

## Supplementary Information

### **Intramolecular Oxidative Cyclodehydrogenation Route for Strap-like Conjugated Polymers Synthesis**

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## S1. The detailed calculated procedures for the charge carrier mobility.

According to the obtained  $V_{th}$  values and the metal-oxide semiconductor FET formula for the saturation regime,  $I_{DS} = \frac{\mu W C_i}{2L} (V_G - V_{th})^2$ , the calculations of the charge carrier mobility ( $\mu$ ) are below:

### OPTVB

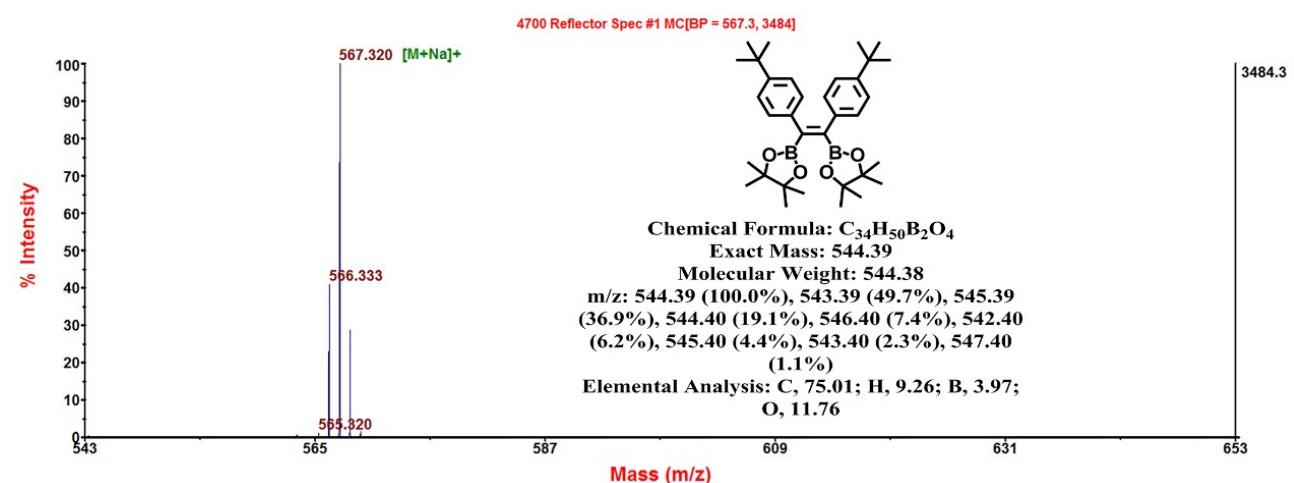
$$V_G = 0 \text{ V}, I_{DS} = 1.78 \times 10^{-7} \text{ A}, C_i = 20 \mu\text{F}/\text{cm}^2, W = 0.6 \text{ mm}, L = 1 \text{ mm}, V_{th} = -0.28 \text{ V}$$

$$\begin{aligned} \mu &= 2LI_{DS}/[WC_i(V_G - V_{th})^2] = 2I_{DS}/[WC_i(V_G - V_{th})^2] \\ &= 2 \times 1.78 \times 10^{-7} / [0.6 \times 20 \times 10^{-6} \times (0 + 0.28)^2] \\ &= 0.38 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \end{aligned}$$

### OPTVN

$$V_G = -3 \text{ V}, I_{DS} = 1.73 \times 10^{-5} \text{ A}, C_i = 20 \mu\text{F}/\text{cm}^2, W = 0.6 \text{ mm}, L = 1 \text{ mm}, V_{th} = -0.54 \text{ V}$$

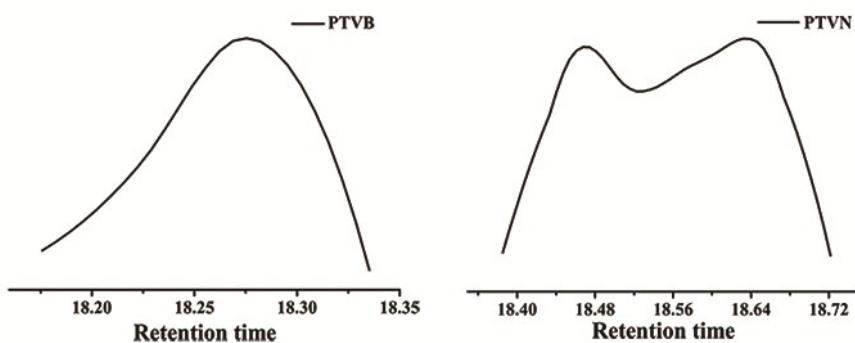
$$\begin{aligned} \mu &= 2LI_{DS}/[WC_i(V_G - V_{th})^2] = 2I_{DS}/[WC_i(V_G - V_{th})^2] \\ &= 2 \times 1.73 \times 10^{-5} / [0.6 \times 20 \times 10^{-6} \times (-3 + 0.54)^2] \\ &= 0.48 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \end{aligned}$$



**Fig. S1** The MALDI-TOF of 2.

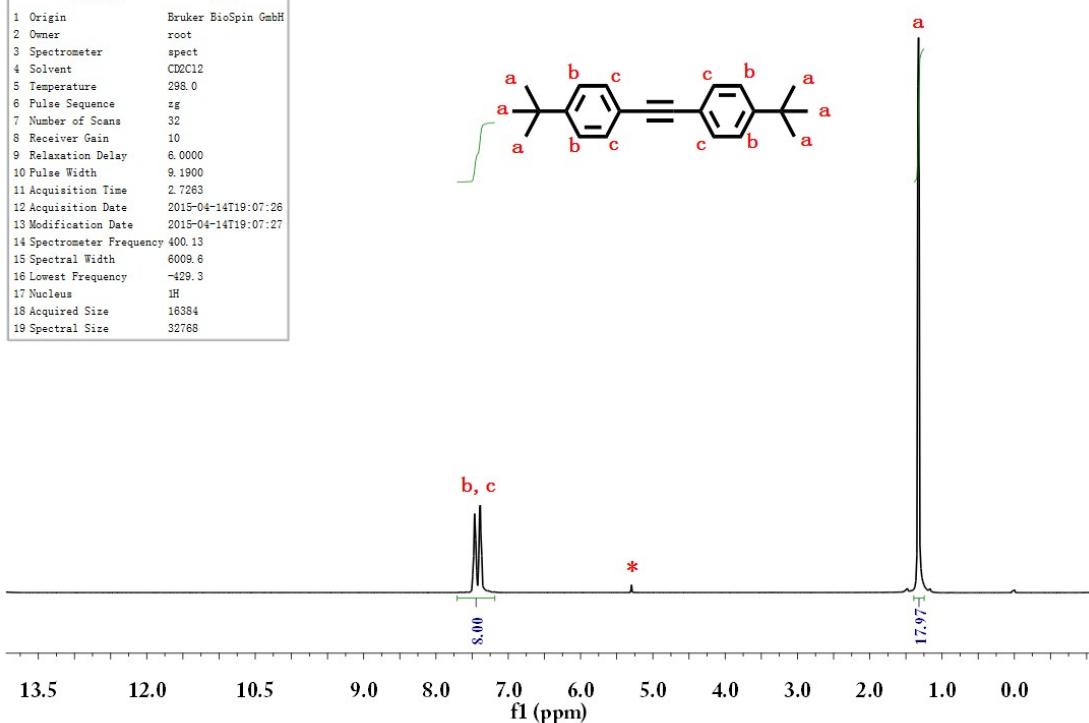
**Table S1** Summary of crystal data and reflection collection parameters for **1** and **2**.

Empirical formula	C <sub>22</sub> H <sub>26</sub>	C <sub>34</sub> H <sub>50</sub> B <sub>2</sub> O <sub>4</sub>
Formula weight	290.43	544.36
Crystal size, mm	0.32 x 0.28 x 0.24	0.26 x 0.21 x 0.18
Crystal system	Monoclinic, P21/c	Triclinic
space group	P2(1)/c	P-1
a, Å	11.731(4)	10.991(18)
b, Å	10.216(4)	12.54(2)
c, Å	15.667(6)	13.97(4)
a, deg	90	108.83(5)
β, deg	96.915(7)	103.58(5)
γ, deg	90	104.77(3)
V, Å <sup>3</sup>	1863.9(12)	1653(6)
Z	4	2
Calculated density, Mg/m <sup>3</sup>	1.035	1.094
F(000)	632	592
Temperature, K	293(2)	296(2)
Wavelength, Å	0.71073	0.71073
μ(Mo Ka), mm <sup>-1</sup>	0.058	0.068
2θ <sub>max</sub> , deg (Completeness )	25.00 (99.8 %)	24.99(97.8 %)
no. of collected reflections	9206	8152
no. of unique ref.(R <sub>int</sub> )	3272 (0.0387)	5701 (0.0933)
Data/restraints/parameters	3272 / 6 / 200	5701 / 0 / 362
R <sub>1</sub> , wR <sub>2</sub> [obs I>2σ (I)]	0.0967, 0.1832	0.1322, 0.2363
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.1394, 0.1951	0.1805, 0.2686
residual peak/hole, e. Å <sup>-3</sup>	0.486 /-0.290	0.436/-0.302
transmission ratio	0.9863 /0.9817	0.9878/0.9824
Goodness-of-fit on F <sup>2</sup>	1.013	1.196



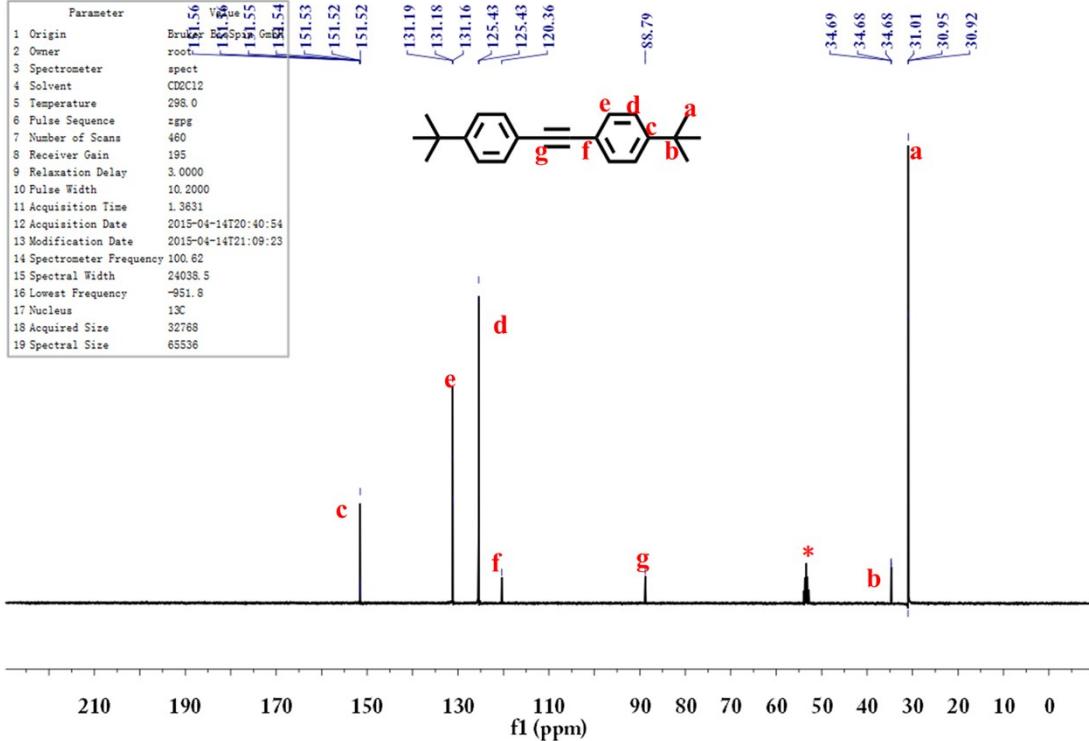
**Fig. S2** The GPC data of **PTVB** and **PTVN**.

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	root
3 Spectrometer	spect
4 Solvent	CDCl <sub>3</sub>
5 Temperature	298.0
6 Pulse Sequence	zg
7 Number of Scans	32
8 Receiver Gain	10
9 Relaxation Delay	6.0000
10 Pulse Width	8.1900
11 Acquisition Time	2.7263
12 Acquisition Date	2015-04-14T19:07:26
13 Modification Date	2015-04-14T19:07:27
14 Spectrometer Frequency	400.13
15 Spectral Width	6009.6
16 Lowest Frequency	-429.3
17 Nucleus	<sup>1</sup> H
18 Acquired Size	16384
19 Spectral Size	32768



**Fig. S3** <sup>1</sup>H NMR spectrum of **1**.

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	root
3 Spectrometer	spect
4 Solvent	CDCl <sub>3</sub>
5 Temperature	298.0
6 Pulse Sequence	zgpg
7 Number of Scans	460
8 Receiver Gain	195
9 Relaxation Delay	3.0000
10 Pulse Width	10.2000
11 Acquisition Time	1.3831
12 Acquisition Date	2015-04-14T20:40:54
13 Modification Date	2015-04-14T21:09:23
14 Spectrometer Frequency	100.62
15 Spectral Width	24038.5
16 Lowest Frequency	-951.8
17 Nucleus	<sup>13</sup> C
18 Acquired Size	32768
19 Spectral Size	65536



**Fig. S4** <sup>13</sup>C NMR spectrum of **1**.

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	root
3 Spectrometer	spect
4 Solvent	CDCl <sub>3</sub>
5 Temperature	298.0
6 Pulse Sequence	zg
7 Number of Scans	32
8 Receiver Gain	10
9 Relaxation Delay	6.0000
10 Pulse Width	9.1800
11 Acquisition Time	2.7263
12 Acquisition Date	2015-04-14T19:17:40
13 Modification Date	2015-04-14T19:17:41
14 Spectrometer Frequency	400.13
15 Spectral Width	6009.6
16 Lowest Frequency	-429.3
17 Nucleus	1H
18 Acquired Size	16384
19 Spectral Size	32768

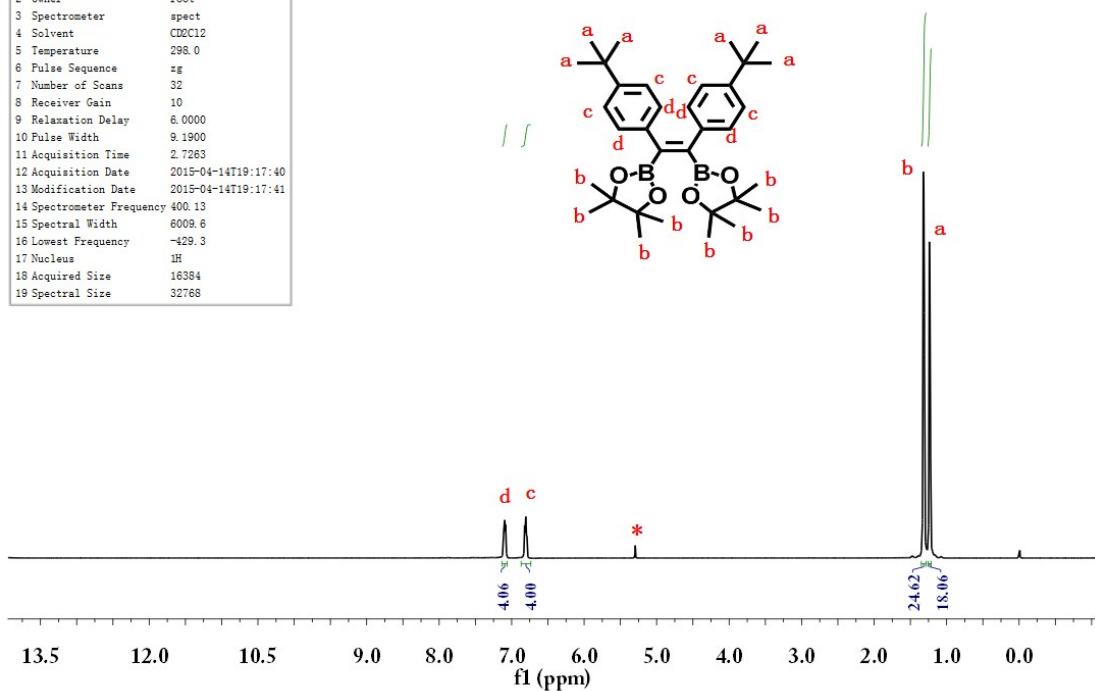


Fig. S5 <sup>1</sup>H NMR spectrum of 2.

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	root
3 Spectrometer	spect
4 Solvent	CDCl <sub>3</sub>
5 Temperature	298.0
6 Pulse Sequence	zgpg
7 Number of Scans	920
8 Receiver Gain	195
9 Relaxation Delay	3.0000
10 Pulse Width	10.2000
11 Acquisition Time	1.3631
12 Acquisition Date	2015-04-14T20:28:53
13 Modification Date	2015-04-14T20:29:56
14 Spectrometer Frequency	100.62
15 Spectral Width	24038.5
16 Lowest Frequency	-951.8
17 Nucleus	<sup>13</sup> C
18 Acquired Size	32768
19 Spectral Size	65536

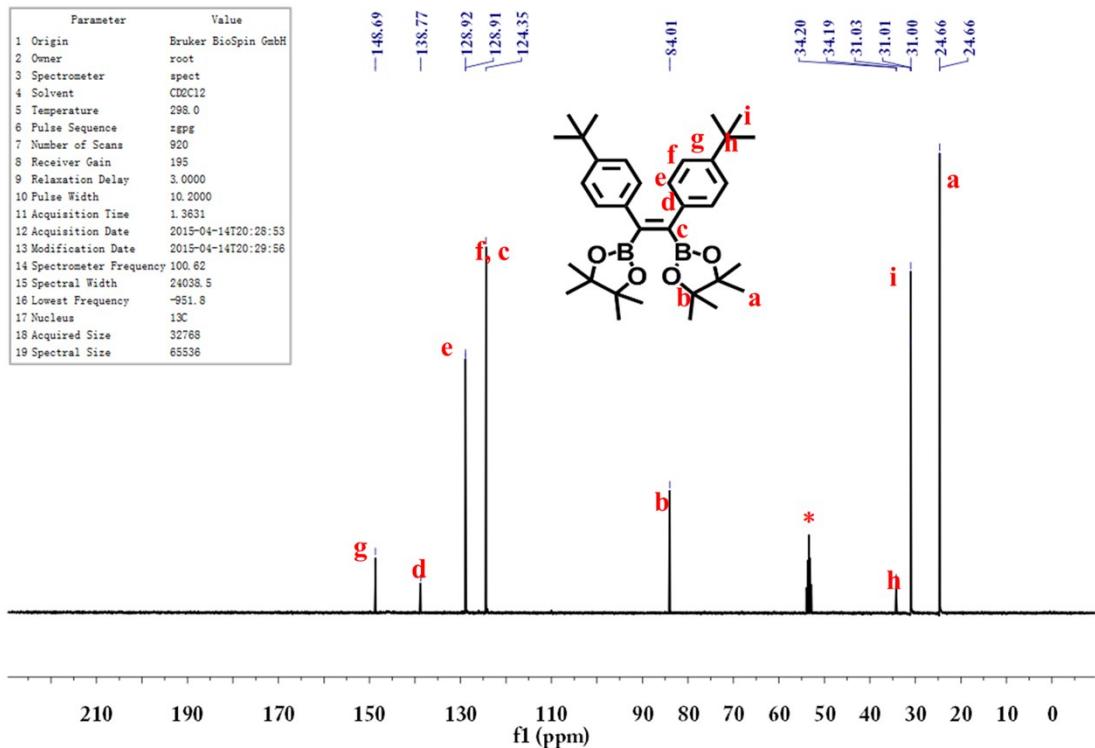


Fig. S6 <sup>13</sup>C NMR spectrum of 2.

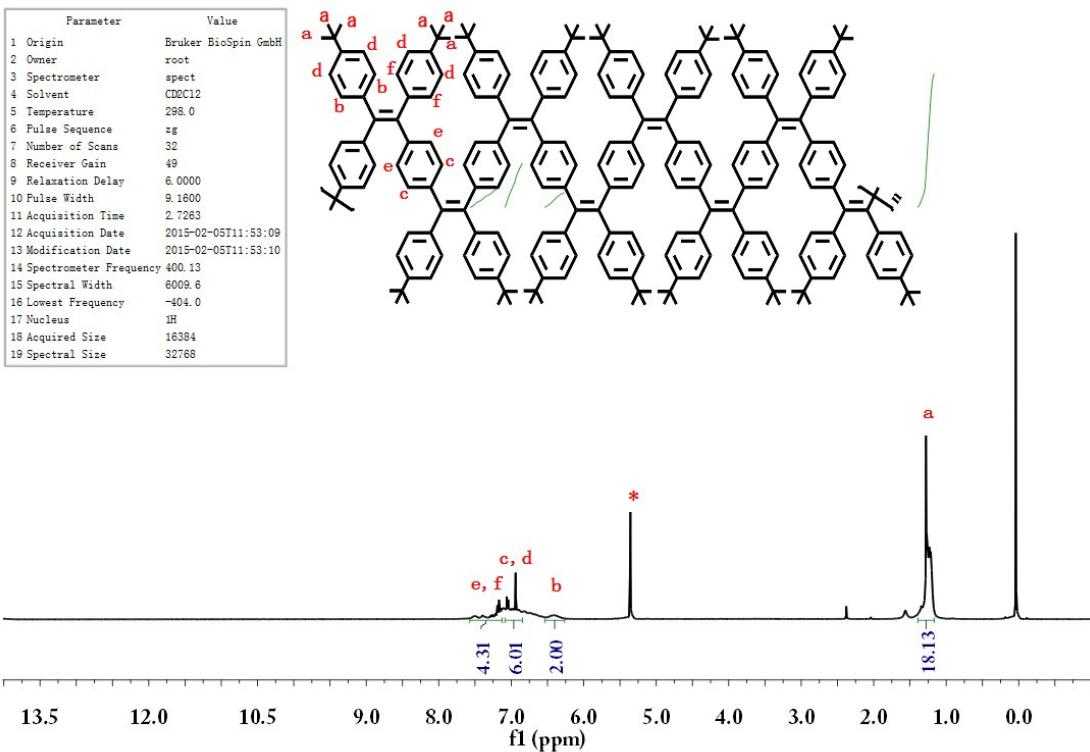


Fig. S7 <sup>1</sup>H NMR spectrum of PTVB.

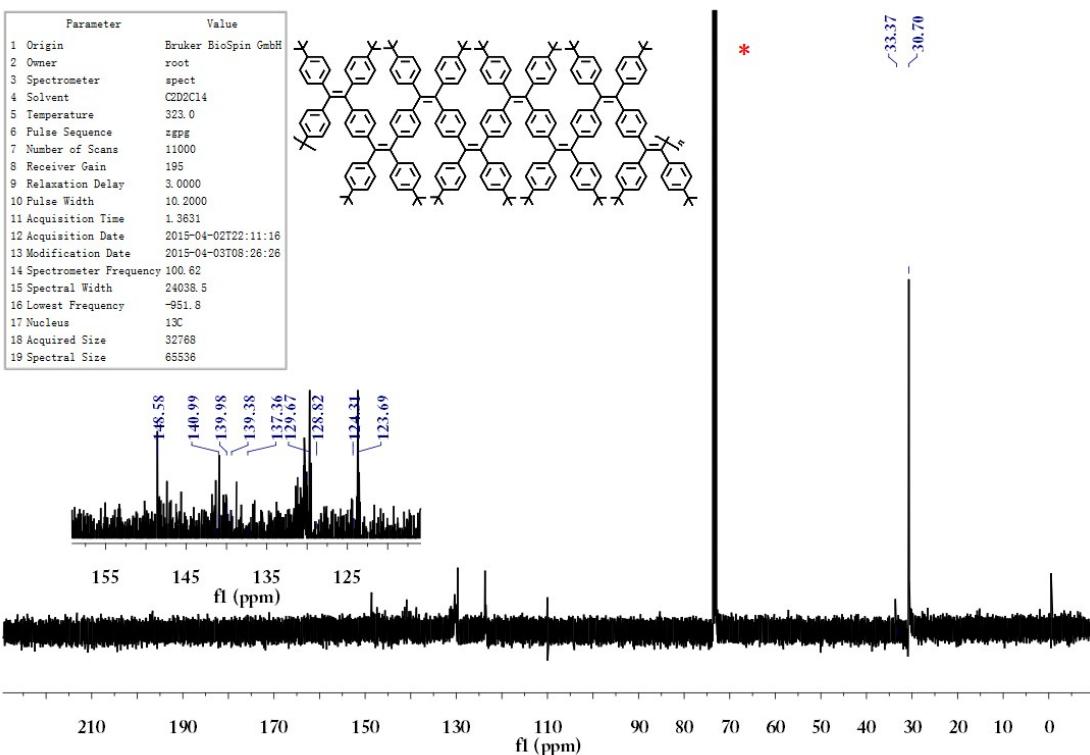


Fig. S8 <sup>13</sup>C NMR spectrum of PTVB.

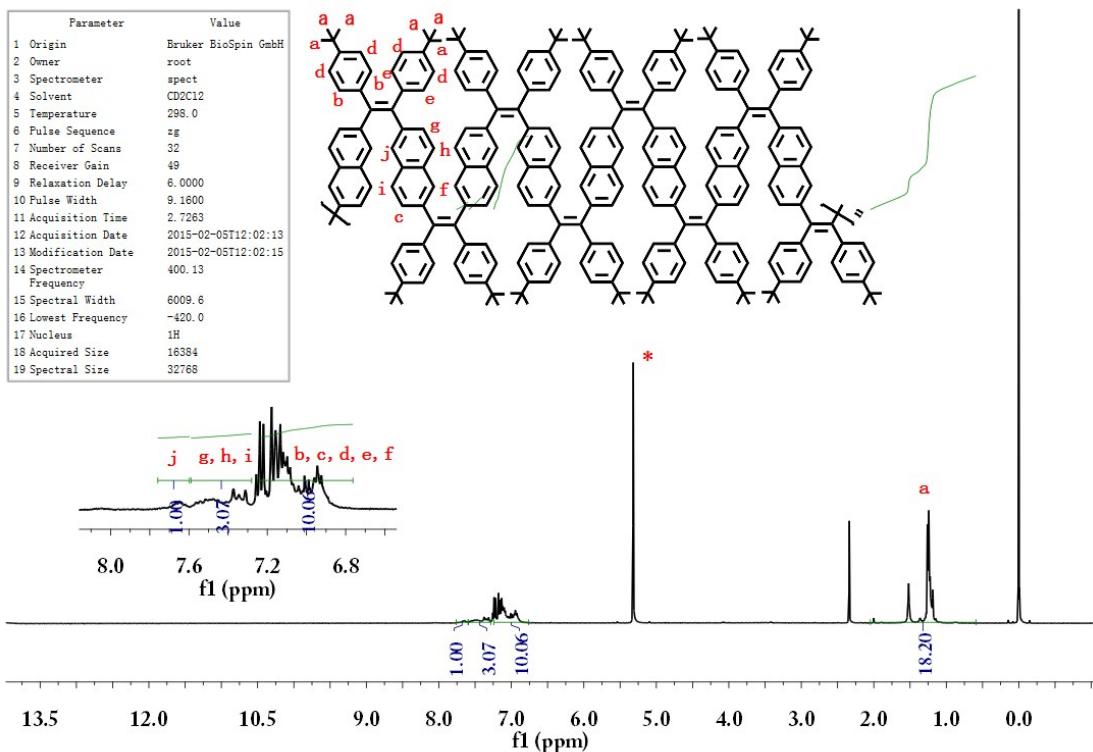


Fig. S9 <sup>1</sup>H NMR spectrum of PTVN.

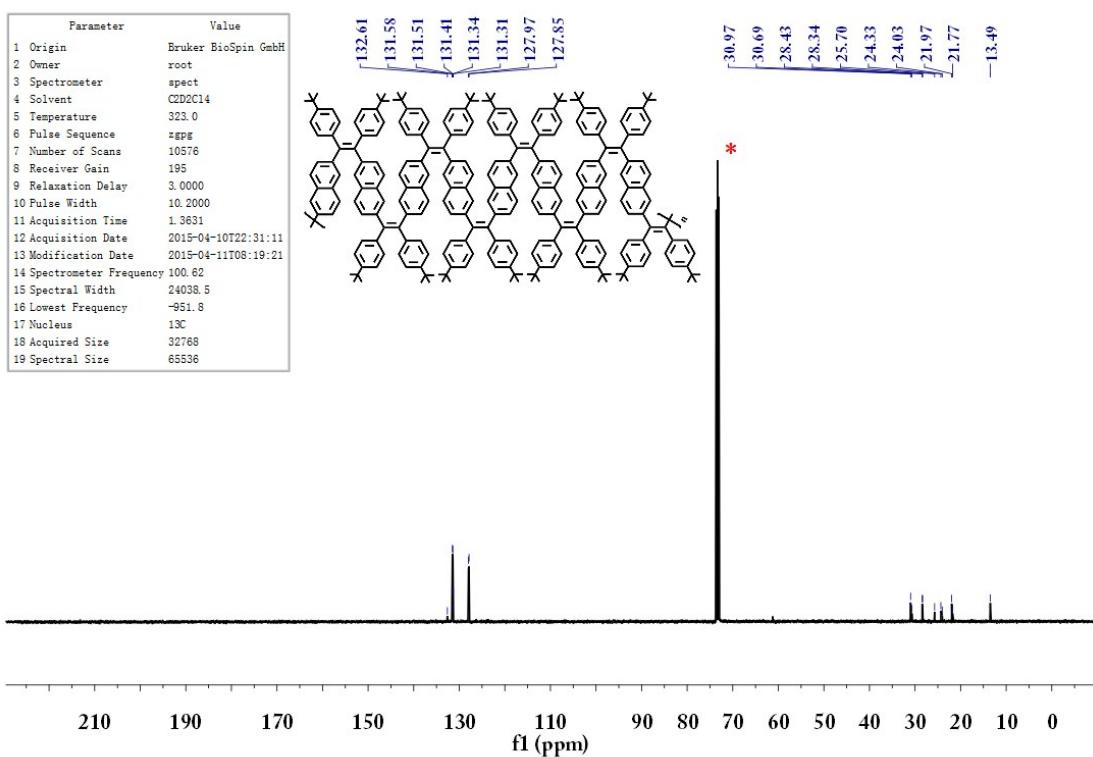
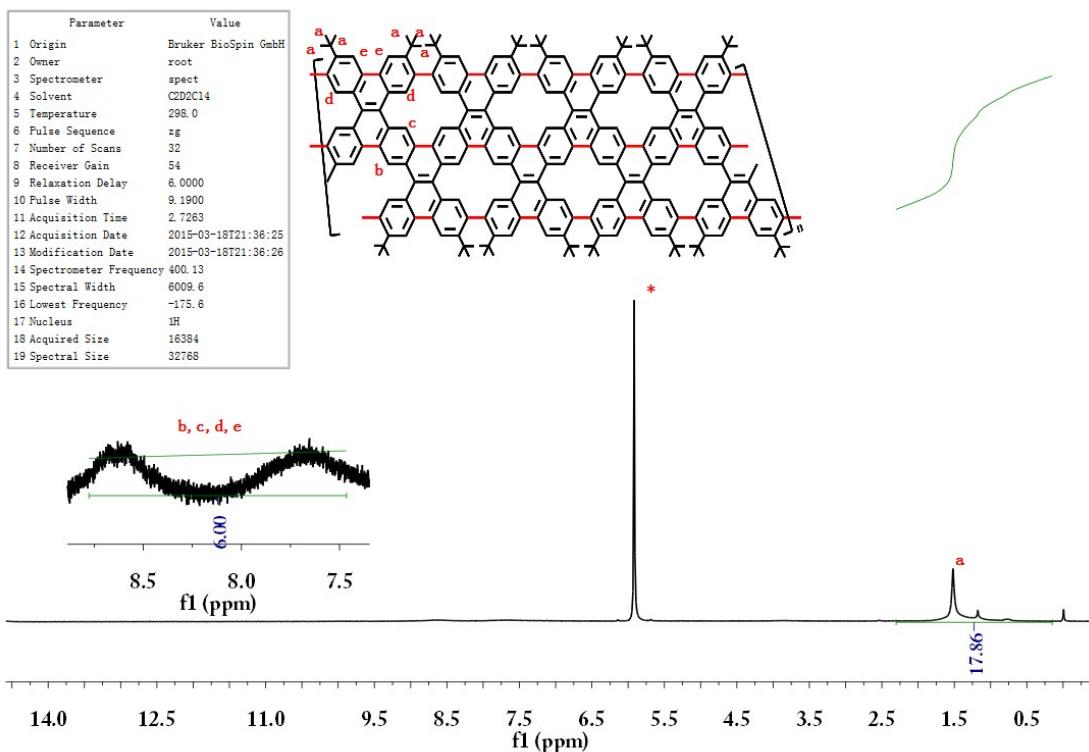
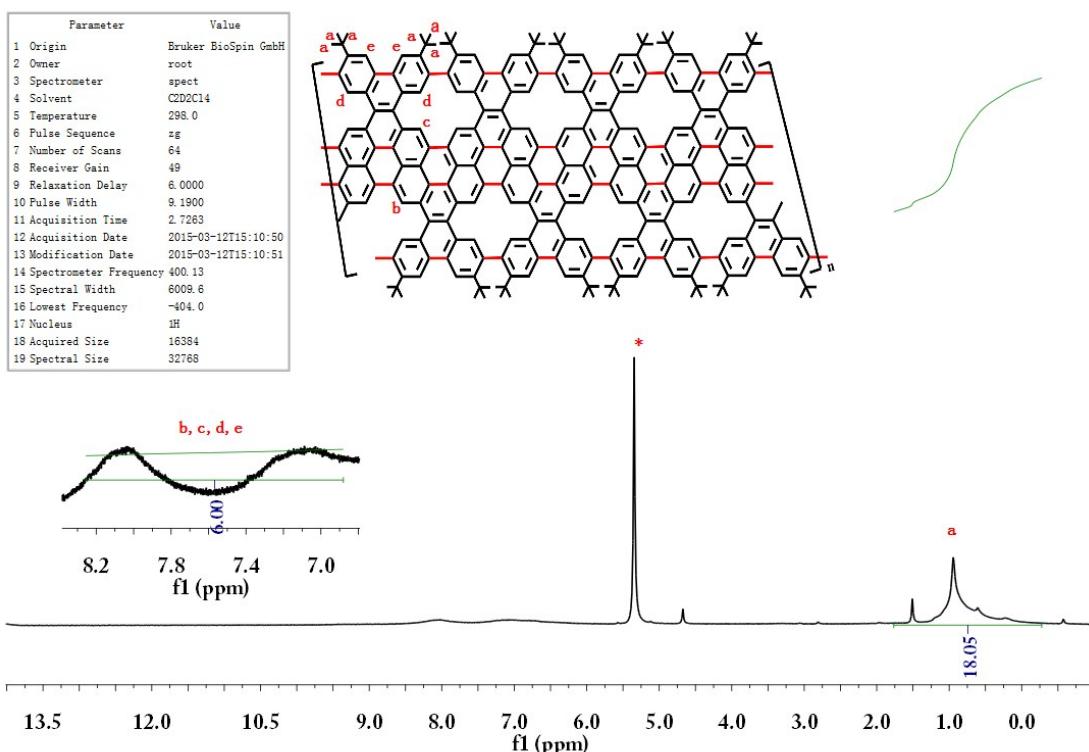


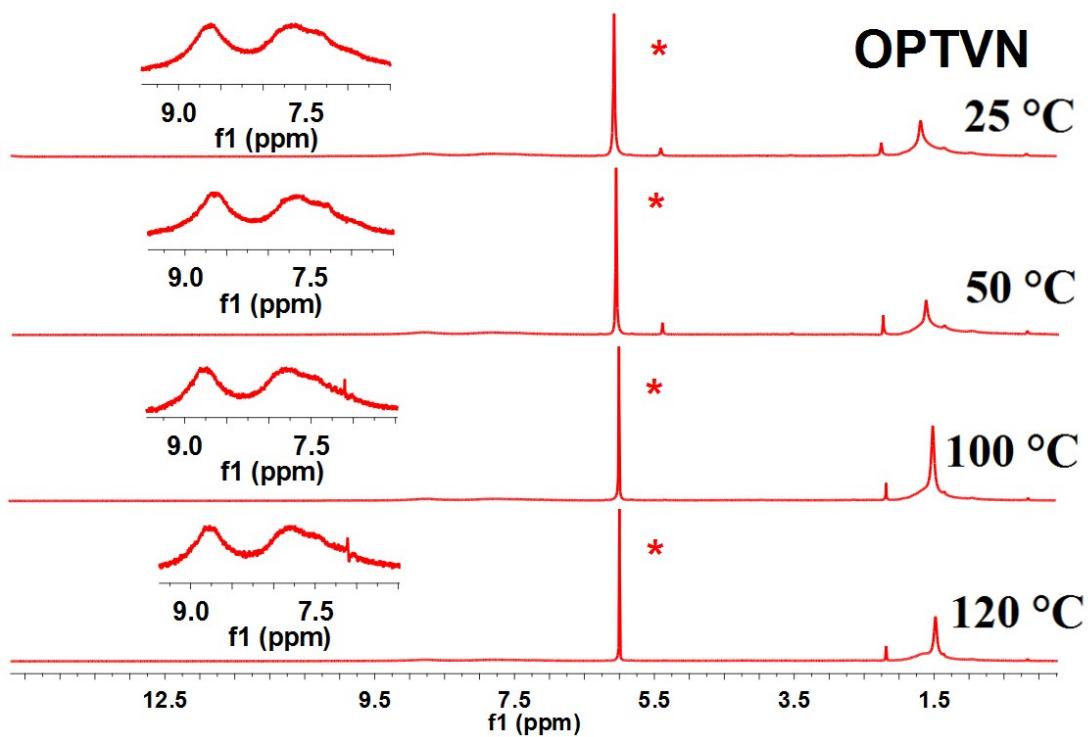
Fig. S10 <sup>13</sup>C NMR spectrum of PTVN.



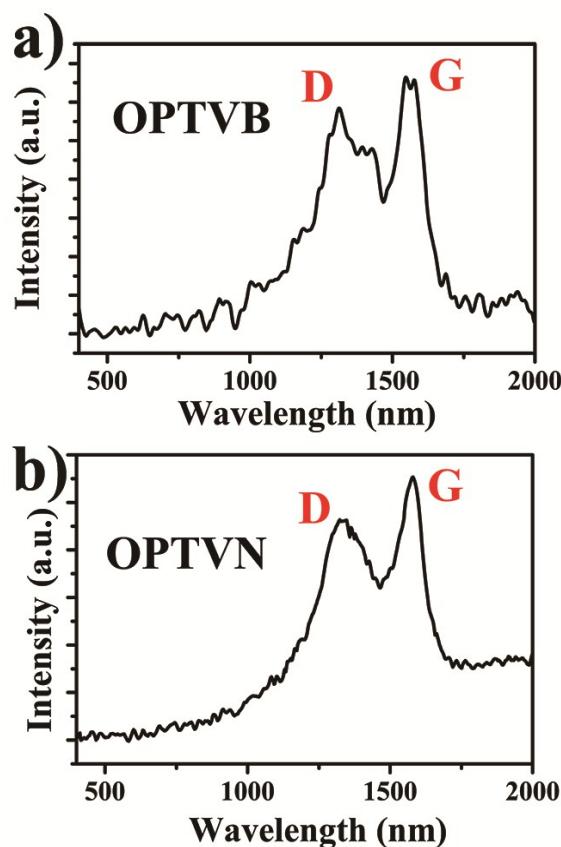
**Fig. S11** <sup>1</sup>H NMR spectrum of OPTVB.



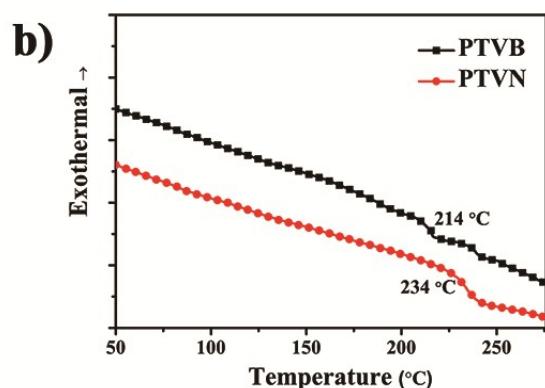
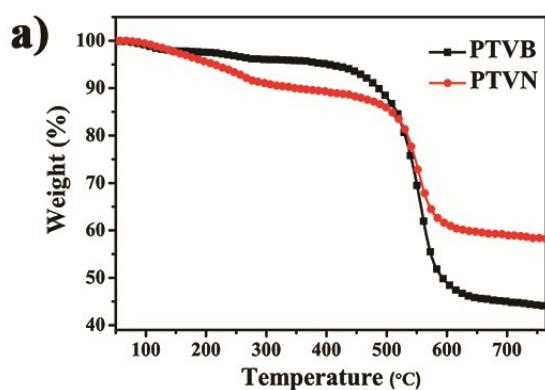
**Fig. S12.** <sup>1</sup>H NMR spectrum of OPTVN.



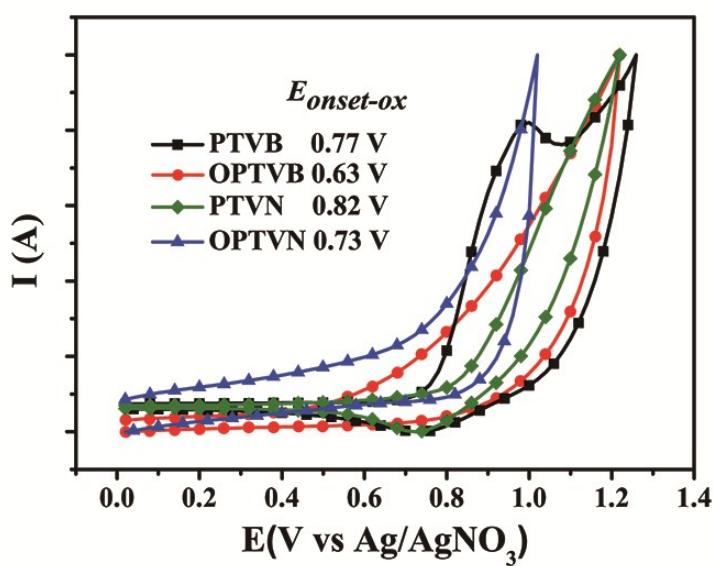
**Fig. S13**  $^1\text{H}$  NMR spectra of **OPTVN** at the variable temperatures (25 °C to 120 °C) in  $\text{C}_2\text{D}_2\text{Cl}_4$ . The inserted images are the amplifications of the aromatic domain.



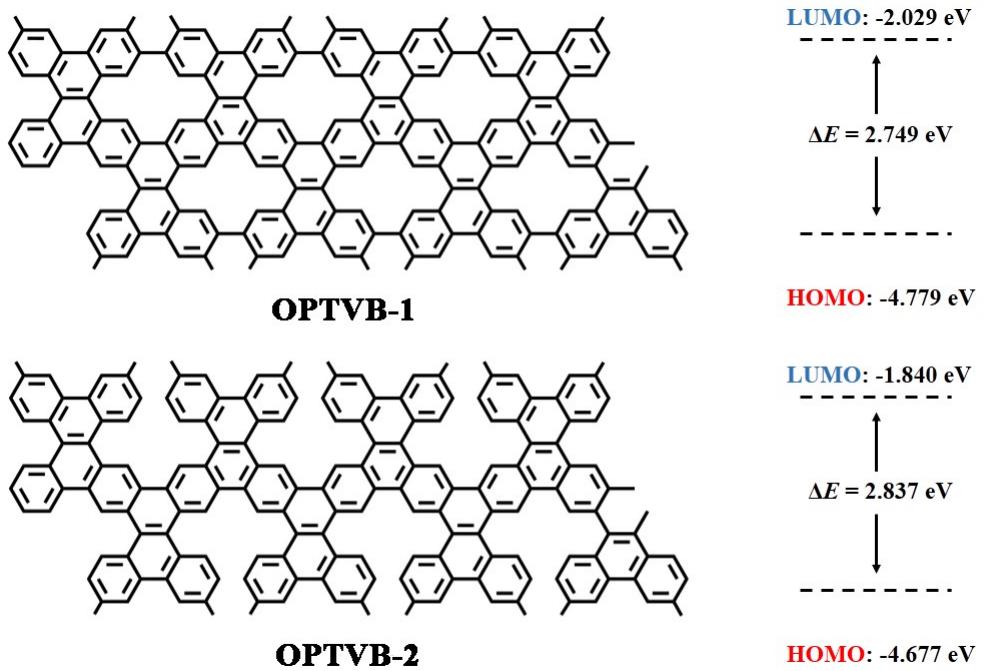
**Fig. S14** (a) Raman spectrum of **OPTVB**. (b) Raman spectrum of **OPTVN**.



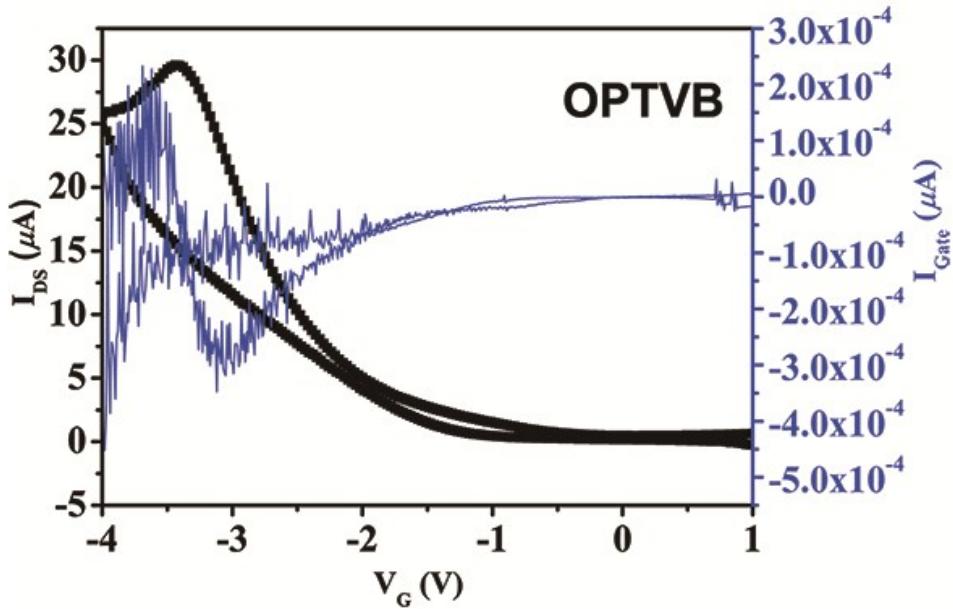
**Fig. S15** (a) The TGA data of **PTVB** and **PTVN**; (b) The DSC data of **PTVB** and **PTVN**.



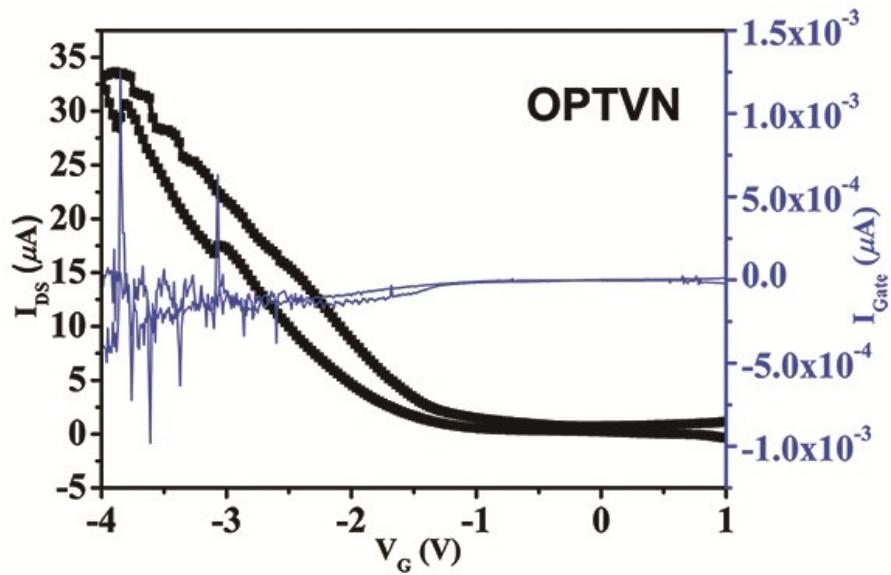
**Fig. S16** The CV curves of **PTVB**, **OPTVB**, **PTVN** and **OPTVN**.



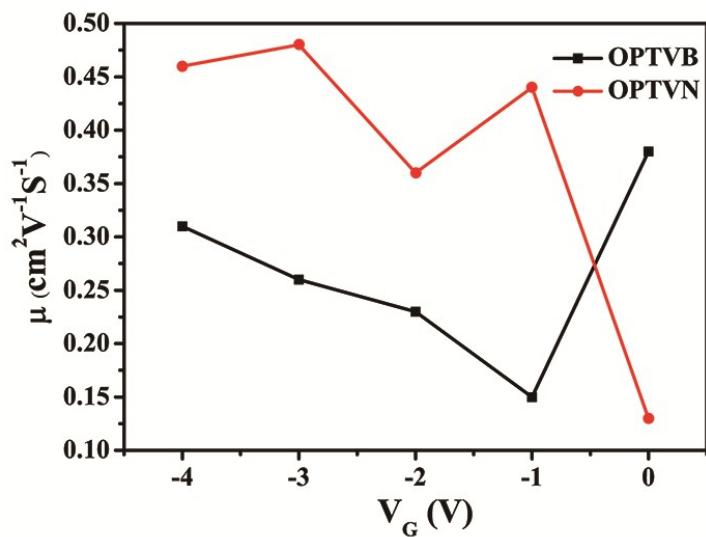
**Fig.S17** The calculated HOMO and LUMO energy levels of **OPTVB-1** and **OPTVB-2**.



**Fig. S18** The original charge transfer curve (black) and gate leakage curve (blue) of the FETs containing **OPTVB**.



**Fig. S19** The original charge transfer curve (black) and gate leakage curve (blue) of the FETs containing **OPTVN**.



**Fig. S20.** The mobility plots versus gate voltages of **OPTVB** and **OPTVN**.