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Single-Step Access to series of D-A π-conjugated oligomers with 3-10 nm chain lengths

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Contents

Materials and methods

Unless otherwise specified, all conventional chemicals were purchased from Energy Chemical. The starting DPP was purchased from Sun Tech Inc. Anhydrous toluene was obtained from treating conventional one with CaH_2. All ^1H and ^{13}C NMR spectra were obtained in chloroform-*d*, with Bruker 400, (^1H NMR 400MHz and ^{13}C NMR 101 MHz) spectrometer. MALDI-TOF MS was performed on a Bruker Auto flex II using 2,5-dihydroxybenzoicacid or α-cyano-4-hydroxycinnamicacid as the matrixes. Samples for MS were prepared by diluting the molecules in $CHCl_3$. Elemental analysis was taken on a Vario MICRO cube spectrophotometer. UV-vis absorption spectra were taken on a Shimadzu UV-2450 spectrophotometer. Theoretical calculations based on DFT methods have been performed for the oligomers with Gaussian09 program. Becke's three-parameter gradient-corrected functional (B3LYP) with 6-31G(d,p) basis for geometric optimization. The Mw, Mn and PDI of polymer **P**1 were measured with the GPC equipped with a Viscotek TDA302 triple detector (Waters1515-Wyatt DAWAN 8+-ViscoStar II).

Synthetic procedures

Synthesis of oligomers O1, O2, O3, O4 and O5

DPP (200 mg, 0.27 mmol), 2,7-dibromo-9,9-dioctylfluorene (DBFL, 104.6 mg, 0.19 mmol), anhydrous Cs_2CO_3 (180 mg, 0.54 mmol), PivOH (8 mg, 0.12 mmol), $Pd_2(dba)_3$ (3.7 mg, 1.5 mol %), tris(o-methoxyphenyl) phosphine (2.9 mg, 3 mol %) were added successively into a Schlenk tube. The tube was purged by repetitions of vacuum and argon filling (×3). Then 5 mL anhydrous toluene was added into *via* syringe. The reaction solution was deoxygenated by freeze-vacuum-thaw cycles three times, and then rigorously stirred at 100 ^oC for 24 h under argon atmosphere. Removal of the toluene by rotary evaporator afforded the crude product, which was then purified by column chromatography on silica gel using mixed CH_2Cl_2 and hexane as eluent (gradually increased the ratio of CH_2Cl_2 to hexane between 1.5:1~2:1, v/v) and successively gave oligomers **O**s1~5, **O**1 (57 mg, yield 23%), **O**2 (56 mg, yield 21%), **O**3 (47 mg, yield 17%), **O**4 (45 mg, yield 16%), and **O**5(35 mg, yield 12%).

Oligomers **O**1, DPP-Fl-DPP: ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 4.0 Hz, 2H), 8.87 (d, *J* = 3.2 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 4H), 7.55 (d, *J* = 4.0 Hz, 2H), 7.28 (d, *J* = 3.9 Hz, 2H), 4.07 (dd, *J* = 8.1, 7.4 Hz, 8H), 2.04 (m, 8H), 1.27 (m, 120H), 0.85 (m, 24H), 0.76 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.88, 161.70, 152.18, 150.40, 141.26, 140.30, 139.93, 136.89, 135.04, 132.48, 130.89, 130.31, 129.97, 128.85, 128.62, 128.38, 125.49, 124.40, 120.61, 120.22, 108.26, 108.11, 55.55, 46.30, 40.33, 38.01, 37.78, 31.89, 31.82, 31.76, 31.74, 31.42, 31.25, 30.59, 30.10, 30.02, 29.95, 29.70, 29.57, 29.50, 29.32, 29.18, 26.41, 26.24, 22.66, 22.57, 19.19, 14.10, 13.96.

MALDI-TOF MS (m/z): $[M]^+$ calcd. for $C_{121}H_{182}N_4O_4S_4$: 1885.058, found 1885.157.

Elemental analysis: calcd for $C_{121}H_{182}N_4O_4S_4$, C, 77.10; H, 9.73; N, 2.97%. Found: C, 77.04; H, 9.64; N, 2.98%.

Oligomers **O**2, DPP-$(Fl\text{-}DPP)_2$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 4H), 8.87 (d, J = 2.8 Hz, 2H), 7.75 (d, J = 7.9 Hz, 4H), 7.70 (d, J = 7.6 Hz, 4H), 7.66 – 7.60 (m, 6H), 7.55 (s, 4H), 7.28 (d, J = 3.7 Hz, 2H), 4.08 (m, 12H), 2.06 (m, 14H), 1.24 (m, 178H), 0.85 (m, 36H), 0.79 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.89, 161.70, 152.19, 150.40, 150.27, 141.28, 140.30, 139.93, 139.77, 136.89, 135.03, 132.52, 130.94, 130.29, 130.04, 128.75, 128.63, 128.39, 125.49, 124.42, 120.62, 120.22, 108.44, 108.21, 108.12, 55.55, 46.31, 40.34, 38.01, 37.78, 31.89, 31.83, 31.75, 31.44, 31.26, 30.10, 29.96, 29.77, 29.70, 29.58, 29.32, 29.18, 26.44, 26.22, 23.85, 22.67, 22.57, 14.10, 14.01.

MALDI-TOF MS (m/z): $[M]^+$ calcd. for $C_{196}H_{292}N_6O_6S_6$: 3020.888, found 3020.716.

Elemental analysis: calcd for $C_{196}H_{292}N_6O_6S_6$, C, 77.93; H, 9.74; N, 2.78%. Found: C, 77.74; H, 9.84; N, 2.74%.

Oligomers **O**3, DPP-$(Fl\text{-}DPP)_3$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (t, J = 4.3 Hz, 6H), 8.87 (d, J = 3.6 Hz, 2H), 7.75 (d, J = 7.7 Hz, 6H), 7.70 (d, J = 7.5 Hz, 6H), 7.63 (d, J = 8.7 Hz, 8H), 7.55 (dd, J = 7.5, 6.3 Hz, 6H), 7.30 – 7.27 (m, 2H), 4.21 – 4.03 (m, 16H), 2.06 (m, 20H), 1.37 – 1.13 (m, 239H), 0.85 (t, J = 5.2 Hz, 48H), 0.79 (t, J = 6.8 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.96, 161.90, 161.83, 161.69, 152.19, 150.41, 150.23, 141.28, 140.34, 139.75, 136.70, 132.51, 128.75, 128.39, 125.51, 124.42, 120.60, 120.21, 108.40, 55.58, 46.38, 40.35, 38.02, 31.91, 31.84, 31.75, 31.44, 31.26, 30.12, 29.96, 29.77, 29.70, 29.58, 29.50, 29.34, 29.18, 26.41, 26.25, 23.86, 22.66, 22.57, 14.10, 14.01.

MALDI-TOF MS (m/z): $[M]^+$ calcd. for $C_{271}H_{402}N_8O_8S_8$: 4156.725, found 4156.347.

Elemental analysis: calcd for $C_{271}H_{402}N_8O_8S_8$, C, 78.31; H, 9.75; N, 2.70%. Found: C, 78.22; H, 9.69; N, 2.72%.

Oligomers **O**4, DPP-(Fl-DPP)$_4$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (t, *J* = 4.4 Hz, 8H), 8.87 (d, *J* = 3.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 8H), 7.71 (d, *J* = 8.7 Hz, 8H), 7.63 (d, *J* = 8.7 Hz, 10H), 7.56 (d, *J* = 4.2 Hz, 8H), 7.28 (d, *J* = 4.9 Hz, 2H), 4.09 (m, 20H), 2.07 (m, 26H), 1.26 (m, 294H), 0.85 (m, 60H), 0.78 (m, *J* = 7.0 Hz, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.89, 161.83, 161.77, 152.19, 150.41, 141.31, 141.26, 140.31, 139.93, 139.73, 136.79, 132.49, 130.86, 128.75, 125.49, 124.43, 120.62, 120.20, 108.40, 68.20, 65.54, 55.55, 46.30, 40.35, 38.77, 38.04, 37.78, 31.91, 31.84, 31.75, 31.44, 31.32, 31.25, 30.59, 30.39, 30.13, 29.96, 29.78, 29.70, 29.59, 29.34, 29.19, 28.94, 26.41, 26.21, 23.85, 22.98, 22.68, 22.57, 14.09, 14.01.

MALDI-TOF MS (m/z): $[M]^+$ calcd. for $C_{346}H_{512}N_{10}O_{10}S_{10}$: 5292.562, found 5292.161.

Elemental analysis: calcd for $C_{346}H_{512}N_{10}O_{10}S_{10}$, C, 78.52; H, 9.75; N, 2.65%. Found: C, 78.50; H, 9.77; N, 2.63%.

Oligomers **O**5, DPP-(Fl-DPP)$_5$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (t, *J* = 4.2 Hz, 10H), 8.87 (d, *J* = 3.2 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 10H), 7.72 – 7.68 (m, 10H), 7.67 – 7.61 (m, 12H), 7.58 – 7.53 (m, 10H), 7.30 – 7.26 (m, 2H), 4.06 (m, 24H), 2.06 (m, 32H), 1.35 – 1.15 (m, 354H), 0.86 (m, 72H), 0.78 (m, 30H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.83, 152.19, 150.28, 141.26, 140.28, 139.93, 139.78, 136.82, 135.04, 132.51, 130.91, 128.89, 128.75, 128.39, 125.49, 124.43, 120.62, 120.22, 108.40, 65.56, 55.56, 46.31, 40.33, 38.12, 31.92, 31.84, 31.76, 31.44, 31.26, 31.20, 30.98, 30.59, 30.13, 29.97, 29.78, 29.70, 29.59, 29.35, 29.19, 26.41, 23.86, 22.68, 22.58, 14.09, 14.02.

MALDI-TOF MS (m/z): $[M]^+$ calcd. for $C_{421}H_{622}N_{12}O_{12}S_{12}$, 6428.399, found 6428.399.

Elemental analysis: calcd for $C_{421}H_{622}N_{12}O_{12}S_{12}$, C, 78.66; H, 9.75; N, 2.61%. Found: C, 78.54; H, 9.80; N, 2.59%.

Synthesis of polymer P1, P(DPP-Fl)

DPP (100 mg, 0.135 mmol), 0.135 mmol 2,7-dibromo-9,9-dioctylfluorene (DBFL, 73.2 mg), anhydrous Cs_2CO_3 (90 mg, 0.27 mmol), PivOH (4 mg, 0.06 mmol), $Pd_2(dba)_3$ (1.9 mg, 1.5 mol %), tris(o-methoxyphenyl) phosphine (1.5 mg, 3 mol %) were added successively into a Schlenk tube. The tube was purged by repetitions of vacuum and argon filling (×3). Then 3 mL anhydrous toluene was added into *via* syringe. The reaction solution was deoxygenated by freeze-vacuum-thaw cycles three times, and then rigorously stirred at 100 °C for 48 h under argon atmosphere. After polymerization, the

polymers were purified by precipitation in methanol, filtered, and washed on Soxhlet with methanol, acetone, hexanes, and chloroform successively. The chloroform fractions were condensed under reduced pressure, and the polymers **P**1 was obtained: (125mg, yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (br, 2H), 7.84 – 7.67 (br, 4H), 7.65 (br, 2H), 7.56 (br, 2H), 4.13 (br, 4H), 2.05 (br, 6H), 1.33 (br, J = 50.9 Hz, 71H), 0.85 (br, 12H), 0.79 (t, J = 6.8 Hz, 6H); GPC: Mn=39115, Mw=110910, PDI=2.836.

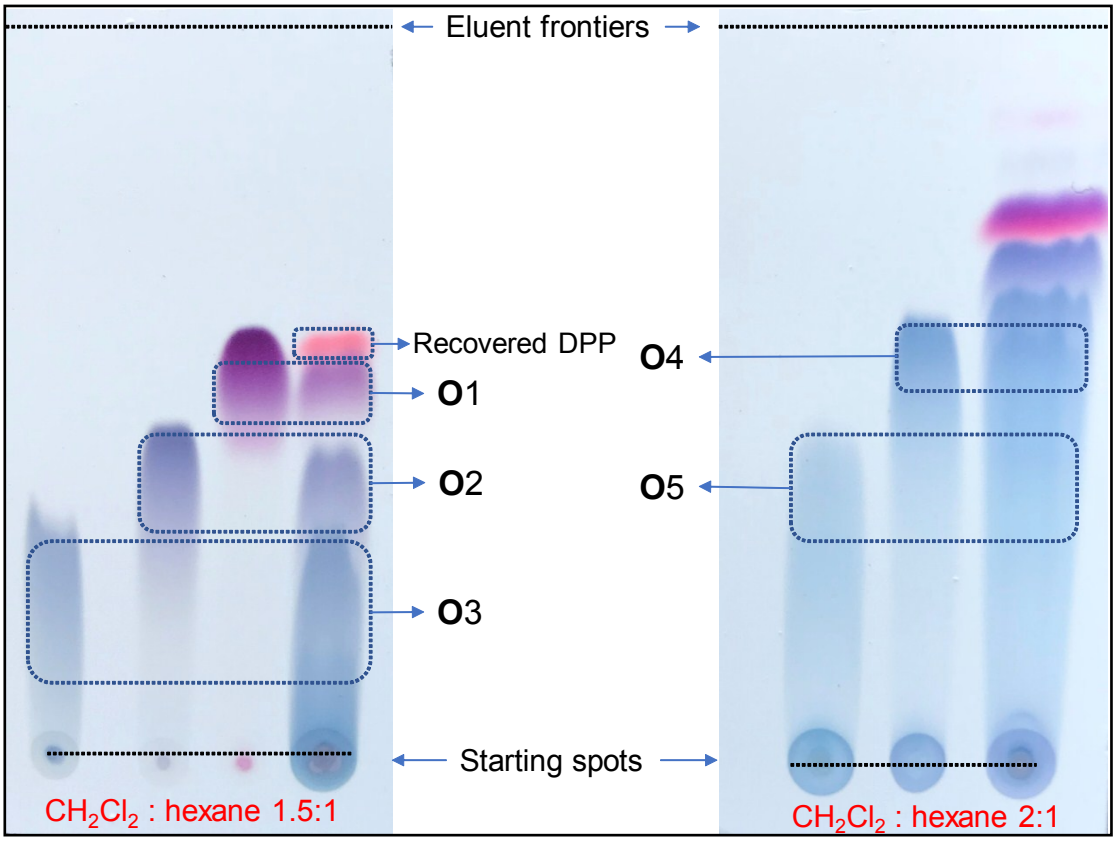


Fig. S1 TLC analysis of the direct arylated coupling between DPP and 2,7-dibromo-9,9-dioctylfluorene in molar ratio of 1.4/1 using CH_2Cl_2 : hexane (1.5:1 and 2:1 respectively, v/v) as eluent . The starting spots on each TLC plate involved the reaction mixture and the corresponding purified oligomers.
(Because that the oligomers **O**4 and **O**5 remained unmoved under the eluent of 1.5:1 ratio of CH_2Cl_2 to hexane (left plate), a higher ratio of 2:1 was applied instead (right plate).).

Table S1 Dependence of the chain lengths of oligomers and distribution of corresponding yields on the molar ratios between DPP and DBFL

Molar Ratio [a]	**O**1 [b]	**O**2 [b]	**O**3 [b]	**O**4 [b]	**O**5 [b]
2:1	35%	24%	16%	trace	trace
1.6:1	30%	26%	18%	5%	4%

1.2:1	Polymeric mixture

[a] Molar ratio between DPP and DBFL. [b] Isolated yields.

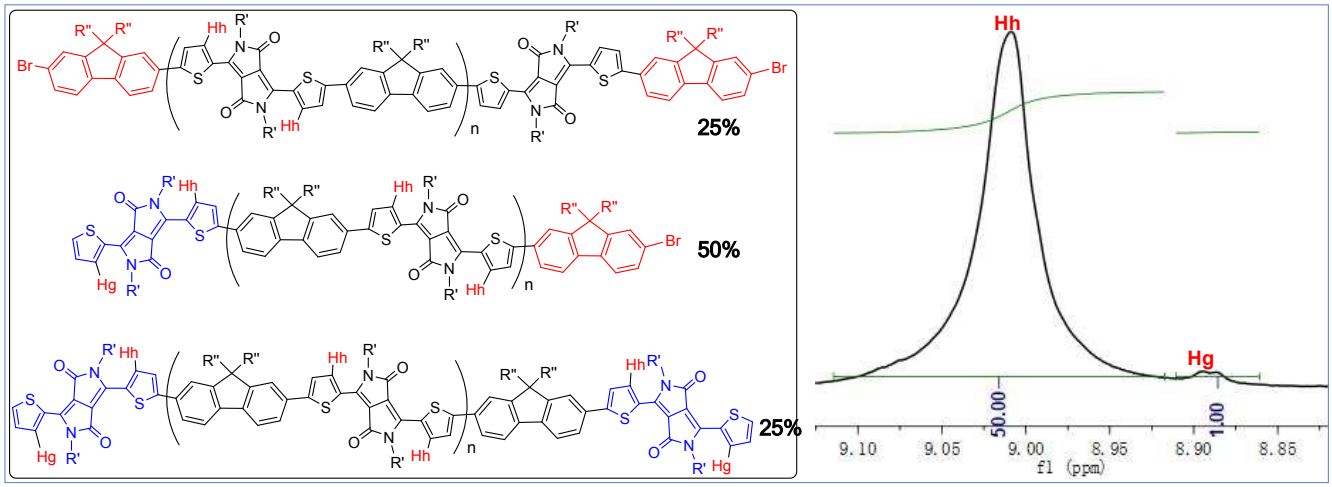
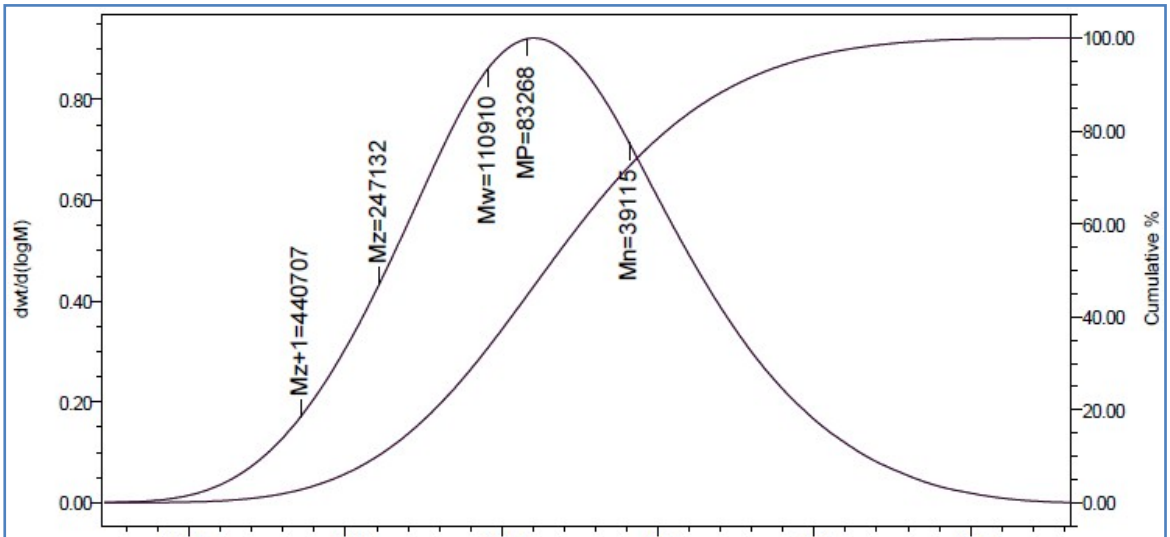


Fig. S2 Statistical distribution of chain ends of P(DPP-Fl) (**P**1), and the ratio of ^{1}H NMR integration of backbone H_h and chain-end H_g.

(In the above Figure, the value of n should be 25. Taking the chain-ended groups into account, the average number of repeat units for polymer should be 26, which equals 25 plus 1. Thus, the average molecular weight of the polymer chains can be calculated as 26×1135 = 29,510, among which the 1135 is the molecular weight per unit.)



Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
39115	110910	83268	247132	440707	2.835517	2.228221

Fig. S3 GPC profile of **P**1 and the corresponding list of the obtained data.

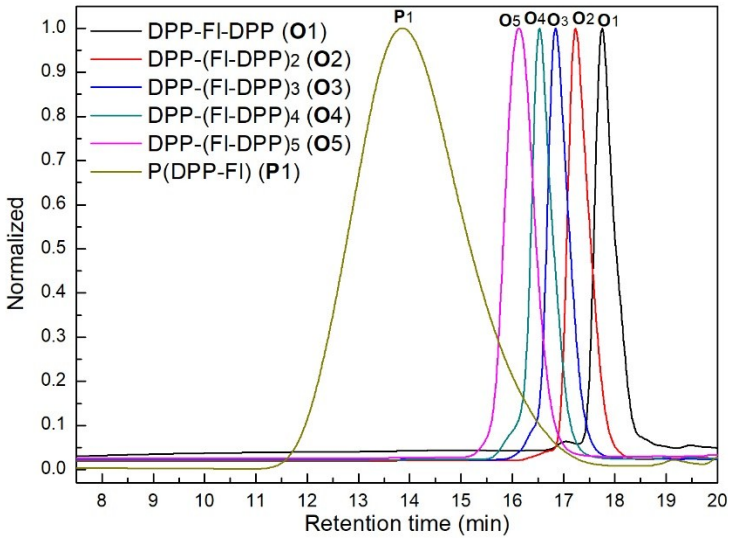


Fig. S4 GPC profiles of oligomers **O**s1~5 and **P**1

Table S2 Summary of retention time in GPC, and GPC/Maldi-Tof/NMR molecular weights

	O1	**O**2	**O**3	**O**4	**O**5	**P**1
Retention time	17.75	17.23	16.85	16.53	16.13	13.86
Mn	1912	3085	4230	5464	8505	39,115
Mw	2046	3301	4569	5907	9281	110,910

PDI	1.07	1.07	1.08	1.08	1.09	2.84
MW by maldi-tof or NMR	1885	3020	4156	5292	6428	29,510

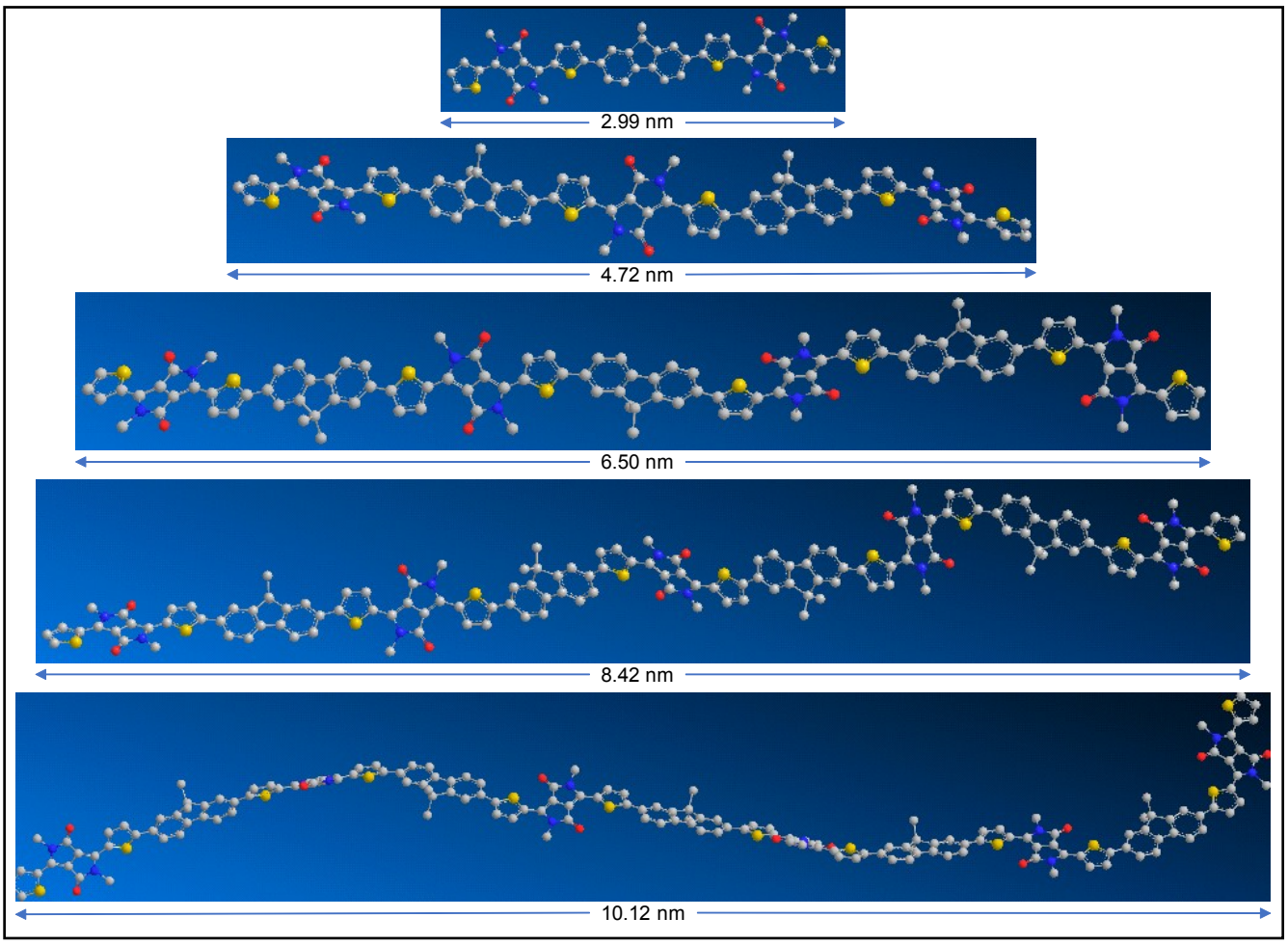
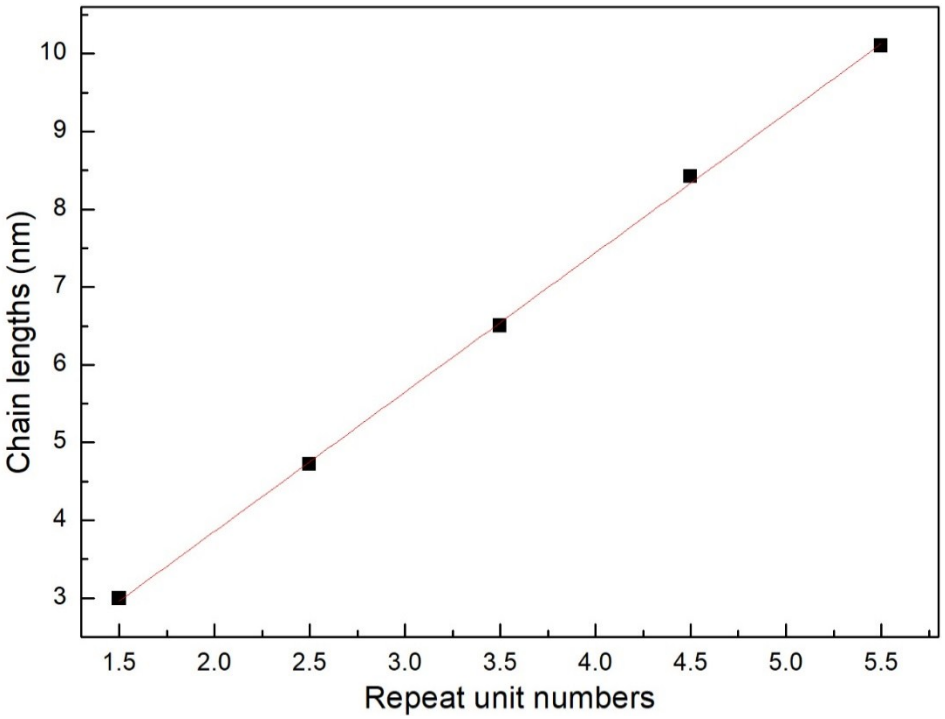


Fig. S5 DFT-optimized geometries of oligomers **O**s1~5 (the alkyl chains replaced by methyl groups).



oligomers	**O**1	**O**2	**O**3	**O**4	**O**5
repeat unit numbers	1.5	2.5	3.5	4.5	5.5
length (nm)	2.99	4.72	6.50	8.42	10.12

Fig. S6 Linear correlation between the repeat unit number and chain lengths of the oligomers **O**s1~5.

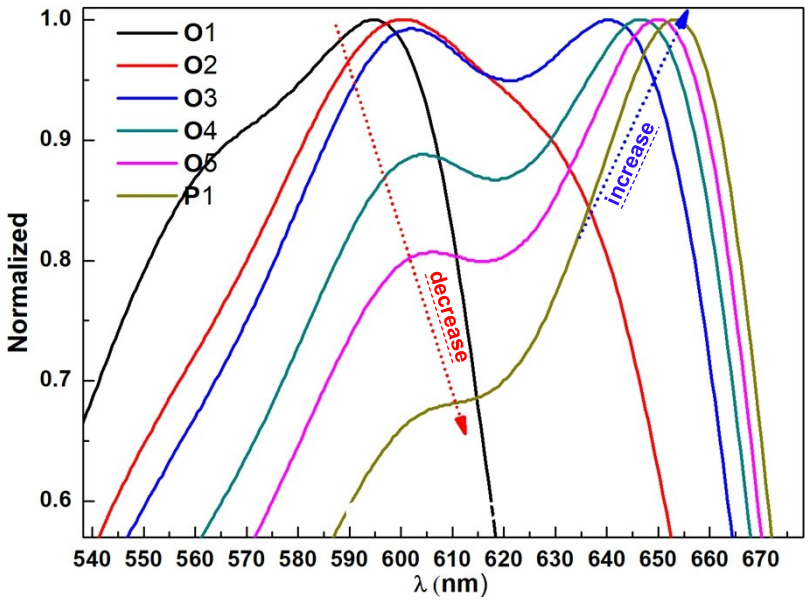
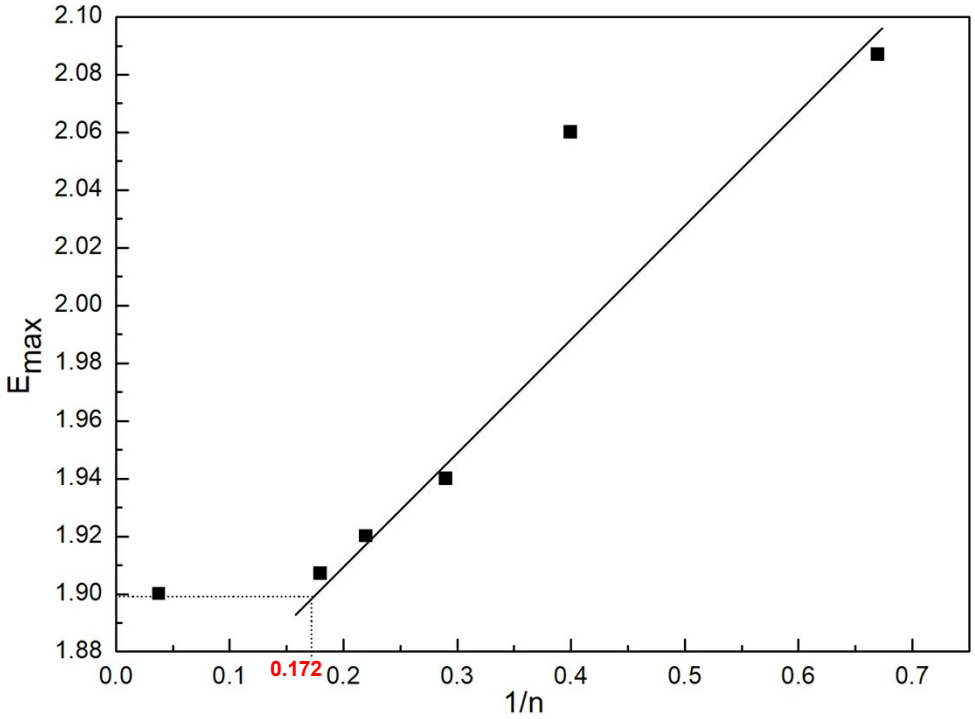
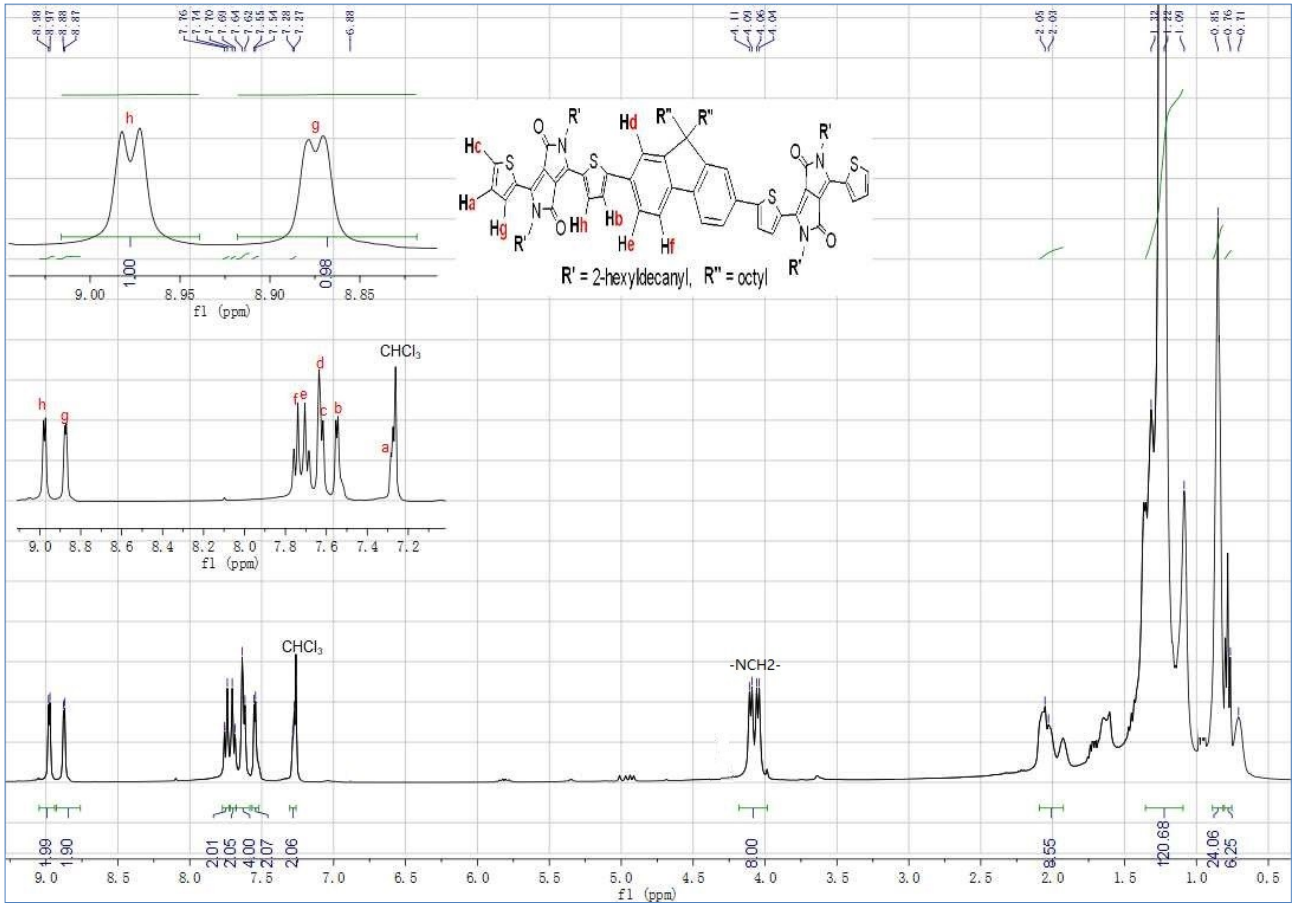


Fig. S7 Partial enlargement of the absorption peaks of Uv-vis spectra of **O**s1~5 and **P**1



Oligomers & polymer	**O**1	**O**2	**O**3	**O**4	**O**5	**P1**
λ_{max} (nm)	595	600.5	640	646.5	650.5	652.5
E_{max} (eV)	2.08	2.06	1.94	1.92	1.91	1.90
Repeat unit numbers	1.5	2.5	3.5	4.5	5.5	26

Fig. S8 Correlation between absorption energies (E_{max}) and inverse repeat unit numbers (1/n) of oligomers **O**s1~5, [S1] where the repeat unit number (n) of **O**s1~5 are set as 1.5, 2.5, 3.5, 4.5 and 5.5, respectively, the repeat unit number of **P**1 are calculated based on ^{1}H NMR.



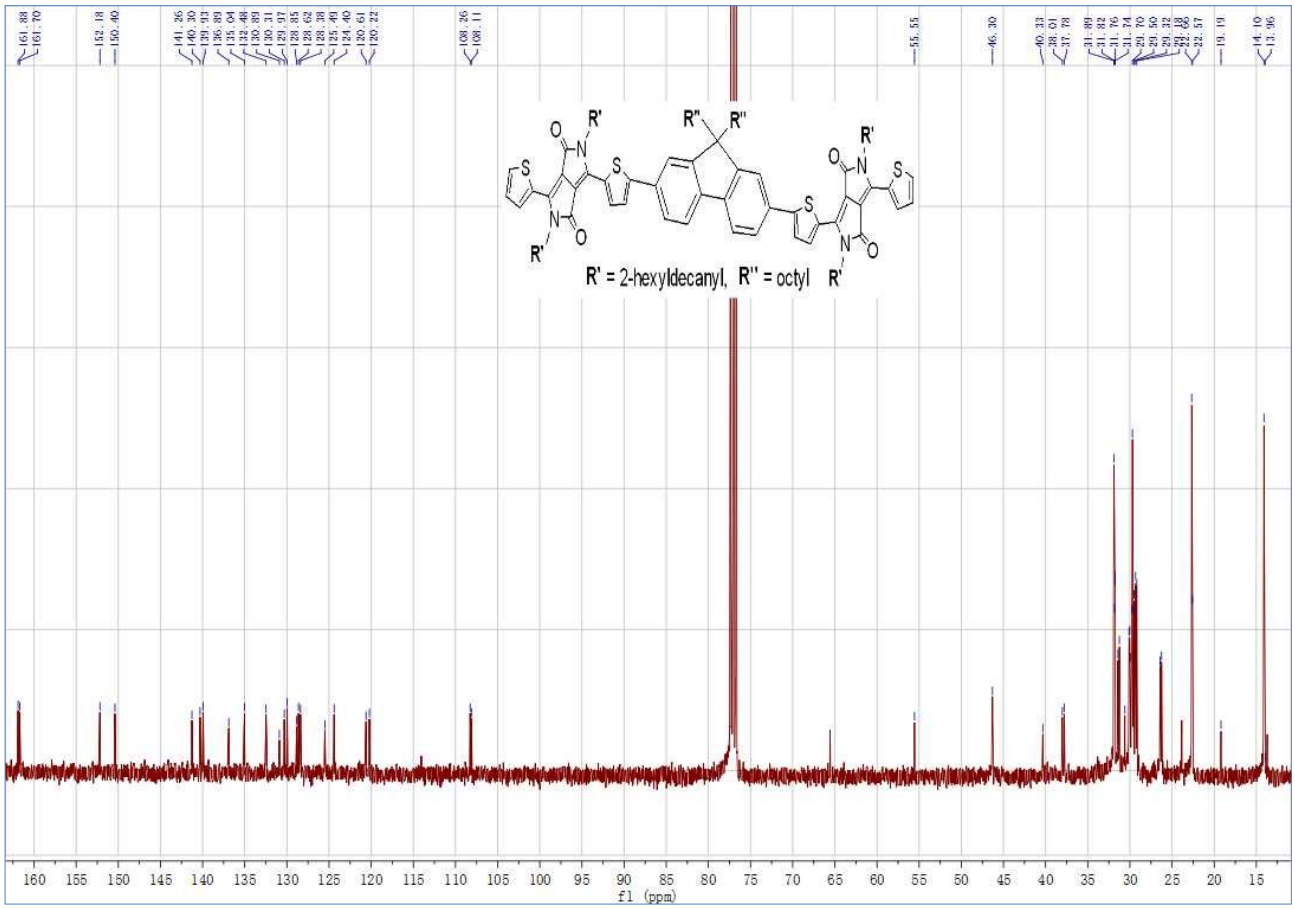
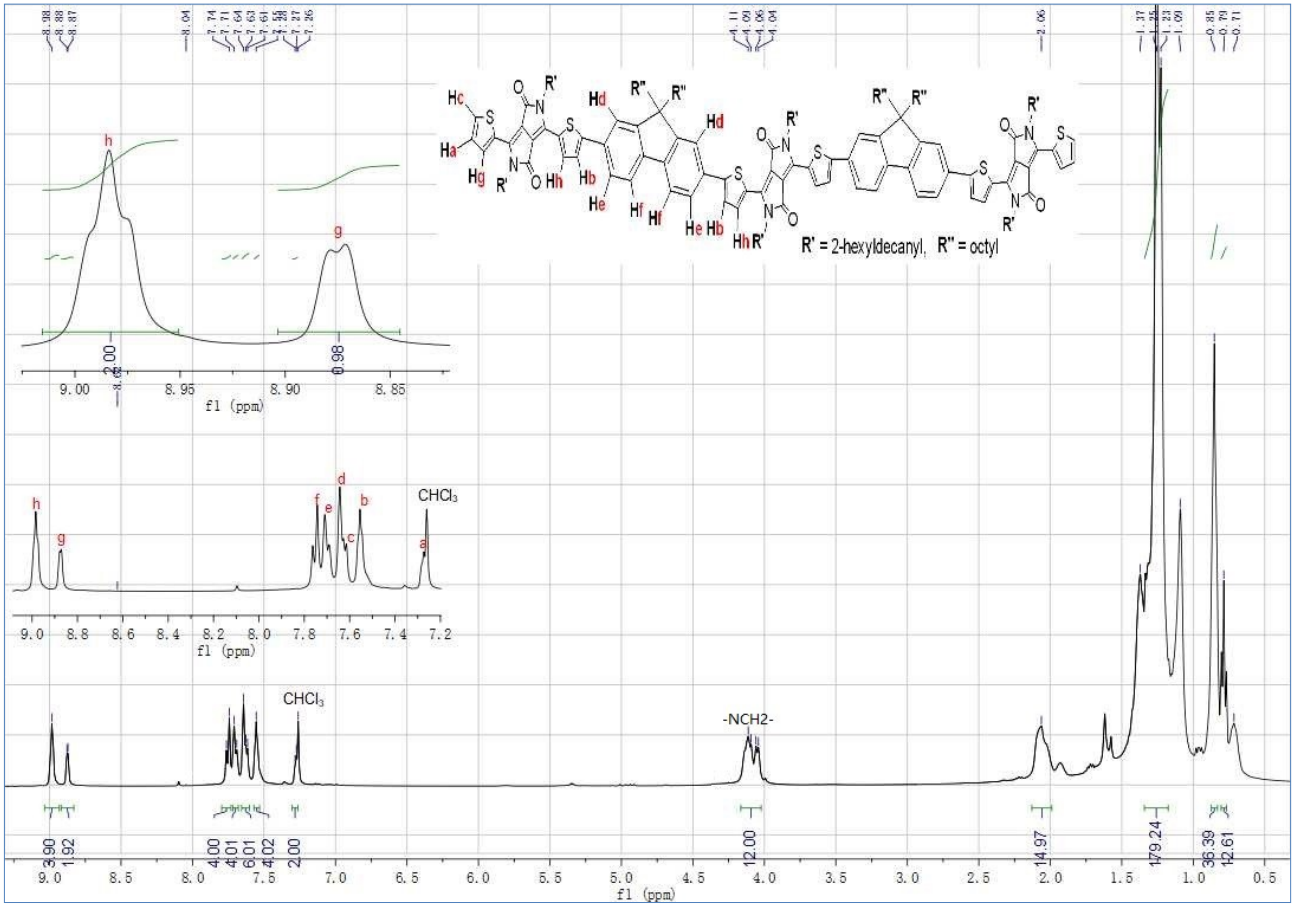


Fig. S9 ^{1}H and ^{13}C NMR spectra of **O**1 in $CDCl_3$.



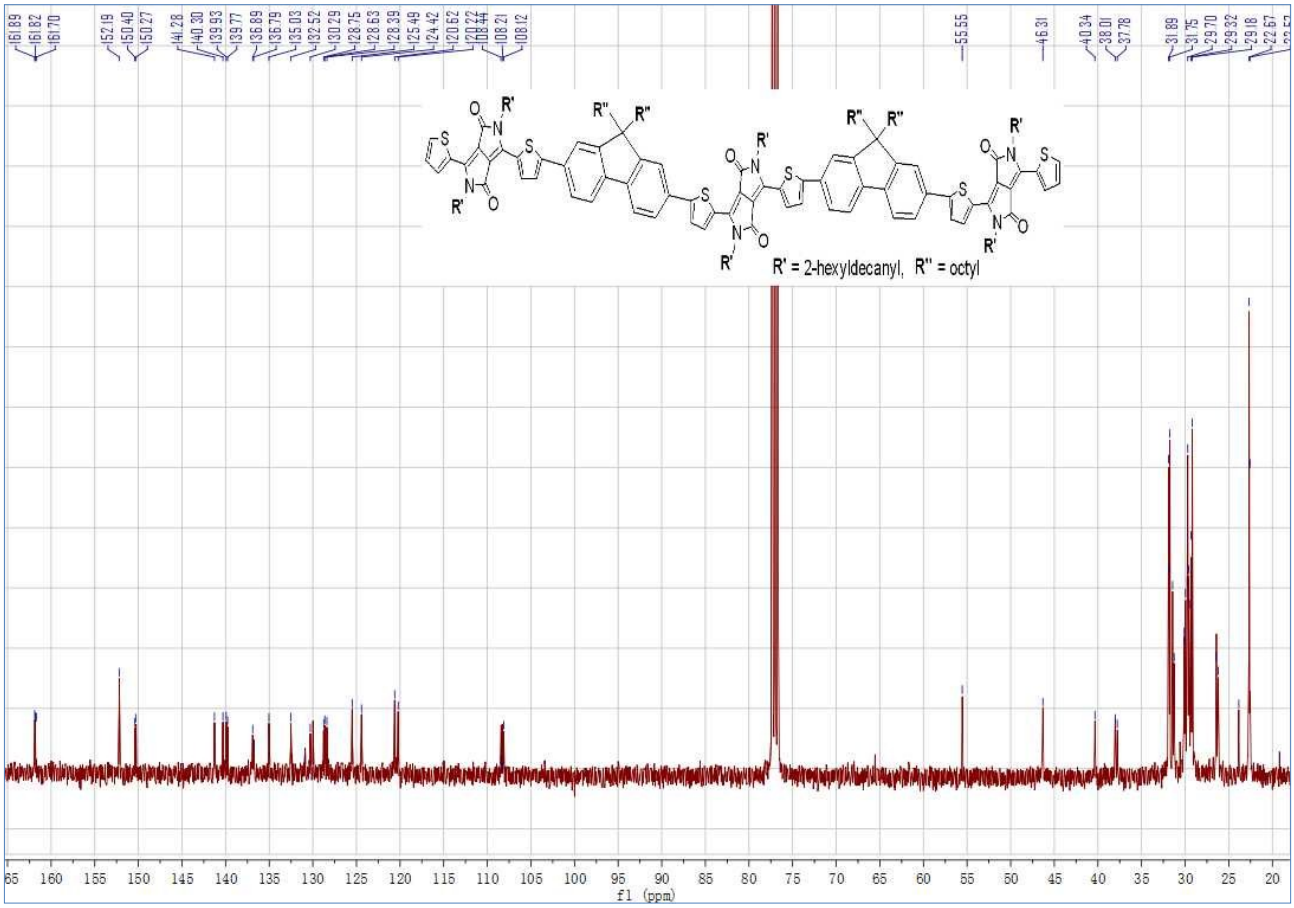
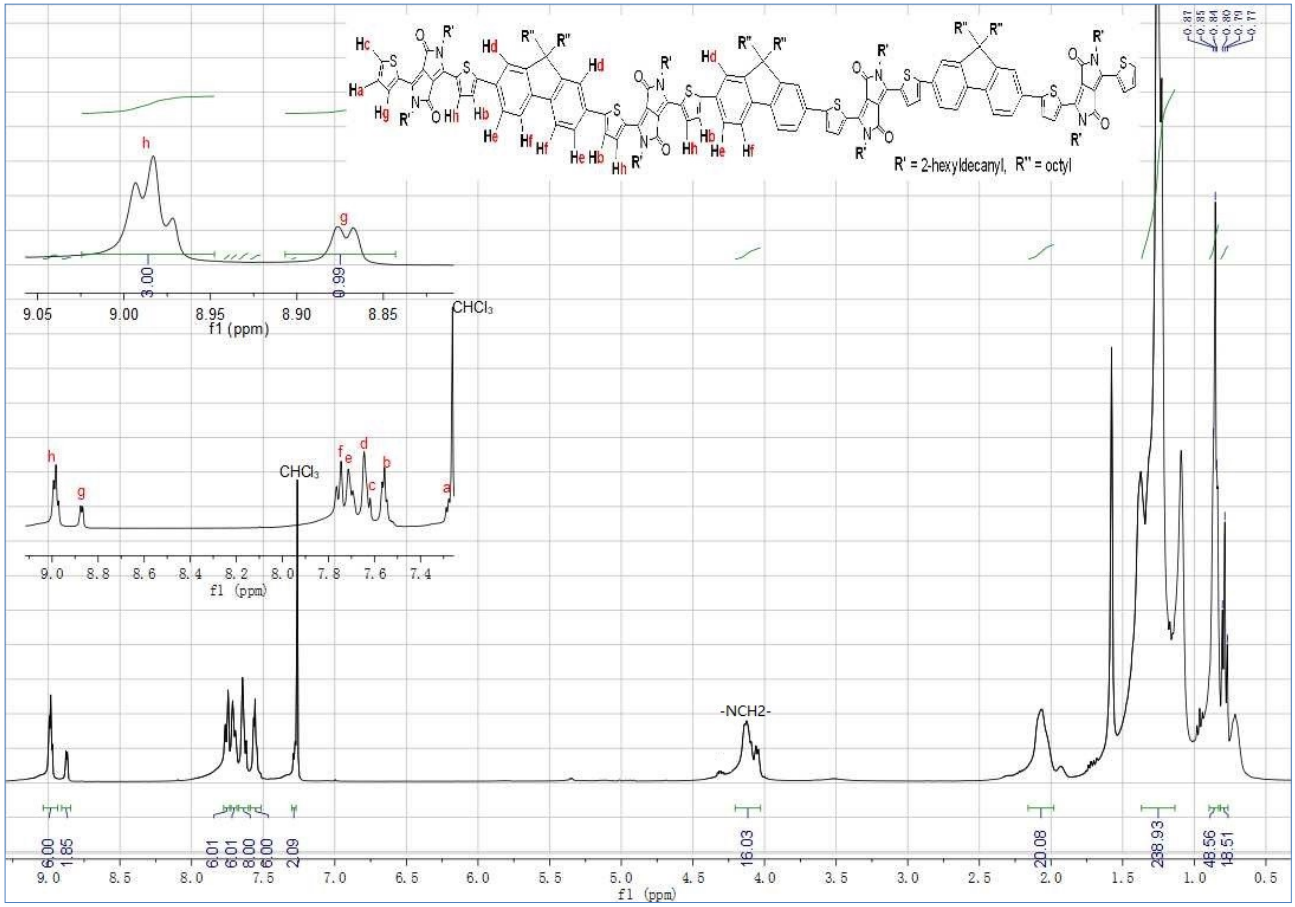


Fig. S10 ^{1}H and ^{13}C NMR spectra of **O2** in $CDCl_3$.



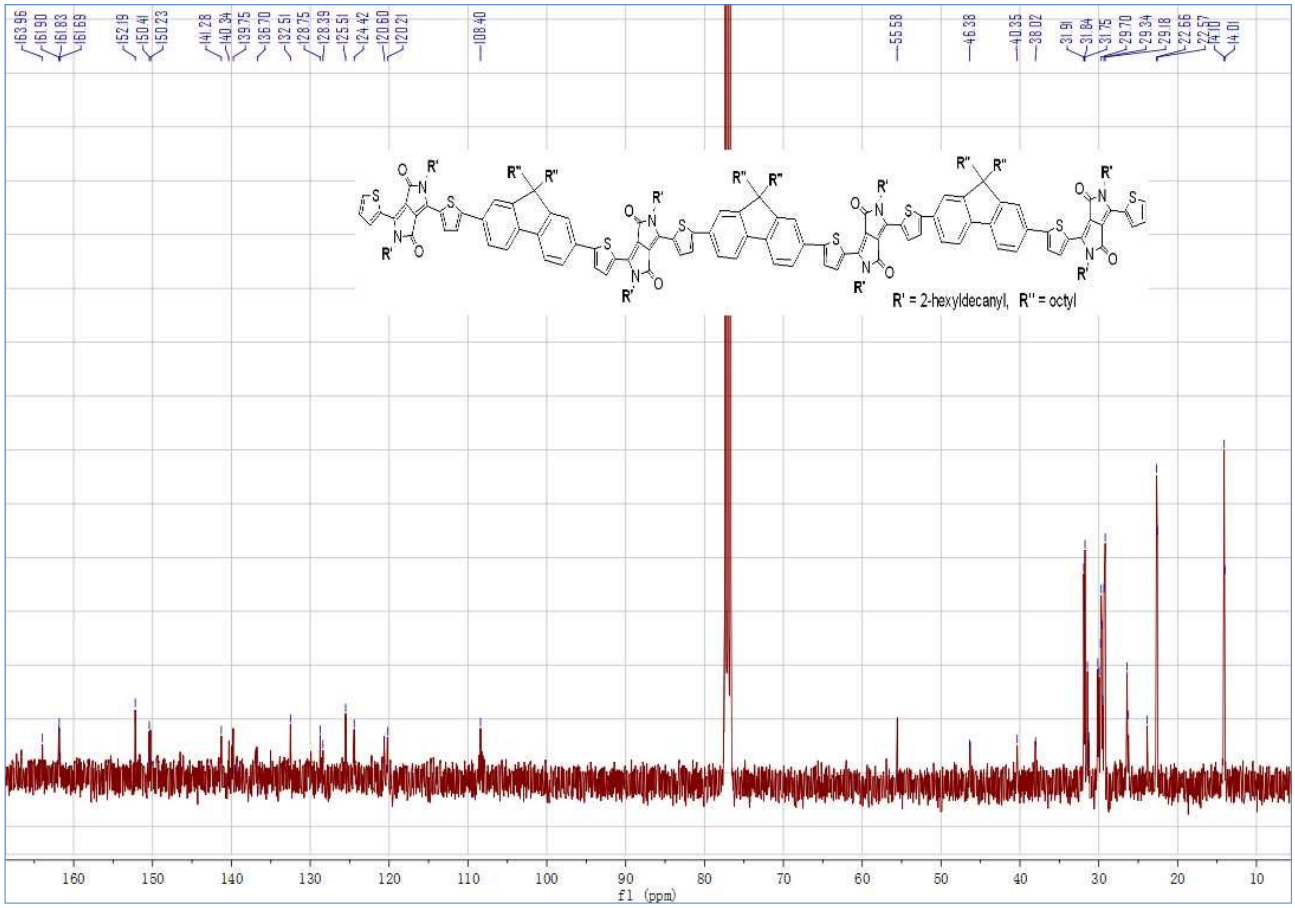


Fig. S11 ^{1}H and ^{13}C NMR spectra of **O3** in $CDCl_3$.

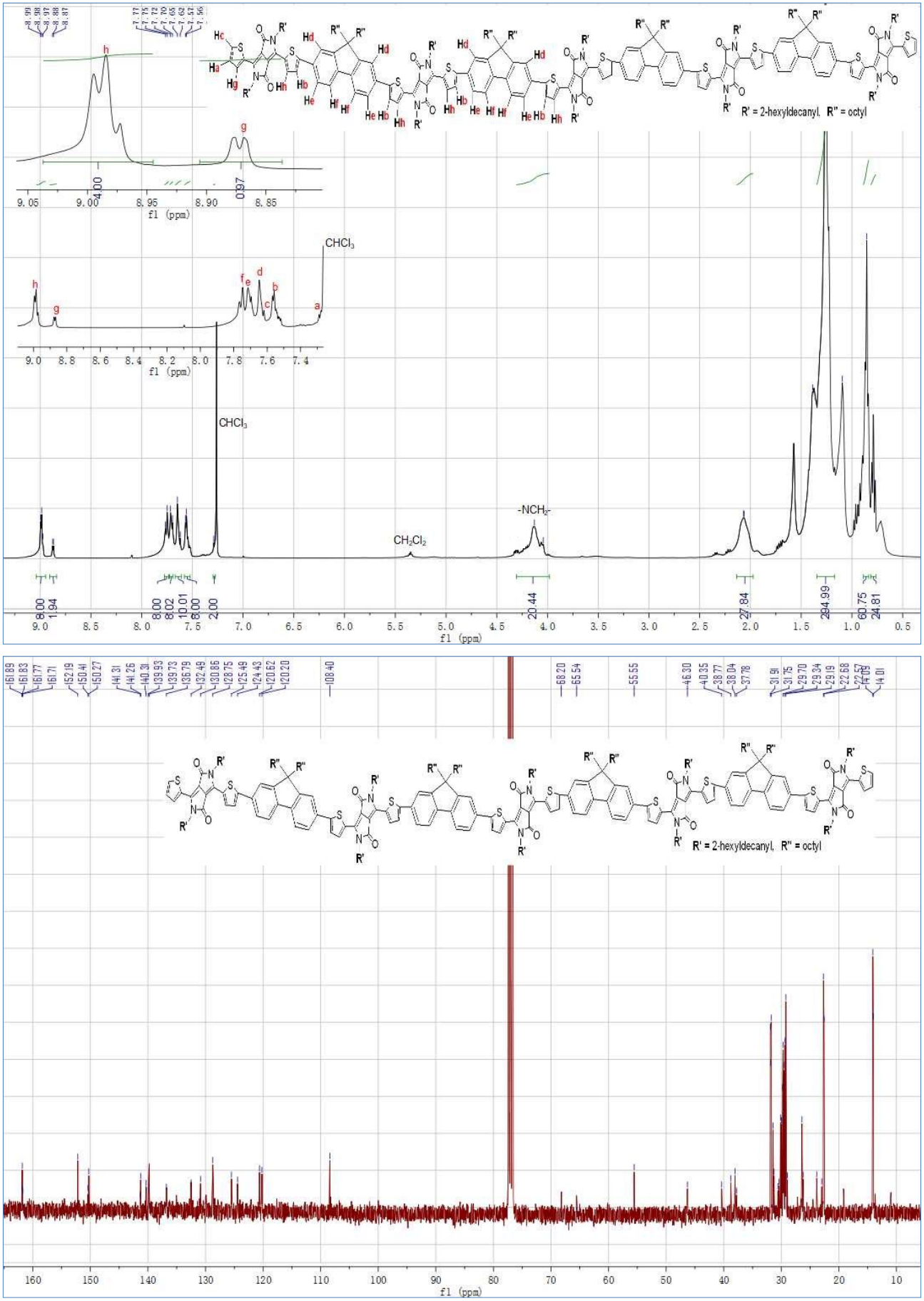


Fig. S12 ^{1}H and ^{13}C NMR spectra of **O**4 in $CDCl_3$.

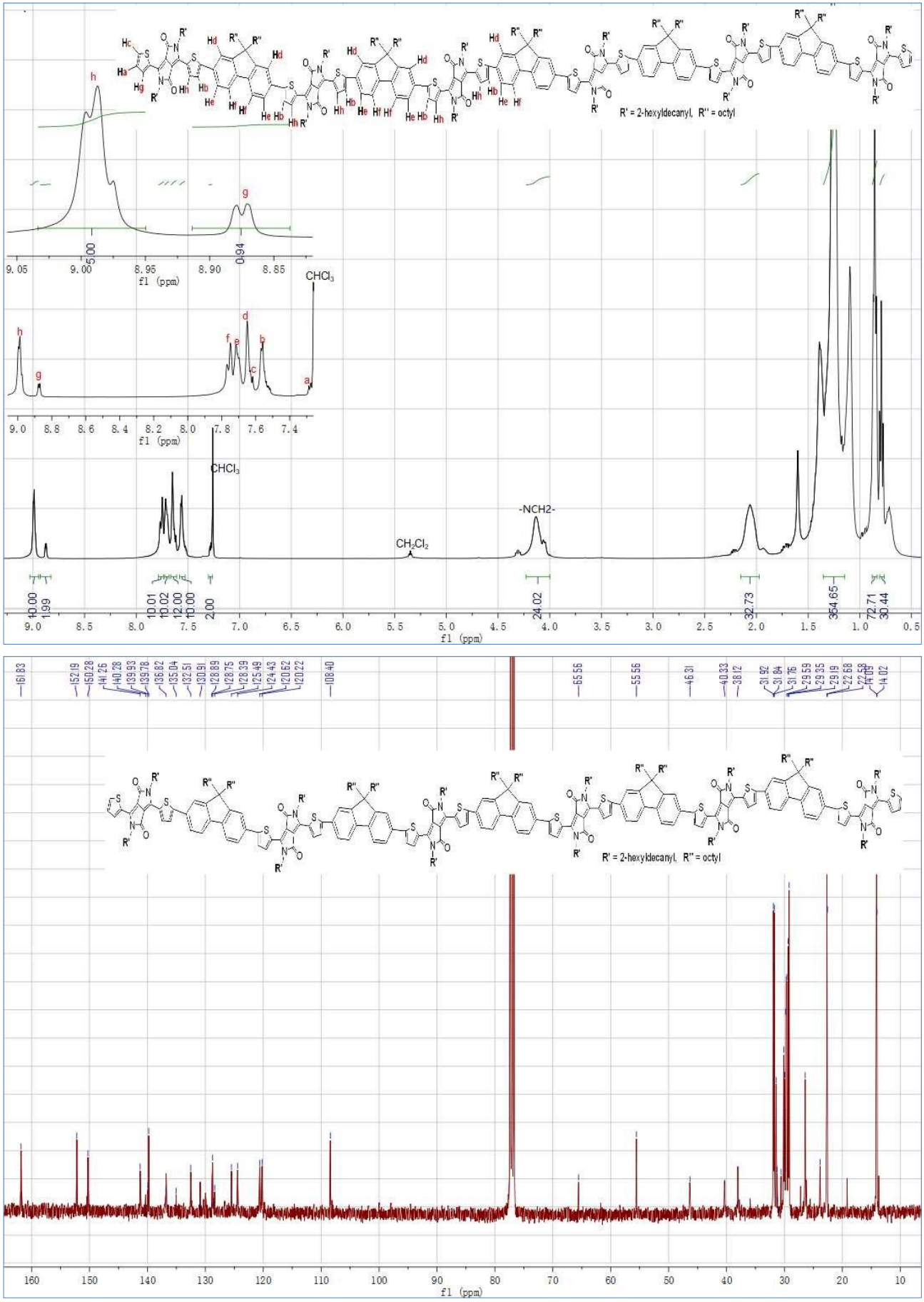


Fig. S13 ^{1}H and ^{13}C NMR spectra of **O5** in $CDCl_3$.

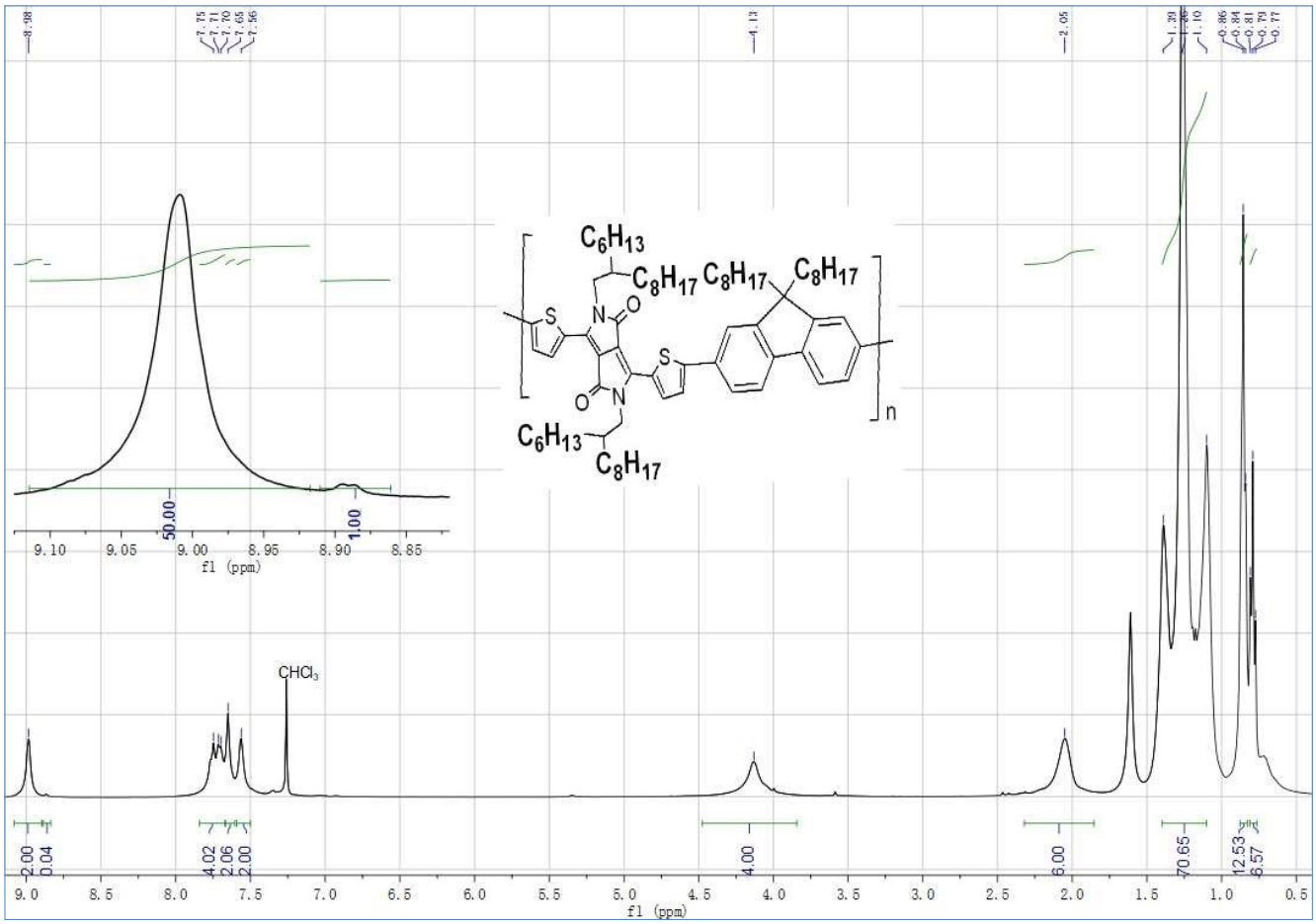


Fig. S14 ^{1}H NMR spectra of **P**1 in $CDCl_3$.

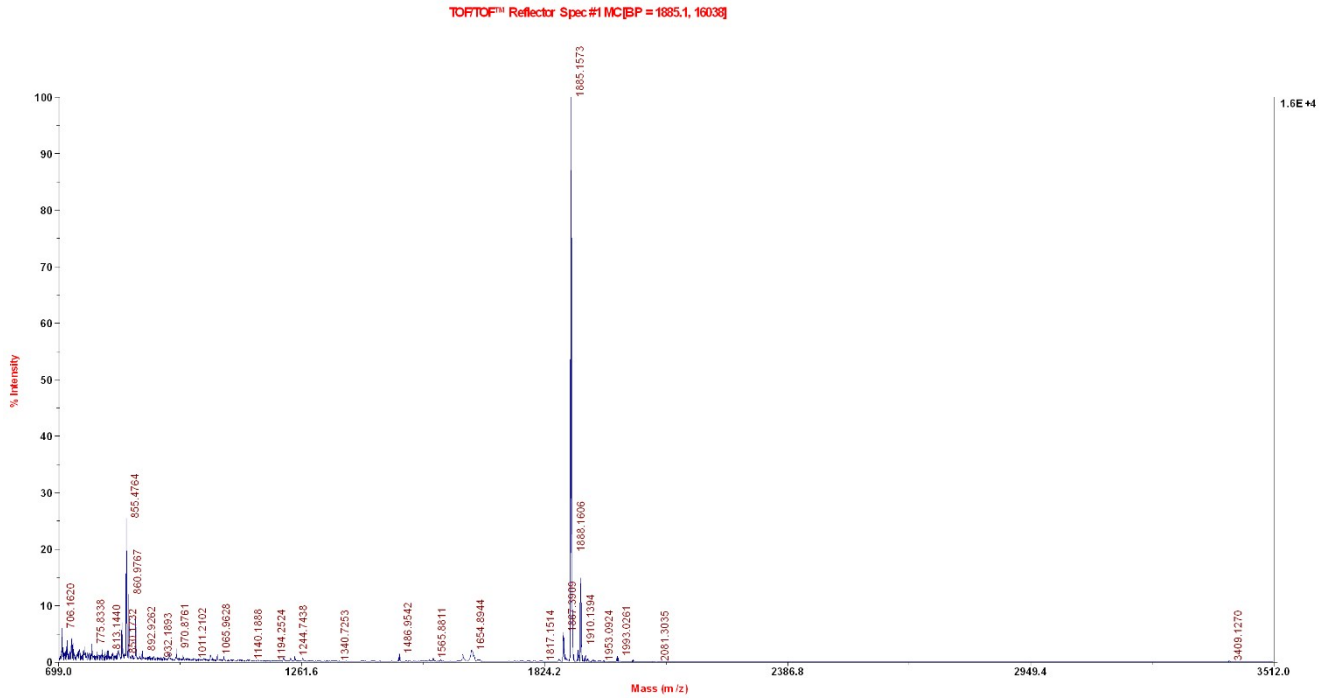


Fig. S15 MALDI-TOF MS of **O**1, calcd. 1885.05, found 1885.16.

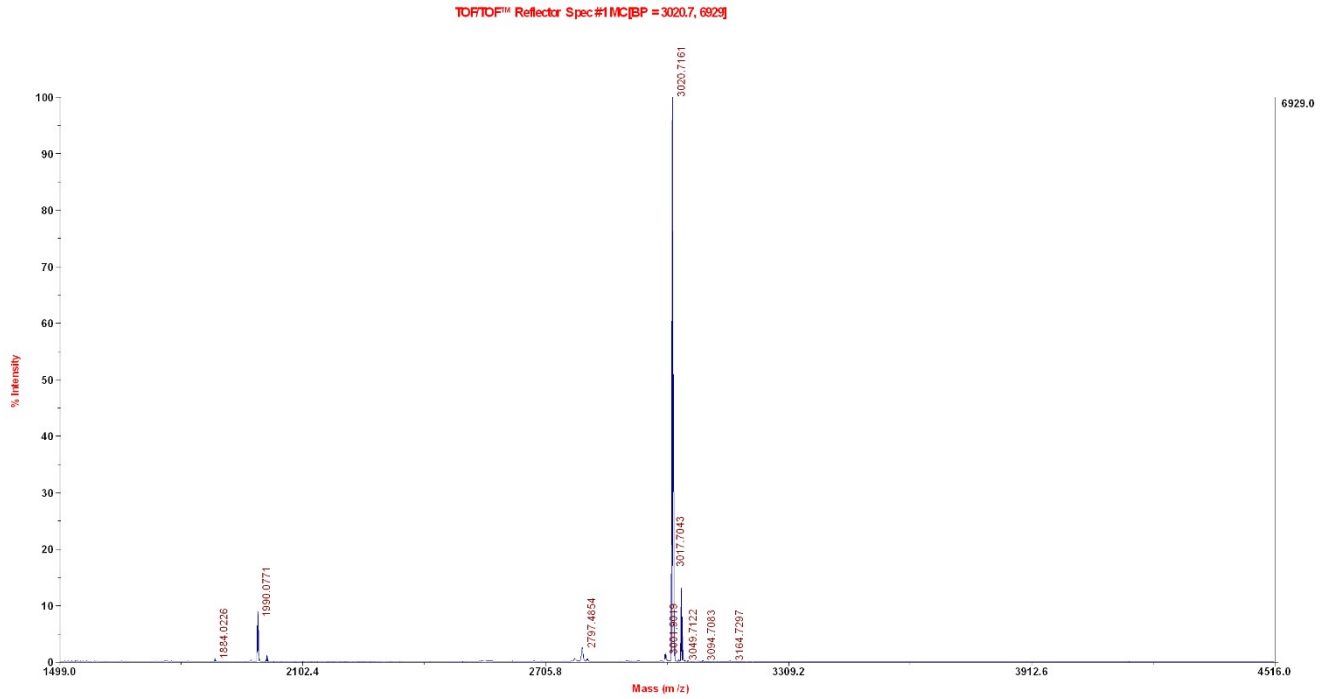


Fig. S16 MALDI-TOF MS of **O**2, calcd. 3020.88, found 3020.72.

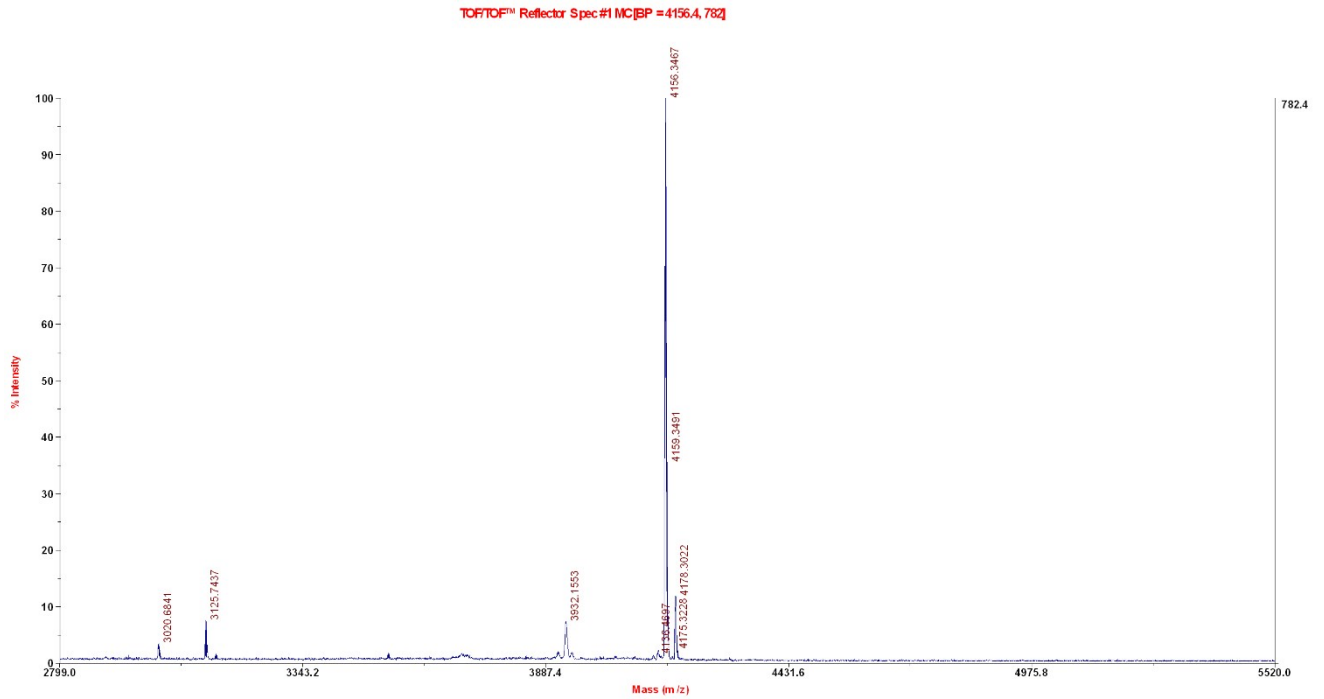


Fig. S17 MALDI-TOF MS of **O**3, calcd. 4156.73, found 4156.35.

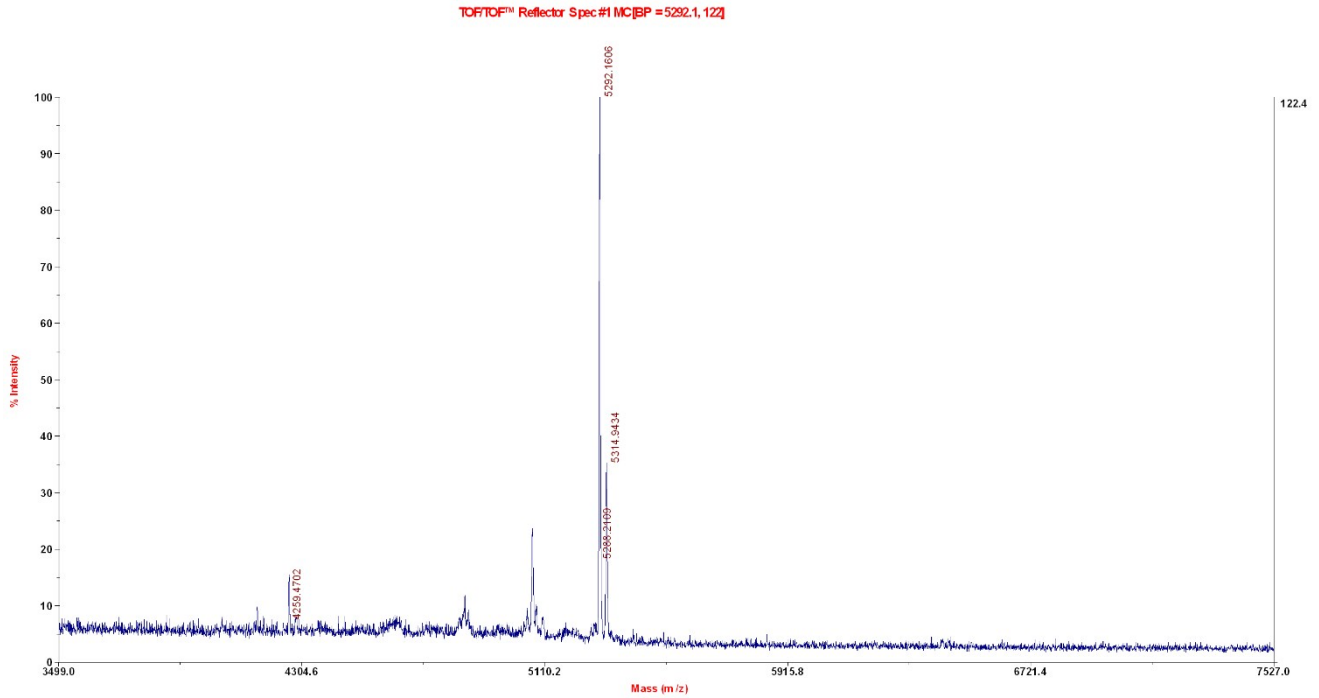


Fig. S18 MALDI-TOF MS of **O**4, calcd. 5294.56, found 5292.16.

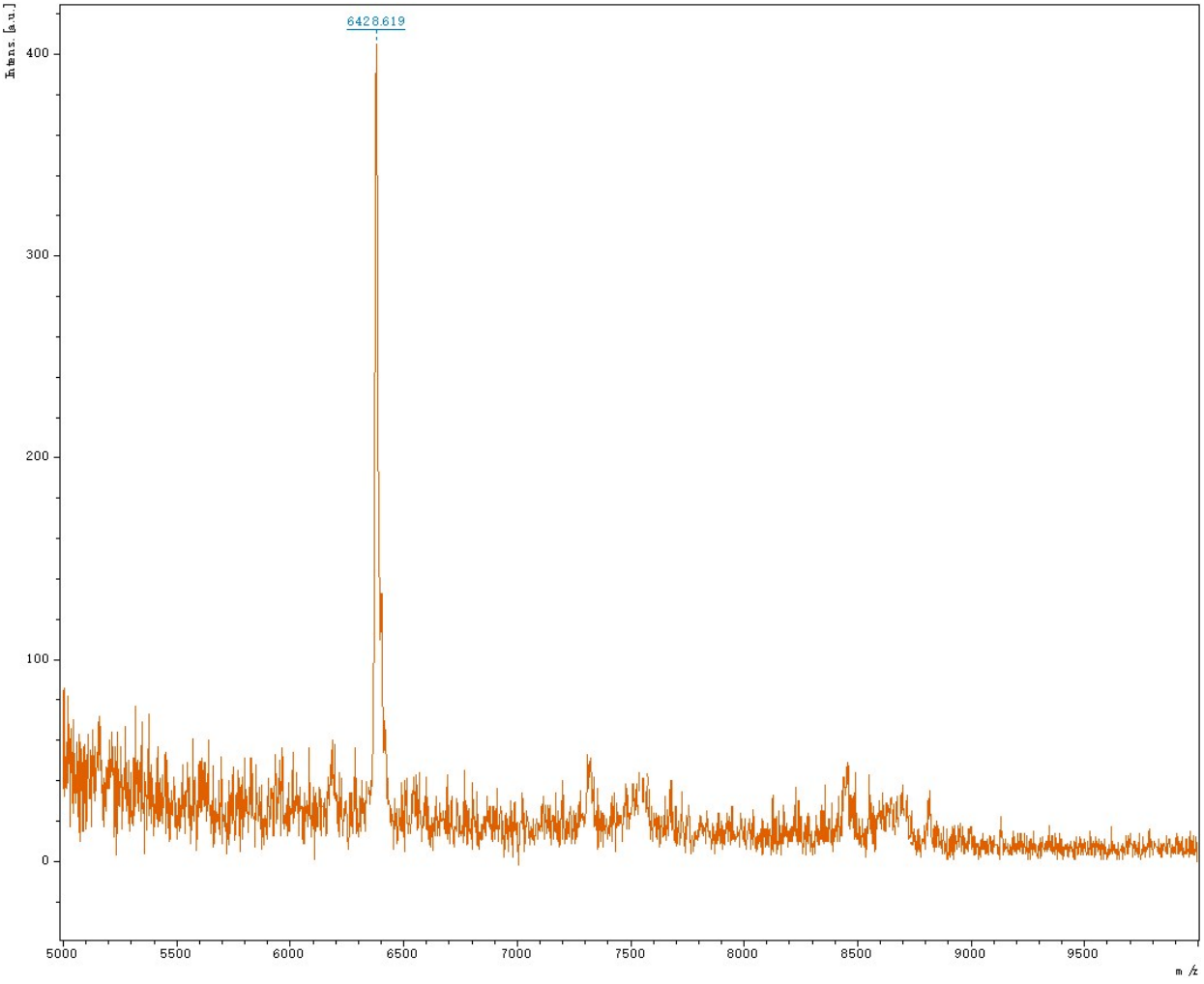


Fig. S19 MALDI-TOF MS of **O**5, calcd. 6428.40, found 6428.62.

Reference

S1 Q. Wang, Y. Qu, H. Tian, Y. Geng, and F. Wang, *Macromolecules*, 2011, *44*, 1256.