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Recently, the thermoelectric (TE) properties of single-walled carbon nanotubes (SWCNTs)/polymer semiconductors composites have been dramatically improved; however, there are no examples of SWCNTs/organic small molecule semiconductors (OSMSs) composites as TE materials, although OSMSs are more attractive due to their exact structure, easy structure optimization, high purity for performance optimization, etc. In this work, four p-type OSMSs are designed and synthesized as p-type binders for application in SWCNT-doped composite films. The relationship between the TE properties and the structure including the conjugated-backbone and the peripheral substituents is investigated. Photophysical spectroscopy and scanning electron microscopy studies indicate that the variation of the molecular geometries and hybrid ratios result in obvious changes in the morphologies, interfacial contacts and grain boundaries of the composite films, subsequently affecting the TE properties of the samples. Notably, the SWCNT/TC2PY (1:1)-based hybrid film exhibits the best performance with an average power factor of $108.4 \pm 4.8 \,\mu$ W m⁻¹ K⁻², which is three times higher than that of SWCNT/TDOPAPy. The results demonstrate that fine tuning the π -extensions of the central core or peripheral substituents of organic semiconductors is a good strategy for designing high-performance p-type organic small molecular TE materials.

Introduction

Thermoelectric (TE) devices providing direct energy conversion between electricity and heat have aroused great interest due to their potential applications in industrial waste heat recovery and natural heat utilization.¹⁻⁶ Until now, the application of TE devices are still restricted in certain situations due to the lack of suitable TE materials,⁷⁻¹² and thus, devoted endeavors to exploit new TE materials are of critical significance.¹³⁻¹⁷ The performance of TE materials is determined by the dimensionless figure of merit, $ZT = S^2 \sigma T/\kappa$, and therefore, materials with high Seebeck coefficients (*S*, $\mu V K^{-1}$), high electrical conductivities (σ , S cm⁻¹), and low thermal conductivities (κ , W m⁻¹ K⁻¹) are required.¹⁸⁻²² Despite high *ZT* values over 1.0 being achieved by certain excellent inorganic TE materials, such as α -MgAgSb, FeNbSb, CulnTe₂, Bi₂Te₃, and PbTe alloys,²³⁻²⁷ most inorganic materials suffer from low *S* and high κ . In addition, high cost, toxicity, brittleness and inelasticity of inorganic TE materials restrict mass production applications.²⁸⁻³³ Alternative strategies involving organic π -conjugated semiconductors offer new opportunities to acquire desirable TE materials,³⁴⁻³⁷ as organics are associated with low κ values, non-toxicity, earth abundance, light weight and mechanically flexibility.³⁸⁻⁴³ Due to the intrinsically low κ of organic TE materials, the power factor (PF = $S^2 \sigma$) remains the fundamental parameter for optimization for efficient TEs.⁴⁴⁻⁴⁹

Owing to their prominent high electrical conductivity and mechanical robustness, single-walled carbon nanotubes (SWCNTs) have emerged as a possible TE material.⁵⁰⁻⁵¹ Nevertheless, the intrinsic low *S* and high κ partly discourage their utilization in TE devices.⁵²⁻⁵⁶ In this context, hybrid materials that incorporate organic semiconductors with SWCNTs have been developed, and exhibited fascinating TE performances compared to the corresponding individual components, as interfacial charge transport across the hybrid nanocomposites can be carefully controlled by matching the work function and bandgap of the different components to obtain both high *S* and σ .⁵⁷⁻⁵⁹ To date, endeavors on organic/SWCNT composites have mainly concerned π -conjugated polymers as binders or linkers for SWCNT-based composite.⁶⁰⁻⁶⁵ In comparison to the polymers, organic small

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⁺Electronic Supplementary Information (ESI) available: Materials synthesis and characterization, composite films preparation, TGA and DSC curves of these OSMSs, absorption spectra and XPS spectra of the samples, CV curves of these OSMSs. See DOI: 10.1039/x0xx00000x.



Scheme 1. Molecular structure of the studied OSMSs (a), illustration of the efficient interactions between the SWCNTs and OSMSs (b), and preparation process of the composite films (c).

molecule semiconductors (OSMSs) are more attractive due to their exact structure and high purity for performance optimization, as well as their regulable molecular size for potential orientation enabling more-efficient contact with the SWCNT surfaces (Scheme 1b).⁶⁶⁻⁶⁸ However, there are few examples of TE materials involving p-type OSMSs, and their performances are significantly lagging behind that of polymers, for example, pentacene (PF < 13 μ W m⁻¹ K⁻²) and tetrathiafulvalene derivatives (< 39.2 μ W m⁻¹ K⁻²), which remain a big room for improvement.²

Our group has developed series of polymers or OSMSs as functional materials, such as TE materials, $^{69-72}$ light-emitting diodes, $^{73-76}$ etc. Here, to further improve the performance and explore new structure of TE, four OSMSs were designed and synthesized as potent p-type TE materials. The SWCNTs/OSMSs composite films were firstly prepared, and the highest PF of 108.4 ± 4.8 μ W m⁻¹ K⁻² was achieved. In addition, the relationship between the TE properties and the structure including the conjugated-backbone and the peripheral substituents was investigated.

Results and Discussion

2.1. Molecular design and DFT calculation

It is well known that diphenylamines and carbazoles are classical hole transport moieties.⁷⁷⁻⁷⁹ If they are incorporated into π -delocalized scaffold such as pyrene or phenylbenzene, especially when different substituents are introduced, the highest occupied molecular orbital (HOMO) distributions, energy gaps and molecular geometries can be finely tuned. Therefore. four p-type OSMSs, namely, N^1 , 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), N¹, N¹, N³, N³, N⁶, N⁶, N⁸, N⁸-octakis (4-methoxyphenyl) pyrene-1,3,6,8-tetraamine (TDOPAPy), N^1 , N^1 , N^3 , N^3 , N^6 , N^6 , N^8 , N^8 -octa-ptolylpyrene-1,3,6,8-tetraamine (TDPAPy) and 1,3,6,8tetrakis(3,6-di-tert-butyl-9H-carbazol-9-yl)pyrene (TCzPy)

(Scheme 1a) were prepared. Density Functional Theory (DFT) calculations were firstly executed to discuss the geometrical and electronic natures of these OSMSs and thus their impacts on the thermoelectric parameters (σ and S). The calculated frontier molecular orbital (FMO) distributions and energy levels of these four OSMSs were shown in Figure 1. Obviously, the lowest unoccupied molecular orbitals (LUMOs) of these pyrene-core OSMSs were effectively confined on the pyrene units, while the HOMOs scattered over the entire molecules, especially for TCzPy, offering more-efficient charge-transfer integrals for hole transport across the molecular junctions.⁸⁰ Both the HOMOs and LUMOs of TDOPABP distributed across the central biphenyl and peripheral bis(4methoxyphenyl)amine moieties.



Figure 1. Calculated energy levels and orbital distributions of these OSMSs.

For an intrinsic organic semiconductor, the HOMO and LUMO levels form the valence band (E_v) and conduction band (E_c) , respectively, and the Fermi level (E_F) is located near the middle of the bandgap $(E_F \approx (E_V + E_C)/2)$ and gradually approaches E_v for p-type doping.¹² To obtain high TE performances, both high σ and S are preferable, and these two

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parameters are interrelated with the carrier concentration and restrict each other. In this respect, TE materials with appropriate bandgaps ($E_{\rm g}$ s) and HOMO levels for p-type doping are essential, as the carrier concentration strongly depends on the activation energy ($E_{\rm F} - E_{\rm V}$).² The calculated HOMO levels and $E_{\rm g}$ s of these OSMSs are presented in Table 1, and all these compounds reveal adequate high HOMO levels (*c.a.* -4.2 eV ~ -5.2 eV) for p-type doping. Noticeably, the intrinsic activation energy of TDOPABP is approximate to 1.95 eV (Figure 1), which will be beneficial to achieve the optimal *S* among these OSMSs.

2.2. Synthesis and Characterization

The synthetic routes of these p-type OSMSs are depicted in Scheme S1. The aromatic halogenated hydrocarbon intermediates of 1,3,6,8-tetrabromopyrene and 3,3',5,5'-tetrabromo-1,1'-biphenyl were synthesized *via* electrophilic substitution and CuCl₂-catalysed oxidative coupling reactions, respectively. The target products TDOPABP, TDOPAPy, TDPAPy and TCzPy were synthesized by Buchwald-Hartwig cross coupling of the halogenated hydrocarbon precursors and the corresponding aniline derivatives. All the intermediates and target products were purified by column chromatography and successive recrystallization. The accurate structural information of these p-type OSMSs were well confirmed by ¹H NMR and ¹³C NMR spectroscopies, elemental analysis and mass spectrometry.

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out to investigate the effects of the various central cores and peripheral substituents of these OSMSs on the thermal properties. The TG curves (Figure S1) revealed that the thermal-decomposition temperatures (T_d , defined as 5% weight loss) of TDPAPy and TCzPy were 475 °C and 468 °C, respectively, which were considerably higher than those of TDOPAPy (436 °C) and TDOPABP (446 °C). The inferior $T_{\rm d}s$ of the latter two OSMSs can be ascribed to the poor stability of the peripheral bis(4-methoxyphenyl)amine moiety. The DTA traces of these pyrene-core OSMSs exhibited gradually enhanced glass-transition temperatures (T_g), from 162 °C for TDOPAPy to 217 °C for TDPAPy and then to 227 °C for TCzPy (inset of Figure S1), which can be attributed to the more rigid pyrene core of latter. For TDOPABP, no considerable decalescence signal was identified before the melting point. Noticeably, all these OSMSs exhibited sufficiently high T_{g} s and $T_{\rm d}$ s, indicating their suitability as candidates for TE application.

2.3 Electrochemical properties

Electrochemical studies using cyclic voltammetry (CV) were performed to evaluate the ionization properties of these OSMSs. As displayed in Figure S2, all the OSMSs exhibited reversible oxidation waves in tetrahydrofuran (THF) solution. The onset oxidation potentials (E_{onset,ox} versus Fc/Fc+ couple) were 0.02 V for TDOPAPy, 0.41 V for TDOPABP, 0.16 V for TDPAPy and 0.15 for TCzPy. According to the equation E_{HOMO} = - $[4.8 + (E_{onset.ox} - E_{1/2(Fc/Fc+)})]$ eV, their HOMO energy levels were estimated to be -4.82 (TDOPAPy), -5.21 (TDOPABP), -4.96 (TDPAPy) and -4.95 eV (TCzPy), respectively, revealing efficient HOMOs for hole transport, and which were follow the same trends of DFT results. In comparison to TDOPAPy, the significantly lowered HOMO levels of TDOPABP could be attributed to the lesser π -delocalization areas of biphenyl, since the HOMOs of these OSMSs were partially distributed on the central cores (Figure 1). Due to the poor electronic affinities of these OSMSs, the reduction processes were not observed, and thus, their LUMO levels were deduced to be -2.51 eV (TDOPAPy), -2.23 eV (TDOPABP), -2.52 eV (TDPAPy) and -2.52 eV (TCzPy) from the optical energy gaps (E_{e} , Figure S8 and Table 1) and HOMO levels (Table 1).

2.4 Thermoelectric properties

To evaluate the potential of thermoelectric conversion capabilities of these OSMSs, composite films incorporated with different amount of SWCNTs were prepared (Scheme 1c) and their electrical conductivities and Seebeck coefficients were investigated. Figure 2a-c exhibits the σ , S and PF as functions of the dopants concentration of these samples and the detailed comparisons of the performance were listed in Table 2 and S2. All the four OSMSs displayed increasing conductivity with the increasing SWCNT loading, as the SWCNTs should effectively decrease the $E_{\rm F}$ of the sample and hence dramatically improve the carrier density for electric conduction (Figure 2a).³⁷ In addition, introduction of different scaffold and substituents has a remarkable influence on electrical conductivities. Among these samples, the highest conductivity (189.4 ± 9.0 S cm⁻¹) was achieved by SWCNT/ TCzPy (1:1), indicating efficient hole transport in the SWCNT/ TCzPy composites, which could be understood in terms of raman spectrum and scanning electron microscopy (SEM) image studies discussed below.

Table 1. Photophysical, electrical and thermal properties of these compounds.

Compounds	λ _{abs,max} a) [nm]	λ _{abs,max} b) [nm]	λ _{em,max} a) [nm]	λ _{em,max} ^{b)} [nm]	E ^{c)} [eV]	E _g d) [eV]	HOMO ^{c)} [eV]	HOMO ^{e)} [eV]	LUMO ^{†)} [eV]	Τ _g / Τ _m / Τ _d ^{g)} [°C]
TDOPABP	301	298	443	455	3.89	2.98	-4.38	-5.21	-2.23	/ 238/ 446
TDOPAPy	496	485	538	536	2.74	2.31	-4.21	-4.82	-2.51	162/ 269/ 436
TDPAPy	479	470	516	512	2.83	2.44	-4.43	-4.96	-2.52	217/ 373/ 475
TCzPy	478	471	533	509	3.04	2.43	-5.21	-4.95	-2.52	227/ 373/ 468

^{a)}Measured on film states, and ^{b)}measured in dilute chloroform solution, ($\lambda_{abs,max}$ was the first absorption peak scanning from the long wavelength region), ^{c)}obtained from DFT calculation, ^{d)}estimated from the optical absorption edge, ^{e)}determined from the onset of the oxidation potential, ^{f)}deduced from the HOMO and optical E_g , ^{g)}obtained from the TG and DTA curves.

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Figure 2. The σ (a), *S* (b), PF (c) values of these samples *versus* different dopant ratios, and the temperature dependence of the σ (e), *S* (f), PF (g) values of these composite films.

Table 2. Thermoelectric parameters of these samples.

Composite films	Seebeck co [µV	oefficient K ⁻¹]	Electrical co [S cr	onductivity n ⁻¹]	Power factor [μW m ⁻¹ K ⁻²]	
	Average	Maximum	Average	Maximum	Average	Maximum
SWCNT/TDOPABP ^{a)}	97.2 ± 11.1	108.3	43.6 ± 3.0	46.6	41.3 ± 6.7	48.0
SWCNT/TDOPAPy ^{a)}	68.9 ± 2.9	71.8	69.3 ± 11.9	81.2	34.0 ± 1.5	35.4
SWCNT/TDPAPy ^{b)}	64.2 ± 6.2	70.4	91.3 ± 5.7	97.0	37.7 ± 5.1	42.8
SWCNT/TCzPy ^{b)}	75.9 ± 3.3	79.2	189.4 ± 9.0	198.4	108.4 ± 4.8	113.2

^{a)} With an optimized doping ratio of 1:2, ^{b)} With an optimized doping ratio of 1:1.

As expected, the Seebeck coefficients of all the SWCNTs/ OSMSs composite films are positive, confirming that p-type electrical transport is dominant. The Seebeck coefficients of SWCNT/TDOPABP and SWCNT/TDOPAPy composite films considerably increased as the hybrid ratios elevated from 1:1 to 1:2 (Figure 2b). Noticeably, the accessory OSMSs increased the coverage area of SWCNTs, which selectively prevented the passage of low-energy carriers by sandwiching organic particles between the nanotubes, thus leading to increases in the mean carrier energies and Seebeck coefficients.61 Additionally, the TDOPABP possess a deeper HOMO levels (-5.21 eV) to trap the low-energy carriers and thus result in a higher Seebeck coefficient. However, the excess TDOPABP or TDOPAPy may induce aggregation, adversely affecting the monodispersity on the SWCNTs and thus decreasing the Seebeck coefficient (Figure 2b). On the other hand, for SWCNT/TDPAPy and SWCNT/TCzPy composite films, the variations of hybrid ratios have a marginal effect on the Seebeck coefficients, which reflect their parallel contacts between the SWCNTs and organics (Figure 2b). The optimized PFs of these composite films were 41.3 \pm 6.7, 34.0 \pm 1.5, 37.7 \pm

5.1, and 108.4 \pm 4.8 $\mu W~m^{-1}~K^{-2}$ for SWCNT/TDOPABP, SWCNT/TDOPAPy, SWCNT/TDPAPy and SWCNT/TCzPy, respectively (Figure 2c), among which the highest PF value of SWCNT/TCzPy is considered with the expectation of DFT calculations and electrochemical data.

To assess the thermostabilities of these composite films, the S, σ , and PF values of the SWCNT/OSMS hybrid films (with moderate doping ratio of 1:2) at different temperatures were shown in Figure 2d-f. As displayed in Figure 2d and 2e, both of the Seebeck coefficients and electrical conductivities of the SWCNT/TDOPAPy and SWCNT/TCzPy hybrid films exhibited slight ascent with the increasing of temperature, and thus result in improved PFs (Fig. 2f), which were coincided with the common tendencies for p-type materials.¹⁴ However, for SWCNT/TDPAPy, especially for SWCNT/TDOPABP, the Seebeck coefficients and electrical conductivities decreased remarkably with the increasing of temperature, which may presumably due to the relatively weak π - π interactions between the organic molecules and the SWCNT interfaces, which lowered their thermostabilities. Such inferences were confirmed in the Raman spectra part.



Figure 3. SEM images of the SWCNT/TDOPABP (a), SWCNT/TDOPAPy (b), SWCNT/TDPAPy (c), and SWCNT/TCzPy (d) composite films with ratios of 1:10, 1:5, 1:2, and 1:1 for 1-4, respectively.

2.5 SEM image studies

SEM measurements were performed to provide insight into the morphologies of the composite films, as the altered molecular structures and SWCNTs/OSMS hybrid ratios impact the phase boundaries of the samples, thus producing analogous contacts that influence the electrical properties.⁶⁰ The SEM images of these SWCNT/OSMS composite films with various hybrid ratios were shown in Figures 3. Clearly, all these composite films exhibited visually homogeneous surfaces at high hybrid ratios (SWCNT/OSMS, 1:1 and 1:2) revealing that the carbon nanotube bundles firmly connect with each other whereby the coated OSMSs, and thus leading to favourable and long interbundle connections and continuous conductive networks, which coincided with their corresponding high σ . Remarkably, the SWCNT/TDOPABP and SWCNT/TDOPAPy composite films showed gradually increased sample surface inhomogeneity with the increased hybrid rates from 1:2 to 1:10, and which might be the key reason for Seebeck coefficients decrease of the samples. However, for SWCNT/TDPAPy and SWCNT/TCzPy composites, the excess organics (at the hybrid ration of 1:5 and 1:10) gathered to form regular crystals (Figures 3c and 3d), rendering homogeneous surface at the SWCNT-rich regions (Figures S4-S7), and therefore result in analogous Seebeck coefficients in contrast to the high hybrid ratio (1:2 and 1:1) films (Figure 2b). Noticeably, the distinct crystallinities of these OSMSs

originating from the diverse molecular structures lead to different morphology trend, which affect the TE performances.



Figure 4. Kelvin probe measurements of these composite films.

2.6 Kelvin probe measurements

To explore the variation of $E_{\rm FS}$ of these hybrid films, Kelvin probe measurements were performed, and the results were shown in Figure 4 and Table 3. As displayed in Figure 4, the work functions (WFs) of all these composite films increased with the increasing of SWCNT/OSMS hybrid ratios. Noticeably,

the increased WFs indicated the downward shift of the $E_{\rm F}s$ in the bandgap and result in increased carrier density, consequently improving the electrical conductivity,³⁷ which agreed with the aforementioned σ results.

Table 3. Work functions of these SWCNT-doped interfaces.

Interfaces	1:10 ^{a)}	1:5 ^{a)}	1:2 ^{a)}	1:1 ^{a)}
	4.287 ±	4.643 ±	4.786 ±	4.774 ±
SWCN1/IDOFABP	0.049	0.043	0.032	0.039
	4.727 ±	4.813 ±	4.826 ±	4.833 ±
SWCNT/TDOPAPy	0.052	0.038	0.043	0.049
	b)		4.875 ±	4.920 ±
SWCN1/IDPAPy			0.043	0.041
SWCNT/TC-DV			4.913 ±	4.929 ±
SWCN1/TC2Py			0.040	0.039

^{a)}SWCNT:OSMS ratio, ^{b)}not obtained due to the high roughness of the interfaces.

2.7. Photophysical properties and Raman spectroscopy

The UV-Vis absorption and photoluminescence spectra of these OSMSs and SWCNT/OSMSs samples were displayed in Figures S8 and S9, and the detailed data were presented in Table 1. As shown in Figure S9, no significant changes can be observed after the treatment of SWCNTs in contrast to the originally absorption spectra of the corresponding OSMSs (Figure S8), revealing no cation radical generating after physical mixture with the SWCNTs. In addition, the X-ray photoelectron spectroscopy analysis confirmed this assumption that no symbolic ammonium salts signals (~ 402 eV) emerged after physical hybridization (Figures S10 and S11).⁴⁰

Raman spectra of these SWCNT/OSMS hybrid films were obtained to discuss the interactions between the two components as well as the structural integrity of the SWCNTs after the fabrication process. The results were shown in Figure 5 and S12-S15, and the details were presented in Table S3. As displayed in Figure 5, the characteristic Raman bands of the SWCNT-based composite films involved the graphite-like G band (at \sim 1593 cm⁻¹), D band (at \sim 1346 cm⁻¹), radial breathing mode (RBM), and G' band (at ~ 2681 cm⁻¹).⁸¹⁻⁸² Here, the graphite-like G band was derived from the optical vibration of two adjacent carbon atoms on the wall of a SWCNT, and the D band was related to defect-induced resonant scattering. Noticeably, all the samples exhibit tiny D band intensities relative to the G band intensities, indicating that no distinct structural defects were introduced upon the drop-casting hybrid process.¹⁶ In comparison with the pure SWCNT, the composite SWCNTs exhibited obviously blue-shifted G bands. suggesting the π - π interactions between nanotubes were impeded by the inserted OSMS particles. This coincided with the enhanced Seebeck coefficients. Another characteristic signature of the SWCNTs was observed at relatively low frequencies (100 \sim 200 cm⁻¹) associated with the RBM, where all the carbon atoms coherently move in a radial direction.¹⁶ As shown in Figure 5, the intensity of the RBM decreases from TDPAPy to TDOPABP, and then TDOPAPy and TCzPy, revealing

stronger interactions with the SWCNTs of the latter two than the formers, since the attached OSMSs on the SWCNT surfaces hinder carbon atom oscillation in the radical direction.¹⁶ Noticeably, the strong interactions between OSMSs and SWCNTs were beneficial to form continuous conductive networks. However, the variation of the RBM intensity imperfectly correlates with the SWCNT/OSMS ratios in the composite films presumably due to the different crystallinity of the OSMSs (Figure 3). Additionally, the G' band was caused by the existence of a double electron-phonon resonance mechanism, and the high-energy shift from TDPAPy to TCzPy (Figure 5) supports shallow hole injection to the SWCNTs.⁸¹⁻⁸² Overall, based on the Raman spectra and SEM images, the SWCNT/TCzPy (1:1) hybrid film bears the lowest RBM intensity and D/G intensity ratio (Table S3), the largest high-energy shift of the G' band and a homogeneous surface, which were beneficial for electrical conductivity.⁸³⁻⁸⁴



Figure 5. Raman spectra of the pure SWCNT and SWCNT/OSMS composite films with the doping ratio of 1:1.

3. Conclusion

In conclusion, four new p-type OSMSs were elaborately designed and adapted for TE application. Noticeably, the bandgaps and HOMO levels of the OSMSs essentially affected the $E_{\rm FS}$ in the SWCNT-hybrid system and thus determined the carrier concentration, while the geometries dictated the contact and interfacial morphologies, hence influencing the conductivity and Seebeck coefficient value. Raman spectra and SEM images revealed that the interfacial contacts and morphologies of the SWCNT/OSMS hybrid films can be manipulated by changing the hybrid ratios, enabling broad prospects for these organic small molecules as binders to achieve high performances, since the definite structures of organic small semiconductors can be optionally regulated. Among these four OSMSs, the TCzPy-based composite film with a hybrid ratio of 1:1 exhibited the best performance, with a conductivity approaching 200 S cm⁻¹ and a Seebeck coefficient over 80 μ V K⁻¹ enabling a high PF over 110 μ W m⁻¹ K⁻².

Conflicts of interest

There are no conflicts to declare.

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Regulating the structure of p-type organic small molecules to generate thermoelectric composites achieve a high power factor of 113.2 μ W m⁻¹ K⁻².