A TCBD-based AB_2-type Second-order Nonlinear Optical Hyperbranched Polymer Prepared by a Facile Click-type Postfunctionalization

Xiaobo Zang,[a, b] Hongtao Liu,[a] Qianqian Li,[c] Zhong'an Li[a, b*] and Zhen Li[c, d*]

[a] Key Laboratory for Material Chemistry of Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China. E-mail: lizha@hust.edu.cn

[b] Shenzhen Institute of Huazhong University of Science and Technology, Shenzhen 518000, P. R. China

[c] Department of Chemistry, Sauvage Center for Molecular Sciences, Wuhan University, Wuhan, 430072, P. R. China. E-mail: lizhen@whu.edu.cn

[d] Institute of Molecular Aggregation Science, Tianjin University, Tianjin 300072, P. R. China.

Table S1. Elemental analysis results.[a]

No.	N[%]	C[%]	H[%]
HP1	2.27 (2.57)	65.58 (74.84)	4.27 (4.99)
HP2	5.90 (7.99)	63.56 (71.97)	5.23 (6.33)
HP3	6.24 (/)	61.21 (/)	5.30 (/)

[a] The theoretical EA values of **HP1** and **HP2** are listed in brackets for comparison, except **HP3** due to the uncertainty of the exact ratio of TCBD groups. Note: A large deviation between experimental and theoretical data has been obtained. Bases on the data of DSC measurements, we attribute the deviation to the occurring of the cross-linking for **HP1** at 132 °C, while at 190 °C for **HP2** and **HP3**, which would make the HPs more thermally stable and thus lead to a large deviation for EA results.

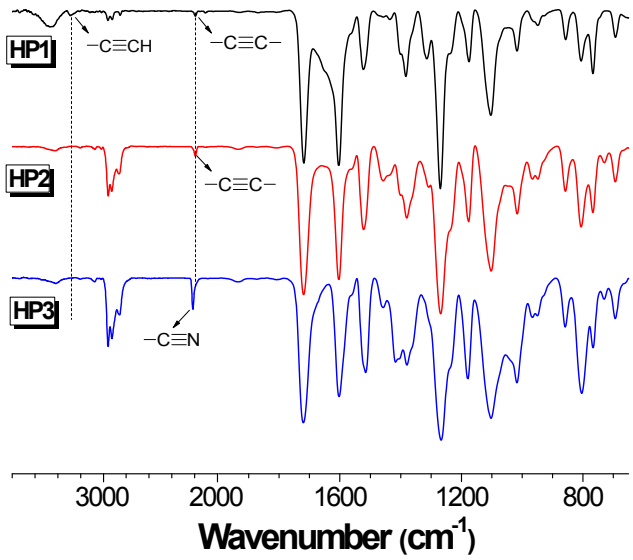


Fig. S1 FT-IR spectra of **HP1-HP3**.

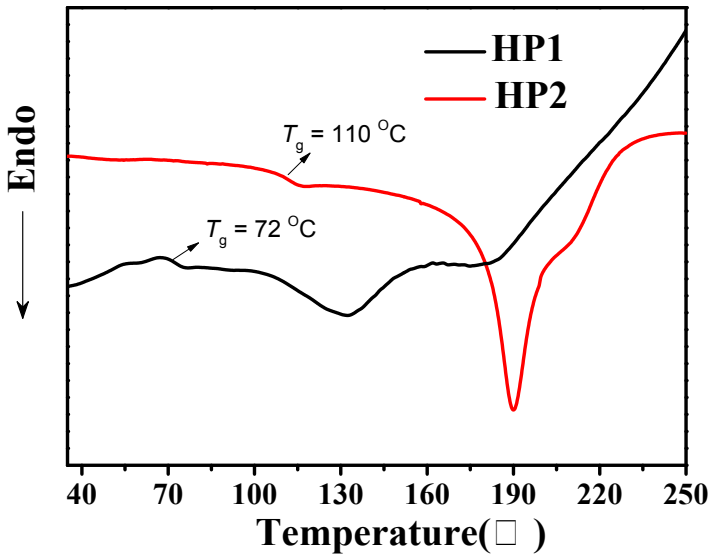


Fig. S2 DSC curves of **HP1-HP2** measured under nitrogen at a heating rate of 10 °C/min.

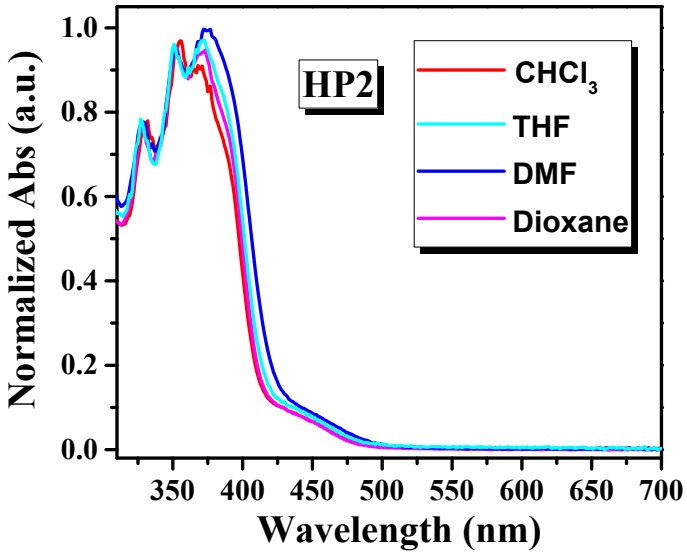
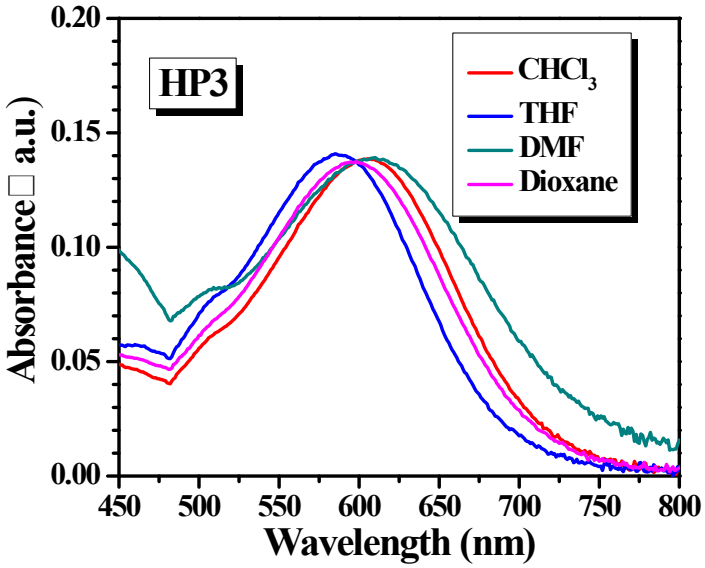


Fig. S3 Solution absorption spectra of **HP2** in different solvents.



Solvents	THF	Dioxane	$CHCl_3$	DMF
λ_{max}	587 nm	598 nm	608 nm	610 nm

Fig. S4 Solution absorption spectra of **HP3** in different solvents, with the absorption maxima listed in Table.

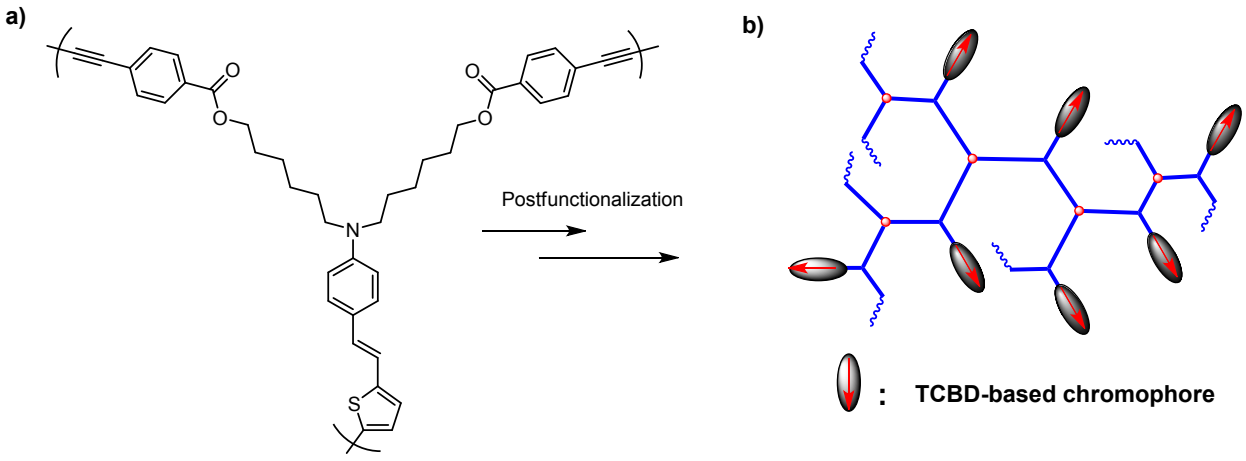


Fig. S5. Proposed two design strategies for improving the NLO effects of TCBD-based hyperbranched polymers.

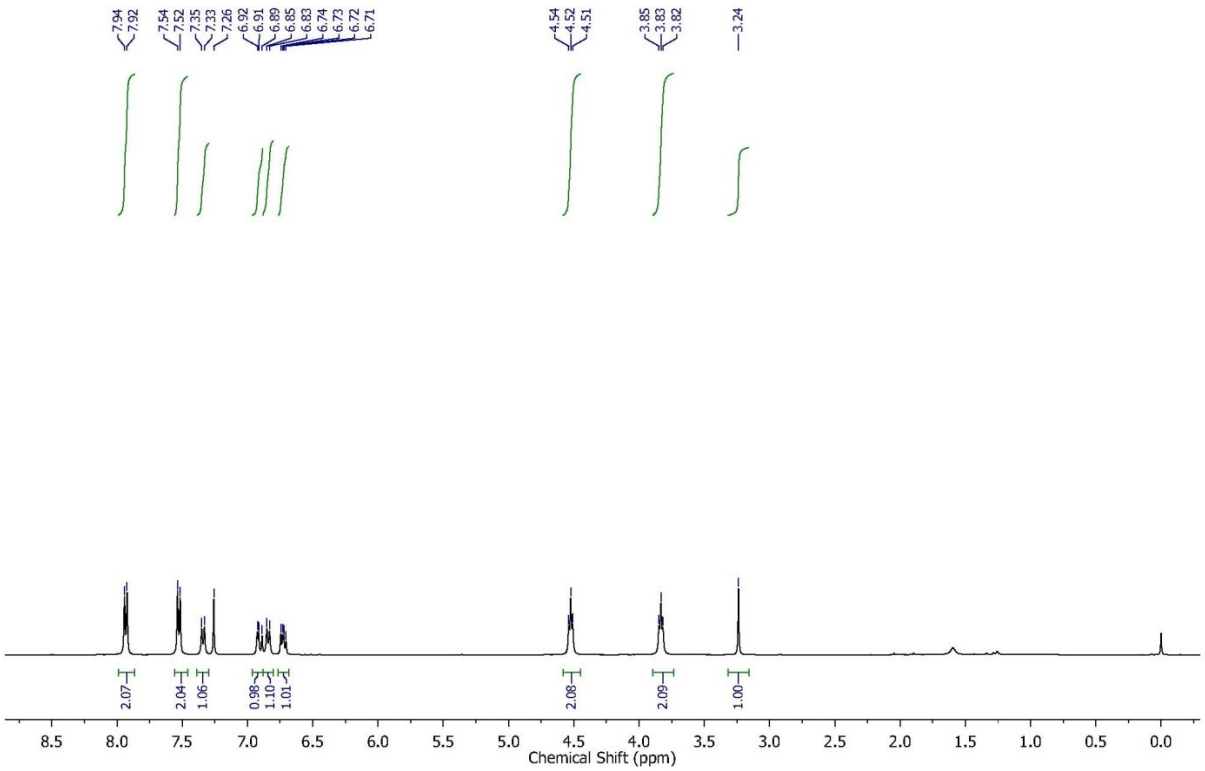


Fig. S6 ^{1}H NMR spectrum of monomer **3** conducted in $CDCl_3$.

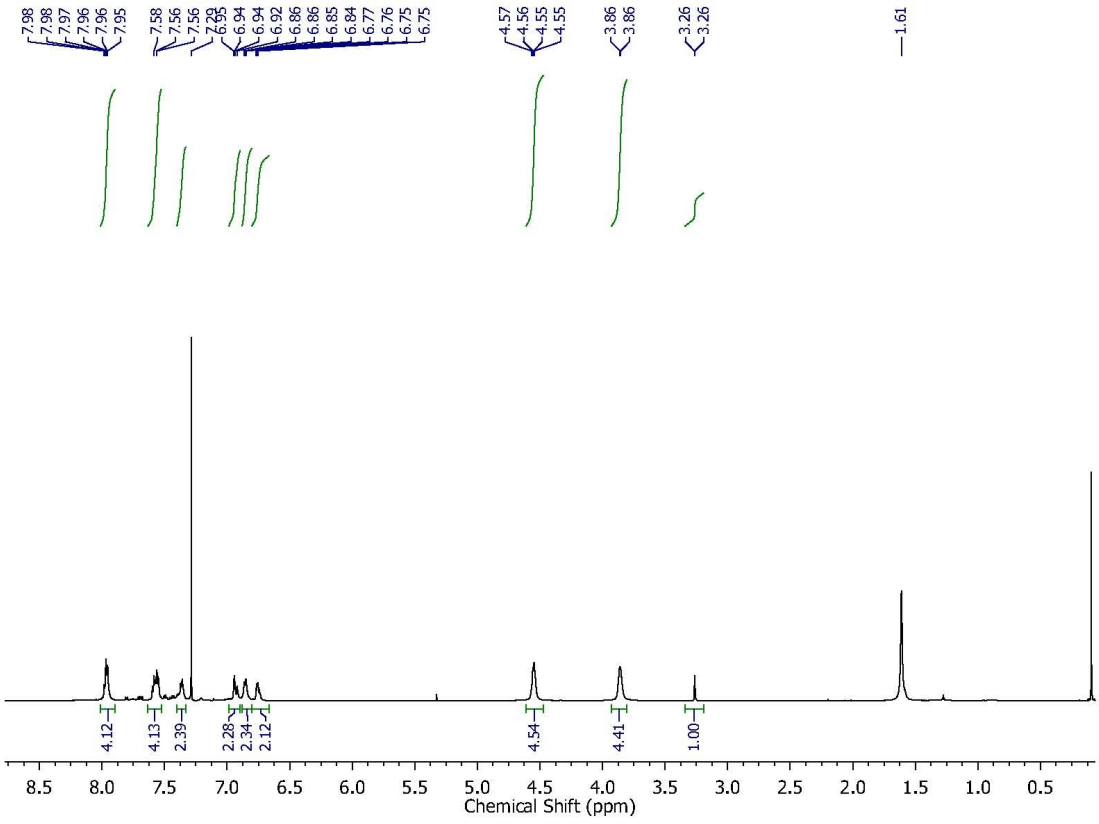


Fig. S7 ^{1}H NMR spectrum of **HP1** conducted in $CDCl_3$.

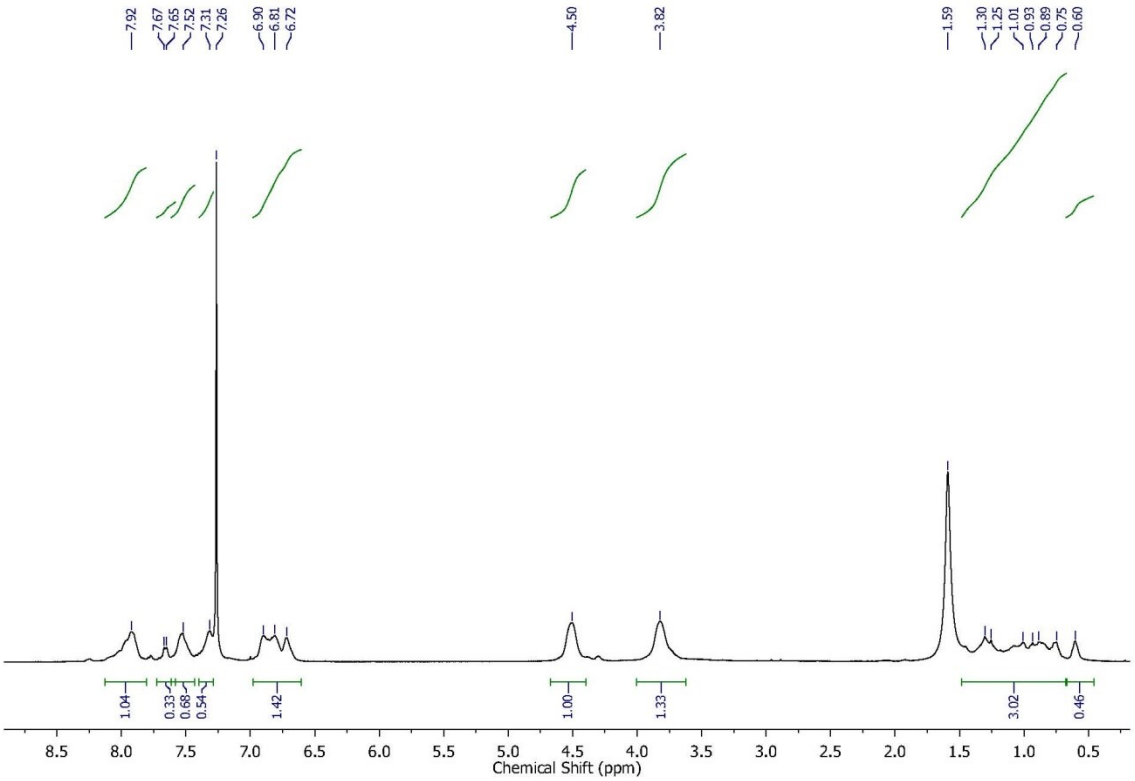


Fig. S8 ^{1}H NMR spectrum of **HP2** conducted in $CDCl_3$.

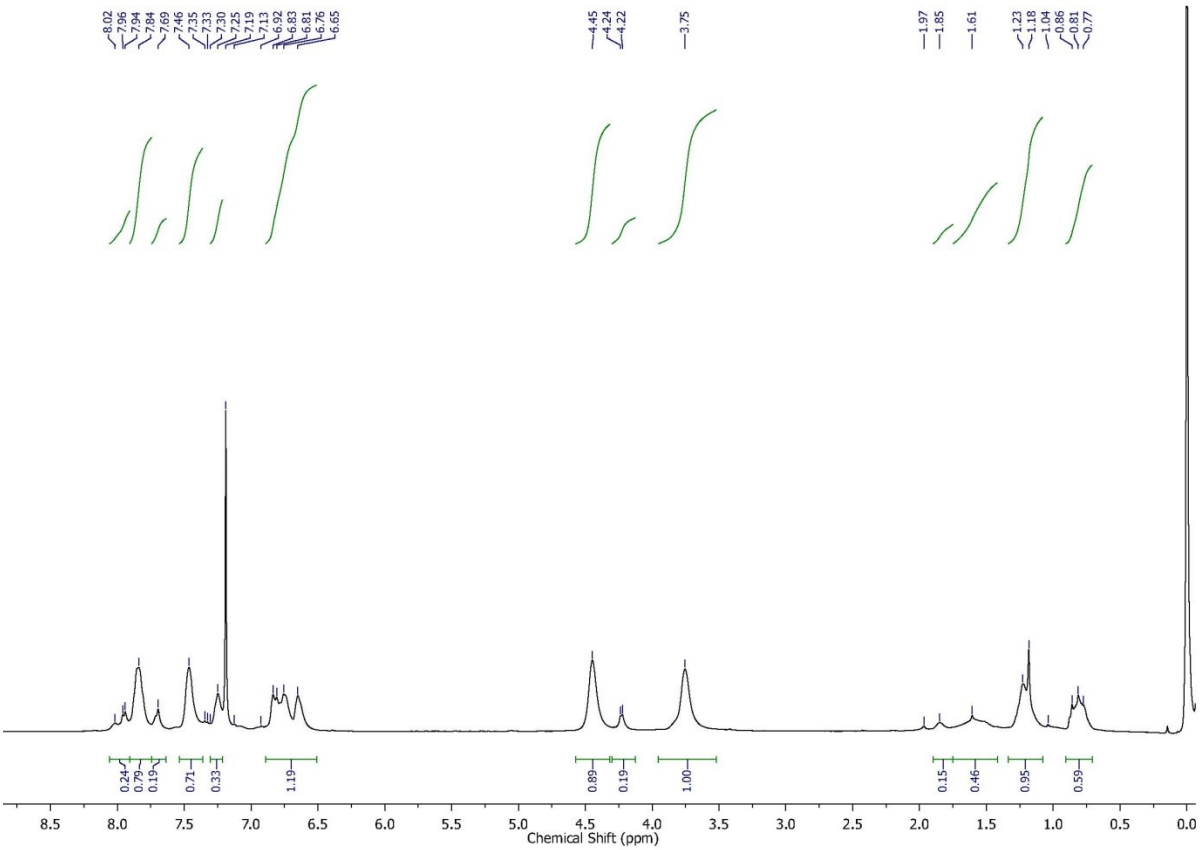


Fig. S9 ^{1}H NMR spectrum of **HP3** conducted in $CDCl_3$.

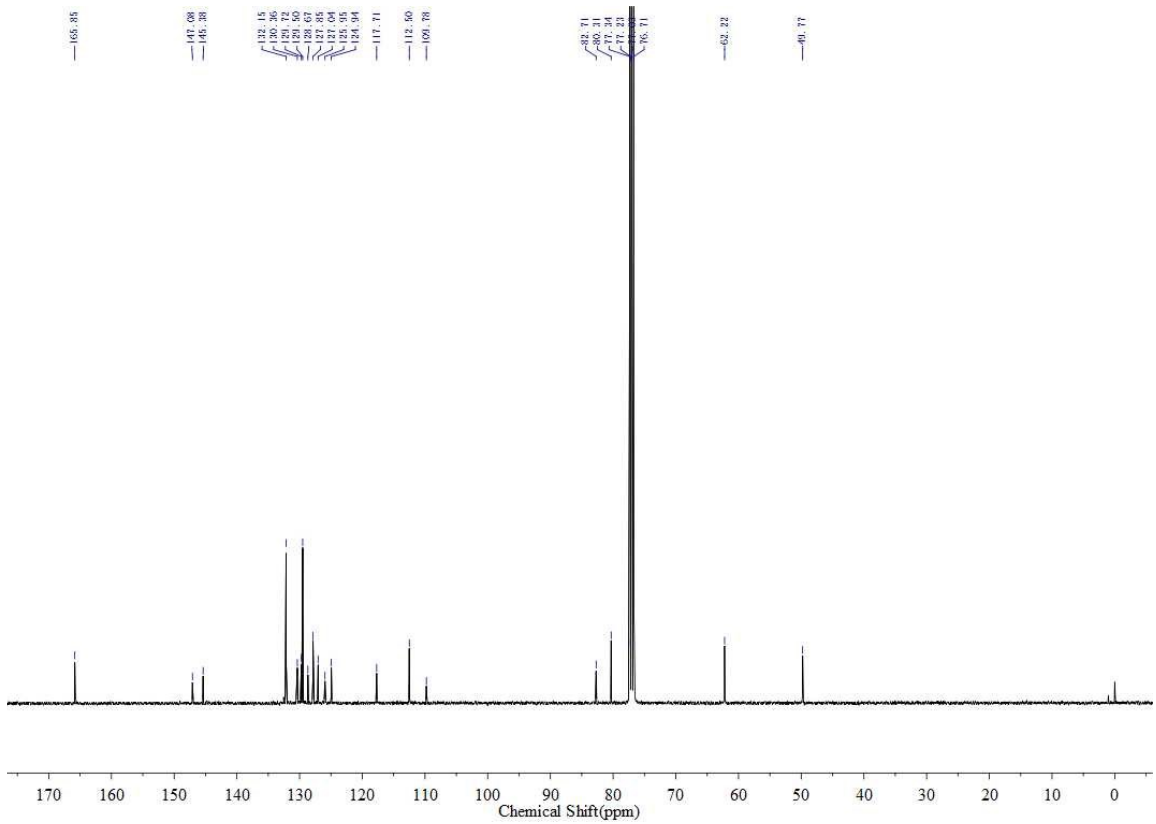


Fig. S10. ^{13}C NMR spectrum of **HP1** conducted in $CDCl_3$.

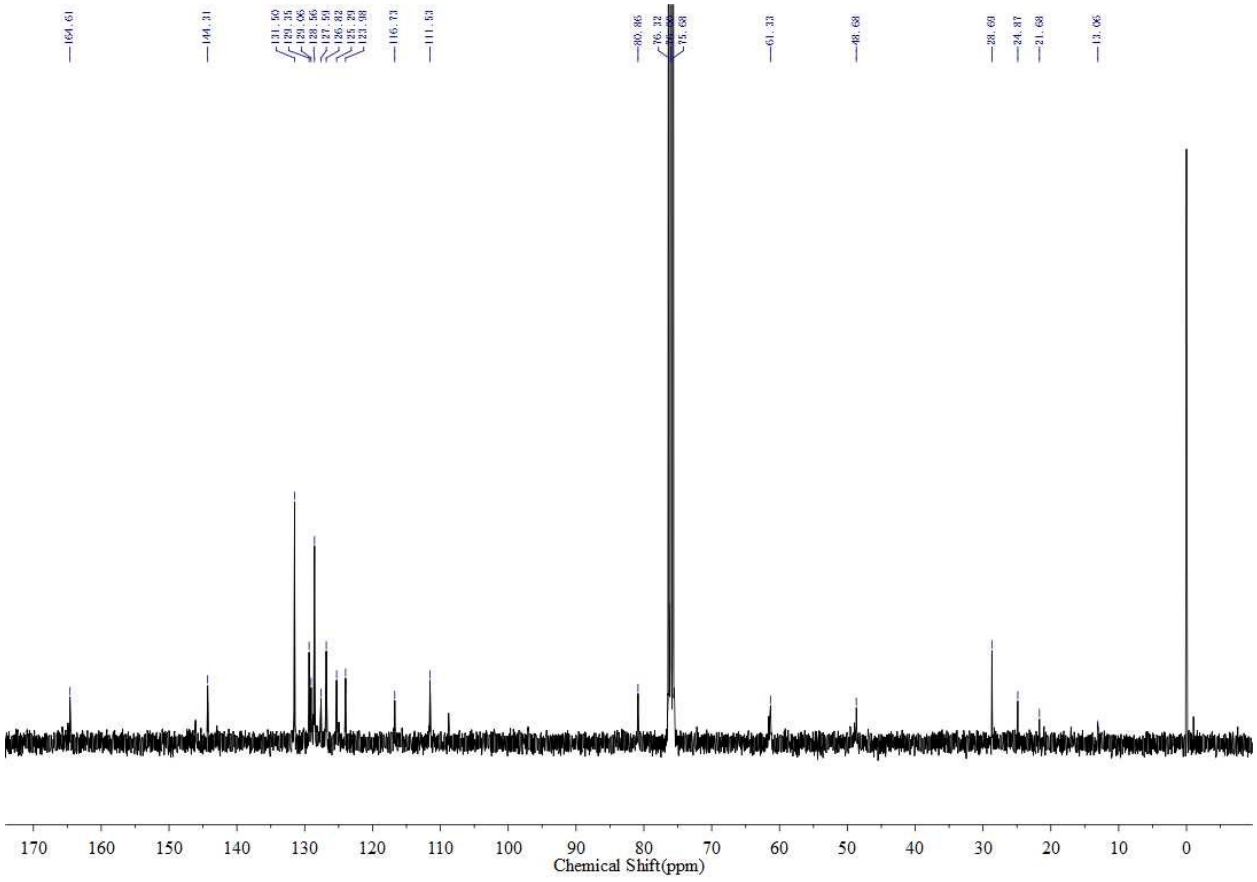


Fig. S11. ^{13}C NMR spectrum of **HP2** conducted in $CDCl_3$.

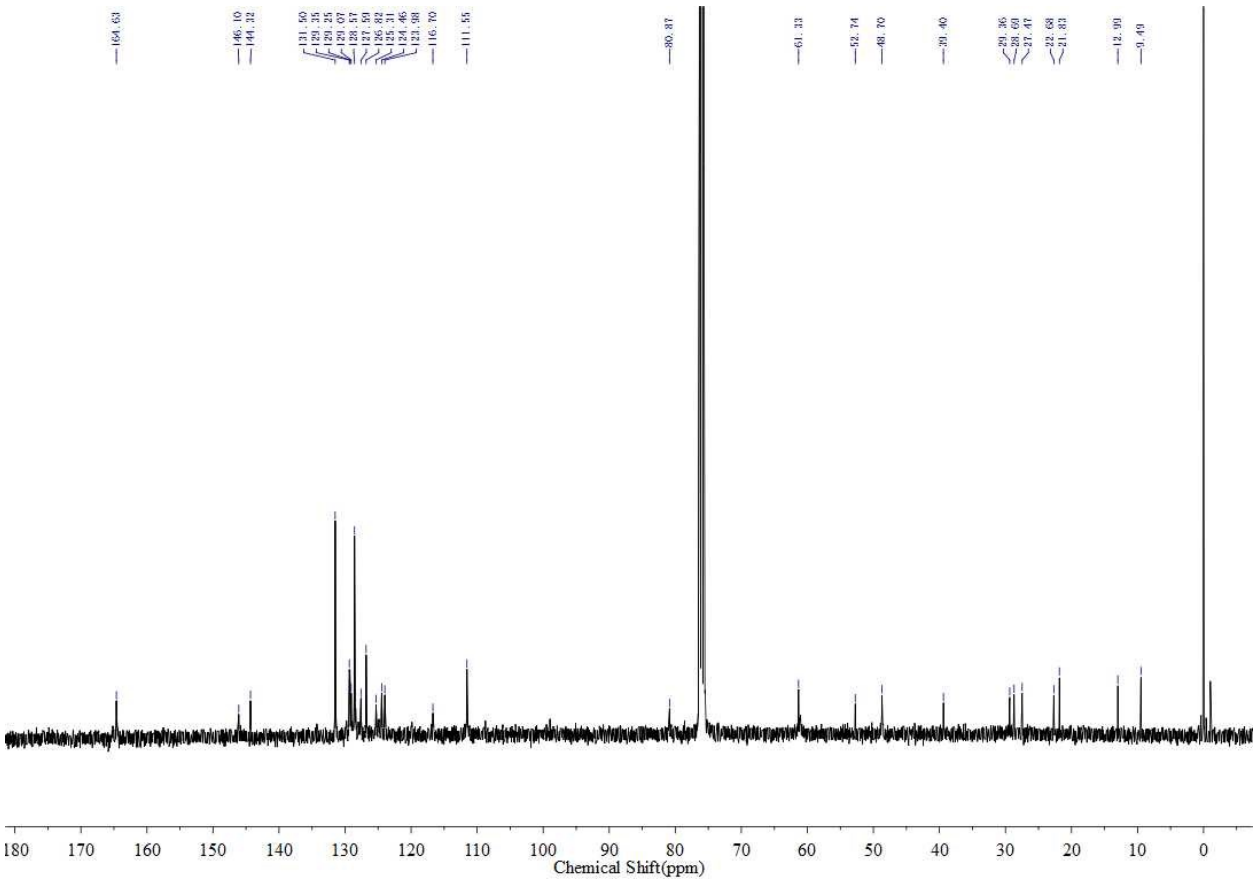
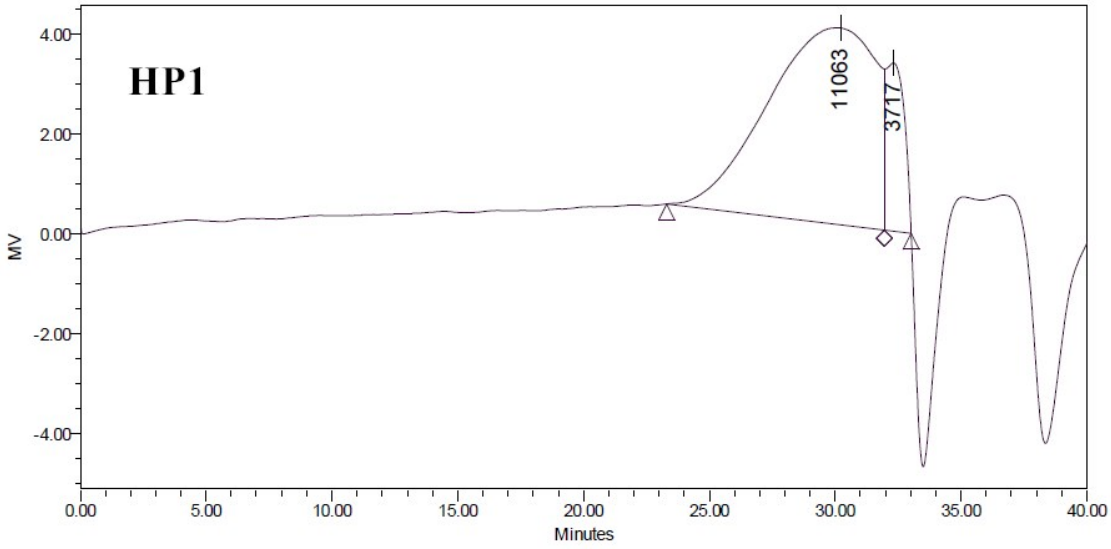


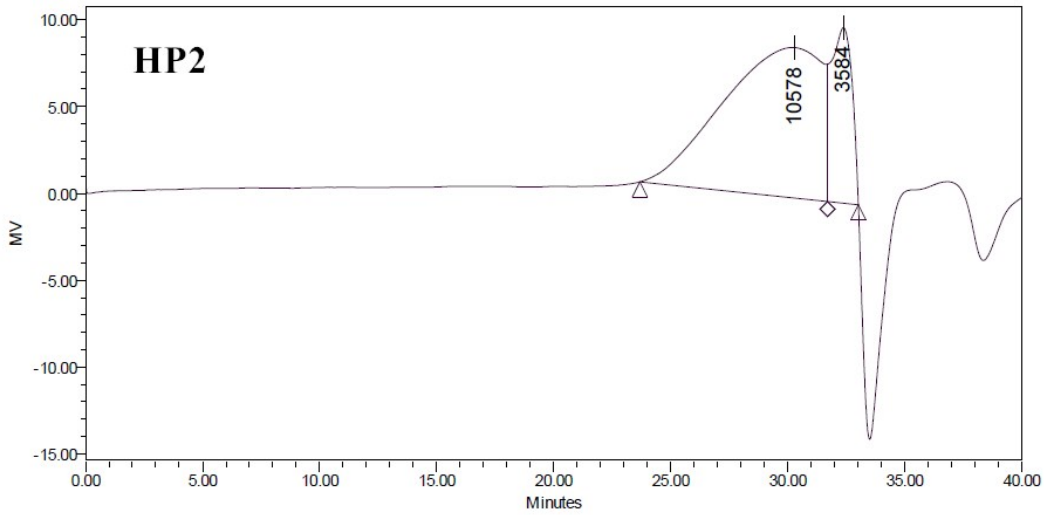
Fig. S12. ^{13}C NMR spectrum of **HP3** conducted in $CDCl_3$.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						12962	22112	11063	38146	58197	1.705968	1.725086
2								3717				

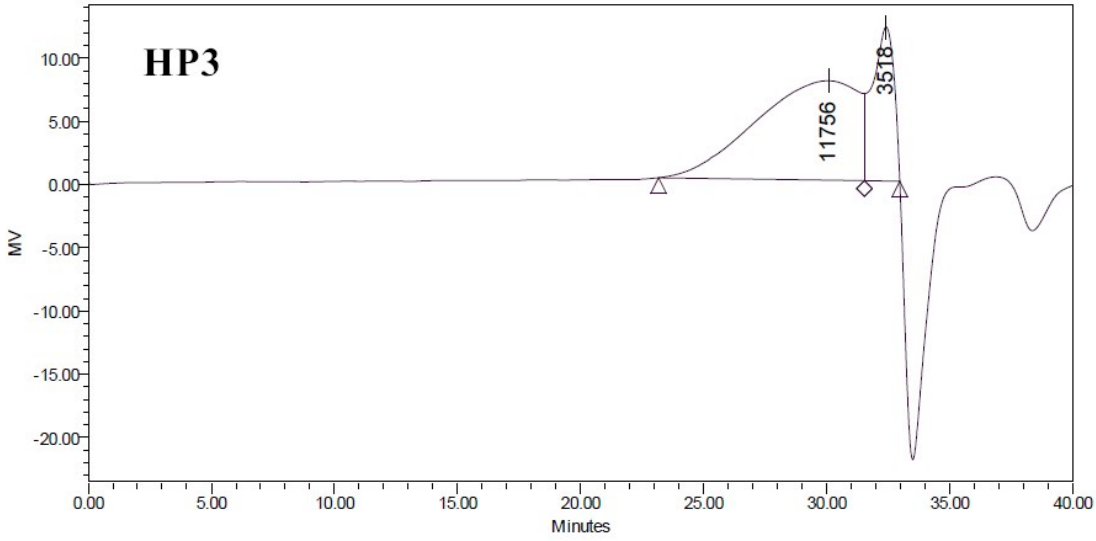
Fig. S13. GPC curve and data of **HP1**.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1								3584				
2						14128	23746	10578	40050	58621	1.680735	1.686634

Fig. S14. GPC curve and data of **HP2**.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						15240	25330	11756	43440	66150	1.662149	1.714945
2								3518				

Fig. S15. GPC curve and data of **HP3**.

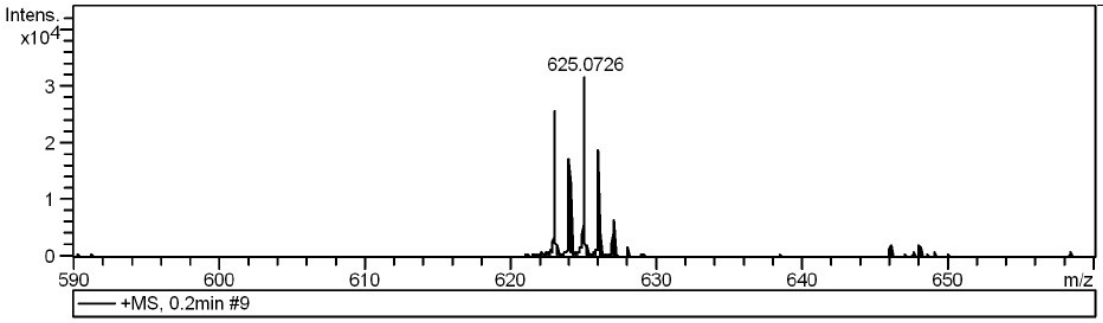
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\Lizhongan\li-zangxiaobo20190710-1.d	Acquisition Date	7/10/2019 10:52:20 AM
Method	tune_low_20170906_50-1200.m	Operator	BDAL@DE
Sample Name	li-zangxiaobo20190710-1	Instrument / Ser#	micrOTOF 10401
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	623.0726	10188	204.0	25590	0.0612
2	624.0777	9805	135.7	17036	0.0636
3	625.0726	10566	252.2	31742	0.0592
4	626.0754	10675	148.0	18636	0.0586
5	627.0781	10532	51.3	6462	0.0595
6	628.0778	10744	12.7	1605	0.0585

Fig. S16. HR-mass spectrum of monomer **3**.