Organic Thermoelectric Materials and Devices Based on p- and n-Type Poly(metal 1,1,2,2-ethenetetrathiolate)s

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Due to their capability of converting heat into electricity (and vice versa), thermoelectric (TE) devices are expected to play an important role in addressing today's global energy issues.[1] At present, research in this area mainly focuses on developing high-performance TE materials. TE efficiency of a material is evaluated by its TE figure of merit (*ZT*), which is expressed by: $ZT = S^2\sigma T/\kappa$, where *T* is the absolute temperature, *S* is the Seebeck coefficient, σ is electrical conductivity, and κ is thermal conductivity. Since inorganic materials normally have high σ, researchers have been working on them extensively. In contrast, much less attentions have been paid to developing organic TE materials. Although organic materials normally have low σ, they usually exhibit low κ, which could compensate the negative effects caused by its low σ. And unlike inorganic TE materials, almost all of which contain toxic and rare elements of Bi, Te, Sb and Pb,[2] organic materials are based on abundant elements (such as C, O, N and S…) in nature. They could result in light weight, low-cost large-area flexible and non-toxic TE modules. Therefore, efforts are worth to be devoted in developing organic TE materials, doing so not only could offer alternative opportunity for green energy generation, but also could significantly contribute to fundamental science.

It has been demonstrated that p-type material poly(3,4-ethylenedioxythiophene) exhibits a high *ZT* value of 0.25.[3] This finding is exciting and encouraging, for the first time it shows that organic materials could also be very good thermoelectric materials despite their intrinsic low conductivity. In this paper, we investigated the TE properties of a series of metal coordination n and p-type polymers containing 1,1,2,2-ethenetetrathiolate (ett) linking bridge: poly[A$_x$(M-ett)] (A = tetradecyltrimethyl ammonium, tetrabutyl ammonium, Na$^+$, K$^+$, Ni^{2+}, Cu^{2+}, M = Ni, Cu). We found that n-type materials poly[Na$_x$(Ni-ett)] and poly[K$_x$(Ni-ett)] exhibit excellent TE characteristics (among best organic TE materials). By combining n-type poly[Na$_x$(Ni-ett)] and p-type poly[Cu$_x$(Cu-ett)], TE module contains 35 n-p single couples is fabricated, it demonstrates an output power of 750 μW, which is the highest for organic materials ever reported. It is

worth to note here that this is the first time n-type organic TE material is demonstrated.

Poly[A$_x$(M-ett)] system was first reported by H. Poleschner et al. nearly 30 years ago.[4] Polymers of this system are very conductive (σ: 10^{-5}~50 S cm^{-1}), and their synthesis, electrical/magnetic properties and structure have also been studied by several groups.[4–9] However, there is no investigation on their TE performances. Considering their amorphous nature, their thermal conductivities should be low, combining with their high conductivities, they could exhibit very good TE performances. Motivated by this idea, we studied the TE properties of Poly[A$_x$(M-ett)]s.

Poly[A$_x$(M-ett)]s were synthesized following a reported procedure with some slight modifications (**Scheme 1**). Ethylene tetrathiolate anion C$_2$S$_4^{4-}$ was generated in situ by reaction of 1,3,4,6-tetrathiapentalene-2,5-dione (TPD) with 4 mol. equiv. sodium methoxide or potassium methoxide in methanol solution, then poly[A$_x$(M-ett)]s were obtained by adding corresponding transition metal salts, complexes with alkyl ammonium as counter cations (A = C$_{14}$Me$_3$N$^+$ or Bu$_4$N$^+$) were then obtained by adding the corresponding ammonium salts. It was reported that the center metals, counter cations and intentional oxidation all have significant effects on the conductivities of poly[A$_x$(M-ett)]s. In this paper a series polymers were synthesized: poly[Na$_x$(Ni-ett)], poly[K$_x$(Ni-ett)], poly[Ni$_x$(Ni-ett)], poly[(C$_{14}$Me$_3$N)$_x$(Ni-ett)] and poly[(Bu$_4$N)$_x$(Ni-ett)]), and poly[Na$_x$(Cu-ett)] and poly[Cu$_x$(Cu-ett)]. Regretably, these polymers are totally insoluble, so common-used structure-characterization method such as NMR can not be applied to them. And they are amorphous, so it is impossible to use X-ray diffraction to analyze their structures. So, we employed Elemental Analysis (EA) to do the characterization, but it still can not give the accurate structures of these polymers, since the data measured could not be expressed by the formula of [A$_x$(MC$_2$S$_4$)]$_n$ (**Table 1**). This might be induced by the following two reasons: (i) As highly rigid molecules, their solubility is very poor, it is very difficult for them to polymerize into large molecular-weight. Therefore, they always precipitate from the reaction mixtures at a low-molecular weight, and the fraction of the terminal groups in the whole polymer increases, leading to the uncertainty of the molecular formula. (ii) Some should-be center metal might become counter cation accidentally, contributing to difficulties of determining the accurate amount of center metal ions. Despite the complexity and uncertainty of the structures of these polymers, the electrical properties and related structure data (EA, X-ray and XPS) are highly reproducible, this provides us a good opportunity to systematically investigate their TE properties.

The basic formula of such polymers was initially suggested by H. Poleschner et al.. Based on their experiments, they supposed that C$_2$S$_4^{4-}$ was formed as the intermediate, which could chelate

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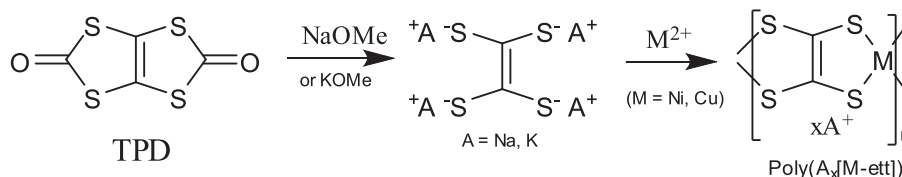
Scheme 1. Synthesis of poly(M-ett).

the transition metal ions to form the linear polymer chains.[4] Later, such polymers were further characterized by P. Cassoux et al. using extended X-ray Absorption Fine Structure (EXAFS) studies.[7,8] Here, we investigate the polymers we made by X-ray Absorption Spectroscopy (XAS) (X-ray Absorption Near Edge Structure (XANES) and EXAFS). XANES provides information about the coordination geometry of the transition metals and EXAFS gives the average distances between the center metal and its surrounding atoms. For poly($Na_x[Ni$-ett]), a comparison of the K-edge XANES spectra with three square planar four-coordinate Ni bis-dithiolene complexes ($TBA_2[Ni(dmit)_2]$, $TBA[Ni(dmit)_2]$ and $TBA[Ni(dmid)_2]$, TBA = tetrabutylammonium, dmit = 1,3-dithiole-2-thione-4,5-dithiolate, dmid = 1,3-dithiole-2-one-4,5-dithiolate), nickel acetate (($CH_3COO)_2Ni$) and five-coordinate NiS (millerite) and six-coordinate NiS_2 were investigated (**Figure 1**a). It is well-known that for 3d-transition metals with noncentrosymmetric geometry display pronounced a pre-edge peak in their K-edge XANES spectra, and the intensity of this pre-edge peak increases in sequence of octahedral, tetragonal and tetrahedral structures.[10–12] This pre-edge peak is clearly observed for tetragonal pyramidal NiS (marked by an arrow in Figure 1a), but is very weak for those square planar dithiolene complexes and poly[$Na_x(Ni$-ett)]. In the XANES range, the peak position and shape of poly[$Na_x(Ni$-ett)] are different from those of its references Ni bis-dithiolene complexes, NiS and NiS_2 and Ni(AcO)$_2$. Considering their similar coordination environment of the center metal in poly[$Na_x(Ni$-ett)] and those Ni bis-dithiolene complexes, both the pre-edge spectra and XANES of them should be similar. In our experiments, as stated above only pre-edge spectra are similar, and XANES are not. The reasons for such observation are not clear at present and further investigation is under way.

The Fourier transform of the k-weighted EXAFS shows a predominant peak, which is originated from the nearest-neighbor sulfur coordination shell around the Ni atoms. Base on this peak, Ni-S distance is calculated to be 2.15 Å, identical to the reported results.[7,8] Besides this first-shell interaction, the second-shell and the third-shell atomic interactions were also observed (Figure 1b), based on which distance of Ni-C of 3.18 Å and Ni-S of 4.71 Å were calculated. These bond lengths are very close to that determined in the single crystal of trimetallic complex with tetrathiooxalate ligands as bridge,[13] where the distances between the center metal Ni and the second-shell carbon atoms and the third-shell sulfur atoms are 3.07 and 4.72 Å respectively.

To further characterize the coordination environment of center metals in our polymers we performed X-ray photoelectron spectroscopy (XPS) experiments. For poly[$Na_x(Ni$-ett)], in the range of 850 ~ 860 eV of the spectra, two Ni($2p_{3/2}$) peaks with bonding energies of 854.1 and 855.7eV can be discerned, indicating that there are two kinds of Ni atoms with different chemical environment in the material(Figure S1a). Considering the very close binding energy value to that of Ni bis-dithiolates ever reported.[14] The dominant peak located at 854.1 eV can be attributed to the center metal Ni in the material. The intensity of the shake-up satellite peak (around 860 eV) is very weak, this suggests that the center Ni atom possesses a square-planar structure and is in the low-spin state.[15] We believe the peak located at 855.7 eV is from the Ni atoms co-act as the counter cations with Na$^+$, this is consist with our further experiment: when we double amount of Ni salt in the reactions, thereby the number of Ni atom act as counter ion is expected to increase considerably. As expected, the resulted product poly[$Ni_x(Ni$-ett)] displays a much stronger

Table 1. Elemental analysis data, conductivities, Seebeck coefficients and power factors of the polymers.

Sample	Elemental Analysis [%] C	σ_{300K} [S cm^{-1}]	S_{300K} [µV K^{-1}]	PF_{300K} [µW m^{-1}K^{-2}]	H	N	M	Na/K
Poly[$C_{14}Me_3N_x(Ni$-ett)]	20.29	2.45	1.02	16.47	–	0.3	−80	0.19
Poly[$Bu_4N_x(Ni$-ett)]	20.60	2.30	1.00	18.96	–	0.2	−25	0.01
Poly[$Na_x(Ni$-ett)]	13.63	1.22	–	27.62	3.00	40	−75	23
Poly[$K_x(Ni$-ett)]	12.99	1.12	–	25.85	0.57	44	−122	66
Poly[$Ni_x(Ni$-ett)]	12.05	1.62	–	31.00	0.47	6.6	−84	4.7
Poly[$Na_x(Cu$-ett)]	11.4	1.03	–	27.72	10.25	0.2	79	0.12
Poly[$Cu_x(Cu$-ett)]	7.26	0.76	–	38.6	0.58	9.5	83	6.5
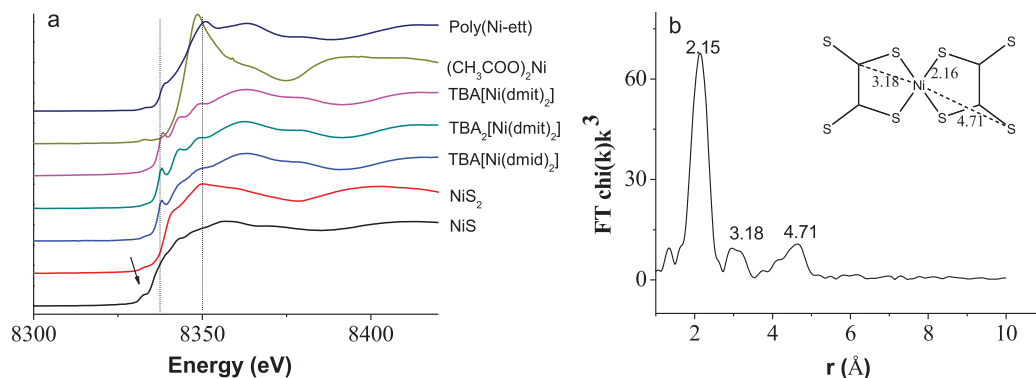
Figure 1. a) Normalized Ni K-edge XANES of poly[Na$_x$(Ni-ett)] and its reference compounds. The pre-edge peak of NiS was indicated by an arrow. b) EXAFS radial distribution curve of poly[Na$_x$(Ni-ett)] (the inset illustrates the coordination shells of nickel).

peak around 855eV, and so does its satellite peak, which is located at about 860 eV(Figure S1a).

For Cu(2p) in poly[Na$_x$(Cu-ett)] and poly[Cu$_x$(Cu-ett)] (Figure S1b), we do not observe the typical configuration interaction satellite, which is normally located in the range of 940 ~ 950 eV, this excludes the existence of Cu^{II}, and only Cu^I or spin paired Cu^{III} could be in the two materials. In the range of 930 ~ 940 eV of the spectra, two peaks can be discerned, which correspond to two Cu(2p$_{3/2}$) binding energies: 932.89 and 934.58 eV. The dominating peak at 932.89 eV is originated from Cu$^+$, while the weaker peak located at 934.58 eV is from Cu^{3+}. This is different from what have been observed in other oxidized Cu bis-dithiolene complexes with Cu^{3+} as the main Cu ions,[9,16,17] where the peak of Cu^{3+} dominates over the peak of Cu$^+$. As we increase the amount of CuCl$_2$ in the reaction, the intensity ratio of Cu$^+$/Cu^{3+} peak does not change, this indicates that the excess copper atoms seemingly act as counter ion actually strongly coordinate with their neighboring sulfur atoms. Thus a cross linked structure for these copper polymers are very possible. This assumption was partially supported by the Cu K-edge XANES spectra, which are quite different from that of two Cu bisdithiolate complexes TBA$_2$[Cu(dmit)$_2$] and TBA$_{1.3}$[Cu(dmit)$_2$] (Figure S2).

Thermal conductivities of amorphous materials with similar composition are expected to be very close, so the parameter power factor ($PF = S^2 \sigma$) was employed to evaluate TE performances of different polymers. As summarized in Table 1, at 300K conductivities of the nickel coordination polymers with tetraalkylammonium are about two orders lower than those of polymers containing Na$^+$ or K$^+$ as counter cations. This can be easily understood: the bulky alkyl groups of the counter cations significantly hinder the close packing of the polymer chains and hence seriously impede the inter-chain charge transport, resulting in low conductivity. Replace of the ammoniums with Ni improves the conductivity, but not as dramatic as Na and K do. The poly[Ni$_x$(Ni-ett)] shows a σ_{rt} about 6.6 S cm^{-1}, while poly[Na$_x$(Ni-ett)] and poly[K$_x$(Ni-ett)] display conductivities around 40 S cm^{-1}. It was noted that Seebeck coefficients of these nickel complexes (except poly[Bu$_4$N$_x$(Ni-ett)]) are much higher in comparison to those highly doped conducting polymers[18,19] and charge transfer salts,[20,21] which have similar conductivities. Among these polymers, Poly[K$_x$(Ni-ett)] possesses the highest

conductivity and Seebeck coefficient, and hence highest *PF* of 66 µW m^{-1}K^{-2} at 300K. To note, the negative (positive) Seebeck coefficient indicates that major carriers are electrons (holes) in corresponding materials, thereby poly(Cu$_x$[Cu-ett]) and poly(Na$_x$[Cu-ett]) are p-type materials and the rest ones in Table 1 are all n-type materials. While conductivity of poly(Cu$_x$[Cu-ett]) is about 50 times higher than that of poly[Na$_x$(Cu-ett)] at 300K, they show close Seebeck coefficient of about 80 µV K^{-1}. The *PF* of poly[Cu$_x$(Cu-ett)] is 6.5 µW m^{-1}K^{-2}, about one-order lower than that of poly[Na$_x$(Ni-ett)] and poly[K$_x$(Ni-ett)].

For poly[Na$_x$(Ni-ett)], poly[K$_x$(Ni-ett)] and poly[Cu$_x$(Cu-ett)], temperature dependence of Seebeck coefficient, electrical conductivity and thermal conductivity were measured in the range of 220 to 440 K (Thermo Gravimetric Analysis (TGA) shows that the polymer starts to lose weight markedly when temperature is above 440 K, so we do not apply this measurement for temperatures higher than 440 K). The electrical conductivities of the three materials all increase with the temperature (**Figure 2**a), which is typical behavior for semiconductors. The Figure S3 shows linear dependence of natural logarithm of conductivity versus $T^{-1/4}$, which indicates charge transport in these polymers follows the famous three-dimensional variable range hopping (3D-VRH) model.[22]

As the Seebeck coefficient is much less susceptible to influences arising from the resistive boundaries in the material because it is essentially evaluated by a zero-current measurement, and temperature drops across such boundaries are much less significant than voltage drops, thus one can gain more information about the conducting mechanism since the effects of boundaries are largely excluded. For poly[K$_x$(Ni-ett)] the Seebeck coefficient is −121.6 µV K^{-1} at room temperature and −151.7 µV K^{-1} at 440 K. As shown in Figure 2b, the absolute values of Seebeck coefficients of both polymers increase almost linearly with the temperature, similar to doped conducting polymers such as polythiophenes[23,24] and polypyrrole.[25] We do not understand well why nickel coordination polymers are n-type, while copper coordination polymers are p-type. One possible reason is that oxidation may selectively mainly on either center metal atoms or ligand bridges, depend on the species of center metal atoms.[17] Such selective oxidation and its effects have been observed in metal phthalocyanine (MPc),[26] where both n and p-type materials can be obtained by employing different metal atoms (NiPcI is p-type but CoPcI is n-type).
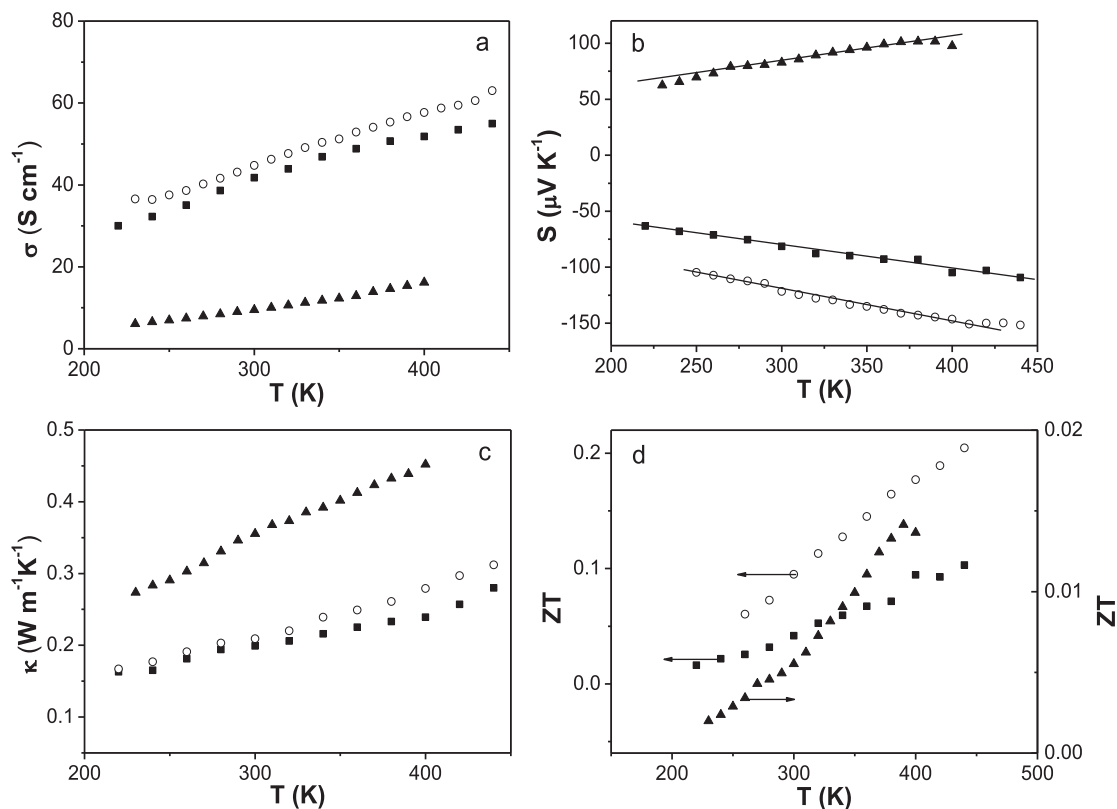
Figure 2. Temperature dependence of a) electrical conductivity, b) Seebeck coefficient, c) thermal conductivity and d) figure of merit for poly[Na$_x$(Ni-ett)] (■), poly[K$_x$(Ni-ett)] (○) and poly[Cu$_x$(Cu-ett)] (▲).

While the thermal conductivities of the two n-type polymers are very close to each other within the temperature range tested (Figure 2c), the poly[Cu$_x$(Cu-ett)] shows much higher thermal conductivity than them (nearly doubled). The higher thermal conductivity of poly[Cu$_x$(Cu-ett)] could be originated from the higher content of metal ions inside it. It is also seen that κ increases almost linearly with the temperature, following the typical behavior of amorphous solids.

Finally, ZT values of these materials are calculated based on the formula: $ZT = S^2\sigma T/\kappa$, and are shown as function of the temperature in Figure 2d. For poly[Na$_x$(Ni-ett)], ZT is 0.042 at 300 K, and it reaches 0.10 at 440 K. Poly[K$_x$(Ni-ett)] shows a ZT value of 0.2 at 440 K. It is seen that for all the materials, ZT tends to increase with the temperature. The ZT value of poly[Cu$_x$(Cu-ett)] varies between 0.002 and 0.014 from 230 to 400 K. Its highest ZT value is 0.014 (at 380 K), about one-order lower in comparison to that of nickel complexes poly[Na$_x$(Ni-ett)] and poly[K$_x$(Ni-ett)].

Motivated by the excellent thermoelectric properties of both p-type and n-type conducting polymers, we built an all-polymer thermoelectric module with 35 legs based on poly[Na$_x$(Ni-ett)] and poly[Cu$_x$(Cu-ett)] on AlN substrate (**Figure 3**a). Both polymers were compressed (hydraulic pressure of 2MPa) into cuboid with dimension of 5 mm × 2 mm × 0.9 mm. After deposition of 50 nm Au on the two opposite sides of the materials, the module was fabricated with silver and Al acting as interconnects at the bottom and top substrates, respectively. The module and temperature gradient (ΔT) control system were shown in Figure 3b.

When a ΔT was applied, a large Seebeck voltage was immediately shown. Both the output voltage and short-circuit current (I_{SC}) increase steadily with the hot-side temperature (T_{hot}) and ΔT (Figure 3c). When T_{hot} is 423 K and ΔT is 82 K, an open voltage of 0.26 V and an I_{SC} of 10.1 mA are generated. This indicates that an output voltage of up to 1.5 V (the operating voltage for many practical devices), can be achieved if the thermoelectric module consists 200 thermocouples.

The power output of the module is measured with different loads (Figure 3d) under various T_{hot} and ΔT. A maximum output power of 750 μW was obtained with a load resistance of 33 Ω (correspond to the internal resistance of the 35 thermocouples), a ΔT of 82 K and a T_{hot} of 423 K. It is worth to note that this is the highest power derived by organic materials based thermoelectric devices ever reported. High power output can also be obtained at much smaller ΔT (≤ 30 K, which is easy to achieve in a natural environment). The thermoelectric device exhibits maximum output power ($P_{max} = U^2/(4R_I)$, where U is the measured Seebeck voltage and R_I is the inner resistance[3]) of 1.2 μW cm^{-2} at ΔT = 30 K when the cold side temperature (T_{cold}) of the device is maintained at room temperature (Figure 3e). Based on this prominent performance, higher P_{max} of 2.8 μW cm^{-2} can be extrapolated assuming an optimum packing density of 0.94 for the module.[3] This very high power out (compared with that already reported value of 0.27 μW cm^{-2})[3] is attributed to the excellent thermoelectric properties and conductivities of both p-leg and n-leg in the module.

Besides its good electric generation ability, the module also shows very good stability. The noncapsulated module does
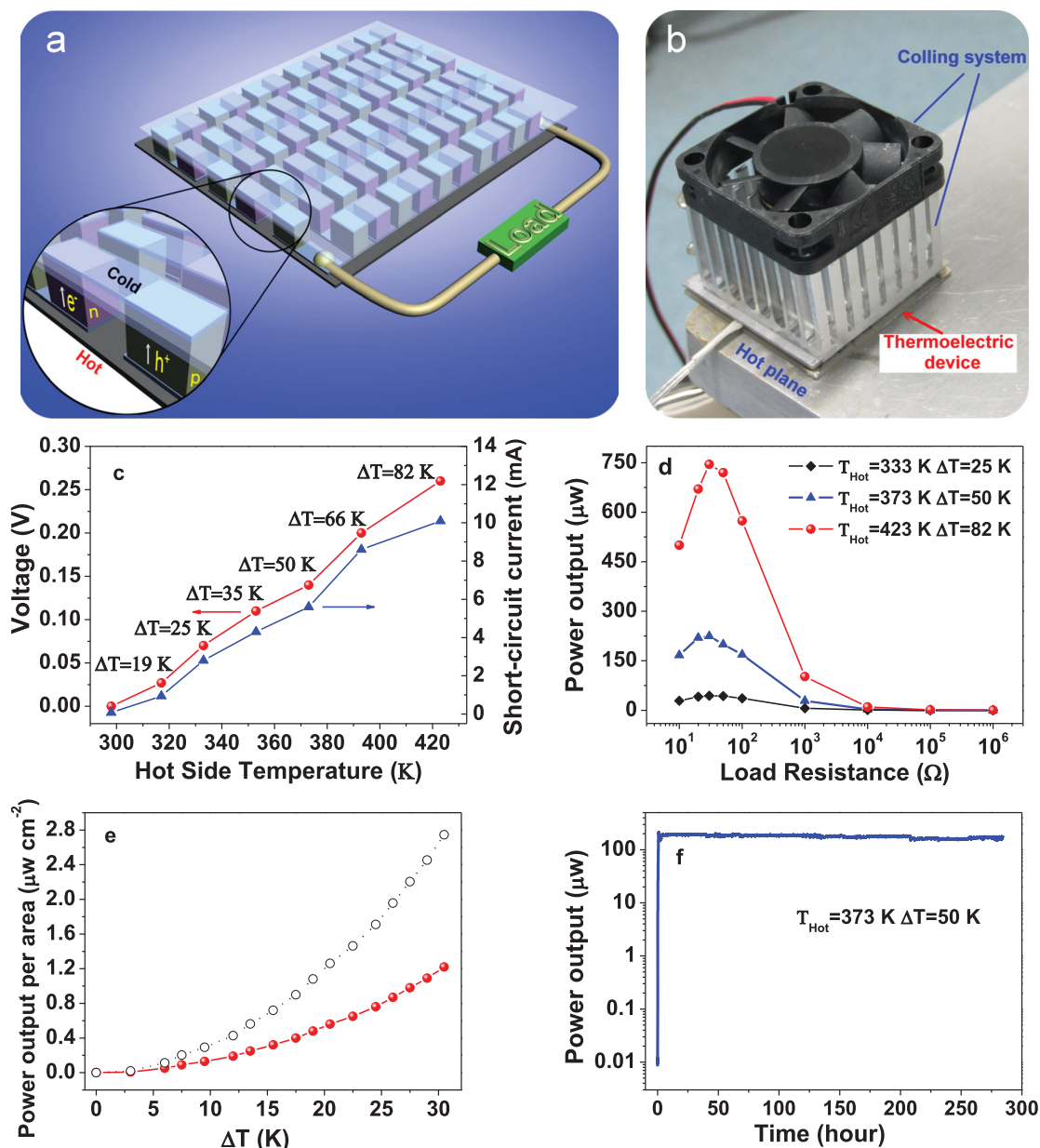
Figure 3. The thermoelectric module consisting of 35 thermocouples. a) Module structure. b) Photograph of the module and the measurement system with hot plane and cooling fan. c) The output voltage and short-circuit current at various T_{hot} and ΔT. d) The measured power output of the module with different loads. e) Maximum power output per area of the module. The packing density, defined as the occupied area of legs divided by the total devices, is 0.40. The extrapolated power output for packing density of 0.94 is plotted as the dashed line. f) Power output stability of the module operating with $T_{hot} = 373$ K and $\Delta T = 50$ K.

not show any obvious degradation after long-time operation of 300 hours at a high temperature of 373 K under ambient atmosphere (Figure 3f). The deduced half-lifetime is even longer than 1000 hours (no lifetime characterization has been done on organic TE devices before). We also tested the ability of the module to act as a thermoelectric refrigerator, but no observable cooling effect was detected. However, single thermocouple indeed displays cooling effect, when a voltage of 0.6 V is applied, a ΔT of 3.5 K can be produced (Figure S4). The absence of cooling effect of the module may be due to its

much larger size, which causes heat dissipated much faster into the ambient environment, and make it difficult to establish a detectable ΔT.

In summary, we have developed both n-type and p-type organic thermoelectric materials with low thermal conductivities, high electrical conductivities, and reasonable Seebeck coefficients: n-type poly[Na_x(Ni-ett)], n-type poly[K_x(Ni-ett)] and p-type poly[Cu_x(Cu-ett)]. The two n-type materials exhibit high ZT values of 0.1 to 0.2 around 400 K (which are among highest for organic materials). Poly[Cu_x(Cu-ett)] also

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shows good ZT value of 0.01 around 400 K. By combining n-type poly[Na$_x$(Ni-ett)] and p-type poly[Cu$_x$(Cu-ett)], thermoelectric module composed of 35 n-p couples was made, which is able to output a voltage of 0.26 V, a current of 10.1 mA, and a power of 2.8 µW cm^{-2} (highest for organic thermal devices ever reported) under a temperature bias of $\Delta T = 80$ K. In addition, the module shows very good stability, and single n-p couple demonstrates its potential of functioning as a thermoelectric refrigerator. Our study indicates that organic materials can also be very promising for future thermoelectric applications, just as its counterpart inorganic materials.

Experimental Section

Synthesis: Synthesis of poly[Na$_x$(Ni-ett)] as a typical procedure for the synthesis of poly[A$_x$(M-ett)]: 1,3,4,6-tetrathiapentalene-2,5-dione (TPD 1 g, 4.8 mmol) was reacted with excess sodium methoxide (1.2 g, 22.2 mmol) in refluxing methanol solution for 12 hours. Then NiCl$_2$ (0.63 g, 4.8 mmol) was added. The resulting solution was refluxed for 12 hours. After placing in atmosphere for a while to let the polymer to precipitate, the solution was filtered and the solid was washed with water, methanol, and diethyl ether separately. The final product was obtained as black powder after drying under vacuum for 12 hours. Poly[K$_x$(Ni-ett)] was synthesized with the similar procedure except using potassium methoxide instead of sodium methoxide. Poly[Cu$_x$(Cu-ett)] was synthesized using the similar procedure of poly[Na$_x$(Ni-ett)] except two equiv. amount CuCl$_2$ was added to the reaction mixture.

Characterization: The analysis of metals (Ni, Cu, Na, K) was carried on inductively coupled plasma optical emission spectrometer (Optima 5300DV, Perkin Elmer). Polymers were dissolved in concentrated nitric acid, and the obtained solution was diluted before analysis. The content of C and H were analyzed by Flash EA 1112 (Thermo Fisher Scientific). TGA was performed on DTG-60 (Shimadzu). XPS was characterized by ESCALab220i-XL (VG Scientific) while the EXAFS was studied at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The polymers were made into compressed cuboid for the thermopower related tests. The Seebeck coefficient, electrical conductivity, thermal conductivity were measured by SB-100 Seebeck Measurement System (MMR Tech.), KEITHLEY 2002 Multimeter (Keithley Instrument Inc.), TCi Thermal Conductivity Analyzer (C-THERM Tech.), respectively. The polymers were synthesized three to five times under the same condition. For each patch, three samples were performed TE measurements. And the measurements were repeated three times to get an average value for each parameter (each time the value is actually very close).

Device fabrication: For the fabrication of thermoelectric module, 42 mm × 42 mm AlN wafer serves as the support substrate. 35 patterned bottom silver electrodes, each 2 mm × 12 mm and 2 mm apart, were inkjet-printed onto the ultraviolet/ozone (UVO) treated substrates. Then the compressed p- and n-type polymer samples (2 mm × 5 mm × 0.9 mm) with 50 nm evaporated Au layer on one side were adhered to bottom substrate using silver paste (EPO-TEK H20E). Then Au electrodes (50 nm) were thermal evaporated onto the other side through a shadow mask, these Au electrodes were then interconnected by Al foils, finalizing the module fabrication. ΔT was created by a hot plane (for T_{hot}) and a cooling fan (for T_{cold}), and was measured by platinum resistance thermometers. The electrical properties were measured by Keithley 4200 SCS under ambient atmosphere.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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