Supporting Information

Extremely High Power Factor in Seebeck Effects Based on New N-Type Copper-Based Organic/Inorganic Hybrid $C_6H_4NH_2CuBr_2I$ Film with Metallic-Like Conductivity

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1. The crystallographic parameter for $C_6H_4NH_2CuBr_2I$ Powder Rietveld Refinement

Table *S1*. The crystallographic parameter for $C_6H_4NH_2CuBr_2I$ (from Powder Rietveld Refinement) [1]	
Wavelength	0.71073Å
Temperature	298 K
2-theta range	10~90˚
Step size	0.02˚
Number of point	4000
Crystal system	hexagonal
Space group	R3
a (b)	3.963(3)Å
c	9.698(5)Å
$\alpha(\beta)$	90˚
γ	120˚
R_{wp}	5.03％
R_{exp}	1.02％
R_p	3.83％
GOF	4.20％
Z	3

2. The thermal conductivity for $C_6H_4NH_2CuBr_2I$ sample

The thermal conductivity (κ) can be determined according to the equation: $\kappa = \kappa_e + \kappa_L$, where κ_e and κ_L is the electronic contribution and lattice contribution, respectively. The electronic part of thermal conductivity κ_e was derived from the measured electrical conductivity according to the Wiedemann–Franz law: $\kappa_e = L\sigma T$, where L is the Lorenz number. Generally, Lorenz number could be

estimated as $L_0 = \frac{\pi^2}{3}(\frac{k_B}{e})^2 \sim 2.45 \times 10^{-8} \text{V}^2/\text{K}^2$ for free electrons, which is suitable for the metals. For most thermoelectric materials, the true Lorenz number is in fact lower than L_0, depending on the reduced Fermi energy $\xi = E_F / k_B T$ and scattering parameter r.[2-3] Assuming the main carrier scattering mechanism around room temperature is the acoustic phonon scattering, r could be -1/2. Then the Lorenz number L can be given as the following:

$$L = \left(\frac{k_B}{e}\right)^2 \left(\frac{3F_0(\xi)F_2(\xi) - 4F_1^2(\xi)}{F_0^2(\xi)}\right)$$

where $F_n(\xi)$ is defined as the Fermi integration

$$F_n(\xi) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \xi}} d\chi$$

Based on the single band approximation,

$$n = 4\pi \left(\frac{2m^* k_B T}{h^2}\right)^{3/2} F_{1/2}(\xi)$$

$$S = \pm \left(\frac{2F_1(\xi)}{F_0(\xi)} - \xi\right)$$

L values were calculated to be $\sim 1.5 \times 10^{-8}$ V^2/K^2. Since the electrical conductivity decrease with the temperature, the κ_e exhibits a decrease-to-increase trend with temperature, as shown in Figure 7(b). At room temperature, κ_e of $C_6H_4NH_2CuBr_2I$ is about 1.6 W/m•K.

To analyses the lattice thermal conductivity κ_L, the Slack's model as empirical formula should be given by:

$$\kappa_L = A \frac{M\theta_D^3 \delta}{\gamma^2 n^{2/3} T}$$

Here n is the number of atoms in the primitive unit cell, δ^3 is the volume per atom, θ_D

is the Debye temperature, M is the average of the atoms in the crystal, γ is the Grüneisen parameter, and A is a collection of physical constants (A~3.1×10⁻⁶ if κ is in W/m·K, M in amu, and δ in Angstroms)[4]. The Debye temperature is estimated by

$$\theta_{\mathrm{D}} \approx \frac{h}{k_B}\left(\frac{v_m}{\delta}\right),$$ where v_m is the mean sound velocity. Ignoring affect of temperature

on the anharmonicity of the bond, the κ_L could be proportional to the T^{-1}.

Table *S2*. The value of parameter for lattice thermal conductivity calculation

A	M (amu)	n	δ (Å)	v_m (m/s)	θ_D (K)	γ
~3.1×10⁻⁶	442.3	17	7.342	~1800 [5]	117.8	2.03 [6]

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