Capturing Waste Heat Energy with Charge-Transfer Organic Thermoelectrics

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Abstract Electrically conducting organic salts, known for over 60 years, have recently demonstrated new abilities to convert waste heat directly into electrical power via the thermoelectric effect. Multiple opportunities are emerging for new structure–property relationships and for new materials to be obtained through synthetic organic chemistry. This review highlights key aspects of this field, which is complementary to current efforts based on polymeric, nanostructured or inorganic thermoelectric materials and indicates opportunities whereby mainstream organic chemists can contribute.

1 What Are Thermoelectrics? And Why Use Them?

Seebeck (in 1821–2) noted that suitably combined p and n thermoelectric (TE) materials generate a voltage (α) when placed between two temperatures: \(T_{\text{hot}}\) and \(T_{\text{cold}}\). Maximising the electrical voltage, current and hence power, induced down the temperature gradient requires electrical carrier transport (via holes or electrons) to outperform heat energy transport (via lattice vibrations). The theoretical maximum (Carnot) efficiency (\(\eta_{\text{max}}\)) of any TE device, all potentially capable of converting waste heat into electrical power, is

\[\eta_{\text{max}} = \frac{1 - T_{\text{cold}}/T_{\text{hot}}}{1 + \sigma\alpha^2/\kappa}\]

For lower temperature operation, e.g., \(T_{\text{hot}} = 200\) to \(T_{\text{cold}} = 25 \degree \text{C}\) (the temperatures where most global waste heat abounds), this corresponds to \(\eta_{\text{max}} = 35\%\) theoretically (and typically <8% in real devices). Using TE materials for waste heat energy extraction is complicated by the fact that thermal (\(\kappa\)) and electrical (\(\sigma\)) conductivity often scale linearly with each other (the Wiedemann–Franz law). The effectiveness of any TE material, at temperature T, is thus usually defined by the dimensionless comparator ZT, where

\[ZT = \alpha^2\sigma/\kappa\]

For efficient energy-harvesting applications, ZT values >1 are needed at the temperature of opera-
tion (T). Simultaneous high electrical and low thermal conductivity are needed to access such performance. Common thermoelectric materials (Figure 1) often underperform (ZT = 0.01–0.25 is not atypical) at lower temperatures, and the few that are effective at 200–25 °C, like Bi₂Te₃, have poor sustainability (tellurium is rarer than gold!). Electrically conducting organic TE materials (Figure 1) potentially could fill this niche offering lower cost, sustainability and waste energy recovery. Saving 8% of the current global heat energy wasted below 200 °C would amount to ~325 TW·h, a value greater than the annual electrical energy consumption of most European countries. As an added advantage, run in inverse operation, highly efficient TE devices allow motionless refrigeration options via the Peltier effect.¹

![Figure 1](https://example.com/figure1.png)

**Figure 1** From unsuitable to ideal materials for low temperature waste heat recovery and some parameters to compare their performance. The power factor \((PF = \sigma\alpha)\) of an ideal organic TE material would be ≥1440 µW m⁻¹ K⁻¹, comparing favourably with that of doped Bi₂Te₃ \((PF = 4160 \mu W \text{ m}^{-1} \text{ K}^{-1})\). These PF values were calculated from the \(\sigma\) and \(\alpha\) values within the Figure.

### 2 Current Organic and Hybrid Thermoelectrics

Organic materials were realised to possess thermoelectric properties from the early 1970s within the fields of organic semiconductors and conducting polymers. In general, organic TE materials offer rather low thermal conductivity \((k)\), significant Seebeck coefficients \((\alpha)\) and tuneable, but often low, electrical conductivity \((\sigma)\). As \(\sigma = q\nu\epsilon\) [where \(q\) is the charge on an electron (or hole), \(\nu\) the free carrier density and \(\epsilon\) the charge carrier mobility], known organic (semi-)conductors showing values of \(n\) and \(\mu\) of \(10^{10}\) to \(10^{16}\) cm⁻³ and \(10^{-4}\) to \(-10^4\) cm² V⁻¹ s⁻¹, respectively, can be theoretically doped into providing \(\sigma\) in the range \(10^{-5}\) to \(10^6\) S cm⁻¹. Rich synthetic methods exist for the synthesis of structurally varied organic (semi-)conductors, offering opportunities for increasing \(\sigma\) while maintaining or degrading \(k\). However, caution should be exercised due to the mutual interdependence of \(\sigma\) and \(k\) in classical conductors. Low temperature waste energy harvesting organic TEs are considered promising due to the potential for new materials discovery via easily prepared libraries, coupled with effective scale-up, reasonable price and very suitable solution-based processes for purification and utilisation in devices. Research activity in organic TE materials has grown rapidly (Figure 2), but the majority of this interest has somewhat remained within the materials (especially polymer) communities and large future potential opportunities for the involvement of mainstream synthetic organic chemists exists.

![Figure 2](https://example.com/figure2.png)

**Figure 2** Number of publications covering the terms ‘organic thermoelectric materials’ and ‘organic thermoelectric’ from 1990 up to the end of 2017 (according to Scopus and Thomson Reuters Web of Science).

Measuring thermal conductivity \((k)\) values can sometimes be challenging and in its absence, the power factor \((PF = \sigma\alpha)\) of a material is a useful alternative comparator. From a chemical point of view, current organic and hybrid TEs can be roughly divided into three classes,¹ leading exemplars of which are shown in Scheme 1:

- Conducting polymers: including purely organic systems such as polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT) together with metallo-coordination polymers such as poly(nickel-1,1,2,2-ethenetetraethiolates).
- Nanocomposite materials: typically, combinations of single- or double-wall carbon nanotubes (or other carbon allotropes) with conducting polymers or other diverse promoters. By using a multi-layering approach very high-power factors have been attained, but empirical optimisation plays a major role in such studies.
- Small molecules: appropriately electron-rich (or poor) molecules with diffuse electron density are known to exhibit significant Seebeck values. For example, pentacene films show \(\alpha \sim 250\) µV K⁻¹, which under appropriate doping afford moderately efficient organic thermoelectric p-type phases. Such strategies are subject to the proviso that the required oxidation or reduction (charge transfer) products are stable.

While representative of the current organic TE area, the compounds shown in Scheme 1 are only a small fraction of those that have been trialled in TE studies. In all cases, appropriate doping (addition or removal of electrons) of the basic TE materials is required to increase \(\sigma\). However, \(\alpha\) is typically found to fall as \(\sigma\) increases and careful optimisation of the doping levels is required in maximising PF and ZT. By using such strategies, remarkable progress has been made towards attaining viable organic TE technology, but
many issues remain to be resolved. For example, while Grunlan’s hybrid carbon nanotube materials\(^7\) (Scheme 1) deliver performance comparable to commercial Bi\(_2\)Te\(_3\), they require the deposition of more than 300 separate layers! Intrinsic constraints may also exist. Recent data mining revealed that most organic TEs show interdependence of the electrical conductivity and Seebeck coefficient, such that \(\alpha \propto \sigma^{-1/4}\), leading to \(PF \propto \sigma^{-1/2}\).\(^10\) These relationships suggest that (re)investigating ‘synthetic metals’ (organic phases ranging from \(~10^{-4}\) S cm\(^{-1}\) for impure (aerobic oxidised samples) to \(10^{-5}\) to \(10^{-6}\) S cm\(^{-1}\) for pristine vacuum-sublimed TTT) leads to stable (p-type) charge-transfer complexes of approximate stoichiometries \([TTT]X\) or \([(TTT)\_2]X\), where \(X\) is a mononuclear or polynuclear anion, often based on iodine.

### 3 Unique Materials from Tetrathiotetra
cenes

Bechgaard and Jerome’s seminal 1979 observation\(^11\) of superconductivity in the organic salt \((TMTSF)_2PF_6\) precipitated a global (but ultimately unsuccessful) quest for related organic materials that could remain superconducting above more than a few Kelvin. Tetrathiotetrace (1) shows that (re)investigating ‘synthetic metals’ (organic phases ranging from \(~10^{-4}\) S cm\(^{-1}\) for impure (aerobic oxidised samples) to \(10^{-5}\) to \(10^{-6}\) S cm\(^{-1}\) for pristine vacuum-sublimed TTT) leads to stable (p-type) charge-transfer complexes of approximate stoichiometries \([TTT]X\) or \([(TTT)\_2]X\), where \(X\) is a mononuclear or polynuclear anion, often based on iodine.

The latter can be isolated as lustrous golden needles of \((TTT)\_2I\_3(\delta \sim 0.1)\) showing a high electrical conductivity of \(\sigma \sim 10^3\) S cm\(^{-1}\) (about a tenth that of liquid mercury) down the needle length (which corresponds to the crystallo-

graphic \(b\)-axis, Figure 3).

Theoretically, the one-dimensional electrical conductivity shown by \((TTT)\_2I\_3\) should be prevented by a Peierls transition to an insulating phase.\(^13\) However, disorder in the \(I_3\) chains allows \((TTT)\_2I\_3\) to achieve the simultaneous short- and long-range (dis)order necessary for a 1D quasi-

crystal phase to be attained.\(^14\) This prevents the symmetry necessary for Peierls effects to manifest themselves; the \(I_1\) chains can be thought of as being composed of: \(\delta\), \(I_3\), and \(I_3^\prime\) leading to an absence of translational symmetry down the
iodine-based counter anion chain. Two factors theoretically combine in (TTT)$_2$I$_{3\delta}$ to facilitate the thermoelectric efficiency of the phase. Firstly, the quasi-one-dimensionality leads to an increase of the density of carrier density of states in (TTT)$_2$I$_{3\delta}$. Secondly, and most importantly in the case of (TTT)$_2$I$_{3\delta}$, there is partial compensation of two of the most important electron-phonon interactions for a narrow strip of states in the conduction band. This affects the relaxation time associated with charge transfer within (TTT)$_2$I$_{3\delta}$, which becomes a sharp function of carrier energy leading to a sharp increase in the mobility of the charge carriers in these states. Provided the Fermi level of the (TTT)$_2$I$_{3\delta}$ phase can be displaced (by optimisation of the carrier concentration) towards this strip of states (those with increased mobility), dramatic increases in electrical conductivity and Seebeck coefficients are predicted. As the derived electrical conductivity grows faster than the electronic contribution to thermal conductivity, the solid is predicted to show non-Wiedemann-Franz-type behaviour. The combination of these two factors suggest, theoretically, that (TTT)$_2$I$_{3\delta}$ should be highly suited for thermoelectric applications. Unfortunately, these same theoretical studies also suggest that carrier scattering by impurities or defects and inter-chain vibrations will have significant negative effects on the observed electrical conduction and hence TE applicability. Similar preliminary studies indicate that n-type charge-transfer complexes could be formed from mixtures of TTT and tetracyanoquinodimethane (TCNQ). However, prior to 2017, the preparative and purification issues associated with TTT (see above) severely limited experimental study of TE behaviour in these materials. Thus, in the next section it is appropriate to overview known classical and modern approaches to TTT molecules, and their tetracene precursors, applicable to eventual device preparation.

4 Synthesis of Tetrathiotetracenes

The synthesis of TTT refers to a handful of synthetic approaches in which tetracene (T) (2) is the core starting material. In some cases, an alternative suitably substituted tetracene derivative is used. Access to definitive synthetic procedural information in the primary literature is complicated. In some cases the initial reports are described only in patents or are limited to early Soviet literature. An overview of known syntheses of unsubstituted and substituted TTT has recently been collected and this also demonstrates these literature accessibility issues. Evaluating the known experimental details, supplemented by our own experiences in this area, it is justified to suggest the direct reaction of tetracene (2), or one of its derivatives, with sulfur in refluxing DMF is the most appropriate method for the synthesis of TTTs. This path (A) was first outlined by Perez-Alberne (Scheme 2) as long ago as 1973. Typically, >90% yields of crude products, containing only small amounts of poly-sulfide materials, are attained.

For the synthetic approaches of pathways B, E and F, there are insufficient data to estimate their efficiency and therefore they do not possess much practical importance at present. The synthesis of TTT (1) by using the substituted species in routes C, D, F and G is described to proceed in yields in the range 40–85%. However, in these cases, previous multistep synthetic approaches to the precursors are necessary in which the 6,11-dihydroxy-5,12-naphthacenodione (DND) (3) is the key intermediate (the starting

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Scheme 2  Synthetic pathways for the preparation of tetrathiotetracene (TTT) (1)
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compound in path C is further used for the synthesis of all chloro-substituted tetracenes). The cost of DND (3) ca. 20–100+ €/mmol makes such manipulations viable on small scale, but the large-scale preparation of 3 has not yet been widely taken up, even after significant process optimisation has appeared.21 Given the wider availability of various tetracenes (at similar cost), the method of choice, in our opinion, is pathway A which typically offers good yields and simple work-ups.20 For example, reaction of the parent tetracene (2) and elemental sulfur in DMF afforded, after refluxing the mixture (4–5 h) and hot filtration, the desired TTT (1) in crude yields above 95%. For purification, a simple Soxhlet extraction with toluene and/or CS2 is effective in removing sulfur impurities and a by-product identified as dithiotetraene. In this manner TTT (1) is produced in >95% purity and good yield. To obtain TTT (1) for thermoelectric applications further purification by applying high-vacuum sublimation is necessary.22 The most important properties of TTT have been demonstrated in Section 3 (above).

A key prerequisite in the production of TTT (1) is the availability of tetracene (2). As of 2018, we were able to identify eight providers of T (2) at prices between 22 to 140 €/mmol (for quantities between 100 mg to 5 g). While custom synthesis of T (2) on larger scales is commonly offered, very few (even simple) tetracene derivatives are commercially available. Practical syntheses of T (2) and substituted derivatives ideally need to fulfil the following criteria for maximum utility: (i) minimised total step-count, (ii) use of only low-cost, sustainable starting materials, (iii) diversity-oriented intermediates facilitating the preparation of substituted tetracene libraries, (iv) simple (chromatography-free) work-up procedures providing analytically pure intermediates and final tetracenes, and (v) applicability to gram scales without yield or purity degradation issues. Synthetic approaches aspiring to these criteria and leading to generalised unsubstituted tetracenes are presented in Scheme 3.

Some of these routes are also suitable for the synthesis of substituted tetracenes. In previous review articles different approaches for the synthesis of tetracenes and high acenes have already been summarised.23 Therefore, here we present only the most practical synthetic approaches to producing tetracenes relevant for elaboration into TTTs.

Traditional routes to tetracene derivatives typically involve unidirectional synthesis from ortho-substituted phenylene units wherein only one aryl ring is formed at a time (routes II–IV and VI), or in rare cases from di-ortho-substituted naphthalenes allowing bidirectional synthesis with formation of two rings at a time (routes I and V). Potentially, bidirectional approaches allow more rapid tetracene synthesis and this idea has been recently investigated (route I).24 This bidirectional synthesis of tetracenes calls for the initial preparation of intermediates 4 and 5 (Scheme 4) by using: (i) copper-catalysed direct addition of ArCH2MgCl to HOCH₂C≡CCH₂OH leading to an (E)-carbenemagnesiouation intermediate which smoothly intercepts iodine providing compounds 4 (in 50–55% yield) on 10 g scales, or (ii) equally conveniently 5 is directly precipitated as an off-white solid from the simple reaction of 2-butyne-1,4-diol with iodine in CHCl₃ on >10 g scales (90% yield).24

For the synthesis of the key diols 6 efficient Negishi-type couplings were developed followed by relatively simple purification. No protection of the free hydroxy groups is required in these reactions as C–C coupling is faster than deprotonation events. Modified high yielding aerobic oxidation by CuI/TEMPO-based catalysis provides the aldehydes 7. The transformation of 7 into 2 occurs in poor to excellent yields depending on the substituents R¹ and R² and the Lewis acid applied. Normal S₂Ar behaviour is observed, if R¹/R² are electron-releasing (e.g., alkyl, OMe, Ph) high yields are realised (typically above 80%). However, if R¹/R² are electron-withdrawing only small amounts of tetracene 7 are produced (e.g., R¹ = H, R² = F gives 2d in only 9% yield).
The majority of the product, 37%, being due to closure on just the electron-rich aryl group). The simplicity of the work-up procedures and the very low cost of the starting materials (both the acetylene and benzyl chloride are only cents/g) means that the route of Scheme 4 is rather attractive for the synthesis, on gram and above scales, of electron-rich tetracenes.

The preparation of the parent tetracene (2) itself can be attained in higher efficiency by using the approaches in Scheme 5 (cf. route II, Scheme 3). The reaction of 1,2-bis(halogen-methyl)benzene (8, X = Cl is commercially available; X = Br is easily prepared by bromination of o-xylene) and 9 provides intermediate 10 in good yield via a published procedure. In our hands, the synthesis of 10 has been further developed for both unsubstituted and substituted variants of 8 and 9. Alternatively, compounds of type 10 can be synthesised (both unsubstituted and substituted) through reaction of phthalaldehyde (11) and dihydroxynaphthalene 12 applying a published procedure. A practical reduction of 10 to give tetracene could be performed with aluminium alkoxides [using commercial Al(O-t-Bu)₃ to provide good yields]. The materials costs for the synthesis of tetracene on a 10 g scale starting from 1,2-bis(chloromethyl)benzene (8a) is ca. 1 €/mmol, and from phthalaldehyde (11) is 2.50 €/mmol; this is at least 10× less than the typical commercial retail cost of the parent tetracene (2).

The ‘furan/benzyne’ approach (routes IV and V, Scheme 3) has been presented in two literature variants, both of which are practical and viable approaches, although multi-step synthesis is necessary in this case. In one case the readily available acetal 13 is converted into the bis-silylfuran intermediate 14 and reacted with in situ generated benzyne 15 providing reactive 16 in good yield (Scheme 6). Derivative 16 reacts rapidly and almost quantitatively with TFA to form 5(12H)naphthacenone 17, which leads after reduction/dehydration to tetracene (2).
A second variant of the ‘furan/benzyne’ approach\(^{28b}\) refers to the bidirectional approach of route V (see Scheme 3), in which benzyne formation is performed in situ from 18 followed by reaction with furans 19 leading to the di-epoxy-tetrahydronaphthalenes 20 in moderate yields. The catalytic hydrogenation of unmodified 20a to give 21a is high yielding and the subsequent dehydration (TFA/CHCl\(_3\) or HCl/MeOH) provides easily tetracene (2) (Scheme 7). The tetramethyl-substituted compound 21b possesses extreme acid lability and is thus directly converted with aqueous HCl into the tetramethyaltetracene 22.

A final feasible, but less common, strategy in tetracene formation is the cycloaddition of benzocyclobutane (23) to epoxides 24 (route VI, Scheme 3), providing the intermediates 25 in good yields (Scheme 8).\(^{29}\) The further conversion into compounds 26 and subsequent aromatisation provides tetracene (2) and dibromotetracene 27 in excellent yields.\(^{29}\) One advantage of such approaches is that dihydroacenes\(^{23c}\) such as 26 are frequently significantly more soluble than their aromatic analogues, which obviously facilitates their purification by chromatography. In balance to this, an additional (slow, high catalyst loading) step is required at the end of the sequence for aromatisation and any functional groups present must also be tolerant of Pd/C.

In summary, based on their frequency of use and ease of implementation, routes I–VI (Scheme 3) as exemplified above, presently offer the most attractive approaches for the preparation of tetracene (T) (2) and its substituted derivatives, allowing access to TTT derivatives on multigram scales and substituted TTTs in research amounts suitable for device preparation. The latter is considered in the next section.

5 Materials and Device Applications

Typically, TE device preparation requires a p/n conductor junction that spans the temperature gradient so that the charge carriers (e\(^-\) or positive holes h\(^+\)) both flow down the ‘legs’ towards the cold surface (Figure 4, a). When screening for improved materials one of the n- or p-type legs is typically of known performance so that the characteristics of the new TE species is extracted more easily. The majority of organic devices prepared so far have used the p-type copolymer PDOT-PSS, which is attractive as thin films of this material are easily cast. The poor solubility of TTT material makes vacuum deposition of thin films more attractive as gas-phase doping also allows preparation of both the n- and p-legs (Figure 4, b) into a functioning in-plane generator (Figure 4, c).\(^{30}\)

![Figure 4](image)

Only very small amounts of power (50 pW at 1 mV) are attained by the device in Figure 4. Greater amounts of power in such thin-film configurations would be attained by use of multiple junctions in series or by increasing the thickness and length of the p/n legs. One alternative method to increase TE device performance for TTT systems is through use of single-crystal devices as formally no crystal grain boundaries exist leading to greatly improved carrier
mobility. This approach has been partially realised by Huewe, Steeger and PfLaum who have successfully developed apparatus (Figure 5) for the simultaneous measurement of $\sigma$, $\alpha$ and $\kappa$ on single crystals of (TTT)$_2$I$_3$. The electrical conductivity of these single crystals ($2.1 \times 10^3$ S cm$^{-1}$ at room temperature) is ideal for an organic TE device and the $\alpha$ values are acceptable ($+42$ $\mu$V K$^{-1}$). Unfortunately, the crystal's thermal conductivity was much higher than anticipated $\kappa = (3.7 \pm 0.2)$ W(m K)$^{-1}$ leading to a poor $ZT_{RT} = 0.03$ value. Nevertheless, single crystals of (TTT)$_2$I$_3$ combined with the n-type material Cu(DNDQI)$_2$ provide a device generating $-20$ nW from only a 30 °C temperature difference. This power is being driven off a total crystal cross-sectional area of only ca. 10$^{-8}$ m$^2$. If many such crystals could be bundled into a 1 cm$^2$ array, then enough power could theoretically drive small personalised electronics ($-1$ mW, about a thousand times higher than current PDOT/PSS-based devices).

**6 Future Perspectives**

Although the results of Section 5 demonstrate proof-of-concept in the use of thio-substituted tetracenes, especially TTT, a great deal of optimisation will be required to develop materials and devices of practical utility. In particular, improvement of $\sigma$ and $\alpha$, ideally with reduction of the thermal parameter $\kappa$ needs to be achieved. There are indications that this is possible as the tetracenes shown in Scheme 9 (see also Section 4) are converted into substituted TTTS.$^{24}$ Known derivatives 1b,c,e provide films with Seebeck coefficients of similar level to the parent TTT on doping with iodine ($\alpha = 17$–25 $\mu$V K$^{-1}$). However, the new 2,8-disubstituted derivatives 1f,g,i,j show significantly increased $\alpha$ values (Scheme 9). Recent analyses show strong correlations between $\alpha$ and $\sigma$ and indications that crystalline conductors behave significantly differently to their polymer analogues.$^{31}$ This, together with the possibilities to use TTT cores in both p- and n-type conductors, means that significant potential exists for the development of these materials in both TE and other applications.

Further, very useful approaches to obtain substituted tetracenes 2 can also be envisaged and these are summarised in Section 10. Especially promising are the organocatalytic approaches for construction of tetracene precursors that have been recently published.$^{32}$

![Scheme 9 2,8-Disubstituted TTTS with improved Seebeck coefficients on I$_2$ doping$^{24}$](image)

Tetracenediones 28 are thus synthesised in one step in yields in the range 60–86%. The development of a suitable reduction procedure seems very feasible and would provide tetracenes in just two steps. As an alternative, a Friedel-
Crafts approach by using naphthalic anhydride and the subsequent reduction to 1,4-tetracenequinone (29) is high yielding33 and may find further development to an efficient procedure for tetracenes (2), or indeed pentacenes, and their sulfur derivatives. Such ideas clearly indicate the significant opportunities that exist for the involvement of mainstream organic chemists in the development of new thermoelectric materials. New exemplars of sustainable chemistry and future exciting and exceptional materials should be expected.

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