Supporting Information

Synthetic procedures for product a, b, c, d, e and f:

5-Bromoisatin, Bromoethane and 4-methylbenzoyl chloride were purchased from Alfa Aesar. Diphenyl ether, 1-(4-fluorophenyl)ethanone, anhydrous aluminum chloride and trifluoromethanesulfonic acid (TFSA) were obtained from China National Medicines Corporation Ltd. TFSA was distilled before use and other chemicals were used as received without further purification.

Synthesis of compound **a** (5-bromo-1-ethylindoline-2,3-dione): A 50 mL flask was charged with 1.13 g (5 mmol) 5-Bromoisatin, 0.65 g Bromoethane (6 mmol), 0.83 g K_2CO_3 (6 mmol) and DMF 30 mL. The flask was degassed with nitrogen. After heating at 60℃for 12 h, DMF and the excess bromoethane were removed by vacuum. The residue was dissolved with dichloromethane and then purified by filtration. After removal of the solvent, the product was obtained as a red solid. Yield: 98.4% (1.25 g). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.68 (m, 2H), 6.81 (d, *J* =10 Hz, 1H), 3.77 (q, *J* = 8.4 Hz, 2H), 1.30 (t, *J* = 8.4 Hz, 3H); ^{13}C NMR (600 MHz, $CDCl_3$, δ): 182.4, 157.1, 149.3, 140.5, 128.2, 118.7, 116.4, 111.7, 35.1, 12.4.

Compound **b** (5-bromoacenaphthylene-1,2-dione) and **c** ((4-phenoxyphenyl)(p-tolyl)methanone) were synthesized by literature.[1, 2]

Synthesis of product **d**: A 25 mL flask was charged with 0.13 g (0.5 mmol) compound **b**, 0.13 g (0.5 mmol) compound **a**, 0.28 g compound **c** (1 mmol) and TFSA

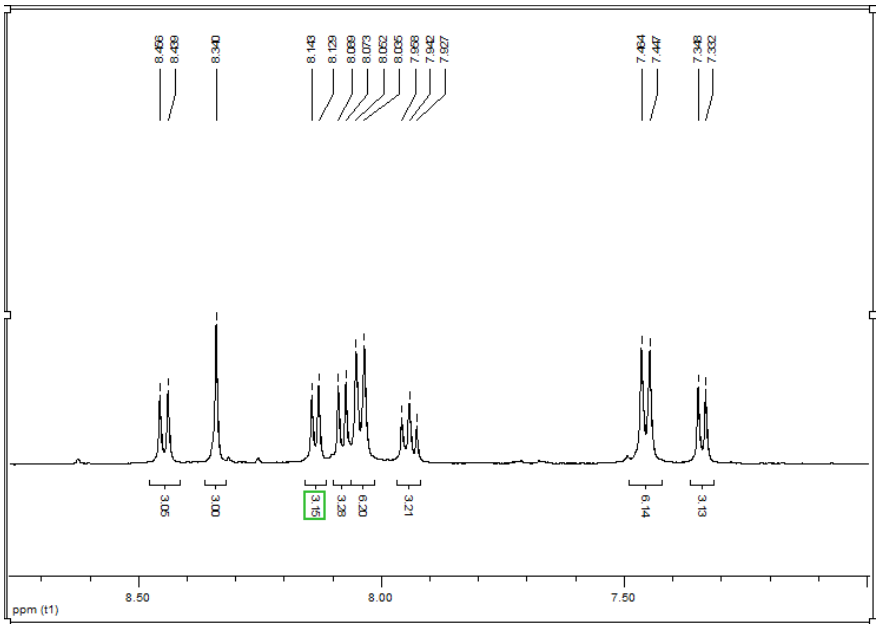
15 mL. The solution was stirred at 30℃. After 6 h, the mixture was poured into distilled waterand extracted with CH_2Cl_2. After washing with distilled water, the organic layer was dried over anhydrous $MgSO_4$. After removing the solvent by vacuum, the product was obtained as a red solid and characterized by ^{1}H NMR. Yield: 94% (0.51 g).

Synthesis of product **e**: A 25 mL flask was charged with 0.63 g (2.5 mmol) compound **a**, 1.44 g compound **c** (5 mmol) and TFSA 10 mL. The solution was stirred at 30℃. After 6 h, the mixture was poured into distilled waterand extracted with CH_2Cl_2. After washing with distilled water, the organic layer was dried over anhydrous $MgSO_4$. After removing the solvent by vacuum, the product was obtained as a red solid. Yield: 97% (1.97 g). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.8 (d, *J* = 10.2 Hz, 4H), 7.68 (d, *J* = 9.6 Hz, 4H), 7.46 (d, *J* = 10.2 Hz, 1H), 7.38 (s, 1H), 7.25 (m, 8H), 7.04 (m, 8H), 6.84 (d, *J* = 10.2 Hz, 1H), 3.84 (q, *J* = 9 Hz, 2H), 2.43 (s, 6H), 1.32 (d, *J* = 9 Hz, 3H); ^{13}C NMR (600 MHz, $CDCl_3$, δ): 195.2, 176.5, 160.7, 155.4, 143, 141.1, 137, 135.1, 135, 132.7, 132.3, 131.5, 130.1, 130, 129.2, 129, 120, 117.6, 115.4, 110.4, 35.3, 21.6, 12.6.

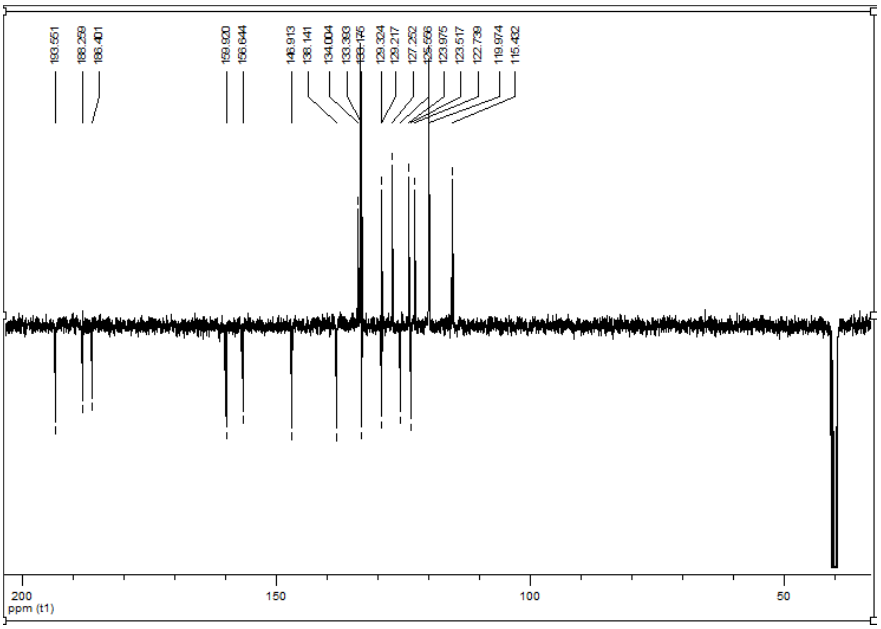
Synthesis of product **f**: A 25 mL flask was charged with 0.65 g (2.5 mmol) compound **b**, 1.44 g compound **c** (5 mmol) and TFSA 10 mL. The solution was stirred at 30℃. After 6 h, the mixture was poured into distilled water and extracted with CH_2Cl_2. After washing with distilled water, the organic layer was dried over anhydrous $MgSO_4$. After removing the solvent by vacuum, the product was obtained

as a red solid. Yield: 95% (1.95 g). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.81 (d, *J* = 9 Hz, 1H), 8.75 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 7 Hz, 1H), 8.26 (br, 4H), 8.18 (d, *J* = 7.8 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.85 (m, 8H), 7.71 (m, 16H), 7.53 (m, 8H), 7.27 (m, 8H), 7.14 (d, *J* = 7.8 Hz, 5H), 7.11 (d, *J* = 8.4 Hz, 3H), 2.44 (s, 12H); ^{13}C NMR (600 MHz, $CDCl_3$, δ): 195.2, 161.2, 160.8, 155.3, 155.2, 153.9, 143, 140.1, 137.7, 137.1, 132.7, 132.5, 132.4, 131.5, 131.1, 131, 130.1, 129, 126.9, 126.8, 126.7, 125.4, 125.1, 124.6, 124.4, 121, 120, 117.6, 117.3, 114.2, 21.6.

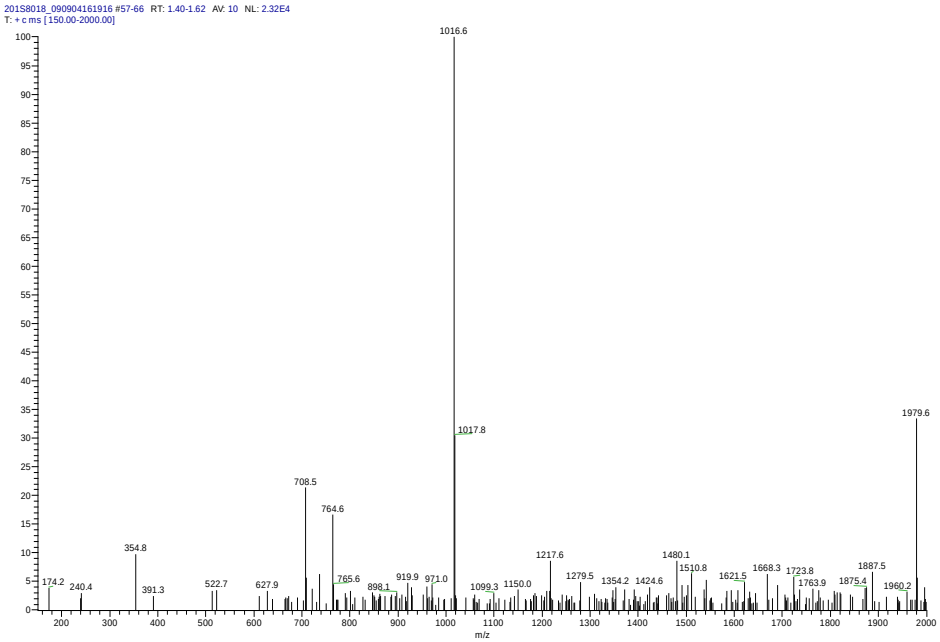
The spectra of the core:



^{1}H NMR spectrum of the core (600 MHz, DMSO).

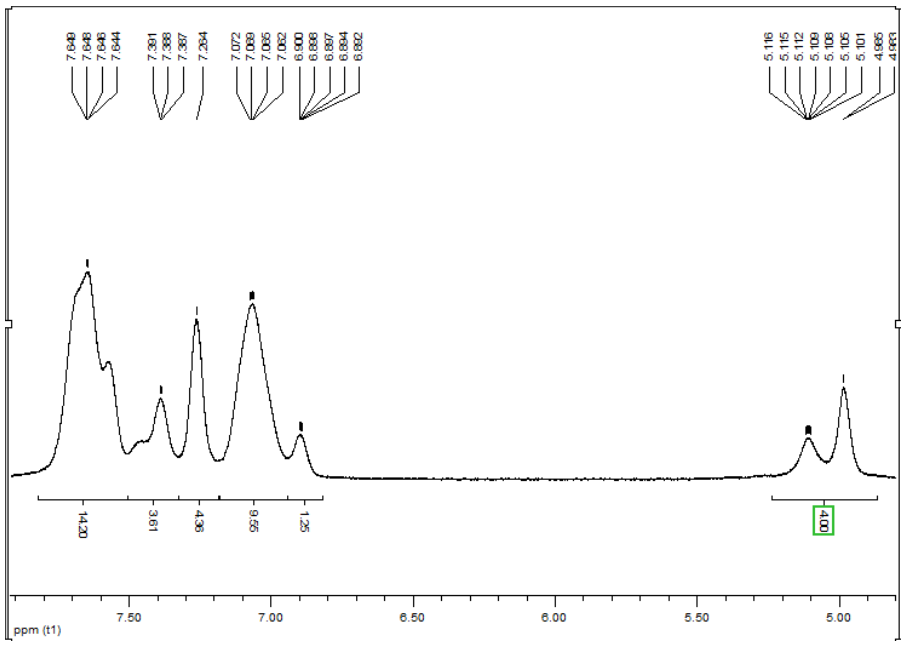


DEPTQ ^{13}C NMR spectrum of the core (600 MHz, DMSO).[3]

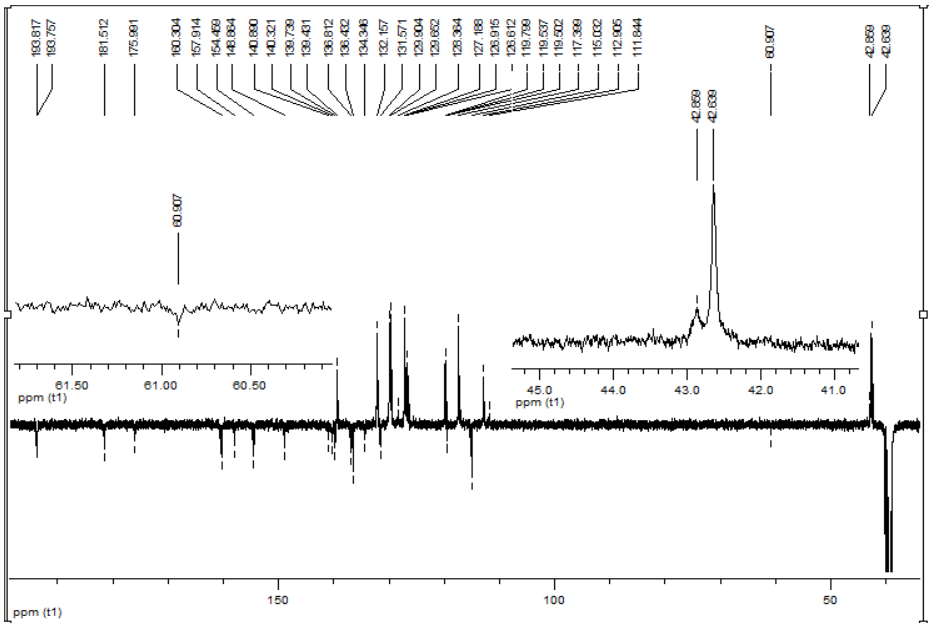


MS (ESI) spectrum of the core.

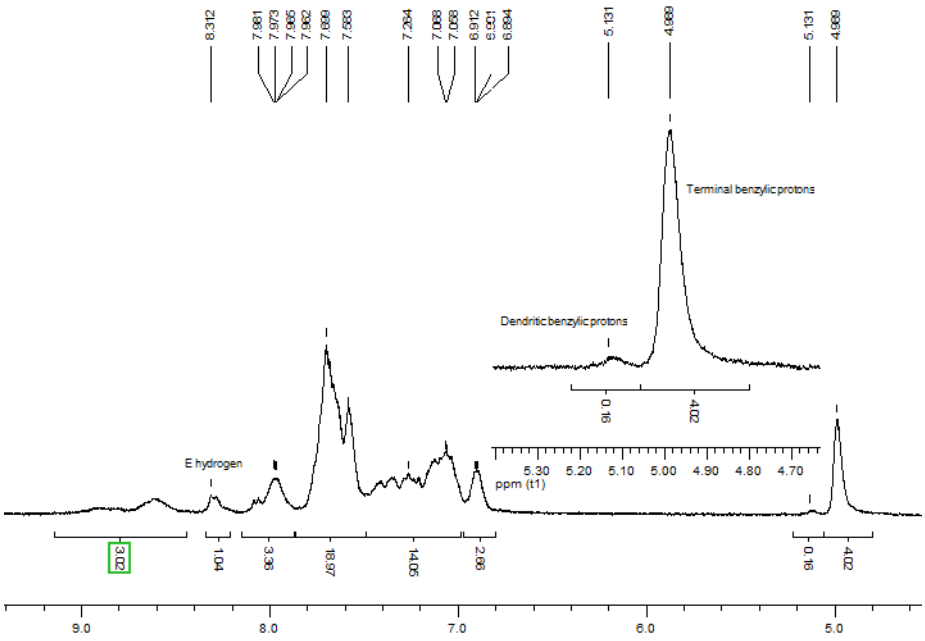
The spectra of the polymers:



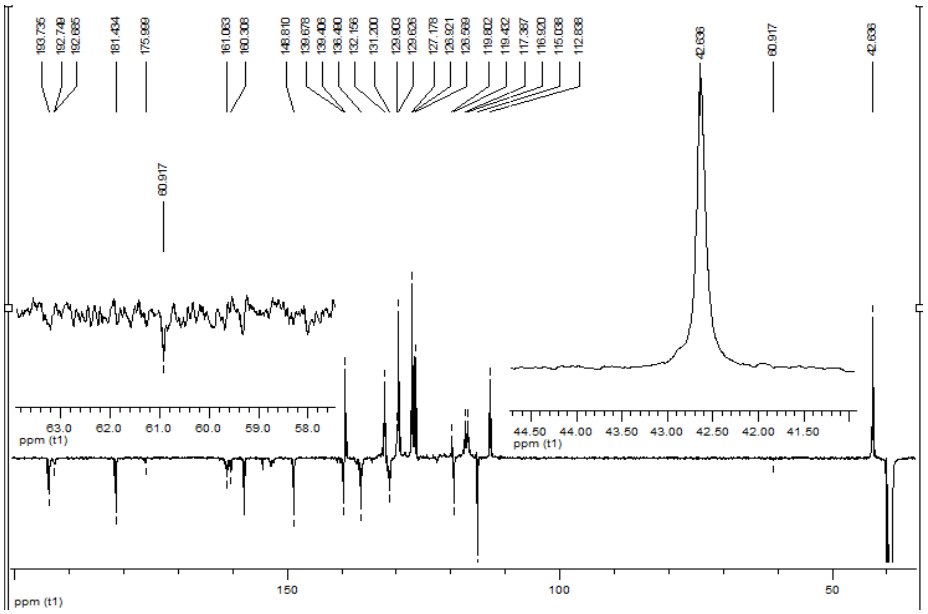
^{1}H NMR spectrum of the polymer **1** (600 MHz, DMSO).



DEPTQ ^{13}C NMR spectrum of the polymer **1** (600 MHz, DMSO).



^{1}H NMR spectrum of the polymer **3** (600 MHz, DMSO).



DEPTQ ^{13}C NMR spectrum of the polymer **3** (600 MHz, DMSO).

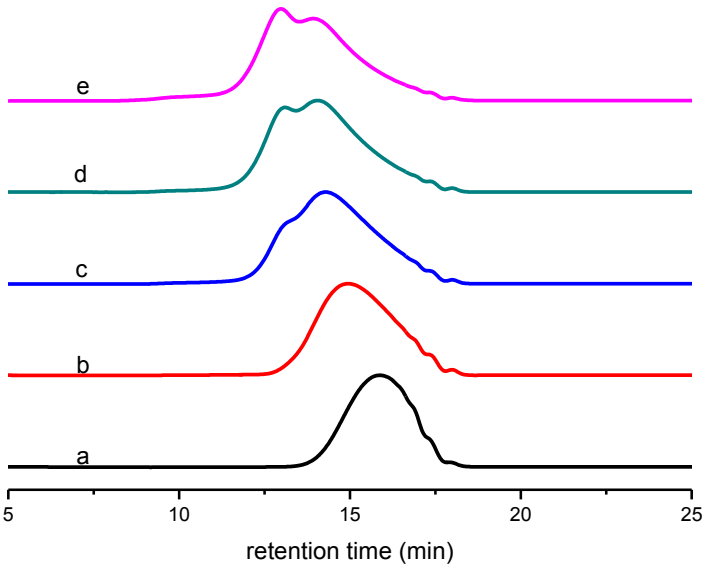


Figure S1.GPC curves of the polymers without core: (a) 20 mg/mL PDI = 1.33 M_n = 6900, (b) 40 mg/mL PDI = 1.55 M_n = 9200, (c) 60 mg/mL PDI = 2.04 M_n = 13100, (d) 80 mg/mL PDI = 2.24 M_n = 15700 and (e) 100 mg/mL PDI = 2.36 M_n = 18200.

Table S1. The synthesis parameters for Polymer **2**, **3**, **4**, **5**, **6** and **7**.

Polymer	Mole Ratio (monomer/core)	Core [mg]	Monomer [mg]	TFSA [mL]	Monomer Concentration [mg mL^{-1}]
2	4	5	10.5	0.52	20
3	6	5	16	0.80	20
4	8	5	21	1.05	20
5	18	5	47	1.17	40
6	30	5	79	1.31	60
7	42	5	110	1.37	80

All the polymers were synthesized in a batch-wise way and the monomer mass of each batch was 5 mg.

Picture S1. TLC performance for product **a** (A), **b** (B), **c** (C), **d** (F), **e** (E) and **f** (D).

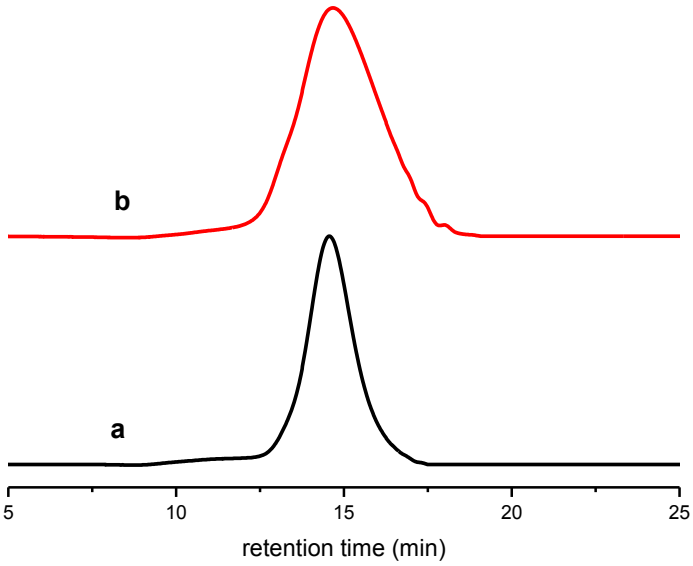


Figure S2. GPC curves of the polymers with the monomer to core ratio of 42, (a) prepared in the slow-addition way, PDI^a = 1.22, PDI^b = 1.56; (b) by one-pot polymerization PDI^a = 1.66, PDI^b = 1.96, PDI^a obtained from the integration of the main peak, excluding the faint shoulder, PDI^b integration of the whole peak.

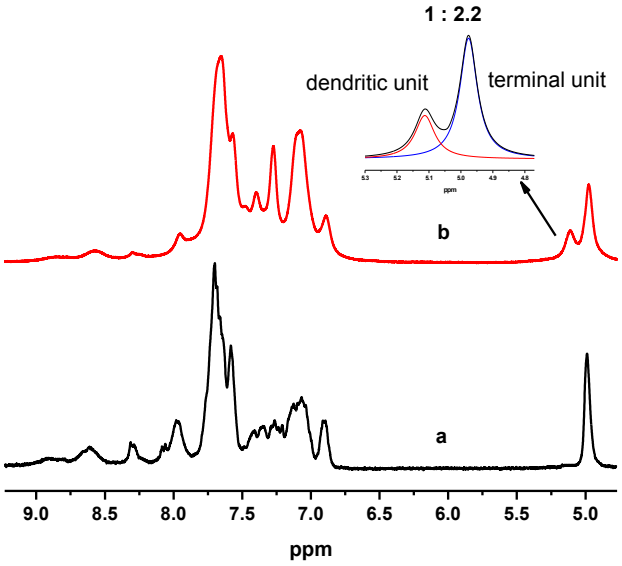


Figure S3. ^{1}H NMR spectra of the polymer **3** (a) and polymer **5** (b) (600 MHz, DMSO).

Table S2. Molecular weight of the individual fitting peaks.

Fitting peak	Retention time (min)	M_1	M_2
a	16.17	6012	6679
b	16.58	5006	5121
c	16.95	3999	3999
d	17.36	2992	3024
e	17.96	1985	1980

M_1 calculated molecular weight of the individual fitting peaks. M_2 molecular weight of the individual fitting peaks according to GPC standard curve.

Table S3. Calculated value of the terminal to dendritic benzylic proton ratio and the monomeric repeating unit to the core moiety ratio of the polymer **3**.

Fitting peaks	A	B	C	D
Peak area	15693	66779	19009	7230
M	2992	3999	5006	6012
P (%)	19.1	62.1	14.1	4.5
T	$8\times P_{(A)}$	$12\times P_{(B)}$	$14\times P_{(C)}$	$16\times P_{(D)}$
D	$0\times P_{(A)}$	$0\times P_{(B)}$	$2\times P_{(C)}$	$4\times P_{(D)}$
N	$3\times P_{(A)}$	$3\times P_{(B)}$	$3\times P_{(C)}$	$3\times P_{(D)}$

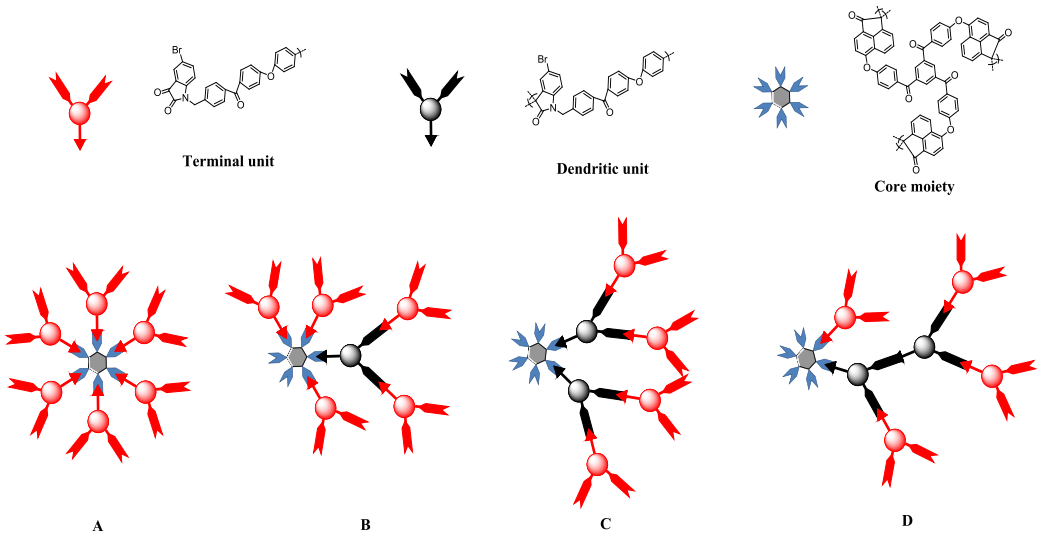
M represents the molecular weight of the hypothetic oligomer. T stands for the number of the terminal benzylic proton. D stands for the number of the dendritic benzylic proton. N stands for the number of the *E* hydrogen (*E* hydrogen: the tricarbonylbenzene proton of the core moiety).

$T_{sum} = T_{(A)} + T_{(B)} + T_{(C)} + T_{(D)}$,

$D_{sum} = D_{(A)} + D_{(B)} + D_{(C)} + D_{(D)}$,

$N_{sum} = N_{(A)} + N_{(B)} + N_{(C)} + N_{(D)}$,

$T_{sum}/D_{sum} = 25.4$, $[(T_{sum} + D_{sum})/2]/(N_{sum}/3) = 6.1$.



Isomer	A	B	C	D
The ratio of the terminal/dendritic units	∞	5	2	2

Scheme S1. Schematic representation of the isomers of the oligomer with six monomeric repeating units.

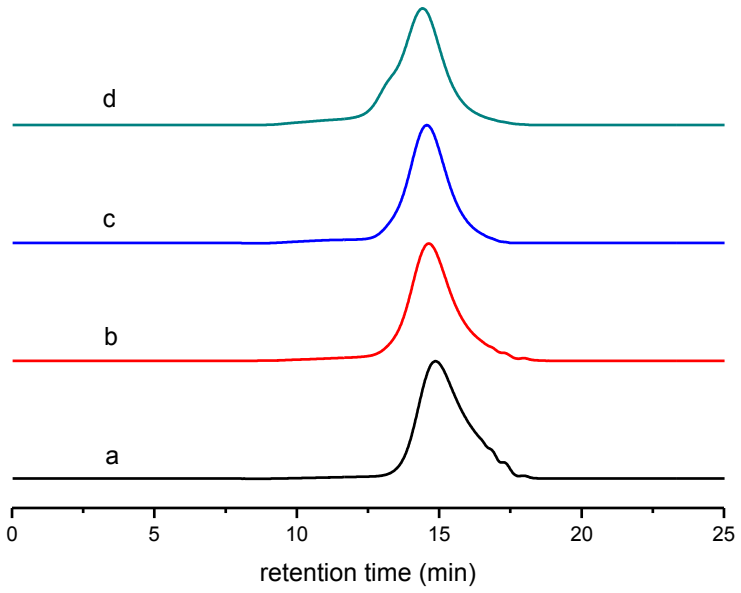


Figure S4. GPC curves of the polymers **7** with different concentration: (a) 20 mg/ml, PDI^a = 1.37 (b) 60 mg/ml, PDI^a = 1.32 (c) 80 mg/ml, PDI^a = 1.22 (d) 100 mg/ml, PDI^a = 1.34, PDI^a obtained from the integration of the main peak, excluding the faint shoulder.

1. M. A. P. Martins, C. P. Frizzo, D. N. Moreira, F. A. Rosa, M. R. B. Marzari, N. Zanatta and H. G. Bonacorso, *Catal. Commun.*, 2008, **9**, 1375-1378.
2. H. G. Rule and S. B. Thompson, *J. Chem. Soc. (Resumed)*, 1937, **0**, 1761-1763.
3. R. Burger and P. Bigler, *J Magn Reson*, 1998,**135**, 529-534.