Conjugated Organic Photothermal Films for Spatiotemporal Thermal Engineering

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With the growth of photoenergy harvesting and thermal engineering, photothermal materials (PTMs) have attracted substantial interest due to their unique functions such as localized heat generation, spatiotemporal thermal controllability, invisibility, and light harvesting capabilities. In particular, \(\pi\)-conjugated organic PTMs show advantages over inorganic or metallic PTMs in thin film applications due to their large light absorptivity, ease of synthesis and tunability of molecular structures for realizing high NIR absorption, flexibility, and solution processability. This review is intended to provide an overview of organic PTMs, including both molecular and polymeric PTMs. A description of the photothermal (PT) effect and conversion efficiency (\(\eta_{PT}\)) for organic films is provided. After that, the chemical structure and optical properties of organic PTMs are discussed. Finally, emerging applications of organic PT films from the perspective of spatiotemporal thermal engineering principles are illustrated.

1. Introduction

Photothermal materials (PTMs) exhibit unique phenomena based on conversion of light to heat, which has attracted interest in the study of such highly intriguing phenomena in the condensed phase and the exploration of their application potential, ranging from photothermal therapy (PTT) and photothermal (PT)/photoacoustic (PA) imaging, clean water harvesting, photoactuation, cell sheet engineering, and energy harvesting. The PT effect, or PA effect as originally defined, is observed when photoexcited materials produce thermal energy via nonradiative vibrational relaxation of excited electrons. For example, free electrons in the metallic nanomaterials absorb light, creating a specific oscillation that produces a PT effect from the surface electrons in the metallic nanomaterials absorb light, creating a specific oscillation that produces PT from these films. Due to easy processing and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

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Further, carbon-based nanostructures and hybrid nanocomposites have been reported with an improved \(\eta_{PT}\) over the years. Although carbonaceous nanomaterials and metallic nanomaterials have been examined by numerous researchers, these materials normally comprise NP-shaped powders and are not readily fabricated into various shapes or thin films with large areas. Additional issues related to inorganic PTMs include biocompatibility and environmental safety.

Thus, many organic molecular PTMs (m-PTMs), including molecular dyes such as cyanines (Cys) and croconaines (Crocs), have been investigated, particularly for PTT and photoacoustic therapy (PAT) . However, to apply m-PTMs in PT devices that require film types, polymeric media are required, and thus the content of m-PTMs in the film is rather limited, to lower \(\eta_{PT}\) from these films. Due to easy processability and low toxicity, polymeric PTMs (p-PTMs) are explored for thin film applications. Furthermore, polymers are intrinsically thermal insulators and flexible. Therefore, recent efforts have been devoted to developing p-PTMs. In particular, conjugated polymers (CPs) with long \(\pi\)-conjugated backbones of contiguous sp\(^2\)-hybridized carbon atoms display high absorption in the visible to NIR region and are easily photoexcited. Thus, a variety of CPs, including poly(3,4-ethylenedioxythiophene)s (PEDOTs), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) block copolymers (PEDOT-PSS), poly(3,4-ethylenedioxythiophene)-(poly(ethylene oxide)) block copolymers (PEDOT-PEO), and polyethylenimines (PEIs), are potential candidates as p-PTMs. However, NIR energy utilization is impeded by the narrow absorption bandwidth in the visible region and the low charge-carrier mobility of polymers. Therefore, several strategies have been proposed to broaden the absorption spectra: 1) protonic acid doping and oxidative doping of CPs, 2) copolymerization of electronic donor–acceptors (D–As), and 3) hybridization with carbonaceous materials, metals, and metal oxides, as reported for PANIs, PPys, PEDOTs, polypyrroles (PPys), and carbon nanotubes (CNTs).

While many reviews of PTMs based on inorganic PTMs are available, synthesis and PT mechanisms for thin film applications for organic PTMs remain rare. Nonetheless, the PT applications using organic PTMs have dramatically
increased since 2011. Furthermore, recent advances in the heat maneuvering and energy harvesting fields have led to the fabrication of PTMs as films, which integrate easily with other layers in a device. Thus, in this review, we first focus on PT films based on organic materials by summarizing the basic properties, such as the heat evolution and efficiency of the PT effect. Second, we highlight the state-of-the-art synthesis of organic PTMs and discuss strategies for improving the high NIR absorption, color tunability, and eventually $\eta_{PT}$. Third, the emerging applications for organic PTMs are exemplified. The perspectives and challenges of PTMs for potential applications are discussed. For example, PT films can be used as wireless actuators, film heaters, energy harvesters, and harvesters for single cell and cell sheet, taking advantage of spatiotemporal control by the wavelength, intensity, diffraction, and polarization of light. Therefore, the application potential of PT films can be extended to various fields, not only those areas that have been developed for PT nanoparticles in solution, but also new areas, where spatiotemporal thermal engineering is required. We believe that PT films derived from noteworthy organic PTMs will become promising resources for thermal engineering to advance the science and technologies related to PT effects that utilize light stimuli such as a high degree of spatiotemporal control by the wavelength, intensity, and polarization of light.

2. Photothermal Characterization of Organic PTMs and Their Films

PT phenomena occur in two steps. First, light energy is absorbed by the PTMs and the absorbed energy is partially or completely converted into heat through electronic excitation and nonradiative relaxation of the excited electrons to the ground state ($S_0$). This first step is mediated by in three different mechanisms, depending on the material type: plasmonic (localized) heating of metal nanostructures, carrier generation and nonradiative relaxation of semiconducting materials (e.g., polymers and metal oxides), and thermal vibrational relaxation (thermalization) in conjugated molecules. Second, the generated heat energy is transferred from the hot side to the cold side of the materials or surrounding medium through phonon transfer.

Although free electrons are the key carriers in the metal atoms and their oxides (Figure 1), $\pi$ electrons delocalized along the $\pi$-conjugated bond of organic materials generally generate the major carriers that absorb light and create thermal energy. This process is attributed to the electrons in the $\pi$-bonds that are more loosely bound (e.g., C=C $\pi$-bond energy for ethene = 272 kJ mol$^{-1}$) and much more weakly bound in extended delocalized $\pi$-bonds with low band gaps, than those in the $\sigma$ bonds.
the C-C bond energy for ethane = 439 kJ mol⁻¹). Upon excitation with light beyond their band gap, the electrons of the organic PTMs are activated from S₀ to the upper level (S₁, S₂, etc.) (Figure 1b).⁷,¹³ When the electrons return to S₀ via a nonradiative process, energy is released as heat. Therefore, energy level design of PTMs is important for effective PTMs leading to the desired pathway.

The excited electrons may undergo intersystem crossing (ISC) to reach triplet states by changing the electron spin orientation, where electrons return to S₀ through a nonradiative process to release heat. However, this process competes with others, such as phosphorescence and photochemical reactions that are principally mediated by O₂ producing radicals or O₂⁻ and O₃ (in the NIR-II region), which have been applied to photodynamic therapy. In comparison with molecular materials, conductive polymers usually show more effective PT effect. A low bandgap and polaronic band in conductive polymers promote the PT process over other photophysical processes in Figure 1b, to increase the proportion of nonradiative process.

Thus, to obtain a high ηPT, the energy of excited electrons must not be consumed by other processes such as fluorescence, phosphorescence, chemical reaction, and self-quenching. When a shorter wavelength of light is absorbed by materials, a higher probability of side processes is observed, and thus light in NIR region must be absorbed to achieve a high ηPT. Therefore, major strategies to design PTMs have emphasized a lower band gap by extending π-conjugation, introducing an intramolecular D–A structure, and doping with the conjugated molecules.⁷,¹³ Because the nonradiative decay (NRD) of the excited electrons is important, the NRD efficiency of the materials determines the PT conversion.⁴³ Notably, excited-state intramolecular motions (EXIMs), such as rotation and vibration, enable the absorbed light energy to dissipate as heat, promoting PT conversion.⁴⁶ Thus, a D–A structured aggregation-induced emission luminogen was reported as a PTM with boosted a NRD process in the solid state and aggregate state within NPs arising from the effective EXIMs.⁴¹,⁴⁴

To estimate ηPT, the Grüneisen parameter (Γ) was used based on an initial pressure rise (p₀) in PA tomography.⁴⁵ The heat generated from the PT effect in tissue results in p₀, which creates acoustic waves. The Γ for tissue relates p₀ and light absorption as

\[ p₀ = ΓμₐF \]  

where \( μₐ \) is the absorption coefficient of tissue, and \( F \) is the local light fluency. Using the isobaric volume expansion coefficient (β, specific heat capacity (Cᵥ), isothermal compressibility (α), and mass density (ρ), Γ can be expressed as below:

\[ Γ = β/(kρCᵥ) \]  

The determination of Γ using PA and PT methods is complicated and Γ is inconsistent within the same type of tissue.⁴⁶ Nonetheless, η for PT has been used for PA materials and shows improved imaging properties by either increasing \( μₐ \) or tuning Γ.⁴⁷

In the case of NPs or films containing PTMs, ηPT values have been reported using the temperature increase measured by IR sensors and thermometers. The ηPT value for a film is determined from the ratio of the photothermally converted thermal energy to the absorbed light energy by modifying the equation for the solution case.⁴⁶,⁴⁷ The total energy balance of a system comprising a substrate and a PT film is defined as the sum of the heat for a PT transition (QPT), heat for a substrate, and heat loss to the surrounding environment (Qsurr) by heat conduction (Qcond), radiation (Qrad), and convection (Qconv) (Figure 2a) under light irradiation, as presented in Equation (3):

\[ \sum_j \left( \sum_i m_i C_p,i,j \right) \frac{dT}{dt} = \sum_j \left( Q_{PT,j} + Q_{sub,j} - Q_{surr,j} \right) \]  

where i and j correspond to the system components and specific point (one pixel of a thermal imaging camera), respectively. The parameters \( m, T, \) and \( t \) represent the mass, temperature (the continuously mixed solution), and time, respectively. A large amount of heat must be generated at the irradiated area if Qsurr is small.

The sum of QPT, the PT heat energy produced by light irradiation to the PT film, generates heat through electron-phonon relaxation, which is determined using Equation (4), as follows:

\[ \sum_j Q_{PT,j} = I_0 \left( 1 - 10^{-A} \right) \eta_{PT} \]  

where \( I_0 \) and \( A \) are the laser power and absorbance at the light wavelength; \( Q_{sub} \) is the amount of heat that dissipated following light absorption by the substrate in the absence of the PT film. Because a transparent (non-PT) substrate is generally used, the absorbance of the substrate is very small. Therefore, Qsub is very small compared to QPT and is negligible. Qsurr is the amount of thermal energy released to the surrounding environment through heat convection, conduction, and radiation. It is assumed that Qsurr increases linearly with temperature for the outgoing thermal energy within a small temperature range to minimize the factors of convection and radiation heat energy loss to the surrounding environment, resembling an isolated system and the heat capacity of the system is sufficiently large to diminish the two factors:

\[ Q_{surr,j} = (ha) (T_{j} - T_{j}) \]  

where \( h, a, T_{surr} \) are the heat-transfer coefficient, the surface area, and the surrounding temperature of the system, respectively. The maximum temperature (Tmax) of the PT film is obtained when the heat generated (input) upon light exposure is equal to the heat released (output) in the equilibrium state (Figure 2b):

\[ Q_{PT,j} + Q_{sub,j} = Q_{surr,j, max} = (ha) \left( T_{max,j} - T_{surr,j} \right) \]  

where Qsurr, max is the maximum Qsurr in the equilibrium state. The heat-transfer factor (ha) is determined using a dimensionless temperature ratio term at specific point (θ) and time constant (τ.), in the cooling part without light exposure:

\[ θ = \frac{T_{j} - T_{surr,j}}{T_{max,j} - T_{surr,j}} \]
Equations (6)–(8) can be substituted into Equation (3) and rearranged to yield:

$$\frac{dt}{d\theta} = \frac{1}{\tau_{s,j}} \left[ \frac{Q_{PT,j} + Q_{sub,j}}{(ha)} \left( T_{\text{max},j} - T_{\text{surr},j} \right) - \theta_j \right]$$

The $Q_{PT,j}$ and $Q_{sub,j}$ terms become zero at the cooling part when the laser is turned off:

$$dt = -\tau_{s,j} \frac{d\theta_i}{\theta_i}$$

A linear relationship between $t$ and $\ln \theta_i$ with a slope of $\tau_{s,j}$ by integrating Equation (10) gives the following equation:

$$t = -\tau_{s,j} \ln \theta_i$$

Finally, the $\eta_{PT}$ is determined by above equations:

$$\eta_{PT} = \sum \left[ \left( ha \right) \left( T_{\text{max},j} - T_{\text{surr},j} \right) - Q_{sub,j} \right]$$
function \( \langle \hat{r}(E) \rangle \) and the function of the DOSs \( g_n(E) \) for p-type materials.\[46\]

\[
p = \int g_V(E) \left[ 1 - f(E) \right] dE = \frac{4\pi}{h^2} \left( 2m^* \right)^{\frac{1}{2}} \int g_V(E) \left( \frac{E_V - E} {E_V - E_T} \right) \frac{1}{1 + e^{\frac{E - E_T}{kT}}} dE
\]

where \( E_V \) is the top of the valence band. Thus, the DOS can be correlated to \( \eta_{PT} \). Following the PT heat generation mechanism in a film (shown above), the DOS of the conduction and valence bands is a characteristic determinant. Because the increased degree of crystallinity of materials increases carrier delocalization through the conjugation network and \( \pi \)-orbital overlapping in the \( \pi \)-stacking direction, the change in crystallinity directly modifies the electronic band structure near the Fermi level \( (E_F) \), as well as the DOS shape.\[50,51\] The PT effect is improved as the DOS at \( E_F \) of PTMs becomes broader, which is achieved by increasing the degree of crystallinity of PTMs.

Since the DOS for semiconductive materials is related to the thermoelectric Seebeck coefficient \( (S_{TE}) \), which is calculated using Equation (14) based on Mott’s formula, the PT effect is enhanced in materials with a high \( S_{TE} \).

\[
S_{TE}(T) = \frac{1}{eT} \left[ \frac{E - E_T}{\sigma(T)} \right] \int \sigma(E,T) \left( \frac{\partial f(E)}{\partial E} \right) dE
\]

where \( k_B \) is the Boltzmann constant and \( e \) is the unit charge. Equation (14) can be rewritten as an expression of \( \mu \) and DOS, as given by Equation (15).

\[
S_{TE}(E,T) = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{1}{\mu} \frac{\partial \mu}{\partial E} + \frac{1}{g(E)} \frac{\partial g(E)}{\partial E} \right)_{E=E_F}
\]

To obtain a high crystalline ordering and to increase the DOS of p-PTMs, the twisting angle of the polymer backbone should be minimized.\[30\] N-containing polymers, such as PPys and PANIs, have a low degree of crystalline ordering due to twisting along the backbone, leading to poor \( \pi - \pi \) stacking. These polymers show a lower \( S_{TE} \), \( \sigma_0 \), and \( \mu \) with a relatively lower \( \eta_{PT} \) compared to PEDOTs and polyanilines. In summary, a high light absorption and a high \( \Delta T_{PT} \) with a low thermal conductivity of the PT films are important parameters to obtain a high \( \eta_{PT} \) in PT films. Since PT effect is strongly associated with \( p \) and \( \mu \), the degree of crystallinity and structural order of PTMs in a film are also important to obtain a high \( \eta_{PT} \) in PT films. Therefore, a rational design for efficient PTMs should achieve:

1) a low band gap in conjugated molecules for enhancing nonradiative relaxation and thermalization in the NIR range,
2) a high packing density of conjugated units for a high light absorption,
3) a high degree of crystallinity and \( \mu \), and
4) a low heat loss to the substrate.

3. Organic PTMs in the Film States

3.1. Organic Molecular PTMs

Due to their intense absorption in the NIR range, NIR-absorbing dyes, such as Cys, Crocs, diketopyrrolopyroles (DPPs), and diimmoniums (DIs), have been explored for m-PTMs.\[32–34\] These materials generally consist of long conjugated groups that are bridged between electron donors or donor coupled acceptors. Long alkyl or ionic groups are introduced as the substituents of donor or acceptor to improve the solubility and physical properties of the PTMs. The absorption properties of m-PTMs are easily tuned by varying the donor units that are conjugated with the bridging group.

Cys consist of a lipophilic polyene bridge and two alkyl indocyanine moieties with an ionic terminal group (hydrophilic) possessing amphiphilic properties. The best known structure is indocyanine green (ICG), which consists of a polyene bridge and two 4-(1,2-trimethyl-1H-benzo[e]indolium-3-yl) butane-l-sulfonate groups. ICG was first synthesized by reacting molecule (1) with 1,4-butanone to produce molecule (2), followed by treatment with molecule (3) and the synthesis of a sodium salt (Figure 3a).\[55\] ICG absorbs the NIR light with a maximum absorption wavelength (\( \lambda_{max} \)) at 780 nm and has been used in the clinic because it was approved for use in human subjects by the U.S. Food and Drug Administration in 1959.\[56\]

ICG releases reactive oxygen species (ROS, \( O_2 \)) to exert anti-tumor effects. However, ICG suffers from several major limitations, such as a low \( \eta_{PT} \) (9% max), low thermal stability, and light-dependent optical properties which include photodegradation, discoloration, and ISC shift.\[60,61\] Thus, many other Cy derivatives have been developed by modifying the ICG structure. For example, a series of IR-X, where X is the \( \lambda_{max} \) of dyes in NIR region, were developed by modifying the polyene, the alkyl groups in the indole group, and counter ions, to improve application potential, such as tumor imaging and targeted therapy.\[62\] For example, IR-825 was synthesized from cyclohexane as a bridge and 2,3,3-trimethyl-4,5-benzo-3H-indole as the indocyanine group (Figure 3b).\[57\]

Extensive effort has been devoted to encapsulating ICG and Cys in NPs including liposomes,\[63\] micelles,\[64,65\] and polymers,\[66\] for theranostic applications.\[32,60,63\] However, Cys have rarely been developed for a thin film application, mainly due to their poor compatibility with polymers and limited stability in the film state. Croconic acid, 4,5-dihydroxycyclopentenetrione, contains two hydroxyl groups, which have been used to synthesize Crocs via a one-pot condensation reaction of croconic acid with electron-rich molecules (Figure 3c).\[66–68\] These D–A–D type zwitterionic structures are quite similar to the well-known squaraines; however, the \( \lambda_{max} \) of Crocs redshifted by approximately 100 nm compared with the corresponding squaraines.\[69–71\] Crocs exhibit narrow and strong NIR absorption with high molar extinction coefficients (10^5 M^-1 cm^-1).\[58\] The absorption properties of Crocs are easily tuned by varying the donor and substituents on the donor units that are conjugated with the croconium core. Crocs generally show good photostability and generate PT heating without producing \( O_2 \) because of their low ISC to the triplet state (\( ^1O_2 \)). A water-soluble croconium dye, Cro-c, was obtained by condensing croconic acid with 2-(4-carboxylcypiperidylamino)thiophene to produce 2,5-bis[4-(4-carboxylcypiperidylamino)thiophenyl]-croconium.\[58\] The water solubility of PTM is useful in preparing a therapeutic agent for PTT and PAT applications or in green solution-process. Cro-c showed a sharp and strong absorption at 800 nm and little absorption in visible region in water (Figure 4g). The Cro-c doped
in polyvinyl alcohol film exhibited similar NIR absorption as Croc-c dissolved solution and excellent photostability when incorporated in NIR-blocking plastic filters.\textsuperscript{[58]}

DPP-based m-PTMs have emerged by introducing donor units (triphenylamine, carbazole, or ferrocene), coupling more than one DPP unit (acceptor), or extending $\pi$-conjugation

\textbf{Figure 3.} Synthesis of m-PTMs. a) ICG,\textsuperscript{[55]} b) IR-825,\textsuperscript{[57]} c) Croc-c,\textsuperscript{[58]} and d) DPP1 and DPP2.\textsuperscript{[59]} e) Synthesis of IDI via oxidation of IPA.\textsuperscript{[54]} The core part of the molecule is highlighted in red. DCB, 1,2-dichlorobenzene; DMF, dimethylformamide; DCM, dichloromethane; MW, microwave.
through the 3- and 6-positions of DPP.\[53\] For example, NIR-absorbing low band gap DPPs were synthesized by bridging tetracyanobutadiene with carbazole-functionalized DPPs using the Pd-catalyzed Sonogashira cross-coupling reaction (Figure 3d).\[59\] The absorption of the bis-carbazole modified DPP (DPP2) exhibited a greater redshift than the mono-derivative (DPP1) (Figure 4b).

As an organometallic PTM, porphyrinic compounds have been developed significantly and mixed with a binder polymer, such as polymethylmethacrylate or polyethylene glycol (PEG), to form films.\[72\] The content of m-PTMs in the polymer was controlled to obtain an average visible transmittance (A VT) of 64.5–85.5% in the wavelength range of 380–760 nm. The \(\eta_{PT}\) of the film was determined from the cooling region to be 20.9%, 36.9%, 16.1%, and 16.6% at 64.5% A VT, for chlorophyll a, chlorophyllin sodium copper, heme-b, and copper(II) phthalocyanine (Figure 4a,c), respectively. The highest \(\eta_{PT}\) of 36.9% (chlorophyllin sodium copper) was determined from a \(\Delta T_{PT}\) of 11.30 K upon exposure to solar light (1 Sun, 100 mW cm\(^{-2}\)). However, the \(\Delta T_{PT}\) from the above m-PTMs was low (Figure 4d) due to their low \(\eta_{PT}\). Furthermore, most of them exhibit significant absorption of visible light, limiting their application in invisible PT systems.

Diimmonium salts (IDs), on the other hand, are much more transparent in the visible region, while they absorb IR light due to a low band gap.\[73\] For example, an isobutyl substituted diimmonium salt (IDI, Figure 3e),\[54\] synthesized by oxidizing the corresponding neutral amine, \(N,N,N',N'-\text{tetrakis}[4-(\text{diisobutylamino})\text{-phenyl}]1,4-\text{phenylenediamine} \) (IPA), affords a highly transparent film, when it was doped in a transparent polymer, such as polyethersulfone (PES) and polydimethylsiloxane (PDMS). A 0.4 \(\mu\)m-thick PES film containing 21.0 wt% IDI showed a \(\Delta T_{PT}\) of 80 K and an \(\eta_{PT}\) > 75% due to a charge resonance intervalence state originating from the delocalized dication state resulting in a low band gap (0.91 eV). The \(\eta_{PT}\) is much higher than that obtained for the NIR dyes developed to date. Furthermore, the film containing 16.7% IDI showed a transmittance of >90% and revealed the full color of the underlying color image (Figure 4e).

The structures and absorption spectra for some representative m-PTMs are compared in Figure 4g. Although most of the m-PTMs show a strong absorption tail in the visible range, IDI shows a low level of absorption in the visible range and broad NIR absorption, which might be beneficial for transparent PT applications.

### 3.2. Polymeric PTMs

The m-PTMs have a large structural variation with spectral selectivity, but they are limited for a film type PT system, as described...
in the previous section. On the other hand, p-PTMs have advantages over m-PTMs because they can be prepared as a film using a simple solution process. Furthermore, the π-bonds of p-PTMs are delocalized over their backbone, which might improve carrier transport and provide multifunctionality by combining intrinsic σe and optical properties.

Notable p-PTMs include 1) poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,4-ethylenedioxyselenophene) (PEDOS) (Figure 5a), 2) PANIs and PPys, and 3) polymers prepared from D–A type monomers. Although the PT effect was not characterized, the first example of a p-PTM can be found from the poly(3-hexylthiophene)/PEDOT:polystyrene sulfonate (PSS) film, which was used as a PT detector. A photovoltage of \( \approx 0.6 \text{ mV} \) was detected for the polymer film in the lateral-type field effect transistor upon irradiation with a 630 nm laser at a power of \( \approx 1 \text{ mW} \).

A poly(3,4-propylenedioxyselenophene) (PProDOS) film was reported in 2011 as a p-PTM. The ProDOS monomer (Figure 5b), which is synthesized from 3,4-dimethoxyselenophene with trimethylene glycol, was polymerized and processed as a low band gap film via electrochemical or chemical polymerization. The absorption of a 100 nm-thick film in the NIR region was maximized in the electrochemically doped state (+0.68 V vs Ag/AgCl) (Figure 5c). With a laser power density \( (I_{\text{pd}}) \) of 0.7 W cm\(^{-2}\), the PProDOS film with an optimized doping state and film composition (Figure 5d) showed a \( \Delta T_{\text{PT}} \) of 10.7 K and \( \eta_{\text{PT}} \) of 19.8%, which was comparable to inorganic materials such as Au nanoshells (13%), Au nanorods (21%), CdTe quantum dots (14%), and CuS nanocrystals (25.7%) in early studies. Notably, the PProDOS film on ITO glass showed a color change according to its oxidation state, providing visible to NIR electrochromism and suggesting that it may produce an electrochemically tunable PT effect.

Polyselenophenes with increased ordering of polymer chains afforded a high \( \eta_{\text{PT}} \) as reported for poly(hexyl-3,4-ethylenedioxyxelenophene)s (PEDOS-C6). The morphology and electronic properties of the PEDOS-C6 film were controlled by the polymerization method followed by doping (Figure 5b). The PEDOS-C6 film prepared using the constant potential method (CPM) and partially doped (at \(-0.1 \text{ V} \) vs Ag/ AgCl) showed a higher \( \eta_{\text{PT}} \) of 42.5% than that using a cyclic
voltammetric method (\(\eta_{PT}\) of 31.8%).[26] This result was ascribed to homogeneous film formation and the alignment of polymer chain from the CPM to produce a PEDOS-C6 film with high absorption in the polaron and bipolaron regions (Figure 5e).

With an \(I_{pd}\) of 2.33 W cm\(^{-2}\), the optimized PEDOS-C6 film showed a \(\Delta T_{PT}\) of >30 K which was higher than the PProDOS film (Figure 5f). As shown in Figure 5e,h, the doped PEDOS-C6 film was quite transparent, and thus it provided the most transparent PT film among the p-PTMs. The PEDOS-C6 film showed transparent to visible electrochromism, which was hot and cold, respectively, under NIR light (Figure 5g-i).

While the polyselenophenes provide a high \(\eta_{PT}\), the synthesis of PEDOS and its derivatives is not trivial. On the other hand, based on the studies of PProDOS and PEDOS-C6, the \(\eta_{PT}\) is substantially affected by the doping states, ordering of polymer chains, and homogeneity of the film morphology, which are controlled by the polymer structure, film preparation method, and doping. Thus, easily accessible polymers, PEDOTs, and other heterocyclic polymers have been extensively studied since then.

For example, PEDOT films with an improved \(\eta_{PT}\) of 50–93% were reported by controlling the polymerization composition and condition to vary the \(\pi-\pi\) intermolecular ordering and doping states of polymers (Figure 2c).[28,30] PEDOT films were prepared using solution casting polymerization (SCP) with a solution containing the monomer (EDOT), oxidant, pyridine, and polymeric surfactant (PEPG) (Figure 6a). PEDOT films showed large absorption in the NIR region, which depended on the composition of the polymerizable solution (Figure 6b).

As the thermal conductivity of PEDOT films is generally low (\(\approx 1\) W m\(^{-1}\) K\(^{-1}\)),[78] the photothermally generated heat may be trapped within the film; thus, \(\Delta T_{PT}\) (Figure 6c) and \(\eta_{PT}\) might be high since the surrounding air is a very poor heat conductor. For example, a 180 nm-thick PEDOT film, with an optimized doping state and film composition, exhibited a \(\Delta T_{PT}\) >100 K upon irradiation with an 808 nm laser (0.19 W). The \(\eta_{PT}\) of PEDOTs increased with the increasing \(\sigma_e\) of PEDOTs at the low \(\sigma_e\), but decreased with increasing \(\sigma_e\) at the high \(\sigma_e\) region to yield a maximum \(\eta_{PT}\) of 93% at \(\sigma_e\) of 0.247 S cm\(^{-1}\) upon exposure to 1064 nm laser (Figure 6d). As described in Section 2, the \(\eta_{PT}\) was linearly correlated with the \(\mu\) of PEDOT films (Figure 2c).

Other CPs, such as PANI and PPy, have also been employed for PTMs. PANI was synthesized using aniline with an oxidant to produce an insoluble PANI in the doped state (emeraldine salt, ES) (Figure 7a).[35] The synthesized ES form was dedoped with a base to afford the more soluble neutral type of PANI (emeraldine base, EB), which is used to prepare NPs and films of PANI (Figure 7b). PANI is generally nontoxic toward normal cells, and PANIs in the EB state are conveniently doped with dopants (i.e., strong acids, Lewis acids, transition metals, etc.). This doped polyaniline (ES) absorbs NIR light and produces heat.[35,36,79] Because of the acidic/oxidative conditions near cancer cells, the NPs in the EB state injected into the body become oxidized in cancer cells exhibiting a color change to ES state. The cancer cells treated NPs in the ES state were ablated through laser irradiation by the PT effect of PANI in the ES state, which provided the first example of a PT theranostic

![Figure 6](image_url)

**Figure 6.** a) Schematic presentation of the synthesis of the highly crystalline PEDOT film using SCP.[30] i) Spin-coating of EDOT/Fe(3-Tos)/pyridine/PEPG in \(n\)-butanol solution onto a substrate; ii) Heating at 60 °C for polymerization; and iii) washing with ethanol for two times to obtain a highly crystalline PEDOT film. Inset: Scanning electron microscopy (SEM) image of P4. b) UV–vis-NIR spectra of PEDOT films prepared from different polymerization solutions. c) Evolution of the temperature increase in PEDOT films upon exposure to an NIR laser (808 nm, 0.19 W) with the light switched off after 60 s. Inset: IR images of PEDOT films after irradiation for 1 min. d) Correlation of \(\eta_{PT}\) at 808 nm (red dot) and 1064 nm (blue square) with \(\sigma_e\) of polymer films. a–d) Reproduced with permission.[30] Copyright 2019, The Royal Society of Chemistry.
method with CPs in 2011.[35] Since then, PT applications of PANI, oligoaniline, and other CP-based nanostructures have been extensively reported.[79–83]

PPy has also been explored as PTMs, due to their broad-band absorption spectrum in their bipolaronic state. PPys have been coated or deposited on various substrates, including (non)conductive and porous substrates. Recently, PPy was uniformly deposited onto meshes by electropolymerization, to produce a PPy-coated stainless steel (SS) mesh for solar steam generation (Figure 7c–e).[38] As shown in Figure 7d, the \( \Delta T_{PT} \) of the mesh increased to 28 K upon irradiation with solar light.

Melanin, a family of pigments present in various plants and animals, shows a strong absorbance of NIR light and thus can be potentially applied as a PTM.[84] In a recent report, natural black sesame melanin (BSM) was employed as a PTM, and a \( \Delta T_{PT} \) of 18 K was observed from a BSM NP solution (1 mg mL\(^{-1}\), pH 12) irradiated with an NIR laser (808 nm) for 10 min.[85] BSM is nontoxic toward normal cells and possesses good biocompatibility. PDA, a melanin-like polymer,[86,87] provides a useful platform for applications ranging from bioadhesives,[91] enzyme immobilization,[92] antibacterials to environmental remediation,[93,94] and energy conversion.[95,96]

For example, PDA nanofibers fabricated on the surface of lipid nanotubes exhibited a large \( \eta_{PT} \). A multiple stimuli-responsive PDA-modified nanofibrous mat showed a \( \Delta T_{PT} \) of 24.9 K upon irradiation with an NIR laser (808 nm) (Figure 7f,g). \[98\]

DPP potentially represents an electron-deficient bridging group to extend the \( \pi \)-conjugation length,[100,101] and thus a tunability of the band gap of D–A type CPs into the NIR region via copolymerization with aromatic heterocycles such as various thiophene derivatives (monothiophene, bithiophene, and benzodithiophene) has been provided using the Stille coupling reaction.[53,101–108] For example, a vinylene bridged DPP polymer (DPPV) was synthesized from monomers \((4)\) and \((5)\) (Figure 8a).\[105\] Interestingly, DPPV showed a higher absorption in the NIR region than its analog DPPT, in which the vinylene bond is absent. In addition, co-precipitation method was used for the DPPV and a biodegradable amphiphilic polymer to form a NP with good water solubility, and this biodegradable NP showed enhanced a PA imaging and a PTT effect. Recently, D–A\(_1\)–D–A\(_2\)–type DPP polymer (PDPPTDQ) was synthesized, where D, A\(_1\), and A\(_2\) are thiophene, DPP,
and thiadiazoloquinoxaline, respectively (Figure 8c). Compared with its analog PDPPTh, a D–A alternating backbone structure (D = thiophene and A = DPP), PDPPTDQ exhibited a lower band gap energy, leading to absorption in the NIR-II region, thanks to the presence of a much stronger electron-withdrawing A₂ in the polymer backbone (Figure 9i).

Other PT polymers were designed as a D–A structure bridged with a π-linker in polymer backbone, to introduce ICT along the backbone, resulting in redshift in absorption. For example, D–A type porphyrin-based CPs (PorCP1 and PorCP2) were reported (Figure 8d,e). Because of the extended D-A conjugation along the backbone, the PorCP2 showed a redshifted broad Q band up to 800 nm and increased extinction coefficient. Through nanoencapsulation, a large number of PorCP2 molecules were densely packed in a single NP to produce favorable NRD, good photostability, and the highest ηₚₜ of 63.8% among porphyrin based polymer NPs.

Recently, thiophene-fused benzodifurandione polymer (TBDOPV-DT) was synthesized via the Stille coupling between TBDOPV acceptor (6) and bithiophene donor (7) (Figure 8f).
The absorption spectra of a spin-coated polymer film (thickness ∼13 nm) displayed a π−π∗ transition at 477 nm and a strong NIR-II absorption at 1093 nm (Figure 9i) arising from the ICT.

ηPT of the TBDOPV-DT film was 50.5%, and the ΔTPT ranged from 25 K to 86 K upon exposure to a 1064 nm laser at a power ranging from 0.27 W to 0.98 W, respectively.

Poly[9,9-bis(4-(2-ethylhexyl)phenyl)-fluorene-alt-6,7-bis(4-(hexyloxy)phenyl)-4,9-di-(thiophen-2-yl)thiadiazoloquinazoline], PFTTQ, is also known as a PT polymer, which contains a highly electron-rich fluorene unit and a highly electron-deficient thiadiazoloquinoxaline unit, synthesized by Suzuki coupling. The PFTTQ NPs fabricated through a precipitation method using 1,2-distearoylsn-glycero-3-phosphoethanolamine-N-[amino(polyethylene glycol)-2000 (DSPE-PEG2000) as a surfactant as the encapsulation matrix showed a ΔTPT of 20 K within 3 min after exposure to an NIR laser (Figure 9a,b).[112]

Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)], PCPDTBT, was prepared as nanoellipsoids with octanoic acid via emulsification (Figure 9c,d).[113] By adding the nanoellipsoids into an elastomeric polyurethane (PU), the resulting PU nanocomposite films showed a ΔTPT of 19 K upon irradiation with solar light for 60 min (Figure 9e). Other D-A types of p-PTMs have been reported using 4H-dithieno[3,2-b:2′,3′-d]pyrrole (DTP) as a planar donor and benzothiadiazole (BT) derivatives and DPP as electron-deficient acceptors via the Stille coupling (Figure 9f).

Waster dispersible NPs were prepared via nanoprecipitation using DSPE-PEG2000 as a surfactant to achieve highly efficient PA and PT performance in killing cancer cells (Figure 9g–h).[104]

Recently, poly(2-phenyl-benzobisthiazole) (PPBBT) was synthesized via click condensation reaction between monomers (8) and (9) (Figure 8g).[114] PPBBT showed a broad absorption spectrum in UV-Vis-NIR range similar to a single-wall carbon nanotube (Figure 9i). PPBBT-based water-soluble and biocompatible NPs generated a ΔTPT of 25 K within 5 min upon exposure to an NIR laser and exhibited ηPT of a 32.4%, which maintained good photostability. Although many previous reports have described the clinical use of CPs for the effective eradication of tumors, the clinical use of these CPs remains controversial because of their poor biodegradability and potential toxicity to the human body.

4. Application Potential

Although the applications of PTMs have been investigated for more than 50 years, organic PTMs were mainly applied in PT deflection spectroscopy[115] and laser ablation until 2005.[24,116]
Since then, their applications have been extended to precise therapeutic and imaging technology utilizing the localized heat generated at the laser-exposed area. Furthermore, they have been applied to organic solar energy harvesting devices, sensors, and many other emerging technologies including photoactuators, desalination, and photoablation. In particular, application to NIR laser treatment (PTT, photodynamic therapy, and PA imaging) has emerged as a promising technology, due to its controllable operation of therapeutic moieties (e.g., heat, reactive oxygen species and drugs), noninvasive signal detection, high spatiotemporal resolution, and low photodamage, without affecting normal cells.[2,3,117] Initially, m-PTMs, which mainly absorb the first biological window (NIR-I, 700–950 nm), were explored and processed as NPs composed of m-PTMs.[118] However, usage of light within the second biological window (NIR-II, 1000–1350 nm) is more effective than the NIR-I region, because of the lower absorption of water in NIR-II, high light permissibility to skin (1 W cm$^{-2}$ for 1064 nm and 0.33 W cm$^{-2}$ for 808 nm) and lower light scattering by blood corpuscles and tissues which are the major light-tissue interactions.[119] Thus, PTMs absorbing light within the NIR-II region have emerged as a solution for PTT and for various applications.[21]

As a thin film in spatiotemporal thermal engineering, a PT layer functions as a light absorber and heater to 1) sense and attenuate NIR radiation, 2) evaporate water on a PT surface, 3) promote the thermal response of the contacting layer to lead actuation, 4) facilitate the thermal reaction at the substrate or PT layer, etc. On the other hand, the PT layers provide active carriers that can generate electricity via photovoltaic (PV), photothermoelectric (PTE), piezoelectric, and photo–mechanical mechanisms, enabling the PT layer to serve as a photodetector and an energy harvester. As presented in Figure 10, a device structure can be as simple as a single layer, in that a PT film is used as a heater that consists of a single free-standing PT film or a PTM or its composite-coated film on a passive substrate. The heat generated from this film can be used for NIR sensors, desalination, and bacterial killing. In bilayer or multilayer applications, PT films are coated onto thermally responsive or reactive layers. For example, a PT actuator is assembled with a thermally responsive layer. Furthermore, the PT film can be coated onto a conductive layer to harvest energy by PT conversion.

The $\Delta T_{PT,j}$ of the PT layer by light exposure can be estimated from the $\eta_{PT}$ of a PTM and the intensity of light according to Equation (16), which is derived from Equation (12)

$$\Delta T_{PT,j} = \frac{I_0(1 - 10^{-A_i}) \eta_{PT} + Q_{sub,j}}{(k\alpha)_j}$$

Figure 10. Potential applications of PT films. Schematic illustrating the generation of thermal energy in PT films derived by the PT effect upon light irradiation or the simultaneous action from thermal energy transfer to the combining substances on PT films. a) PT film heater. b) Solar water evaporator. c) PTE energy harvester. d) Three bending mechanisms of PT actuators according to their structures. i) Expansion of the thermally responsive elastomer layer (C-type), ii) reduction in the volume of the phase change liquid-crystalline layer (L-type), and iii) water evaporation of the humidity-responsive layer (H-type). e) Light triggering cell sheet harvesting. iv) Unfolding process of the thermally sacrificial layer (collagen) to dissociate into aqueous media upon selective PT heating.
However, other parameters such as the thickness and morphology of the film, wavelength of the light illumination, and $Q_{\text{sub}}$ may affect the $\Delta T_{PT}$ of the PT film. Furthermore, m-PTMs are difficult to process without dispersing them in a polymer binder and these films have evolved a low $\Delta T_{PT}$,[72] possibly due to the limited content of m-PTMs and their low carrier mobilities. One exception is the IDI dispersed polymer film.[14] The 16.7 wt% IDI-PES film on a 60 μm-thick PDMS layer showed a $\Delta T_{PT}$ of 87 K in 5 s by exposing the film to a 1064 nm laser (0.23 W) (Figure 4f). This can be ascribed to the high $\eta_{PT}$ (75.2%) and transparency of the film. Therefore, it is interesting to review and compare the reported $\Delta T_{PT}$ values for different PTMs, especially for p-PTMs.

As a first example of a PT film, the 100 nm-thick PProDOS film coated onto ITO glass showed a $\Delta T_{PT}$ greater than 13 K upon irradiation at an 808 nm laser ($I_{pd}$ of 0.7 W cm$^{-2}$).[23] The $\Delta T_{PT}$ increased to 30 K when PProDOS was replaced with transparent PEDOS-C6[26] upon irradiation at a higher $I_{pd}$ (Figure 5f). A PEDOT film with a high $\eta_{PT}$ of 93% was reported by optimizing the degree of crystallinity and doping state, which reached $\Delta T_{PT} >$120 K (Figure 6c).[30]

Figure 11a shows the correlation of $\Delta T_{PT}$ with $\eta_{PT}$ upon exposure to different light sources and summarizes the state-of-the-art PT films summarized in Table 1. In general, the higher the $\eta_{PT}$, the higher the $\Delta T_{PT}$ that is observed (Region I). However, it is noteworthy that some PEDOTs show higher $\Delta T_{PT}$ values (Region II), possibly due to the improved $\mu$ in highly ordered polymer chains, as described in Section 3. The $\eta_{PT}$ value of the PTMs roughly shows a linear relationship with their $\lambda_{abs}$ (Figure 11b) under the condition that the excitation sources for PT experiments were different for each samples. The PEDOT film (No. 6) shows the state-of-the-art $\Delta T_{PT}$ of the PTMs exposed to a light source with different wavelengths (Figure 11c). While the MXene $(Ti_3C_2T_x)$@PDA-PU composite (No. 10) shows the highest $\eta_{PT}$ in the visible region, the p-PTM, such as PEDOTs, shows the highest $\eta_{PT}$ in the NIR region. Starting from an $\eta_{PT}$ of 13% for PProDOS in 2011 (No. 5), an $\eta_{PT}$ of >90% for p-PTMs has been reported in 2019. Furthermore, light excitation at a short wavelength in the visible region is shifted to the NIR region to reduce unwanted side reactions of p-PTMs and IDI (No. 15). Thus, PT heaters working in the NIR-II region are now available, which will lead a substantial progress in PT science and engineering. The state-of-the-art PTMs are summarized in Table 1.

4.1. Photothermal Water Evaporation and Desalination

PT films have been rapidly applied to solar-driven steam generation, desalination, and water purification.[7,38,81,99,120–123] A hydrophilic surface for an efficient water supply and a high solar thermal (or vapor generation) efficiency ($\eta_{STE}$) in the spectrum of the PT film are important points to consider when fabricating a system for robust and efficient clean water production. The light is absorbed by the PT film to generate a heat gradient from the top to bottom of the device, where water is pumped from the bottom of the device by the capillary effect to the hot zone, resulting in solar steam generation. The $\eta_{STE}$ or photothermal efficiency of water vaporization ($\eta_{PTW}$) is defined as Equation (17):

$$\eta_{STE} = \eta_{PTW} = \frac{H \times \Delta \nu}{Q_i}$$

where $H$ is the enthalpy of liquid-vapor phase change at the surface temperature of the membrane, $\Delta \nu$ is the difference in evaporation rates with and without light, and $Q_i$ is the incident $I_{pd}$. Similarly, the water evaporation efficiency ($\eta_w$) of a PT film based on photon energy was determined using Equation (18) as follows:[38]

$$\eta_w = \frac{Q_e}{Q_i}$$

where $Q_e$ is the power density for the evaporation of water, which is estimated using Equation (19) as follows:

$$Q_e = H_e \frac{dm_w}{dt} = \nu_w \times H_e$$

where $m_w$ is the mass of the evaporated water, $\nu_w$ is the water evaporation rate, and $H_e$ is the heat of evaporation of the water (≈2260 J g$^{-1}$). The $Q_e$ and the $\eta_w$ of the PT heater were determined based on the slope of the mass change in the water droplets over the irradiation period, after deducting the natural evaporation rate.

The $\eta_{STE}$ and $\eta_{PTW}$ have been improved using a substrate with low thermal conductivity to ensure that the generated heat is used to evaporate the water on the top of the device. Furthermore, structural modification using nano- and
Table 1. Summary of the benchmark PTMs and their applications.

| Application | Sample number | Organic PTMs | λ_{abs} [nm] | ε_a [S cm^{-1}] | λ_{PT} [nm] | ΔT_{PT} [K] | η_{PT} [%] | Output | Performance | Ref. |
|-------------|---------------|--------------|--------------|----------------|-------------|------------|-----------|--------|-------------|------|
| PTH         | 1             | Chlorophyll a| 415          | 2.3f)         |             |            |           |        |             | [72] |
|             | 2             | Chlorophyllin sodium copper | 400 | 6.2f)         |             |            |           |        |             | [72] |
|             | 3             | IDI          | 1130         | 1.3f)         |             |            |           |        |             | [54] |
|             | 4             | IDI-PES      | 1135         | 0.68h)        | 1064        | 87         | 75.2      |        |             |      |
|             | 5             | PProDOS      | 626          | 0.70h)        | 0.001       | 808        | 10.7      | 19.8   |             | [25] |
|             | 6             | PEDOT        | 1250         | 0.21h)        | 0.247       | 1064       | 143       | 93     |             | [30] |
|             | 7             | PU–PPy      |              |              |             |            |           |        |             | [148]|
|             | 8             | MXene@PDA-PU |              |              |             |            |           |        |             | [149]|
|             | 9             | PVPS-PANI    | =700         |              | 808         | 30         |          |        |             | [150]|
|             | 10            | AgNP@MXene-PU| 470         |              | 808         | 111        |          |        |             | [151]|
|             | 11            | PDA coated mat| 980         |              | 808         | 24.9       |          |        |             | [98] |
|             | 12            | TBDOPV-DT    | 1102         | 1.1h)         |              |            |           |        |             | [111]|
|             | 13            | TBDOPV-DT    | 1093         | 1.6h)         |              |            |           |        |             |      |
| PTW         | 14            | IDI          | 1130         | 1.3f)         | 1064        | 87         | 75.2      | η_{PTW} (ν_{PTW}) | 68.8 (3.65) | [54] |
|             | 15            | IDI-PES      | 1135         | 0.68h)        | 1064        | 87         | 75.2      | η_{PTW} (ν_{PTW}) | 75     |        |
|             | 16            | PPy-coated air-laid paper | 400–1300 | 0.45h)        | 1064        | 87         | 75.2      | η_{PTW} (ν_{PTW}) | 81.9 (1.41) | [122]|
|             | 17            | PPy-PVDF     | 300–2500     |              | 1064        | 107        | 50.5      |        |             |      |
| PTA         | 18            | IDI          | 1130         | 1.3f)         | 1064        | 87         | 75.2      | η_{PTW} (ν_{PTW}) | 68.8 (3.65) | [54] |
|             | 19            | IDI-PES      | 1135         | 0.68h)        | 1064        | 87         | 75.2      | η_{PTW} (ν_{PTW}) | 75     |        |
|             | 20            | PEDOT        | 1300         | 0.12h)        | 1000        | 808        | 106       | 50     | η_{PTW} (ν_{PTW}) | 150   | [29] |
|             | 21            | PANI (ES)/LCE| 875          | 0.0082d)      | 808         | 112        |          |        |             |      |
|             | 22            | RGO–P3HT     | 581          |              | 532         | 40         | 82        | η_{PTW} (ν_{PTW}) | 30     | [128]|
|             | 23            | f-BNNS/PEDOT:PSS/PNIPAM | 0.0004 | 808         | 59          | –          | η_{PTW} (ν_{PTW}) | 80     | [152]|
|             | 24            | GO–PDA       |              |              | 812         | –          | –         | η_{PTW} (ν_{PTW}) | 120   | [130]|
|             | 25            | PDA-RGO/NOA-63| 800        | 0.012h)       | 812         | –          | –         | η_{PTW} (ν_{PTW}) | 80     | [129]|
| PTE         | 26            | PEDOT        | 1064         | 0.34h)        | 940         | Solar      | 63        | 56     | PF_{PTW}     | 690   | [30] |
|             | 27            | PEDOS-C6     | 763          | 1.1h)         | 335         | 808        | 30        | 42.5   | PF_{PTW}     | 354.7 | [26]|
|             | 28            | Poly[Cu,(Cu-ett)];PVDF | 808 | 76.1       | –          | PF_{PTW}     | –        |        | [146]|
|             | 29            | PTII         | 1369         | 0.022         | 1700        | 11.7       | 25.1      | PF_{PTW}     | 0.18  | [147]|
|             | 30            | TzQl-TDPP    | 1697         | 0.0014        | 1700        | 14.4       | 30.9      | PF_{PTW}     | 0.013 | [147]|
| PTHC(CS)    | 31            | PEDOT        | 808          | 16.4         | 50          | a_{HC(TC)}(η_{HC}) | 19(168) | [10] |
| (SC)        | 32            | PEDOT        | 808          | 22           | 7.4         | a_{HC(TC)}(η_{HC}) | 1.33 | [27] |
| (SC)        | 33            | PDA NP/PNIPAM| 808         | 9            | –          | a_{HC(TC)}(η_{HC}) | 0.2  | [138]|
| NP          | 34            | ICG          | 754          | 2.11c)        |             |            |           |        |             |      |
|             | 35            | ICG          | 785          | 6.6          | 3.37        | FL         |          |        |             | [56] |
|             | 36            | M4 (DMPC-based liposomal ICG) | 800 | 15           | 8.99        | FL         |          |        |             | [63] |
|             | 37            | IR780        | 801          | 808          | 18          | PTT        |          |        |             | [62] |
|             | 38            | IR820        | 820          |              | 808         | PT         |          |        |             | [61] |
|             | 39            | IR825        | 825          | 1.15c)        | 808         | 10.7      | PT        |          | [67] |
|             | 40            | Croc-c       | 787          | 2.10c)        | 808         | 12.8      | PT        |          | [68] |
|             | 41            | Croc-A1      | 795          | 2.00c)        | 808         | 12.8      | PT        |          | [68] |
|             | 42            | Croc-A1      | 795          | 2.90c)        | 808         | 12.8      | PT        |          | [68] |
|             | 43            | Croc-A2      | 795          | 3.10c)        | 808         | PT        |          |        |             | [68] |
|             | 44            | Croc-DA      | 798          |              | 808         | 37        | PATo, PETo, |          | [71] |
|             | 45            | DPPV         | 819          | 0.32c)        | 808         | 30        | 71        | PTT, PAI |             | [105]|

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microporous templates, textiles, membranes, and foams of 1D or 3D structures have afforded an improved \( \eta_{\text{PTW}} \). Because of their simple deposition process and high \( \eta_{\text{PT}} \), p-PTM-based steam generators are competitive with those based on Ti\( ^{3+}\)-TiO\(_2\).\(^{128}\) or reduced graphene oxide (RGO)\(^{125,126}\) on wood.\(^{125-127}\) Among p-PTMs, PPy films are widely used for water vaporization. A PPy-coated SS mesh deposited by electropolymerization\(^{38}\) was treated with fluoroalkylsilane to facilitate selective evaporation upon exposure to an NIR laser (1064 nm, 0.58 W cm\(^{-2}\)). Based on the linear correlation of the droplet weight over time, \( \eta_{\text{PTW}} \) was determined to be 3.65 kg m\(^{-2}\) h\(^{-1}\), which is much higher than the typical solar \( \eta_{\text{PT}} \) (0.08–1.4 kg m\(^{-2}\) h\(^{-1}\) under AM 1.5 irradiation). The \( Q \) and \( \eta_{\text{TE}} \) values of the PT heater were 0.2 W cm\(^{-2}\) and 68.8%, respectively. These results might originate from the high transparency of the film and the low heat loss from the polymeric binder and substrate, which might contribute to such a high \( \eta_{\text{PT}} \) and \( \eta_{\text{TE}} \). Notably, a droplet of saturated brine was selectively evaporated upon exposure to an NIR laser (1064 nm, 0.76 W cm\(^{-2}\)) within 4 min, leaving dried NaCl salt on the surface (Figure 13d).

4.2. Photothermal Actuators

As described above, the temperature induced by the PT effect of organic materials even reached to \( >100 \) °C. This high temperature can induce a spatiotemporal thermal change in the

### Table 1. Continued.

| Application\( ^{a}\) | Sample number | Organic PTMs | \( \lambda_{\text{abs}} \) [nm]\(^{i}\) | \( \varepsilon \) | \( \sigma \) [S cm\(^{-1}\)]\(^{j}\) | \( \lambda_{\text{PT}} \) [nm]\(^{i}\) | \( \Delta T_{\text{PT}} \) [K]\(^{f}\) | \( \eta_{\text{PT}} \) [%] | Output | Performance | Ref. |
|-----------------|--------------|--------------|-----------------|---------|-----------------|-----------------|-----------------|---------|-------------|-----|
| 46              | DPPT         | 828          | 0.26\(^{d}\)    |         | 808             | 20              | 29              | PTT, PAI      | [105]  |
| 47              | DPP1         | 695          | 0.48\(^{d}\)    |         |                 |                 |                 |           |             |     |
| 48              | DPP2         | 726          | 0.72\(^{d}\)    |         |                 |                 |                 |           |             |     |
| 49              | Hemoglobin   | 400          | 0.45\(^{d}\)    |         | 550             | 5.67            | 17.3            | PT           | [72]   |
| 50              | Cu(II) phthalocyanine | 728          | 1.96\(^{d}\)    |         | 550             | 6.53            | 16.6            | PT           | [72]   |
| 51              | PEDOT-SO\(_4\)\(^{2-}\) | 818          |                 |         | 808             | 27              | 31.4            | PTT          | [33]   |
| 52              | PANI (ES)    | 810          |                 |         | 808             | 66              |                 | PTT          | [35]   |
| 53              | PDPPTDQ      | 1253         | 0.57\(^{d}\)    |         |                 | 1064            |                 | PAI          | [108]  |
| 54              | PorCPI       | 673          |                 |         | 635             | 55              | 62.3            | PTT, PAI      | [109]  |
| 55              | PorCP2       | 800          | 0.42\(^{d}\)    |         | 808             | 50              | 63.8            | PTT          | [110]  |
| 56              | PFTTQ        | 800          | 0.05\(^{d}\)    |         | 808             | 40              |                 | PTT          | [112]  |
| 57              | PDPTBT       | 690          | 0.22\(^{d}\)    |         | 808             | 33              |                 | PT, PAI      | [104]  |
| 58              | PDPTPT       | 740          | 0.24\(^{d}\)    |         | 808             | 38.2            |                 | PT, PAI      | [104]  |
| 59              | PDPTDPP      | 783          | 0.75\(^{d}\)    |         | 808             | 45              |                 | PTT, PAI      | [104]  |
| Film            |              |              |                 |         |                 |                 |                 |           |             |     |
| 60              | PCPDTB-PJU   | 718          |                 |         | 11.2            |                 |                 | PT, AM       | [113]  |
| 61              | PPBBT        | 500          | 808             | 25      | 32.4            |                 |                 | PTT          | [114]  |

\( ^{a}\)PHT, PT heater; PTW, PT water evaporation; PTA, PT actuator; PTE, photothermoelastic; PTHC, PT harvesting of cells; CS, cell sheet; SC, single cell; NP, nanoparticle in solution; \( ^{b}\)Maximum absorption wavelength; \( ^{c}\)Absorption coefficient; \( ^{d}\)Electrical conductivity; \( ^{e}\)Light wavelength for PT engineering; \( ^{f}\)Temperature increase; \( ^{g}\)Molar absorption coefficient of solution, \( \times 10^5 \) M\(^{-1}\) cm\(^{-1}\); \( ^{h}\)Absorption coefficient of film, \( \times 10^5 \) cm\(^{-1}\); \( ^{i}\)Water vaporization efficiency, %; \( ^{j}\)Water vaporization rate, kg m\(^{-2}\) h\(^{-1}\); \( ^{k}\)Bending angle, °; \( ^{\circ}\)Power factor by PTE, \( \mu \text{W m}^{-1} \) K\(^{-2}\); \( ^{l}\)Harvested cell sheet area, cm\(^2\); \( ^{m}\)Areal efficiency of cell detachment, %; FL, fluorescence; FLI, fluorescence imaging; PF, NIR-blocking plastic filter; PATo, photoacoustic tomography; PETo, positron emission tomography; PAI, photoacoustic imaging; AM, antimicrobial. Sample numbers correspond to those in Figure 11.
contacting thermally responsive layer of the PT layer, such as a glass transition, volume expansion, melting, degradation, etc., depending on the $\Delta T_{PT}$. Such changes could generate bending and movement of the PT actuators, allowing a remote controlled wireless actuation. Several types of thermally responsive layers are possible: 1) an elastomer with high coefficient of thermal expansion (CTE), 2) liquid crystal (LC)-doped polymer composite or LC polymers (LCPs), and 3) humidity-responsive layer, depending on the driving mechanism of the actuator (Figure 10d). In the PT film with a large CTE elastomer layer (C-type), the bilayer is bent toward the direction of elastomer because it is more expandable than the PT film. Similarly, the bilayer containing LC polymers (L-type) is bent toward the direction of the LC layer. The bilayer with the humidity-responsive layer (H-type) is bent toward the direction of the PT film because it shrinks through the loss of water molecules inside PT layer following PT heating. The bending angle ($\theta_b$) (Figure 14a) is linearly proportional to $\Delta T_{PT}$.

$$\theta_b = \frac{kL}{2} (\alpha_{PT} - \alpha_{TR}) \Delta T_{PT}$$

where $L$ is the length of the actuator, $\alpha$ is the CTE, $E$ is Young’s modulus, and $l$ is the thickness, with the subscripts PT and TR denoting the PT heating film and thermally responsive layer, respectively.

As an example of the C-type actuator, a bimorph consisting of a PEDOT film on a PDMS layer was reported (Figure 14b–d). As an example of the C-type actuator, a bimorph consisting of a PEDOT film on a PDMS layer was reported (Figure 14b–d).
considering Young’s modulus of the two layers to maximize the \( k \) value. The bilayer with 0.4 and 70 \( \mu \)m-thick for PEDOT and PDMS, respectively, showed reversible and fast bending within 2s, a \( \theta_b >120^\circ \), and a displacement of 20 mm upon NIR exposure (198 mW) due to a high \( \Delta T_{PT} \) of 106 K. Since most actuators, regardless of their working mechanism, are deeply colored or turbid, actuators with full color or transparency are rare. However, the NIR-II absorptive IDI allowed the realization of a transparent PT actuator due to its high transparency (93%) (Figure 4g)[54]. The IDI-PES coated PDMS bimorph generated a \( \Delta T_{PT} \) of 98 K and showed a large reversible \( \theta_b \) (>70°) upon exposure to a 1064 nm laser (0.71 W cm\(^{-2}\)) (Figure 14e). The blocking force of this actuator was determined to be 2.6 GPa, which may be useful for creating a transparent artificial muscle. Notably,

Figure 13. a) The weight (black) and the %wt loss (blue) of a water droplet over time for NIR-irradiated (dashed) and nonirradiated (solid) samples in air.[54] b) Photo images of the mass change of a water droplet over time upon exposure to 1064 nm laser. Inset: IR camera images of the IDI-PES surface with a temperature range of 20–60 °C. c) Evaporation of water droplets with large areas. d) Selective evaporation of a brine droplet and the corresponding IR camera images. a–d) Reproduced with permission.[54] Copyright 2020, Wiley-VCH.

Figure 14. C-type actuators. a) Modeling for actuation of the bimorph. b) PT displacement (solid, line) and \( \theta_b \) (empty, dashed line) of PEDOT/PDMS bimorphs upon exposure to different laser intensities with different thicknesses of the bimorph.[29] c) Reversible folding of PEDOT/PDMS upon exposure to an NIR laser. d) A photo image of a venus flytrap upon exposure to an NIR laser. e) \( \theta_b \) (dot) of IDI-PES/PDMS bimorphs with \( \Delta T_{PT} \).[54] f) Photo images and g) IR camera images of the folding and unfolding of IDI-PES/PDMS induced by tuning NIR irradiation on and off, respectively. h) Photo images of a yellow flytrap under room light and i) a luminescent flytrap from IDI-PES/PDMS under UV light by NIR switching. a,e–i) Reproduced with permission.[54] Copyright 2020, Wiley-VCH. b–d) Reproduced under the terms of a CC-BY license.[29] Copyright 2019, The Authors. Published by Springer Nature.
by taking advantage of the high transparency of IDI-PES, the composite film produced an actuator with a vivid color and an emissive actuator upon the addition of dyes and fluorophores (Figure 14f–i). For example, the IDI-PES/PDMS bilayer showed blue-green fluorescence after mixing with Coumarin 153, achieving a yellow-colored and luminescent actuator. Furthermore, the bilayer was stable in water and exhibited free movement on water.

Regarding the H-type actuator, the PT layer consists of polymer and carbon materials, such as graphene oxides (GOs), to improve actuation helped by high humidity responsive properties. The grafting of P3HT onto the surfaces of the RGO composite was reported for the PT layer (Figure 15a).[128] A high ηPT of 82% was achieved from this composite upon exposure to a 532 nm laser, which exhibited a photoswitchable bimetallic strip as a switch for an LED bulb (Figure 15b). In another case, the PDA-modified RGO composite (humidity-responsive layer) onto the NOA-63 layer was applied as a bilayer PT actuator (Figure 15c).[129] The hydrophilic composite layer absorbed moisture leading to swelling (flat) and loss of water occurred following PT heating, which led to shrinking (bending), with a reversible θb of 80° (Figure 15d,e). Subsequently, the humidity-responsive GO-PDA composite on the RGO layer was used as a light-driven actuator,[130] which showed reversible folding within 3 s and a θb = 180° with a ΔTPT of 32 K. Notably, it was applied to a wormlike walking device based on all-graphene self-folding paper (Figure 15f). Compared to the inorganic materials reported for the PT heating layer, such as MoS2 and MXene, organic material-based composite films exhibit a high ηPT and high ΔTPT, as well as flexibility.

Regarding the L-type actuator, PANI with LC elastomer composites was prepared by uniaxially stretching a pre-cross-linked composite following a complete cross-linking reaction.[36] The composite of 1 wt% PANI (ES) showed a reversible NIR-triggered photoactuation and heavy-lift capability (11.3 g) upon exposure to an 808 nm laser that generated a ΔTPT of 112 K. Later, PDA NP-doped LC elastomer composites were synthesized by transesterification.[131] This transesterification of the composite was further triggered by a high Ipd (1.4 W cm−2) to bend at 160 °C and hold a 3D shape after heating to 200 °C. Recently, PDA-coated LC elastomers were applied as light-driven artificial muscles.[132] These elastomers showed fast lifting-recovering cycles within 0.65 s and afforded a prototype robotic swimmer that was able to move on a water surface by reversible bending and unbending motions induced by NIR light.

PT heating can be coupled with other types of actuation mechanisms such as photochemical reactions and molecular motion by photoisomerization. For example, a shape-programming and shape morphing actuator was prepared using an azobenzene-based photoactive LC composite (Figure 16).[133] The azobenzene unit undergoes trans-to-cis photoisomerization by UV light to control the cis content (Figure 16d). The PT heating led to the LC unit transforming in shape under UV light, and cis-to-trans photoisomerization was controlled...
by blue light exposure to switch the actuator to its initial state (Figure 16e,f). Subsequently the LC actuator was reconfigured with UV light followed by red light illumination to adapt to other shapes (Figure 16g). A UV light fuel gripper was demonstrated as a microrobot that lifts an object (Figure 16h,i). The actuating parameters of some representative PT actuators are summarized in Table 1.

4.3. p-PTM films for Cell Sheet Harvesting

As the temperature of the PT layer can be precisely controlled, for example, by varying the $I_{pd}$ and thickness of the PT layer, the PT effect has been applied to cell engineering, including the ablation of unwanted cells such as cancer cells while harvesting wanted cells without heat damage. Live cell sheet harvesting in spatiotemporal tissue engineering provides the reproduction and replacement of nonfunctional tissues and organs. Thus, several methods have been investigated using thermo-, photothermo-, electro- and photochemical stimuli, or a combination of these stimuli, to harvest live cells and cell sheets by inducing the cells to detach from a substrate due to a change in the substrate surface.

Noninvasive and selective harvesting of stem cells was reported with a PEDOT film exposed to an NIR laser. By controlling the doping level of the PEDOT film, cell viability at the PEDOT surface and the $\Delta T_{PT}$ of the laser-exposed area were optimized to proliferate mesenchymal stem cells (MSCs) onto the PEDOT surface and harvest the MSCs via PT heating, respectively. To harvest cell sheets that maintain cell–cell interactions, PT disassembly of triple helix collagen was used.
Thus, the collagen layer was coated on a PEDOT surface, and human dermal fibroblast (HDF) cells proliferated on top of the collagen layer to form a cell sheet. The stable triple-helical conformation of collagen under cell culture conditions ($\approx 37^\circ C$) (Figure 17a) unfolded upon PT heating ($\approx 41^\circ C$) due to exposure to an NIR laser, liberating individual strands of collagen into an aqueous medium and attenuating HDF cell–surface interaction. Simultaneously, the HDF cell sheet is harvested while floating in the medium.[10] Using this highly effective photodetachment method and optical system, live cell sheets were harvested within a short exposure time (5 min) to an 808 nm laser (2.5 W cm$^{-2}$). Notably, the efficiency of cell detachment ($\eta_d$), which is determined from the ratio of the detached cell area over the NIR-exposed area, was determined to be 168% at 2.5 W cm$^{-2}$, indicating that the area of detached cells is larger than the NIR-exposed area (Figure 17b,c). Using this highly effective photodetachment method and optical system, live cell sheets were harvested within a short exposure time (5 min) to an 808 nm laser (2.5 W cm$^{-2}$). Notably, the efficiency of cell detachment ($\eta_d$), which is determined from the ratio of the detached cell area over the NIR-exposed area, was determined to be 168% at 2.5 W cm$^{-2}$, indicating that the area of detached cells is larger than the NIR-exposed area (Figure 17b,c). Taking advantage of the harvesting of cell sheets with precisely controlled light, multiple human adipose-derived stem cell (ADSC) sheets with tailored shapes were harvested from the collagen coated PEDOT film using a patterned PDMS lens for NIR diffraction (Figure 17d–f), to afford a cell sheet with a large area of 19 cm$^2$ (3 cell sheets) after one exposure to an 808 nm laser (Figure 17g–i).[137]

Figure 17. a) Schematic structure of collagens having one $\alpha 2$ and two $\alpha 1$ polypeptide chains i) in the unexposed region and dissociated, unfolded collagens ii) in the NIR-exposed region.[70] The water molecules (I) in the triple helical structure are expelled upon PT heating to generate single helical collagens that form new hydrogen-bonding interactions with warm water molecules (II) and then dissociate into cell media. b) Effect of the diameter of the NIR-exposed area ($d_{\text{NIR}}$) on the diameter of the harvested cell sheet ($d_{\text{HCS}}$, black) and $\eta_d$ (blue). c) Effect of the $I_{\text{pd}}$ value (black) on the temperature increase at the PEDOT surface (red) and on the $d_{\text{NIR}}$ (blue). d) FESEM image of a square patterned PDMS lens.[137] e) Corresponding IR camera image obtained for the PT pattern on the PEDOT substrate. f) Corresponding microscopic image of the harvested HDF cell sheet. g) Schematic illustrating the harvesting of multiple cell sheets with a line patterned PDMS lens. Inset: An FESEM image of the line patterned PDMS lens. h) Corresponding IR camera image of three PT patterns. i) Photo images of the harvested human ADSC sheet. a–c) Reproduced with permission.[10] Copyright 2015, Wiley-VCH. d–i) Reproduced with permission.[137] Copyright 2017, Wiley-VCH.

Recently, PDA NP and poly(N-isopropylacrylamide) (PNIPAM) hydrogel composites have been used for single cell release from the composite surface, which were used as a p-PTM and thermally responsive polymer, respectively.[138] After exposure to an 808 nm laser for 1 min (10 W cm$^{-2}$), the hydrogel released 50% of the seeded cells. The composite layer was photocontrolled from hydrophilic to hydrophobic properties above the lower critical solution temperature, causing a reduction in the volume to release cells from the surface. Finally, these PT cell sheet harvesting results have been incorporated in various studies examining intercellular interactions, artificial tissue engineering, skin reproduction, and organ regeneration.[135]

4.4. Photothermal Energy Harvesting

PT conversions are accompanied by carrier generation and transport to perform PTEs,[16,30,193–195] photothermalvoltaics,[18,163,146] and PT mechanical energy conversions[121,125] integrated with PVs, Peltier modules, piezoelectrics, and Stirling engines. For the efficient conversion of light to thermal energy for useful electric or mechanical energies, a high $\eta_{\text{PT}}$ of the PT film is crucial for energy conversion. The PTE effect consists of two processes: 1) the absorbed light energy is converted into thermal energy, and 2) it spatiotemporally triggers the carriers to move toward the cold part which generates electricity by
the thermoelectric phenomenon.\cite{26} The output power and PTE efficiency ($\eta_{\text{PTE}}$) can be determined from the following equations:

\[ P_{\text{PTE}} = \sigma I^2 S \]  
\[ V_{\text{PTE}} = \frac{\int \nabla T \ dx}{6} \]  
\[ I_{\text{PTE}} = \frac{V_{\text{PTE}}}{R} \]  
\[ P_{\text{PTE}} = V_{\text{PTE}} I_{\text{PTE}} \]  
\[ \eta_{\text{PTE}} = \frac{P_{\text{PTE}}}{P_{\text{input}}} \]

where PF is the power factor, $S$ is the Seebeck coefficient, $V_{\text{PTE}}$ is the output voltage, $V_T$ is the temperature gradient, $I$ is the output current, $R$ is the resistance between the two electrodes, and $P$ is the output power. Therefore, the PTE mechanism (mostly from a single layer) is unlike that in from PVs (multilayers), for which semiconductors are used to convert light into electricity due to the separation of electrons and holes.

Among the p-PTMs, the PTE effect was first reported with a PEDOS-C6 film where the Au electrode was used to collect electricity (Figure 18a).\cite{26} This PTE film affords a $V_{\text{PTE}}$ of 900 mV and a $P_{\text{PTE}}$ of 354.7 mW m$^{-1}$ K$^{-2}$ upon exposure to an 808 nm laser, with stability over 1000 cycles (Figure 18b). It was applied as a body heat generator by touching it to a person’s arm (Figure 18c). Later, the PEDOT film with an optimized degree of crystallinity was recently applied to a PTE device to yield a $P_{\text{PTE}}$ of 620 mW m$^{-1}$ K$^{-2}$, which was 1.7 times higher than the PEDOT-C6 film described above.\cite{26} This substantial increase in $P_{\text{PTE}}$ might be ascribed to the increased $\sigma$, $S$, and DOS in the PEDOT film, according to Equation (15). A solar heat harvester was prepared from a 2.23 mm-thick PEDOT film, which was connected to other 3 PEDOT film devices in parallel (Figure 18d). Upon exposure to solar light, this harvester showed a high $\eta_{\text{PTE}}$ of 38 mW m$^{-2}$ in an absorber-free system (Figure 18e). This harvester also showed a high energy density of 420 Wh g$^{-1}$ compared to the other absorber-free inorganic solar thermoelectric systems.\cite{111}

A Cu-based organic complex polymer, poly[Cu$_x$(Cu-ett)], mixed with PDVF as a polymeric thermoelectric composite was applied as the NIR detection film (Figure 18f).\cite{26} The single and 36-leg integrated device showed $V_{\text{PTE}}$ of 25 mV and 0.9 mV, respectively, upon exposure to solar light, along with a $S_{\text{PTE}}$ of 79 mV K$^{-1}$ (Figure 18g,h). Recently, poly(thienoisoindigo) (PTII) and poly(thiazoloquinoxalinimide-thiophene-flanked diketopyrrolopyrrole) (TzQI-TDPP) polymers showed a high absorption in the NIR-II region as p- and n-type PTE films, respectively (Figure 18i–k), with a $\lambda_{\text{max}}$ of 1295 and 1591 nm, respectively.\cite{111} Notably, the TzQI-TDPP film showed a high $V_{\text{PTE}}$ of $\approx$5.3 mV and $S_{\text{PTE}}$ of $\approx$306 mV K$^{-1}$ upon irradiation with a 1700 nm laser (78 W cm$^{-2}$). However, this film showed a low $P_{\text{PTE}}$ of 0.013 $\mu$W m$^{-2}$ K$^{-2}$ because of its low $\sigma$ (2.2 $\times$ 10$^{-2}$ S cm$^{-2}$).

Other types of PTE energy-harvesting devices are possible, such as PT pyroelectric and piezoelectric devices. Furthermore, these devices can be integrated as a thin film to obtain a hybrid energy harvester that harvests multiple sources of energy. For example, the PEDOT film was coated onto a pyroelectric PVDF film and a Peltier module. Then, these units were integrated with dye-sensitized solar cells (DSSCs) (Figure 19a).\cite{26}

The DSSCs absorbed visible light to generate PV energy, and the NIR light passing through the DSSCs was absorbed by the PEDOT film at the bottom, which heated the poly(vinylidene fluoride-co-trifluoroethylene) film to generate both piezoelectric energy and PT heat energy upon irradiation with solar light (Figure 19b). Finally, the heat generated by the PEDOT film drove the Peltier module, and all the electric energy was accumulated in a capacitor to operate the electrochromic device (Figure 19c,d). The hybrid harvester exhibited a high solar energy conversion efficiency of 11.7%, which was 20% higher than that obtained for the DSSC alone. Notably, an LED lamp and electrochromic display were operated by the solar light harvesting device.

A D–A type PT polymer, TBDOPV-DT was reported along with its–electric and PT–mechanical converters.\cite{111} A high level of absorption in the NIR-II region was observed for the TBDOPV-DT film, with a $\eta_{\text{PT}}$ of 50.5%. A high Seebeck voltage of 29.7 mV was obtained from the hybrid PT film and Peltier module put under a piece of pig skin using a 1064 nm laser (0.82 W). Additionally, the hybrid PT film and Stirling engine displayed a light–mechanical energy conversion efficiency of 0.0054% at a light power of 1.76 W (Figure 19e,f).

5. Summary and Future Outlook

Conjugated organic PTMs have been extensively examined over the last decade due to their unique tunability of heat generated from light, high level of light absorption, ease of synthesis and modification of molecular structures, and low cytotoxicity in various applications. The chemical structures of the organic PTMs have been designed to retain a long conjugated group and a D–A structure, to introduce ICT resulting in a redshift in the absorption toward the NIR region and an increased extinction coefficient. The representative m-PTMs are ICG, IR-X, Croc, DPP, and IDI, which show strong NIR-I absorption to provide maximum $\eta_{\text{PT}}$ values of 9%, 20%, 60%, 71%, and 75%, respectively, in the NP or in polymeric media. On the other hand, a thin film of p-PTMs has been produced without binder through a simple process such as SCP or CVD methods in that monomers are directly polymerized on a substrate. The representative PEDOT film prepared by SCP method showed a maximum $\eta_{\text{PT}}$ of 93% and the PPy-coated air-laid paper prepared by CVD method showed $\eta_{\text{PTW}}$ of 81.9%.

Starting from an $\eta_{\text{PT}}$ of 13% for the PProDOS film reported in 2011, the $\eta_{\text{PT}}$ values for p-PTMs reached 93% by 2019, with maximum $\eta_{\text{PT}}$ values of 93%, 42%, 35%, 65%, 71%, and 66% reported for PEDOT, PEDOS, PANI, PPy, PDDP, and D-A polymers, respectively, which show generally higher $\eta_{\text{PT}}$ values than m-PTMs. The $\mu$ and $\Delta\eta_{\text{PT}}$ are linearly correlated with $\eta_{\text{PT}}$, which conveniently provides the design and programming of thermal engineering with PTMs. While some
inorganic composites, such as MXene@PDA-PU composites, show high $\Delta T_{PT}$ in the visible region. p-PTMs such as PEDOTs show a high $\Delta T_{PT}$ in the NIR region. Furthermore, the light sensitivity of organic PTMs is shifted to the NIR-I and even NIR-II regions, as observed for PEDOTs, TBDOPV-DT, and IDI, reaching $>140$ K upon excitation with a 1064 nm laser. This redshift for light excitation might reduce unwanted side reactions during PT applications.

As summarized in Table 1 for representative examples, organic PTMs possess great potential in the development of PTW, PTA, PTE, and PTCH. The outcome and efficiency of each application are quite promising and some of them show
potential for multiple applications. For example, the transparent IDI exhibited a high $\Delta T_{PT}$, leading to effective water evaporation with a maximum $\nu_w$ of 1.70 kg m$^{-2}$ h$^{-1}$ and transparent actuators which provides new possibilities for colorful actuators. The PEDOT films showed not only a high $\Delta T_{PT}$ but also a high Seebeck effect, to exploit the film for PTA with a high $\theta_b$ of 150°, PTE with a $P_{FTE}$ of 690 $\mu$W m$^{-1}$ K$^{-2}$, and PTCH with a fast live cell sheet harvesting capacity. Transparency of some organic PTMs is an exceptional characteristic which promote multifarious properties such as integrating ability with piezoelectric, pyroelectric, and solar light harvesting devices. The transparency can be controlled by film thickness, ordering of molecules or polymers, porosity, and PTM content in binder.

The PT effect in a film represents a convenient tool for maneuvering heat and can take advantage of light stimuli such as a high degree of spatiotemporal control by the wavelength, intensity, diffraction, and polarization of light. Therefore, the applications have been extended to various fields, not only those areas that have been developed for inorganic PTMs but also new areas, where spatiotemporal thermal engineering is required. [113,148,149,152,153]

In addition, the strong PT effect and compatibility with mechanically synergistic polymers or inorganic PTMs based on CPs afford composite films which increase the application potential due to the enhanced $\eta_{PT}$. For example, a catechol-conjugated poly(vinylpyrrolidone) sulfobetaine (PVPS):PANI film was reported for PT killing of bacteria. [150] Another example is a PT cloth weaved from an elastic PU tube coated with PPy that showed a $\Delta T_{PT}$ of 50 K and $\eta_{PT}$ of 73.9% under solar light irradiation, [148] which is comparable to that obtained for MXene@PDA-integrated PU composites. [149] In addition, a self-healing PT composite with a boron nitrogen nanosheet (f-BNNS)/PEDOT:PSS/PNIPAM hydrogel film exhibited a $\Delta T_{PT}$ of 59 K upon exposure to an 808 nm laser (1.01 W), affording an on-skin motion sensor and heating patch. [152] Compared to inorganic-based composites, such as AgNP@MXene-PU, [151] CP-based composite films have been reported to be a high priority for PT engineering because of their high $\eta_{PT}$ and large stretchability for various applications.

Various PT films with noteworthy organic PTMs are now available; however, understanding the PT effect and the applications of these films has only just begun. Thus, it is expected...
that organic PTMs will shed light on a better understanding of the PT effect and provide a guide for the rational design of the target device for more precise and effective spatiotemporal thermal engineering. For future development of PTMs, several strategies can be conducted as follows. The rational design for efficient m-PTMs should achieve a band gap tuning through intramolecular D–A structure to extend π-conjugation. For the efficient p-PTM design, a low band gap structure could be designed with extension of π-conjugation in the main chain units for a high molar extinction coefficient in the NIR range. Further consideration on the degree of crystallinity and carrier mobility induced by the DOS broadening at $E_G$ is important to enhance nonradiative relaxation. A method of adjusting the band structure using a dopant, which has been actively studied recently, can also be a good challenge for p-PTMs. Since only recently it has been reported that $\eta_{PT}$ and $\mu$ are related to each other in PEDOT films, it is necessary to explore the versatility of various CPs in the future for both theoretical and experimental perspectives, to develop a guiding principles to the PT properties of organic PTMs. As the PT effect in the PTM films provide precise spatiotemporal thermal engineering, the application of these organic PTMs could be extended in various fields including the emerging applications in invisible target PT imaging and therapies, molecular motion controls, artificial neural network, and flexible energy conversion devices.

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

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Conflict of Interest
The authors declare no conflict of interest.

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