

Supplementary materials for

Interface-located Photothermoelectric Effect
of Organic Thermoelectric Materials in
Enabling NIR Detection

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EXPERIMENTAL METHODS

Materials Preparation and Device Fabrication

Poly[Cu_x(Cu-ett)] and poly[K_x(Ni-ett)] were synthesized according to previous reports,¹ which were mixed with poly(vinylidene fluoride) (weight ratio = 1.5:1) in dimethylsulfoxide (DMSO) solution via ball-milling.² PEDOT:PSS (PH1000 from Sigma Aldrich) was mixed with 5 volume % of EG. We fabricated a PTE device comprising poly[Cu_x(Cu-ett)]:PVDF as an organic active layer. Before the deposition of the organic active layer, octadecyltrichlorosilane (OTS) modification on the glass substrates was performed to create hydrophobic substrates. Thereafter, patterned hydrophilic regions on the hydrophobic substrates were created by UV-ozone (UVO) treatment utilizing a shadow mask. By using a drop casting method, the patterned poly[Cu_x(Cu-ett)]:PVDF composite film arrays were deposited. Finally, the device fabrication was completed after the deposition of Au electrodes (Figure 1c-1e).

Measurement of Thermoelectric and Photothermoelectric Properties

A home-built system integrated with an IR camera (FLIR A300), an electrical signal measurement system (Agilent B1500) and a high resolution translation stage was built to perform thermoelectric and photothermalelectric characterization. The photothermalelectric measurement was carried out by scanning the device through a NIR laser (808 nm, 0-340 mW, beam size of 2 mm², 0-17 W/cm²). The film was heated with NIR irradiation and the temperature gradient was simultaneously recorded by Au resistive thermometers deposited on the films and an IR camera FLIR A300

with a minimum threshold of 0.05 K. The I-V curves or V-time curves were tested by an Agilent B1500 semiconductor parameter analyzer at room temperature.

Measurement of UPS spectra

The ultraviolet photoelectron spectroscopy (UPS) analysis was performed in a KRATOS ULTRA AXIS DLD photoelectron spectroscopy system with an unfiltered He I (21.22 eV) gas-discharge lamp. The absolute energy resolution of the analyzer was 100 meV for the UPS. The base pressure in the analysis chamber was better than 2×10^{-9} Torr. The UPS spectra were recorded with sample bias of -9.0 V to allow the observation of the inelastic electron cutoff so that sharp cutoff edges were observed in all the He I UPS spectra.

Table S1. The calculated Seebeck coefficient of poly[Cu_x(Cu-ett)]:PVDF composite under exposure to NIR light (808 nm) with different laser power.

Laser power (W/cm ²)	Voltage (mV)	Average T _{max} (°C)	Average T _{min} (°C)	ΔT (°C)	S (μV/k)
0.54	0.37	34.33	29.96	4.37	84.67
1.14	0.79	40.85	29.97	10.88	72.61
1.74	1.2	45.5	29.96	15.54	77.22
2.46	1.7	51.7	30.19	21.51	79.03
3.12	2.15	56.37	30.45	25.92	82.95
3.77	2.6	62.48	30.59	31.89	81.53
4.01	3.1	71.81	30.76	41.05	75.52
5.36	3.7	81.17	31.07	50.1	73.85
6.23	4.3	89.36	31.27	58.09	74.02
7.25	5	93.53	31.52	62.01	80.63
8.26	5.7	100.59	33.28	67.31	84.68
8.99	6.2	109.76	33.62	76.14	81.43
Average					79.01

Table S2. Seebeck coefficient of poly[Cu_x(Cu-ett)]:PVDF composite, poly[K_x(Ni-ett)]:PVDF composite and PEDOT:PSS (mixed with 5% EG) with and without NIR irradiation.

Sample	S (μV/K)	
	Under NIR irradiation	Without NIR irradiation
poly[Cu _x (Cu-ett)]	79±5.0	52±1.5
poly[K _x (Ni-ett)]	42±1.2	40±0.4
PEDOT:PSS	43±0.6	43±0.2

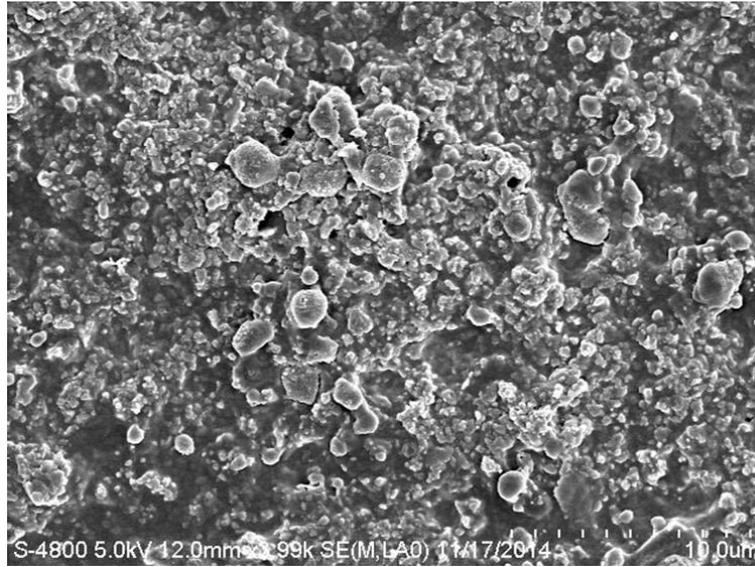


Figure S1. The SEM image of poly[Cu_x(Cu-ett)]:PVDF film

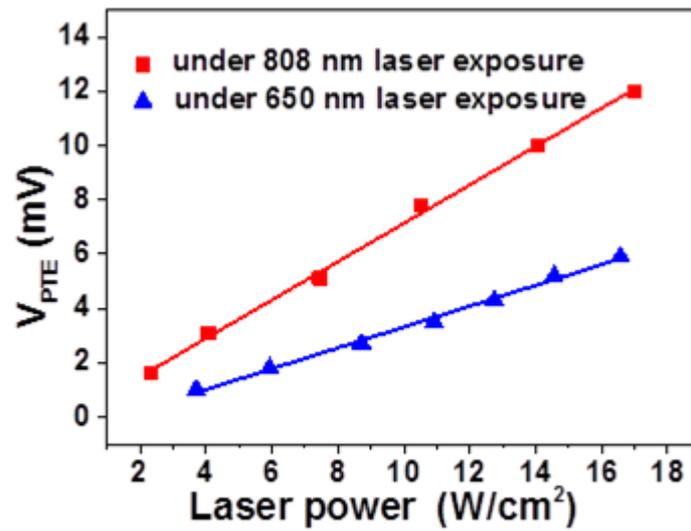


Figure S2. Photothermoelectric voltage generation of poly[Cu_x(Cu-ett)]:PVDF composite film upon light irradiation with different laser intensity and wavelength.

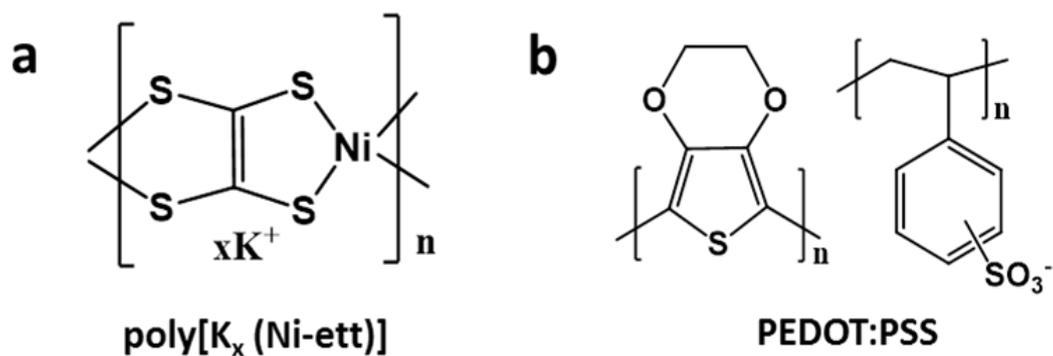


Figure S3. (a) Molecular structure of poly[K_x (Ni-ett)]. (b) Molecular structure of PEDOT:PSS.

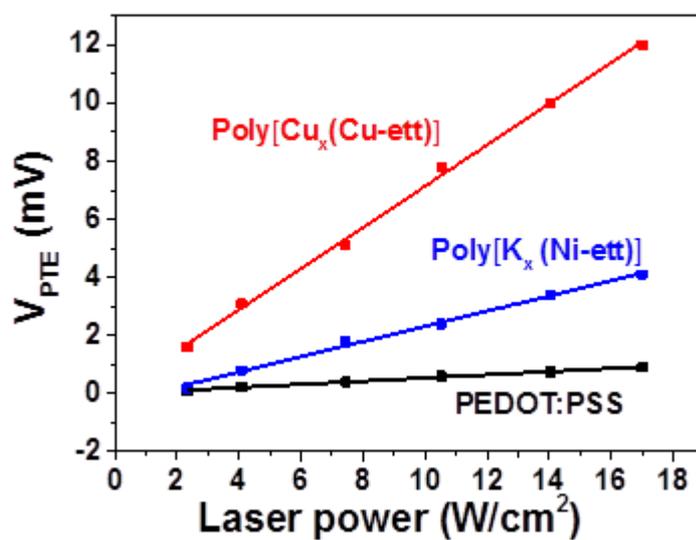


Figure S4. NIR (808 nm) laser power dependent photothermoelectric voltage for the devices based on different materials.

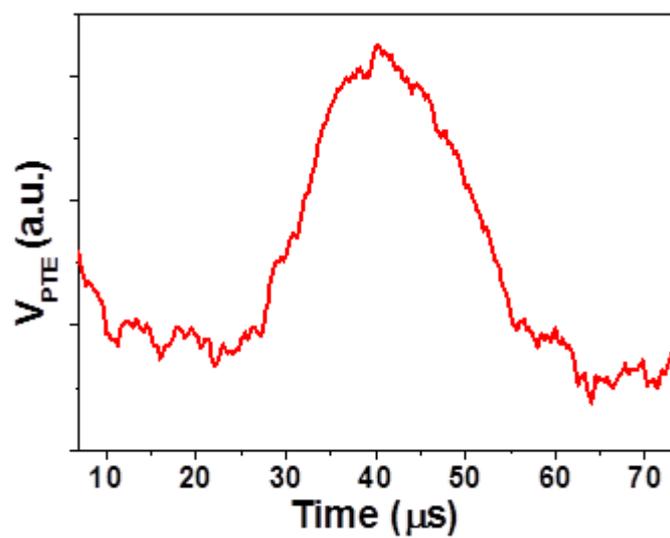


Figure S5. Response curve of poly[Cu_x(Cu-ett)]:PVDF based devices on NIR exposure.

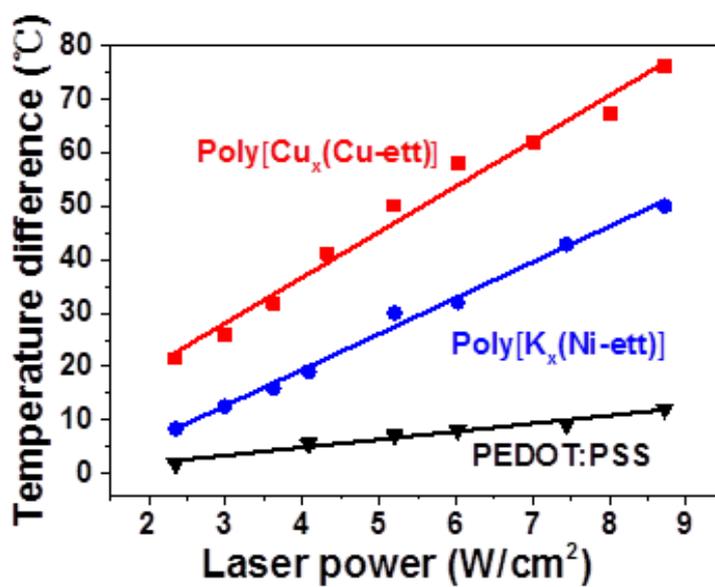


Figure S6. Temperature difference of the active films upon NIR irradiation with different laser power.

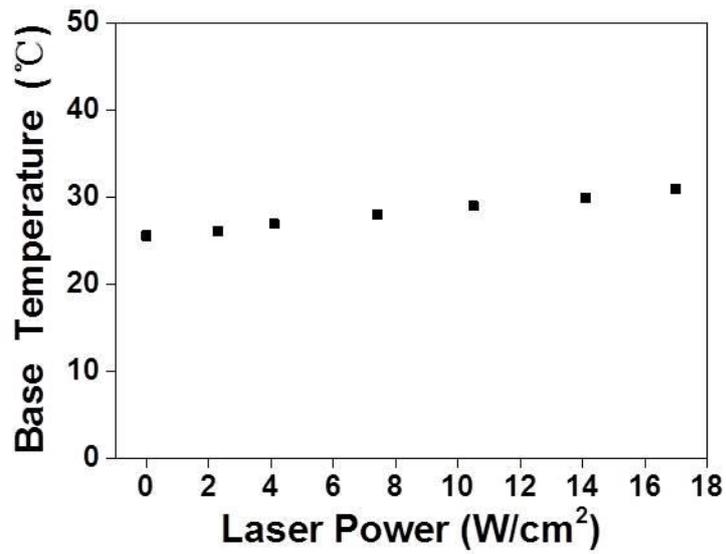


Figure S7. Base temperature of poly[Cu_x(Cu-ett)]:PVDF film upon irradiation of NIR light with different power when the laser is fixed at the electrode/organic layer interface.

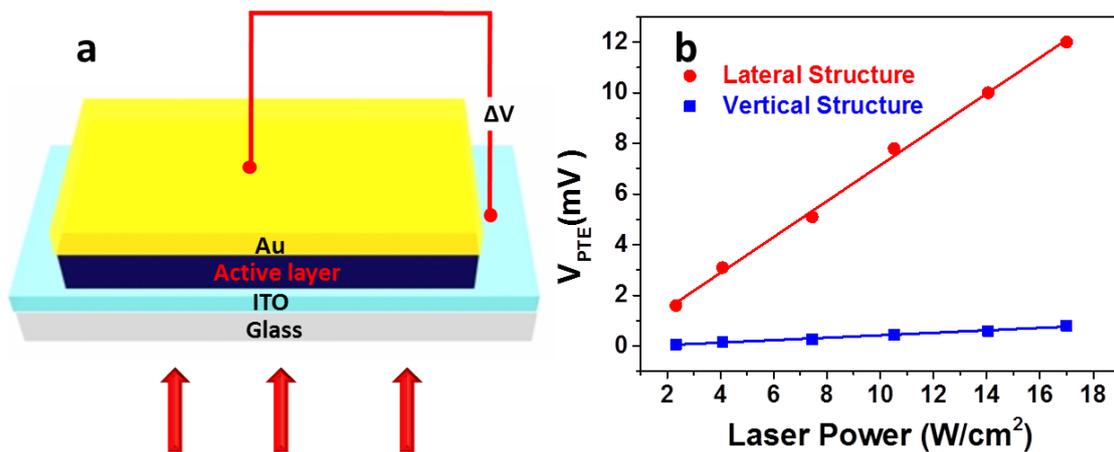


Figure S8. (a) Illustration of vertical photothermoelectric device. (b) Photothermoelectric voltage generated by poly[Cu_x(Cu-ett)]:PVDF composite based devices with varied device geometry (under light irradiation of 808 nm NIR laser).

- (1) Sun, Y.; Sheng, P.; Di, C.; Jiao, F.; Xu, W.; Qiu, D.; Zhu, D. Organic Thermoelectric Materials and Devices Based on p-and n-Type Poly (metal 1,1,2,2-ethenetetrathiolate). *Adv. Mater.* **2012**, *24*, 932-937.
- (2) Jiao, F.; Di, C.-a.; Sun, Y.; Sheng, P.; Xu, W.; Zhu, D. Inkjet-Printed Flexible Organic Thin-Film Thermoelectric Devices Based on P-And N-Type Poly (Metal 1,1,2,2-Ethenetetrathiolate) S/Polymer Composites Through Ball-Milling. *Phil. Trans. R. Soc. A* **2014**, *372*, 20130008.