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Supporting information for:

Tailoring the Framework of Organic Small Molecule Semiconductors towards High-Performance Thermoelectric Composites *via* Conglutinated Carbon Nanotube Webs

Xiaojun Yin,^{a,b} Yuhao Peng,^c Jiajia Luo,^c Xiaoyan Zhou,^{a,b} Chunmei Gao,^{d,*} Lei Wang^{a,*} and Chuluo Yang^{a,c,*}

^{*a*}Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China. E-mail: wl@szu.edu.cn

^{*b*}Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.

^cHubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan, 430072, P. R. China. E-mail: clyang@whu.edu.cn

^{*d*}College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, PR China. E-mail: gaocm@szu.edu.cn

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General Information

¹H NMR and ¹³C NMR spectra of these organic semiconductors were recorded on a Bruker AVANCE III HD 400MHz spectrometer. The exact molecular weights were evaluated by Thermo Scientific LTQ Orbitrap XL Mass spectrometer. MALDI-TOF mass spectra were obtained on a Bruker Biflex III TOF mass spectrometer. UV-Vis absorption spectra and photoluminescence (PL) spectra were obtained on Shimadzu UV-2600 spectrophotometer and Hitachi F-4600 fluorescence spectrophotometer, respectively. Raman spectra were recorded on LabRAM HR800 with wavenumber range from 100 to 3500 cm⁻¹ under an excitation wavelength of 532 nm (Nd-YAG laser). Thermogravimetric and differential thermal analysis (TG-DTA) of the compounds were performed on a Hitachi STA 7300 unit at a heating rate of 20 °C min⁻¹ from 40 to 800 °C under an argon atmosphere. Scanning electron microscope (SEM) imaging were performed on Zeiss Merlin Compact with enlargement factor of 1000, 10000, or 30000. Cyclic voltammetry (CV) measured in nitrogen-purged tetrahydrofuran (THF) solution by using a CHI voltammetric analyzer. The Bu_4NPF_6 (0.1 M) was used as the supporting electrolyte with ferrocenium-ferrocene (Fc/Fc⁺) was identified as the internal standard, and scan rate was 100 mV s⁻¹. The highest occupied molecular orbital (HOMO) energy levels (eV) of the samples were calculated through the following formula: -[4.8 + $(E_{\text{onset oxi}} - E_{1/2(\text{Fc/Fc+})})$] eV and the lowest unoccupied molecular orbital (LUMO) levels were deduced from HOMO and energy gap (E_g) . The X-ray photoelectron spectra were performed on an ESCALAB 250Xi X-ray Photoelectron Spectroscopy (Thermo Fisher Scientific Corporation, Analysis and Test Center of Wuhan University) using a monochromated AlKa (1,486.6 eV) X-ray source.

The electrical conductivities and Seebeck coefficients of these composite films were measured using a TE parameter test system (MRS-3, JiaYiTong Company) from 298 K to 418 K in a vacuum environment. The Seebeck coefficient of Ni at room temperature was measured as a reference sample; the measured value of 16 ± 0.3 mV K⁻¹ was in good agreement with the literature value of 15 mV K⁻¹.¹ An average of four composite samples was tested to determine the TE performances for each SWCNTT loading.

Composite Film Preparation

General procedures for the p-type composite film preparation are described as follow: The SWCNTs (50 mg) was dispersed in anhydrous chlorobenzene (50 mL) by using a probe sonicator (JY99-IIDN, Scientz, China) under ice-water bath for 30 mins. Afterwards, the p-type OSMSs (TDOPAPy, TDOPABP, TDPAPy or TCzPy) were added to the dispersion of SWCNTs (1 mg/mL) and the mixtures were sonicated for 2 h to ensure thorough mixing. The doping ratios of SWCNT/OSMS compositions were varied by adding different dosages of p-type OSMSs. The glass substrates (15×15 mm) were subjected to cleaning using ultra sonication in acetone, deionized water and ethanol, and dried under vacuum. Finally, the gel-like mixtures were dropped on the cleaned glass substrates carefully to form the composite films via volatilizing the solvent.

Materials Preparation

All reagents commercially available were used as received unless otherwise indicated. Solvents were purified according to standard procedures. The starting material of pyrene, 1,3,5-tribromobenzene, di-*p*-tolylamine, bis(4-methoxyphenyl)amine and 3,6-di-*tert*-butyl-9*H*-carbazole were commercially available (purchased from Energy Chemical). The aromatic halogenated hydrocarbon intermediates of 1,3,6,8-tetrabromopyrene and 3,3',5,5'-tetrabromo-1,1'-biphenyl were synthesized according to the literature procedures.²⁻³ Target compounds of $N^1,N^1,N^3,N^3,N^6,N^6,N^8,N^8$ -octakis(4-methoxyphenyl) pyrene-1,3,6,8-tetraamine (**TDOPAPy**)⁴ and $N^1,N^1,N^3,N^3,N^6,N^6,N^8,N^8$ -octa-p-tolylpyrene -1,3,6,8-tetraamine (**TDPAPy**)⁵⁻⁶ were synthesized according to the literature procedures.

Synthesis of $N^1, N^3, N^3, N^6, N^6, N^8, N^8$ -octakis(4-methoxyphenyl)-[1,1'-biphenyl]-3,3',5,5'tetraamine (**TDOPABP**). Palladium acetate (54 mg, 0.24 mmol), tri-*t*-butylphosphine (146 mg, 0.72 mmol) and toluene (120 mL) were stirred about 15 minutes under the nitrogene atmosphere to obtain a palladium-phosphine complex. Then 3,3',5,5'-tetrabromo-1,1'-biphenyl (724 mg, 1.5 mmol), Bis-(4-methoxy-phenyl)-amine (1.84 g, 8 mmol) and sodium *t*-butoxide (1.38 g, 8 mmol) were added to the solution and the reaction mixture was stirred at 110°C for 48 hours under nitrogen. After cooling to room temperature, the product was extracted with CHCl₃, washed with brine water and then dried over anhydrous sodium sulfate. Then, the solvent was removed under vacuum. The crude product was adsorbed in silica gel and purified by column chromatography using petroleum ether/dichloromethane (3:1) as eluent and recrystallization from dichloromethane/methanol to afford the corresponding desired compound **TDOPABP** as reseda crystal (1.21 g, 76%). ¹H NMR (Toluene-*d*₈, 400 MHz): 7.03-7.01 (m, 8H), 7.00-6.99 (m, 8H), 6.98 (s, 6H), 6.60-6.59 (m, 8H), 6.57-6.56 (m, 8H), 3.33 (s, 24H). ¹³C NMR (CDCl₃/CD₂Cl₂, 100 MHz): 155.57, 149.16, 142.99, 140.80, 126.27, 114.43, 112.27, 112.03, 55.47. HRMS (ESI) calcd for C₆₈H₆₃N₄O₈ [M+H]⁺ 1063.46404, found 1063.46387.



Scheme S1. Synthetic routes and molecular structures of these p-type organic small molecule semiconductors (OSMSs).

Synthesis of 1,3,6,8-tetrakis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)pyrene (**TCzPy**). Similar to **TDOPABP**, the **TCzPy** was obtained in yield 86% as yellow orange power. ¹H NMR (Toluene- d_8 , 400 MHz): 8.27 (s, 4H), 7.85 (s, 2H), 6.94-6.92 (m, 12H), 6.77-6.75 (m, 12H), 1.48 (s, 72H). ¹³C NMR (Toluene- d_8 , 100 MHz): not obtained due to the poor solubility in

regular deuterium reagents. MS (MALDI-TOF, m/z): 1310.8 [M]⁺. Anal. calcd for C₉₆H₁₀₂N₄ (%): C 87.89, H 7.84, N 4.27; found: C 87.92, H 7.78, N 4.30.



Thermodynamic properties of these OSMSs

Figure S1. TGA and DTA curves of these p-type OSMSs.

Electrochemistry properties of these OSMSs



Figure S2. CV curves of these compounds in THF solution.

Measurement of the seebeck coefficient (S) of these samples.



Figure S3. Linear fitting the relations between ΔT and ΔV . According to the formula of $S = -\Delta V/\Delta T$,⁷⁻⁹ the slope is the seebeck coefficient of the sample.

Table S1. Film thickness (nm) of these composite samples from step profiler measurements.

Compound	5%	10%	14%	20%	50%	100%
SWCNT/TDOPABP	2.20	1.64	Ø	1.50	1.08	0.88
SWCNT/TDOPAPy	3.20	2.10	Ø	1.42	1.43	0.92
SWCNT/TDPAPy	Ø	8.10	4.20	1.64	1.06	0.85
SWCNT/TCzPy	Ø	11.15	Ø	4.41	0.90	1.02

The electrical conductivity (σ) of these composite films can be calculated according to the following formula:

$$\rho = \frac{V}{I} \times \frac{A}{L} = R \times \frac{A}{L} = \frac{1}{\sigma}$$

Samples		R ₁ ^{a)}	R ₂ ^{a)}	R ₃ ^{a)}	R _{av} ^{a)}	R _{err} ^{a)}	σ ^{b)}	σ _{err} b)	S 1 ^{c)}	S2 ^{c)}	Sav ^{c)}	S _{err} c)
SWCNT		0.247	0.265		0.256	0.01	823.7	2.3	30.8	29.4	30.1	0.7
	5%	446.0	269.0		357.5	88.7	5.4	1.7	58.7	65.3	62.0	3.3
SWCNT:	10%	90.0	93.5	105.4	96.3	9.1	26.8	1.9	68.6	73.0	70.8	2.2
TDOPABP	20%	134.7	136.4		135.5	0.8	20.8	0.2	78.8	97.6	88.2	9.4
(wt%)	50%	95.77	84.0		89.8	5.8	43.6	3.0	108.3	86.1	97.2	11.1
	100%	42.6	40.3		41.5	1.2	115.8	3.5	42.1	40.4	41.3	0.9
	5%	258.3	294.7		276.5	18.2	4.8	0.3	58.8	62.0	60.4	1.6
SWCNT:	10%	155.3	209.6		182.5	27.1	11.0	1.9	57.5	61.1	59.3	1.8
TDOPAPy	20%	107.8	97.5		102.6	5.2	29.1	1.5	58.8	63.6	61.2	2.4
(wt%)	50%	47.0	36.4	44.7	42.7	6.3	69.3	11.9	66.0	71.8	68.9	2.9
	100%	31.2	35.9		33.6	2.4	136.8	10.6	46.3	41.4	43.9	2.5
	10%	431.3	334.0	410.1	391.8	57.8	1.3	0.2	66.7	71.4	69.1	2.4
SWCNT:	14%	104.5	105.5		105.0	0.5	9.6	0.1	58.3	64.5	61.4	3.1
TDPAPy	20%	40.4	37.8	41.5	39.9	2.1	70.7	3.9	63.4	66.0	65.7	2.3
(wt%)	50%	43.4	41.6		42.5	0.9	93.9	2.1	59.1	67.3	63.2	4.1
	100%	57.7	51.3		54.5	3.2	91.3	5.7	58.0	70.4	64.2	6.2
SWCNT	10%	188.2	235.8		212.0	23.8	1.8	0.2	67.4	72.4	69.9	2.5
SWUNI:	20%	198.5	161.6	147.9	169.3	21.4	5.7	0.8	60.1	58.1	59.1	1.0
I UZF y	50%	49.4	56.6		53.0	3.6	88.7	6.5	61.3	63.5	62.4	1.1
(WL/0)	100%	21.1	23.0	21.7	21.9	1.1	189.4	9.0	72.6	79.2	75.9	3.3

 Table S2. Thermoelectric parameters of these samples.

^{a)} Ω , ^{b)} S cm⁻¹, ^{c)} μ V K⁻¹.

SEM images of these composite films.



Figure S4. SEM of SWCNT:TDPAPy (1:5) composite films, 1000 fold (a), and 30000 fold at the SWCNT-rich regions (b).



Figure S5. SEM of SWCNT:TDPAPy (1:10) composite films, 1000 fold (a), and 30000 fold at the SWCNT-rich regions (b).



Figure S6. SEM of SWCNT:TCzPy (1:5) composite films, 1000 fold (a), and 30000 fold at the SWCNT-rich regions (b).



Figure S7. SEM of SWCNT:TCzPy (1:10) composite films, 1000 fold (a), and 30000 fold 30000 fold at the SWCNT-rich regions (b).



Absorption and emission spectra of these OSMSs.

Figure. S8. UV-Vis absorption spectra of these OSMSs in film states (a) and in dilute chloroform solution (c), and photoluminescence spectra of these OSMSs in film states (b) and in dilute chloroform solution (d).



Figure S9. The UV-Vis absorption spectra of these composite systems in chlorobenzene solution (with the remove of SWCNTs *via* centrifugalization).

XPS spectra of the OSMSs doped with SWCNT



Figure S10. X-ray photoelectron spectroscopy of these composite films.



Figure S11. X-ray photoelectron spectra of N 1s of these composite films.

Samples		RBM	D band	G band	G' band	R	$I_{\rm G}/I_{\rm G}$	d_{t}^{a}
		[cm ⁻¹]	[cm ⁻¹]	[cm ⁻¹]	[cm ⁻¹]	$[I_{\rm D}/I_{\rm G}]$		[nm]
SWCN	Т	156, 187	1347	1569, 1590	2682	0.018	6.36	1.28
	1:10			1573, 1593	2682			
SWCNT/	1:5	155, 178	1347	1573, 1593	2681			1.61
TDOPAPy	1:2	155, 177	1345	1573, 1593	2682	0.014	8.48	1.59
	1:1	153, 172	1345	1573, 1593	2681	0.009	8.85	1.62
	1:10	156, 175	1345	1573, 1593	2681	0.009	8.26	1.58
SWCNT/	1:5	155, 177	1346	1573, 1593	2681	0.010	8.26	1.59
TDOPABP	1:2	156, 175	1346	1573, 1593	2682	0.008	8.26	1.58
	1:1	157, 175	1345	1573, 1593	2681	0.009	8.26	1.57
	1:10	157, 171	1344	1573, 1593	2679	0.010	7.46	1.57
SWCNT/	1:5	157, 176	1345	1573, 1593	2681	0.011	8.11	1.57
TDPAPy	1:2	156, 176	1347	1573, 1593	2681	0.009	7.71	1.58
	1:1	159, 177	1346	1573, 1593	2681	0.009	7.71	1.55
	1:10	156, 175	1346	1573, 1593	2680	0.025	8.06	1.58
SWCNT/	1:5	156, 173	1344	1573, 1593	2680	0.010	8.06	1.58
TCzPy	1:2	156, 181	1343	1573, 1593	2678	0.010	6.99	1.58
	1:1	155, 176	1346	1573, 1593	2683	0.008	9.09	1.59

 Table S3. Raman spectra data of these SWCNT/OSMSs composite films.

 $^{a}\omega_{\text{RBM}} (\text{cm}^{-1}) = 204/d_{\text{t}} (\text{nm}) + 27 (\text{cm}^{-1})$



Figure S12. Raman spectra of the SWCNT/TDOPABP composite films with different doping ratio.



Figure S13. Raman spectra of the SWCNT/TDOPAPy composite films with different doping ratio. Remarkably, the background noise synchronously enhanced with the increase of TDOPAPy due to the overlap of absorption at 532 nm and thus result in fluorescence emission at $500 \sim 650$ nm region.



Figure S14. Raman spectra of the SWCNT/TDPAPy composite films with different doping ratio.



Figure S15. Raman spectra of the SWCNT/TCzPy composite films with different doping ratio.



Figure S16. FTIR spectra of these samples. In comparison with the individual FTIR spectra of SWCNT and OSMSs, the characteristic peaks of these OSMSs in corresponding composite films (with hybrid ratio of 1:1) are absent, suggesting the interactions between the SWCNT and the OSMSs.

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