Supporting information for

### Effect of charge distribution at nitrogen atoms of polyaniline copolymers on spindependent transport: experimental analysis and density functional theory calculations

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#### S1. Contents of *o*-TDN/*m*-ABN for copolymers

Samples		Contents (%)
PANI		/
ОМ	OM-1	60.09
	OM-2	84.95
	OM-3	92.87
MCN	MCN-1	11.69
	MCN-2	12.06
	MCN-3	14.12

Table S1. Contents of *o*-TDN/*m*-ABN for copolymers

The obtained polyaniline copolymers were named as "OM/MCN-1, 2, 3", in which "OM" and "MCN" represented the polyaniline copolymers with *o*-TDN and *m*-ABN, respectively.

The polymerization of copolymers is affected by many factors. Elemental analysis of copolymer was conducted by XPS in Fig. S1 to confirm the contents of *o*-TDN and *m*-ABN in their copolymers. With the addition of *o*-TDN, a new peak of C 1s at 284.3 eV belonging to  $sp^3$  hybrid carbon of methyl increases gradually, while pure PANI doesn't have this peak. So, by calculating the ratio of the peak area of  $sp^3$  hybridized carbon to the sum of the peak areas of  $sp^2$  hybridized carbon and  $sp^3$  hybridized carbon, the contents of *o*-TDN in the OM copolymers can be obtained. While with the addition of *m*-ABN, a new peak of C1s at 288.0 eV belonging to *sp* hybrid carbon of nitrile group increases gradually as well, by adopting the same methods, the contents of *m*-ABN in the MCN copolymers



can be gained. The attained results of the contents for PANI and its copolymers are laid out in Table S1.

**Fig. S1.** High resolution XPS C 1s spectra of (a) pure PANI, (b) Pure OM, (c) OM-1, (d) OM-2, (e) OM-3, (f) *m*-ABN monomer, (g) MCN-1, (h) MCN-2, (i) MCN-3.

## S2. Charge transfer values in the charge differential distribution

	C <sub>1</sub>	C <sub>2</sub>
Position 1	0.02	0.13
Position 2	0.14	0.15
Position 3	0.05	0.02
Position 4	-0.03	0.25
Position 5	0.04	-0.002

Table. S2. Charge transfer values in the charge differential distribution of OM oligomer

**Table. S3.** Charge transfer values in the charge differential distribution of MCN oligomer

	C <sub>1</sub>	C <sub>2</sub>	N <sub>1</sub>
Position 1	-0.1	-0.97	0.9
Position 2	0.3	-1	-1.18
Position 3	0.27	-0.97	-0.99

#### S3. FTIR spectra of PANI and its copolymers



**Fig. S2.** FTIR spectra of polyaniline copolymers for (a) OM-1, OM-2, OM-3 and pure PANI; (b) MCN-1, MCN-2, MCN-3 and pure PANI.

Figs. S2a and b show the FTIR spectra of pure PANI and its copolymers with different contents in *o*-TDN/*m*-ABN to aniline. In Figs. S2a and b, the strong absorption peaks at 1577 and 1492 cm<sup>-1</sup> are assigned to the C=C stretching vibrations in benzene and quinone rings, respectively. The absorption peaks at 1245 and 1303 cm<sup>-1</sup> are ascribed to the stretching vibrations of C=N in the quinone ring and C-N in the benzene ring. The absorption peaks located at 1153 and 809 cm<sup>-1</sup> are attributed to the C-H stretching vibrations in quinone and benzene rings. All these peaks are the characteristic peaks of the electrically conductive emeraldine salt (ES) form of PANI, which indicates that these copolymers own the PANI fragments. In Fig. S2a, the absorption peak at 1380 cm<sup>-1</sup> represents the C-H bending vibration of CH<sub>3</sub>, while in Fig. S2b, the absorption peak at 2222 cm<sup>-1</sup> corresponds to the stretching vibration of C=N, and their intensities turn to be higher along with the increasing of contents of *o*-TDA/*m*-ABN. These changes in FTIR spectra demonstrate that the aniline and *o*-TDN/*m*-ABN are both involved in the

copolymerization rather than in the separate polymerization of aniline or o-TDN/m-ABN.



#### S4. XRD patterns of PANI and its copolymers

Fig. S3. XRD patterns of copolymers (a) OM-1, OM-2, OM-3 and pure PANI; (b) MCN-

1, MCN-2, MCN-3 and pure PANI.

S5. TGA curves of PANI and its copolymers



**Fig. S4.** TGA curves of copolymers (a) OM-1, OM-2, OM-3 and pure PANI; (b) MCN-1, MCN-2, MCN-3 and pure PANI.

The thermal stability is closely related to the molecular structure and molecular weight of copolymers. The TGA curves of PANI and its copolymers are shown in Fig. S4.

It is noted that the profile of the TGA curve for copolymers after introducing *o*-TDN is close to that of pure PANI since the molecular of OM is analogous to the pure PANI in Table S3. Meantime, the introduction of *m*-ABN results in a huge difference of thermal stability for MCN, and the MCN is disintegrated at earlier temperatures with low thermal stability due to its severely reduced molecular weight. The molecular weight of MCN-1 is higher than that of MCN-2 and MCN-3, and its thermal stability is more stable than MCN-2 and MCN-3.



#### S6. SEM images of PANI and its copolymers

Fig. S5. SEM images of (a) pure PANI, (b) OM-1, (c) OM-2, (d) OM-3.



Fig. S6. SEM images of (a) pure PANI, (b) MCN-1, (c) MCN-2, (d) MCN-3.

# S7. Resistivity of PANI and its copolymers

Table S4. Resistivit	ty and $E_{g}$ of the	PANI and its	copolymers.
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Samples		Resistivity ( $\Omega \cdot cm$ )	E <sub>g</sub> (eV)
PANI		$0.065\pm0.001$	1.48
ОМ	OM-1	$0.281\pm0.009$	1.56
	OM-2	$0.999\pm0.059$	1.62
	OM-3	$2.359\pm0.054$	1.67
MCN	MCN-1	$4.435\pm0.045$	1.69
	MCN-2	$37.155 \pm 0.754$	1.78
	MCN-3	$(1.212 \pm 0.025) \times 10^3$	1.82

#### **S8.** The molecular weight of PANI and its copolymers

The molecular structure and molecular weight of conductive polymers have a huge influence on their electrical and magnetic property. The molecular weight of PANI and its copolymers is detected by GPC in Table. S3. It is found that the molecular weight of all the OM copolymers is higher than that of pure PANI, which connotes that at the same reaction time, the introduction of *o*-TDN facilitates the polymerization process, elevating the molecular weight. Nonetheless, the molecular weight of MCN copolymers is decreased significantly, due to the strong electron withdrawing group (CN).

Samples		Molecular weight (g·mol <sup>-1</sup> )
PANI		98150
ОМ	OM-1	126762
	OM-2	98168
	OM-3	118555
MCN	MCN-1	6101
	MCN-2	2222
	MCN-3	1301

**Table S5.** Molecular weight for pure PANI and its copolymers.

#### S9. Band gap of PANI and its copolymers





The band gap could be calculated by eqn (S1).

$$\alpha hv = A(hv - E_{\alpha})^n \tag{S1}$$

where A is a constant, v and h are the frequency and Planck constant, respectively, and  $hv=1240/\lambda$ ,  $\lambda$  refers to the absorption wavelength in the UV-vis DRS spectra;  $\alpha$  is the absorption coefficient, and n=0.5 represents the interbond transition mechanism. The extrapolation of the straight part of the plots can be applied to obtain band gap ( $E_g$ ).



**Fig. S8.** Calculation of band gaps for (a) pure PANI, (b) MCN-1, (c) MCN-2, and (d) MCN-3, obtained from UV-vis DRS spectra by plotting  $(\alpha h v)^2 vs. h v.$ 

The electrical conductivity is related to carrier density and carrier mobility as shown in eqn (S2).

$$\sigma = ne\mu \tag{S2}$$

where *n* presents the charge carrier density and  $\mu$  stands for the charge carrier mobility.

The transport model is described as eqn (S3).

$$W(T) = \frac{E(T)}{kT} = \frac{d[\ln(\sigma)]}{d[\ln(T)]}$$
(S3)

where E(T) is the activation energy characteristic of the transport model and k is

Boltzmann constant.

Mott variable range hopping mechanism can be described as eqn (S4).

$$\sigma = \sigma_0 \exp[-(\frac{T_0}{T})^{\frac{1}{n+1}}], n=1, 2, 3$$
(S4)

where the pre-exponential factor  $\sigma_0$  is a constant, which stands for the electrical conductivity at a high temperature limit,  $T_0$  is the hopping barrier, which represents the characteristic Mott temperature, providing the energy needed for charge's hopping conduction and *T* is the Kelvin temperature. The *n* value of 3, 2, and 1 is for three-, two-, and one- dimensional systems, respectively.

MR can be calculated as eqn (S5).

$$MR\% = \frac{\Delta R}{R} = \frac{R(H,T) - R(0,T)}{R(0,T)} \times 100\%$$
 (S5)

where R(H, T) and R(0, T) refer to the resistance under magnetic field H and without magnetic field, respectively.

S10. XPS of PANI and its copolymers



Fig. S9. High resolution XPS N 1s spectra of (a) pure PANI, (b) OM-1, (c) OM-2, (d) OM.



Fig. S10. High resolution XPS N 1s spectra of (a) pure PANI, (b) MCN-1, (c) MCN-2, (d) MCN-3.

The N atom in the imine of PANI is the main position of protonic acid. The higher doping degree means freer electrons and holes, so the proton doping on N is closely related to the electrical conductivity of conducting polymers, and their doping degree can be analyzed by the high resolution XPS N 1s spectra, as shown in Figs. S9 and S10. The binding energies of the four peaks fitted by the high resolution XPS N 1s spectra for pure PANI are 399.14, 400.00, 401.01, and 401.70 eV, representing -N=, -NH-,  $-N^+=$ , and  $-NH^+-$ , respectively. Based on the formula in eqn (S6), the doping degree of copolymers can be calculated by the peak area of these four peaks. According to the results listed in S14 Table S4, the doping degree of pure PANI is 42.28%. With the addition of *o*-TDN, the doping degree is decreased gradually, which is consistent with the trend of electrical conductivity change in OM copolymers. For MCN copolymers, after introducing *m*-ABN, the doping degree is reduced significantly.

doping degree=
$$\frac{-NH^+ - + -N^+ =}{-NH^+ - + -N^+ = + -NH^- + -N^=}$$
 (S6)



Fig. S11. High resolution XPS N 1s spectra of (a) PANI-1 mol/L, (b) PANI-0.1 mol/L, (c) PANI-0.05 mol/L, (d) OM-1-1 mol/L, (e) OM-1-0.1 mol/L (f) OM-1-0.05 mol/L.

The doping degree of OM-1 and PANI at different acid concentrations is also analyzed by the high resolution XPS N 1s spectra in Fig. S11 with the same calculation method. The resistivity, doping degree, and MR of OM-1 and PANI at different acid concentrations are listed in Table S5. It's obvious that the doping degree of PANI and OM-1 decreases with the reduction of acid concentration, and the MR diminishes correspondingly, which is consistent with the results of the doping degree for different contents of *o*-TDN and *m*-ABN.

Sample		Doping degree (%)	MR (%)
PANI		42.28	2.08
OM	OM-1	36.80	1.79
	OM-2	36.39	1.67
	OM-3	32.19	1.29
MCN	MCN-1	31.10	1.32
	MCN-2	27.63	1.10
	MCN-3	22.82	1.04

**Table S6.** Doping degree, and MR of PANI and its copolymers.

Table S7. Resistivity, doping degree and MR of OM-1 and PANI at different acid concentrations

Sample		Resistivity ( $\Omega$ ·cm)	Doping degree (%)	MR (%)
PANI	PANI-1mol/L	$0.065\pm0.001$	42.28	2.04
	PANI-0.1mol/L	$0.976\pm0.047$	33.90	1.70
	PANI-0.05mol/L	$2.068\pm0.097$	27.41	1.42
OM-1	OM-1-1mol/L	$0.281\pm0.009$	36.80	1.79
	OM-1-0.1mol/L	$2.451\pm0.419$	31.05	1.58
	OM-1-0.05mol/L	$3.239\pm0.010$	26.20	1.29