Doped films of organic small molecules are investigated with respect to their thermoelectric properties. A variety of hosts and dopants, for both n and p-doping, are compared. C_{60} n-doped by Cr_2(hpp)_4 and o-MeO-DMBI-I are found to be the most promising material systems with a maximum of ZT_M = 0.069 at T_M = 40 °C, assuming a doping-independent thermal conductivity due to phonon-based heat transport. This value is 16% of the current record reported for optimized devices employing the doped polymer PEDOT:PSS.

I. INTRODUCTION

The thermoelectric (TE) effect allows for generation of electricity from temperature gradients. This opens the path for self-sustaining sensors, power generation from waste heat or a complementary to photovoltaics[1]. In recent years, several approaches for different material systems and device layouts have been developed to achieve a high efficiency at low cost[2]. While the highest efficiencies have been reported for TE elements based on inorganic semiconductors, recently, doped polymers gained attention because despite having lower efficiency they have the potential of a strong cost reduction.[3] [4] Additionally, these organic compounds allow for fabrication of TE devices on flexible foils which are easier to handle and can e.g. be installed on large and curved surfaces like in cooling towers.

In this work, another class of organic semiconducting compounds is studied: small molecules, which so far have hardly been examined with respect to their TE properties, but are predicted to be a promising material class.[5] [6]. Small molecules have the advantage to polymers that due to their low molecular weight they can be deposited by thermal evaporation in vacuum, allowing for high material purity and arbitrary layer stacks, while mass production on large substrates via roll-to-roll fabrication is feasible as well. Doping of small molecules has led to novel devices like organic light-emitting diodes (OLEDs) and organic photovoltaic cells.[7] The electrical conductivity of such doped layers of small molecules typically increases with temperature[8] [9], while their thermal conductivity is rather low[10]. The scope of this publication is the comparison of the TE potential of several material combinations of small molecular hosts and dopants.

It is found that n-doped C_{60} samples show several orders of magnitude higher power factors, compared to p-doped hole transporting compounds. The highest values are obtained for low concentrations of Cr_2(hpp)_4 or high concentrations of o-MeO-DMBI-I in C_{60}. The resulting ZT_M of these first tests for this material class are as high as 16% of the current record reported for optimized devices employing the doped polymer PEDOT:PSS.

II. EXPERIMENTAL

Samples are prepared and measured in-situ in a vacuum setup (base pressure ≈ 3 × 10^{-5} Pa), which has been described in detail earlier[11] [12]. A doped organic layer of mostly 30 nm thickness is deposited by thermal co-deposition of host and dopant onto a glass substrate with two parallel, 40 nm thick gold contacts of 5 mm distance. This sample layout allows for measurement of both, conductivity and Seebeck coefficient at different temperatures, because the substrate is mounted onto two separately heated copper blocks below the gold contacts. All samples are thermally annealed at T = 100 °C in vacuum prior to investigation to ensure reproducibility of temperature-dependent measurements.

Electrical measurements are performed using a Keithley 236 source measure unit. For probing the conductivity σ, a voltage of V = 1 V is applied to the gold contacts and the current flow is measured and averaged over 2 minutes to compensate for statistical fluctuations. As for all samples a linear and symmetric current response is found for V = −10 to 10 V, we assume ohmic injection. For measuring the Seebeck coefficient S, a temperature difference of ΔT = 5 K between the gold contacts is used and the thermovoltage is measured and averaged for several minutes, followed by a measurement at ΔT = −5 K to compensate for measurement artifacts. Both, σ and S, are measured at different mean temperature T_M and for various samples of different doping concentration C.

In the following, C is expressed in terms of molar ratio (MR), being the ratio of the numbers of dopant to host molecules.

Hole transporting materials investigated here are the hosts N,N',N"-tetraakis (4-methoxyphenyl-benzidine (MeO-TPD) and N,N'-bis(9,9-dimethyl-fluoren-2-yl)-N',N"'-diphenyl-benzidine (BF-DPB) p-doped by 1,3,4,5,7,8-hexafluorotetrayanophthoquinodimethane (F_6-TCNNQ) and 36-fold fluorinated C_{60} (C_{60}F_{36}).[13]

As electron transporting material the host C_{60} is studied, comparing 5 n-dopants: tetakis(1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato)chromium (II) and ditungsten (II) (Cr_2(hpp)_4 [14] and W_2(hpp)_4 [15]), 3,6-bis(dimethylamino)acridine (AOB) [11], 2-(1,3-dimethyl-1H-benzoimidazol-3-ium-2-yl)phenolatehydrate (DMBI-POH [11]) and 2-(2-methoxyphenyl)-1,3-dimethyl-1H-benzoimidazol-3-ium.

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FIG. 1. Power factor $S^2 \sigma$, at $T_M = 40 {°}C$, $\Delta T = 5 {K}$ for (a) $p$-doped and (b) $n$-doped samples. For the $n$-$C_{60}$ samples the intrinsic thermal conductivity $\kappa = 10^{-3} \text{W/cmK}$ is used to calculate $ZT_M$ which is displayed at the right hand side axes.

iodide ($\alpha$-MeO-DMBII $^{[12,15]}$). Some of the conductivity and Seebeck data presented in this work have been published earlier in the given references, but so far no conclusion for the TE properties have been deduced.

III. RESULTS

The thermoelectric potential of a material is determined by the material’s figure of merit $ZT_M$

$$ZT_M = \frac{S^2 \sigma}{\kappa} T_M,$$

with Seebeck coefficient $S$, electrical conductivity $\sigma$ and thermal conductivity $\kappa$, measured at the mean temperature $T_M$. Hence, for TE applications, materials of low $\kappa$ but high $S$ and $\sigma$ are desired. The numerator $S^2 \sigma$ in equation (1) is called power factor. Doping a semiconducting TE material allows for manipulating these parameters. The presence of dopants leads to an increasing density of free charge carriers and thus $\sigma$ along with a reduction of $S$, due to the shift of the Fermi level towards the transport level $^{[16]}$. At low doping concentrations, the thermal conductivity $\kappa$ is attributed to phonons while at high $C$ contributions from the electrons dominate. Consequently, the optimum in doping concentration needs to be determined.

For the most extensively studied inorganic TE material system Bi$_2$Te$_3$, record values in the order of $ZT_M = 1.0$ at $T_M = 400 {°}C$ were achieved$^{[2]}$, while for the doped polymer PEDOT-PSS recently a promising record of $ZT_M = 0.42$ at room temperature has been reported$^{[3]}$.

The figure of merit largely affects the efficiency of power generation $\eta$, which is given by the ratio of electrical energy $W$ generated to the net heat flow rate $Q_H$ $^{[17,13]}$

$$\eta = \frac{W}{Q_H} = \frac{T_H - T_C}{T_H} \sqrt{1 + \frac{ZT_M}{T_C}} - 1, \quad (2)$$

were $T_H$ and $T_C$ are the temperatures at the hot and cold side of the material, respectively. For $ZT_M \to \infty$, equation (2) approaches the Carnot limit.

Layers of doped small organic molecules have been found to show an increasing $\sigma$ with temperature in the range of 30 to 100 $°C$, while $S$ stays almost constant $^{[12]}$. Hence, instead of $ZT_M$, the power factor $S^2 \sigma$ is used. This evaluation is performed for a variety of material combinations and doping concentrations. Data measured at $T_M = 40 {°}C$ are chosen, because that temperature was most reliable to control for all samples.

All four $p$-doped material combinations displayed in FIG. 1(a) show an increasing power factor with doping concentration and a saturation at high $C$. The largest values are obtained for MeO-TPD doped by F$_6$-TCNNQ with a maximum of $4.6 \cdot 10^{-3} \mu\text{W/mK}^2$. Several orders of magnitude higher values are obtained for $n$-doped C$_{60}$ samples, as plotted in FIG. 1 (b). This is attributed to the extraordinary high electron mobility of C$_{60}$ $^{[20]}$, determining the conductivity. Hence, C$_{60}$ is the most promising candidate for an organic small molecular TE device of all studied host materials. Applying the dopant $\alpha$-MeO-DMBI-I results in the highest power factors with a maximum of 22 $\mu\text{W/mK}^2$ at $C = 0.310$ MR ($= 9.8$wt%). At lower concentrations the dopant Cr$_2$(hpp)$_4$ results in the best power factors. Interestingly, the dopants Cr$_2$(hpp)$_4$, W$_2$(hpp)$_4$ and AOB yield almost identical values at $C > 0.200$ MR.

The highest value obtained for C$_{60}$ $n$-doped by $\alpha$-MeO-DMBI-I is comparable to the record reported for layers of C$_{60}$ $n$-doped by the inorganic dopant Cr$_2$CO$_3$ in an optimized sample geometry $^{[21]}$. For the purely organic doped layers of Pentacene $p$-doped by F$_6$-TCNNQ,
the current record reported in literature\cite{22} is one order of magnitude lower, despite employing an optimized geometry.

For intrinsic C\textsubscript{60}, the thermal conductivity has been reported to be almost temperature-independent between 30 and 300 K at a value around $\kappa = 10^{-3}$ W/cm K\cite{19}, which is 4 orders of magnitude lower than values observed for PEDOT:PSS\cite{23}. Assuming that $\kappa$ is mainly attributed to phonons and hence unaltered by introduction of dopant molecules, the value for intrinsic C\textsubscript{60} can be used to derive $ZT_M$, which is shown by the right hand axes of FIG. 1(b). A maximum of $ZT_M = 0.069$ at $T_M = 40$ °C is found for the sample of C\textsubscript{60} n-doped by 0.310 MR of O-MeO-DMBI-I. This value is 16% of the current record reported for PEDOT:PSS of $ZT_M = 0.42$ at room temperature\cite{3}.

As $\sigma$ was found to increase with temperature for all investigated samples, it is interesting to study the temperature dependencies of $ZT_M$ (equation (1)) and $\eta$ (equation (2)) for the sample of highest $ZT_M$. Here, the temperatures $T_H$ and $T_C$ are $T_M \pm \Delta T/2 = T_M \pm 2.5$ K, respectively, used during the Seebeck measurements.

FIG. 2 shows that both $ZT_M$ and $\eta$ show an approximately linear increase with $T_M$. Raising $T_M$ from 30 °C to 100 °C, $ZT_M$ almost doubles while $\eta$ rises by 50%. At a typical TE device operating temperature of $T_M = 60$ °C, the values of $ZT_M = 0.084$ and $\eta = 0.039$% are derived.

The efficiency reported here is rather low, compared to optimized polymer devices. Based on equation (2), it is expected that increasing $\Delta T$ should result in an efficiency gain. For example using $T_H = 100$ °C and $T_C = 20$ °C, hence $\Delta T = 80$ K instead of $\Delta T = 5$ K while keeping $T_M = 60$ °C and hence $ZT_M = 0.084$, should result in a 16-fold efficiency gain, reaching $\eta = 0.606$%. However, since in our setup it was impossible to measure at such a large $\Delta T$, this work requires a different experimental approach and will be done in future.

IV. CONCLUSIONS

This simple estimation of the thermoelectric properties of doped organic small molecules yields that the studied $p$-doped material systems generates rather low power factors, while $n$-doped C\textsubscript{60} is a promising candidate for organic TE devices. The best results are obtained for C\textsubscript{60} doped by low Cr\textsubscript{2}(hpp)\textsubscript{4} or high O-MeO-DMBI-I doping concentrations. Assuming the thermal conductivity of intrinsic C\textsubscript{60} is valid for doped layers as well, a maximum of $ZT_M = 0.069$ at $T_M = 40$ °C is derived, being 16% of the current record reported for optimized PEDOT:PSS layers. $ZT_M$ and hence $\eta$ is found to increase with $T_M$ for this material class. It is expected that applying a larger temperature difference of $\Delta T = 80$ K at $T_M = 60$ °C an efficiency of 0.606% can be reached. In a future work, the thermal conductivity of $n$-doped C\textsubscript{60} layers needs to be studied to verify these results.

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\[\text{FIG. 2. } ZT_M \text{ and } \eta \text{ vs. } T_M \text{ at } \Delta T = 5 \text{ K for a sample of C}_{60} \text{ } n\text{-doped by 0.310 MR of O-MeO-DMBI-I.}\]

\[\text{FIG. 2 shows that both } ZT_M \text{ and } \eta \text{ show an approximately linear increase with } T_M. \text{ Raising } T_M \text{ from 30 } ^\circ\text{C to 100 } ^\circ\text{C, } ZT_M \text{ almost doubles while } \eta \text{ rises by 50%. At a typical TE device operating temperature of } T_M = 60 \text{ } ^\circ\text{C, the values of } ZT_M = 0.084 \text{ and } \eta = 0.039\% \text{ are derived.}\]

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