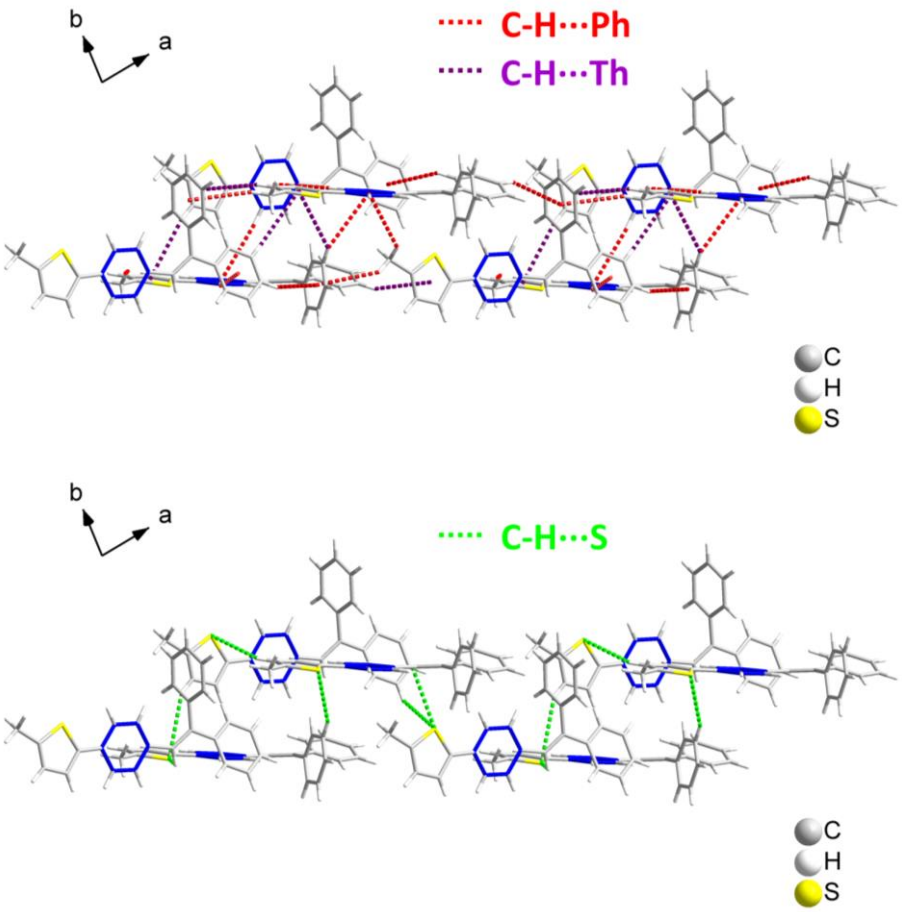


Figure S3. The intermolecular hydrogen bonds including C-H···π (red/violet lines) and C-H···S (green lines) interactions in Crystal-P1 (eight molecules).

Table S2. Summarization of the C-H…π interactions in Crystal-P1.

Type of Interaction	Orientation of Interaction		d /Å [a]	Number	A /º [b]
Intermolecular [c]	1	C-H…Ph	3.097	1	156.536(520)
	2	C-H…Ph	3.107	1	156.896(520)
	3	C-H…Ph	3.237	1	176.953(610)
	4	C-H…Ph	3.248	1	176.710(610)
	5	C-H…Ph	3.301	1	152.205(117)
	6	C-H…Ph	3.312	1	127.528(101)
	7	C-H…Ph	3.372	1	150.251(964)
	8	C-H…Ph	3.385	1	149.886(964)
	9	C-H…Ph	3.393	1	143.806(909)
	10	C-H…Ph	3.398	2	147.227(741)
	11	C-H…Ph	3.398	1	175.070(551)
	12	C-H…Ph	3.422	1	174.861(551)
	13	C-H…Ph	3.458	2	129.698(737)
	14	C-H…Ph	3.460	1	131.991(720)
	15	C-H…Ph	3.465	1	138.330(720)
	16	C-H…Ph	3.524	2	135.503(688)
	1	C-H…Th [d]	3.251	1	148.349(995)

	2	C-H…Th	3.277	2	149.700(736)
	3	C-H…Th	3.355	2	139.714(800)
	4	C-H…Th	3.488	2	152.073(937)
	5	C-H…Th	3.541	2	139.232(711)

[a] Distance of H…benzene ring. [b] Angel of C-H…benzene/C-H…thiophene ring interaction. [c] Intermolecular hydrogen bond interaction. [d] C-H…thiophene ring interaction.

Table S3. Summarization of the C-H…S interactions in Crystal-P1.

Type of Interaction	Orientation of Interaction		d /Å [a]	Number	A /º [b]
Intermolecular [c]	1	C-H…S	3.173	1	131.939(861)
	2	C-H…S	3.413	2	147.114(737)
	3	C-H…S	3.424	1	101.336(640)
	4	C-H…S	3.513	2	151.860(917)
	5	C-H…S	3.525	2	104.995(522)
	6	C-H…S	3.590	2	153.440(705)

[a] Distance of H…S. [b] Angel of C-H…S interaction. [c] Intermolecular hydrogen bond interaction.

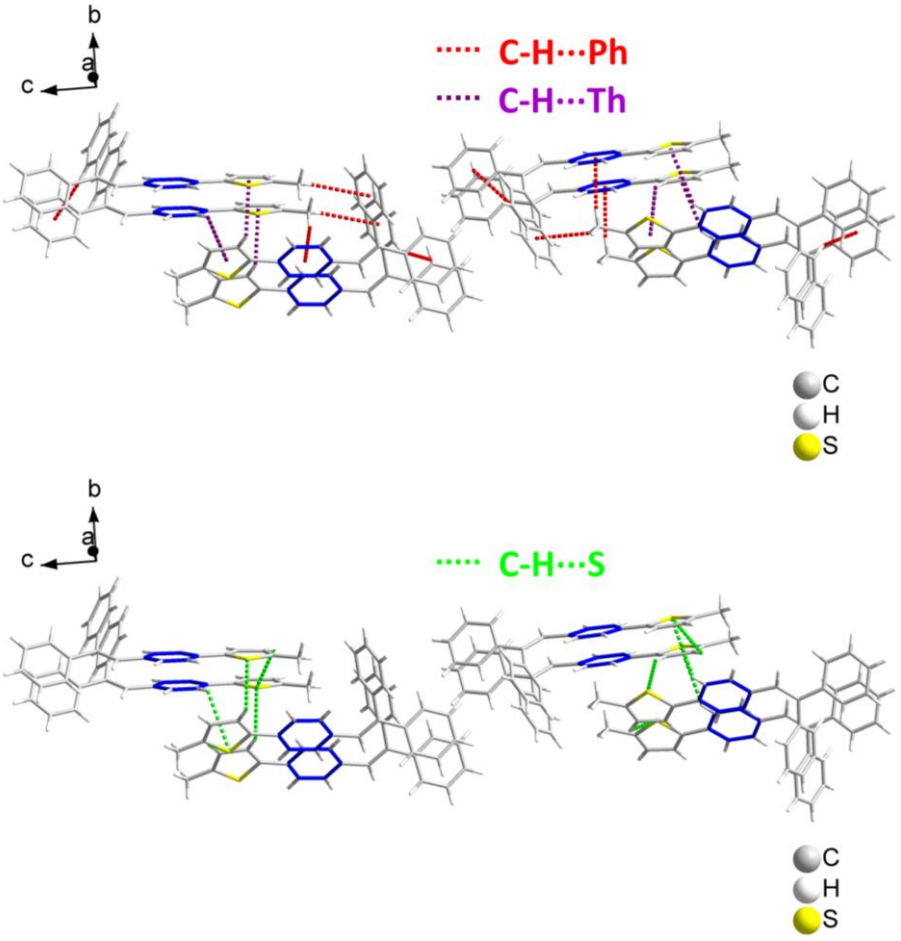


Figure S4. The intermolecular hydrogen bonds including C-H···π (red/violet lines) and C-H···S (green lines) interactions in Crystal-P2 (eight molecules).

Table S4. Summarization of the C-H…π interactions in Crystal-P2.

Type of Interaction	Orientation of Interaction		d /Å [a]	Number	A /º [b]
Intermolecular [c]	1	C-H…Ph	2.911	1	159.425(615)
	2	C-H…Ph	2.917	2	159.304(615)
	3	C-H…Ph	3.408	1	144.613(373)
	4	C-H…Ph	3.421	2	144.644(373)
	5	C-H…Ph	3.426	1	144.792(373)
	6	C-H…Ph	3.471	2	152.717(512)
	7	C-H…Ph	3.487	1	152.510(512)
	1	C-H…Th [d]	2.985	3	129.726(256)
	2	C-H…Th	3.122	3	137.611(305)

[a] Distance of H…benzene ring. [b] Angel of C-H…benzene/C-H…thiophene ring interaction. [c] Intermolecular hydrogen bond interaction. [d] C-H…thiophene ring interaction.

Table S5. Summarization of the C-H…S interactions in Crystal-P2.

Type of Interaction	Orientation of Interaction		d /Å [a]	Number	A /º [b]
Intermolecular [c]	1	C-H…S	3.089	3	148.333(252)
	2	C-H…S	3.521	4	110.647(604)
	3	C-H…S	3.531	3	117.948(321)

[a] Distance of H…S. [b] Angel of C-H…S interaction. [c] Intermolecular hydrogen bond interaction.

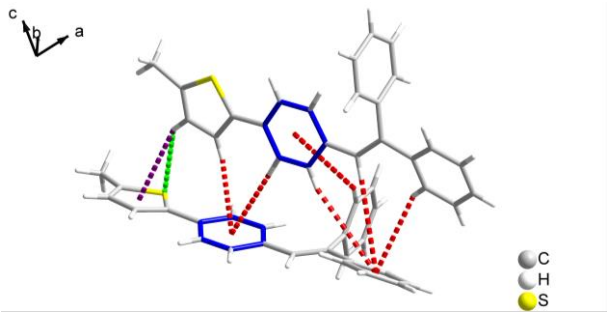


Figure S5. The intermolecular hydrogen bonds including C-H···π (red/violet lines) and C-H···S (green lines) interactions in Crystal-P1 (two molecules).

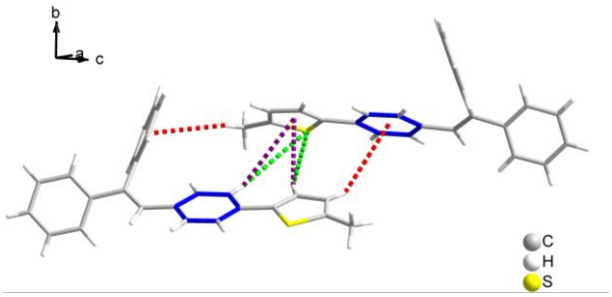


Figure S6. The intermolecular hydrogen bonds including C-H···π (red/violet lines) and C-H···S (green lines) interactions in Crystal-P2 (two molecules).

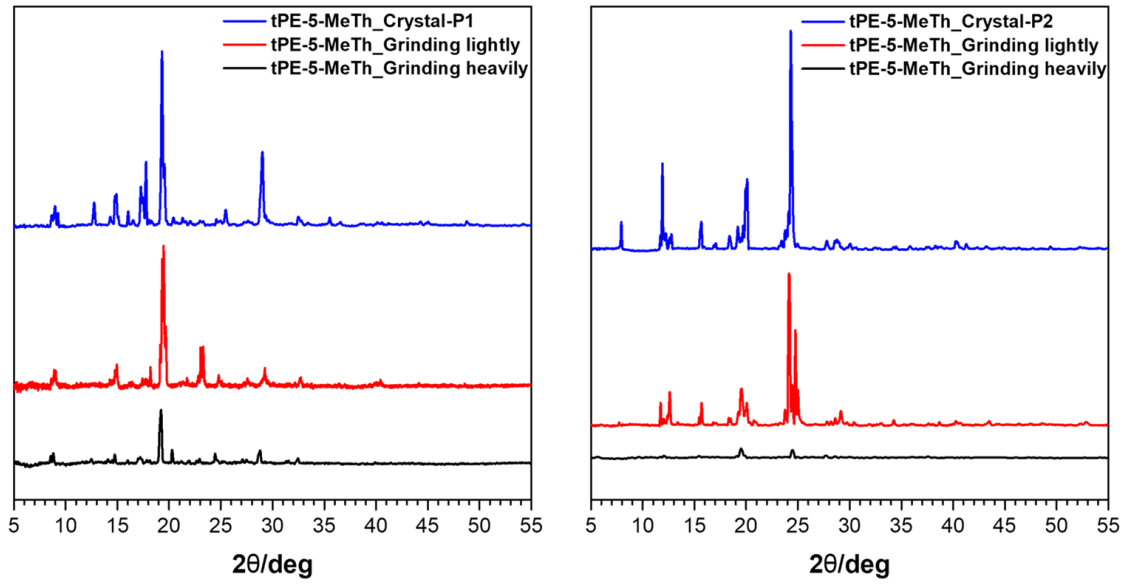


Figure S7. PXRD patterns of crystalline polymorph in different phases.

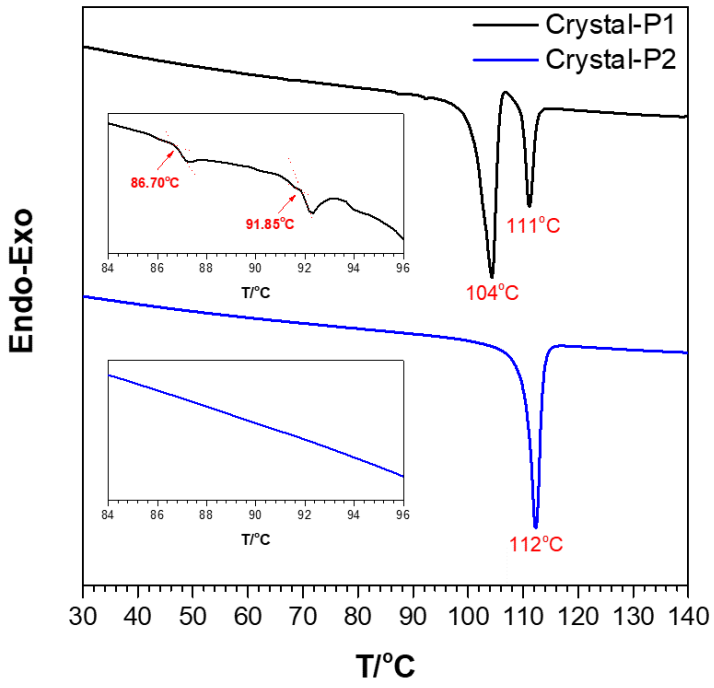


Figure S8. DSC curves of crystalline polymorph in different phases.

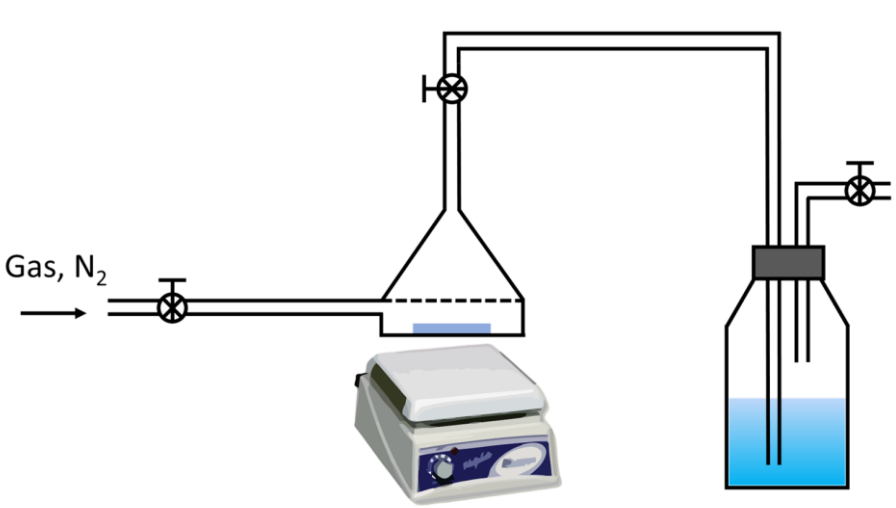


Figure S9. Experimental setup for the heating process under the blowing of dry N_2.

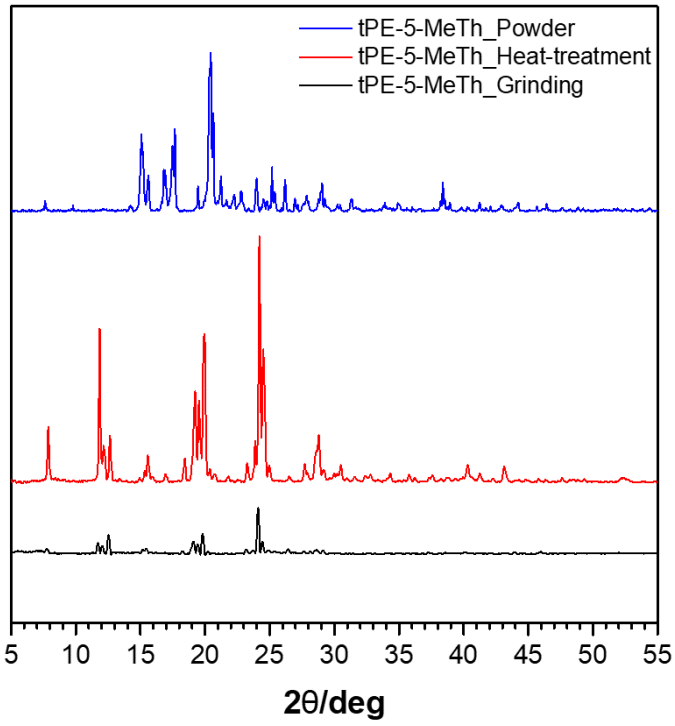


Figure S10. PXRD patterns of thermal-treatment in each step for heating temperature over 95 ^{o}C.

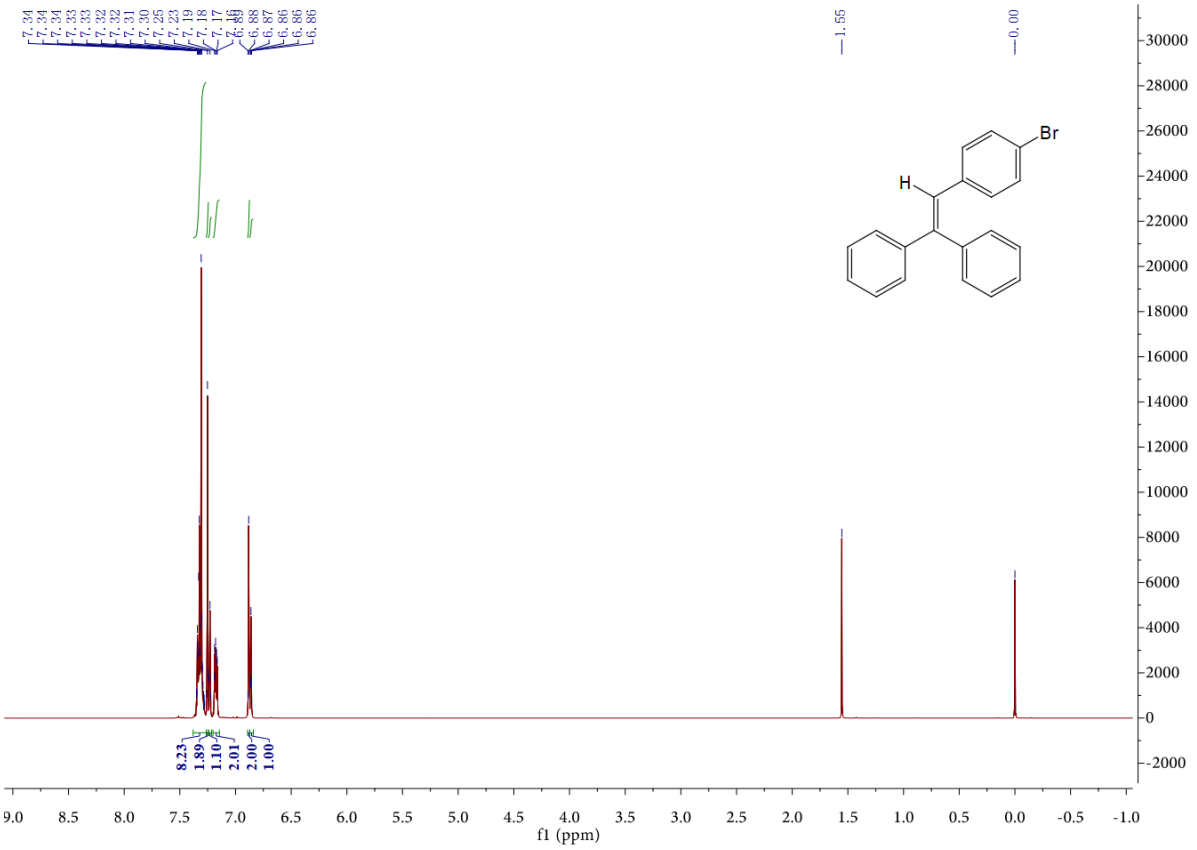


Figure S11. The ^{1}H NMR spectrum of as prepared **tPE-Br**.

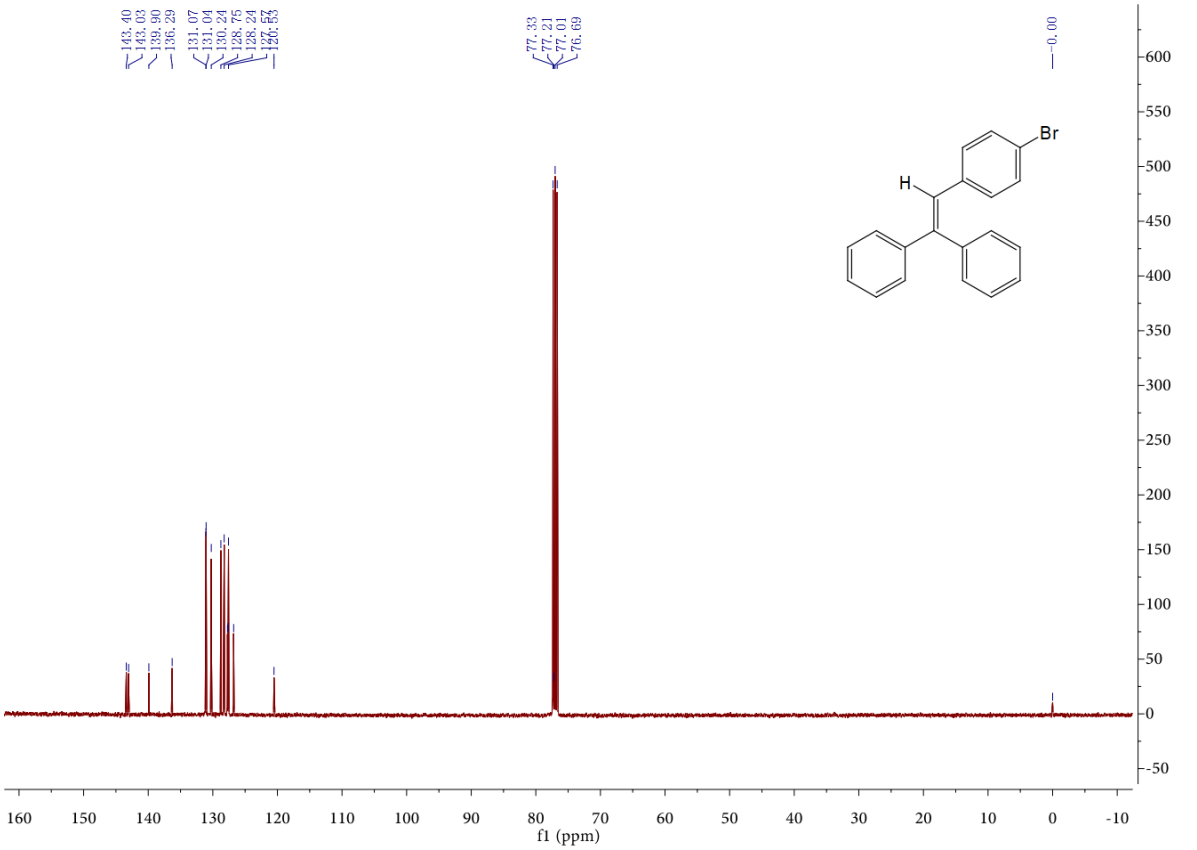


Figure S12. The ^{13}C NMR spectrum of as prepared **tPE-Br**.

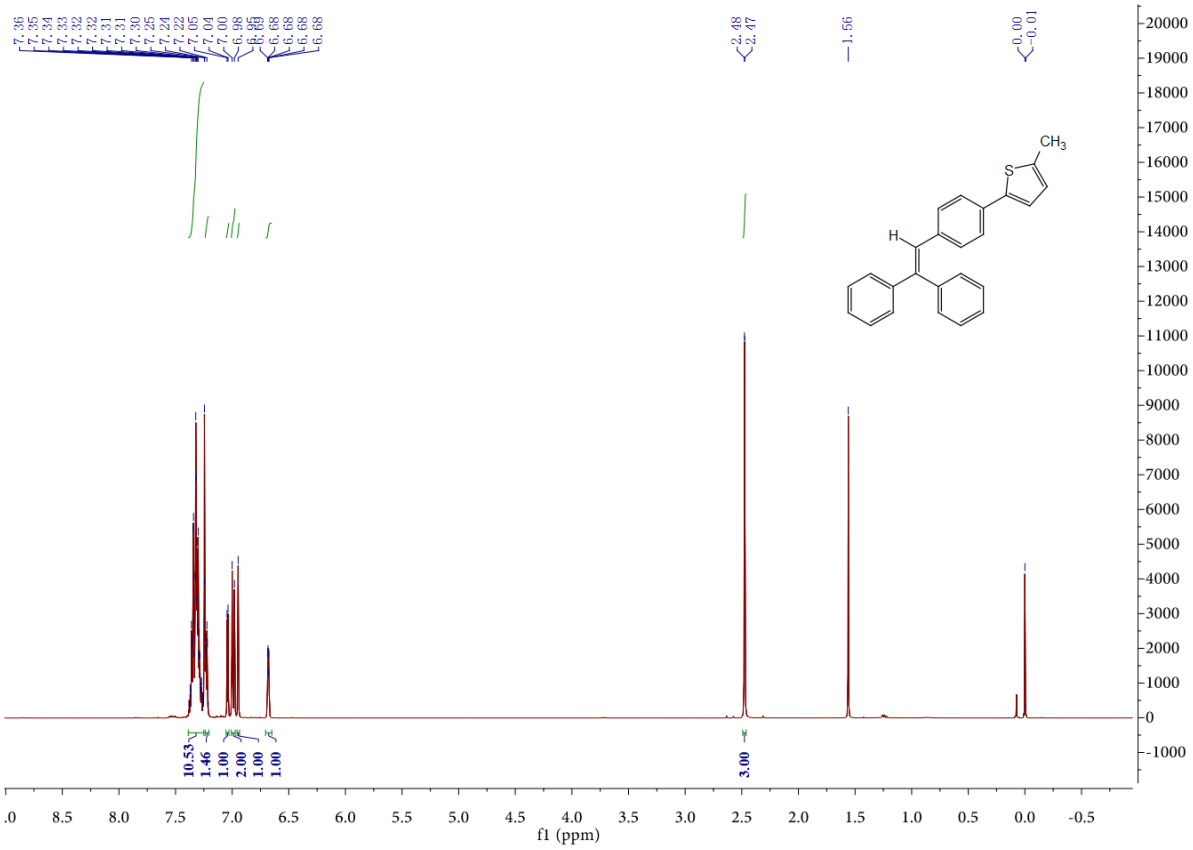


Figure S13. The ^{1}H NMR spectrum of as prepared **tPE-5-MeTh**.

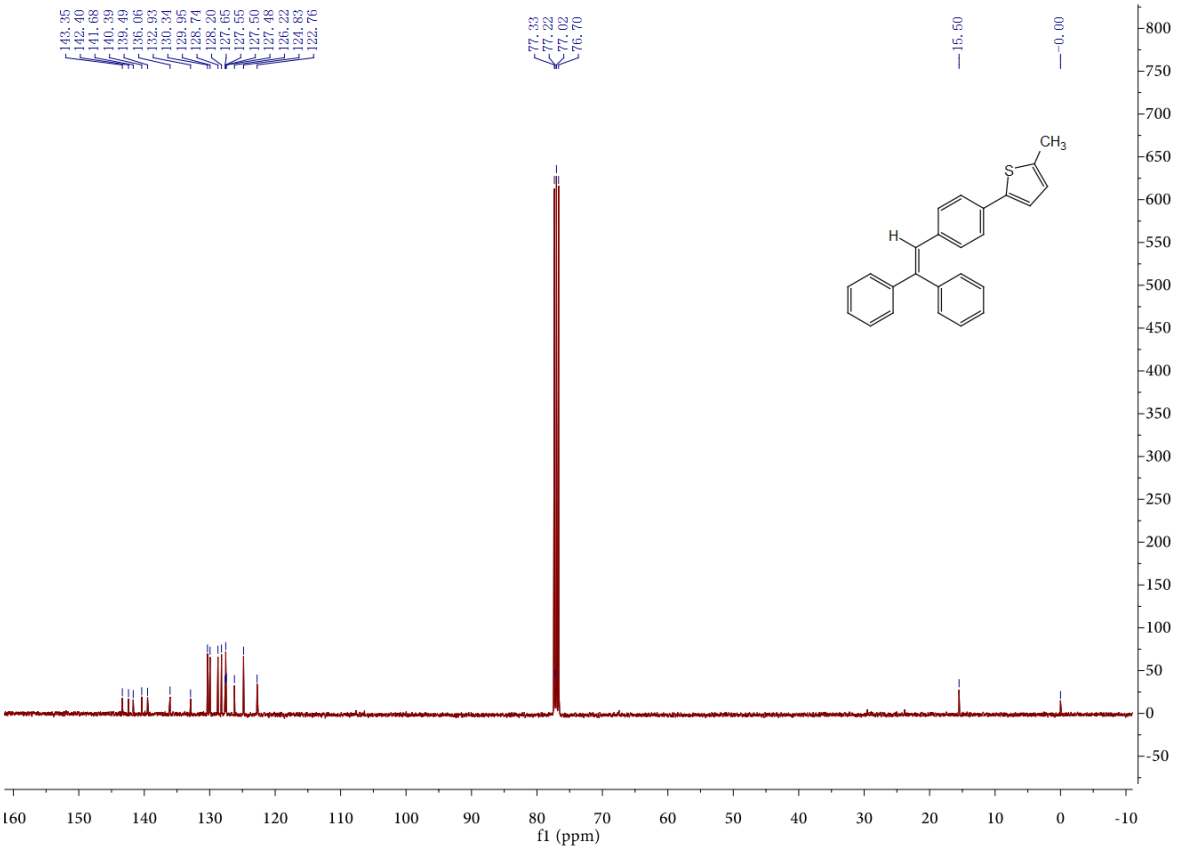


Figure S14. The ^{13}C NMR spectrum of as prepared **tPE-5-MeTh**.

Table S6. Structural data crystal of Crystal-P1 and Crystal-P2.

Name	Crystal-P1	Crystal-P2
Empirical formula	$C_{25}H_{20}S$	$C_{25}H_{20}S$
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	P1	$P2_12_12_1$
Unit cell Angles (^{o})	α = 64.477(7) β = 78.704(7) γ = 77.452(8)	α = 90 β = 90 γ = 90
Unit cell lengths (Å)	a = 8.886(4) b = 10.971(5) c = 11.261(5)	a = 5.988(3) b = 7.360(4) c = 45.02(2)
Unit cell volume (Å^3)	960.5(7)	1984.3(17)
Z	2	4
Density (mg/m^3)	1.219	1.180
F(000)	372	744
CCDC number	1846930	1846929

Reference

1. C. Zheng, Q. Zang, H. Nie, W. Huang, Z. Zhao, A. Qin, R. Hu, B. Z. Tang, *Mater. Chem. Front.*, 2018, **2**, 180-188.

2. X. Ye, Y. Liu, Y. Lv, G. Liu, X. Zheng, Q. Han, K. A. Jackson, X. Tao, *Angew. Chem.*, 2015, **127**, 8087-8091.