FINAL REPORT

1 General Information

DFG reference number:	LE 747/66-1
Project number:	665556
Project title:	“Novel n-Doping Approaches for Organic Semiconductors“
Name(s) of the applicant(s):	Prof. Dr. Karl Leo
Official address(es):	Technische Universität Dresden, 01062 Dresden
Name(s) of the co-applicants:	--
Name(s) of the cooperation partners:	Heliatek GmbH
Reporting period (entire funding period):	01.07.2020 – 31.12.2023

2 Summary

Die Suche nach vielversprechenden n-Dotierstoffen für OPV-Module ist ein wichtiges Gebiet in der organischen Halbleiter Produktion. In diesem Bericht zeigen wir eine einfache Synthesestrategie zur Herstellung von Diaza-s-indacenen, welche vielversprechende Eigenschaften für die n-Dotierung aufweisen. Der Syntheseweg umfasst einfache Verfahren, wenige Schritte, günstige Materialien und hohe Ausbeuten und erfüllt somit alle Voraussetzungen für die Prozess-Hochskalierung. In diesem Bericht wurden zwei Verbindungen dieser Familie vorgestellt, die Aussicht auf eine Kommerzialisierung haben. Eines zeigt ein überzeugendes HOMO-Energieniveau zusammen mit einem sehr guten Leitfähigkeitsverhalten. Darüber hinaus entspricht seine Sublimationstemperatur den Anforderungen an einen OPV-n-Dotierstoff. In Zusammenarbeit mit Heliatek haben wir untersucht, ob diese Verbindungen in industriellen OPV-Stacks verwendet werden können.

Finding promising n-dopants for (organic photovoltaic) OPV is an important field in the organic semiconductor manufacturing. In this report, we show a straightforward synthetic strategy for

the preparation of diaza-s-indacenes which show very promising characteristics for n-doping. The synthetic route includes simple procedures, few steps, cheap materials and high yields, thus fulfilling all prerequisites for an up-scaling process. Two compounds of this family with promise for commercialisation were presented in this report. One shows a convincing HOMO energy level together with very good conductivity behavior. Additionally, its sublimation temperature is in line with requirement for an OPV n-dopant. In collaboration with Heliatek we assessed whether these compounds can be used in industrial OPV stacks.

3 Progress Report

Background and objectives of the project

Devices based on organic semiconductors offer many fascinating new applications since they allow lightweight, flexible electronics and optoelectronics which can be deposited on almost any substrate with comparatively simple methods. It has been shown that blending organic semiconductors with suitable dopants **/Walzer2007/** can increase the conductivity by orders of magnitude and allow better injection at the electrodes. Today, doping is already broadly used in organic light emitting diodes (OLED). It plays an important role in organic solar cells (OSC), also known as organic photovoltaic (OPV), in particular those based on evaporated layers. OPV hold the promise to overcome the limitations of traditional photovoltaics like high-temperature processing with environmentally critical materials, non-flexibility, non-transparency and large weight. The technology allows the coating of plastic substrates in a roll-to-roll process close to room temperature with extremely thin absorbers. This results in flexible modules that are lightweight (around 500 gm^{-2}), display homogeneous surfaces with adjustable color and can be semitransparent. Another important advantage is the superior efficiency when the device is working under diffused light conditions, for example on a cloudy day when the solar panel is not exposed to direct sunlight.

For efficient device operation, organic solar cells need good contact properties, efficient transport layers, and high built-in voltage. All these properties can be achieved by doped transport layers, containing a matrix compound with a suitable redox dopant. OPV very often applies at least one n-dopant in the electron transport layer, or as a pure interlayer promoting electron injection from a conductive layer into a semiconductor or from a semiconductor into another semiconductor. In contrast to molecular p-dopants which are in general air and moisture stable, highly efficient n-dopants are commonly sensitive to rapid degradation in air due to the low ionization energies required for electron donation. Additionally, the insufficient thermostability, especially concerning fast processing in industrial applications and the need of extremely high doping ratios required for sufficient performance as well as cumbersome multi-

step syntheses for some n-dopants (e.g. guanidine and phosphine imine derivatives) are not satisfactory.

As a world-leader in organic photovoltaics, Heliatek GmbH currently holds the world record for cell efficiency in an OPV based on small molecules and is the first company to start the market launch of large OPV solar films. Figure 1 illustrates the rollability and shows the application of their OPV devices.

Figure 1: The rollability of an OPV device of Heliatek (left) and its possible application on the wall of a building (right).

On the other side, we – the IAPP (TU Dresden) – have carried out pioneering work on the doping of small-molecule semiconductors in the last two decades. In the past few years, we have obtained a quantitative understanding of p-type doping **/Walzer2007, Tietze2012, Tietze2015, Tietze2018, Schwarze2018/**. Similarly, it was shown that n-doping is possible using similar principles **/Nollau2000/**. However, n-doping is, as mentioned above, much more challenging in terms of materials. An ideal n-dopant for OPV should have optimal optoelectronic properties, especially fine-tuned donor levels for doping, have a molecular structure that is complementary to C_{60} **/Schwarze2018/** and prevent the formation of large crystalline domains in the electron acceptor layer. Additionally, it should be air- and thermostable for good processability and its synthesis should economically viable and scalable.

The purpose of this project was the transfer of the academical know-how of n-dopants to the commercial sector. We have focused on the development of n-side dopants which should possess a high ionization potential, a suitable sublimation behavior and strong doping ability. Regarding this, we found that tetraamino diaza-s-indacenes are promising candidates. In close collaboration with Heliatek GmbH, we characterized compounds of this substance class in terms of their performance in single layers and solar cell devices to assess their application potential. Heliatek played a key role in this project: They helped to define the goals to achieve with the new n-doping materials and were involved the assessment of the new materials regarding their practical application. This includes preparation of organic solar cells and their evaluations with regard to all important parameters as process stability, efficiency, lifetime etc. Their technological leadership in OPV made them the ideal industry partner for this project.

Description of the project-specific results and findings

Based on DFT-Calculations, we had predicted some possible substance classes (among them: *WP1* cyclopropene imines and *WP2* diaza-s-indacenes) which should possess favorable donor strengths (see Figure 2). Additionally, the retrosynthetic analyses showed that these compound families are easily accessible.

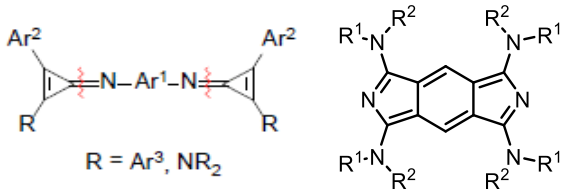


Figure 2: General structures of cyclopropenyl imines and tetraamino diaza-s-indacenes.

WP1: Cyclopropene Imines

Due to their promising characteristics for n-doping, we firstly attempted to synthesize cyclopropenyl imine derivatives like shown in Figure 3.

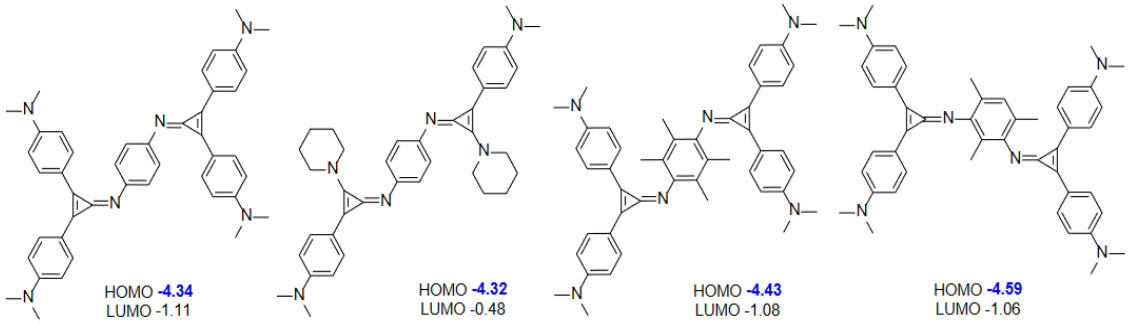
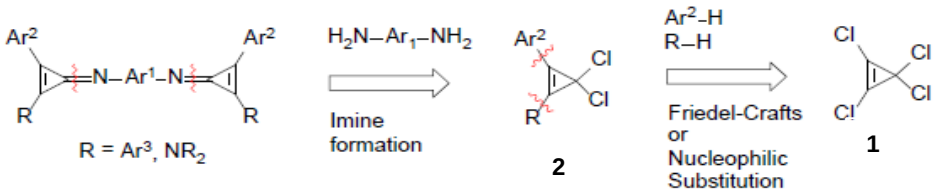


Figure 3: Selected cyclopropenyl imines and their calculated HOMO and LUMO levels.

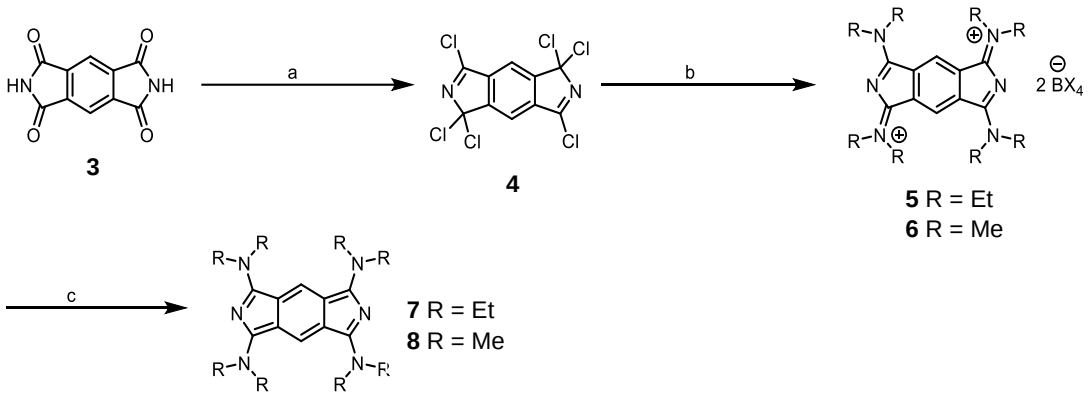
For the preparation of the cyclopropenyl imines we envisioned the synthetic strategy shown in Scheme 1. The synthetic approach started with the readily available tetrachlorocyclopropene **1**. Unfortunately, it was not possible to access any intermediates **2**, neither through Friedel–Crafts alkylation nor nucleophilic substitution of **2** with an appropriate substrate.



Scheme 1: Illustrating retrosynthetic pathway for the preparation of cyclopropenyl imines **2** proceeding from tetrachlorocyclopropene (**1**).

WP2: Tetraamino Diaza-s-indacenes

Because of the difficulties in the synthesis of the cyclopropenyl imines, we proceeded with the syntheses of the tetraamino diaza-s-indacenes. The synthesis of diaza-s-indacene **7** was already developed by Gompper **/Gompper1988/** however, the respective procedures were not described in detail. The synthetic approach starts with the chlorination of the commercially available pyromellitic diimide **3** to afford the hexachloro compound **4** which can be subsequently converted with an amine and a borate salt to obtain the respective compounds **5** and **6** over two steps (Scheme 2). In the final step, the reduction of the compounds **5** and **6** with potassium graphite led to the respective tetraamino diaza-s-indacenes **7** and **8**. Through this strategy we could synthesize a range of tetraamino diaza-s-indacenes of which the two compounds **7** (R = Et) and **8** (R = Me) were promising candidates.



Scheme 2: Synthesis of **7** and **8**; reagents and conditions: a) PCl_5 (4.3 equiv.), $POCl_3$, 120 °C 4 d, 88 %; b) for R = Et: 1. Et_2NH (10 equiv.), THF, rt, 2.5 h, 2. $NaBPh_4$ (3 equiv.), MeCN, rt, 10 min, 93 % (over two steps), for R = Me: 70% ; c) for R = Et: KC_8 (2.05 equiv.), THF, rt, 2.5 h, 50 %, for R = Me: 14%.

Indacenes **7** and **8** were obtained in an overall yield of 41 % and 10 %, respectively. In the following, the results of compound **7** are demonstrated. After synthesizing of indacene **7** successfully, its thermal properties were assessed. **7** sublimed nicely at 165 °C and was obtained in 81 % yield as green to purple crystals (Figure 4). Decomposition starts at about 230 °C according to the TGA. Both sublimation and decomposition temperature are suitable for industrial processing.

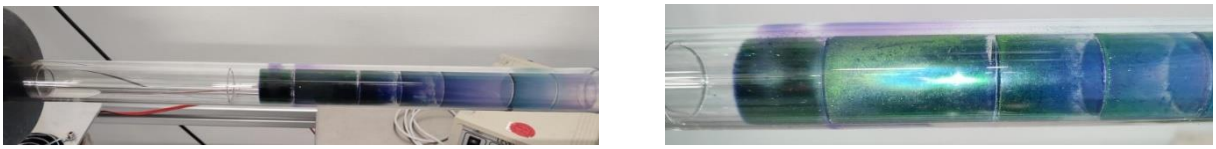


Figure 4: Purple to green crystals of Compound **7** after sublimation in the sublimation tube.

Subsequently, the sublimed material was analyzed by mass spectrometry, cyclic voltammetry (CV), differential scanning calorimetry (DSC) and conductivity tests were carried out. The mass spectrum showed the product peak at $[M+H]^+$ = 439.5 *m*/*z*.

The CV of **7** was measured in acetonitrile (T = 293 K, 0.1 M $[nBu_4N][PF_6]$; v = 200 mV/s; Pt-working, Ag-reference and Pt-counter electrode, see Figure 5).

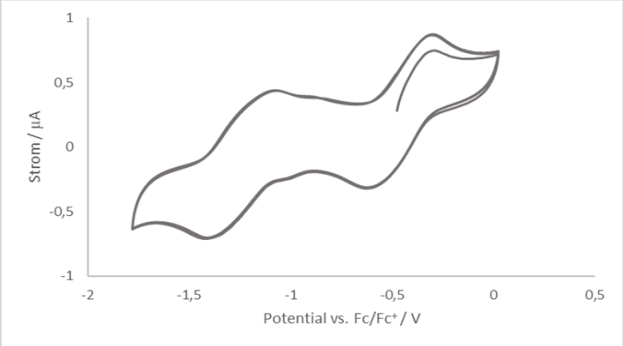


Figure 5: Cyclic voltammogram of **7** (potential vs Fc/Fc^+).

It is remarkable that the HOMO level determined by CV is in excellent agreement with the value calculated by DFT (see Table 1). The energy of the HOMO is quite high, meaning that it can easily donate an electron to the hole transport material.

$E_0^{(0/+1)}$ (CV)	–1.25 V
$E_0^{(+1/+2)}$ (CV)	–0.45 V
HOMO (CV)	–3.55 eV
Calculated HOMO (B3LYP/6-311G**SCRF)	–3.63 eV

Table 1: CV measured values as well as calculated and experimental HOMO energies of compound **7**.

The DSC of **7** showed melting at 115 °C without decomposition, indicated by solidification at 97 °C when cooling the sample down (Figure 6).

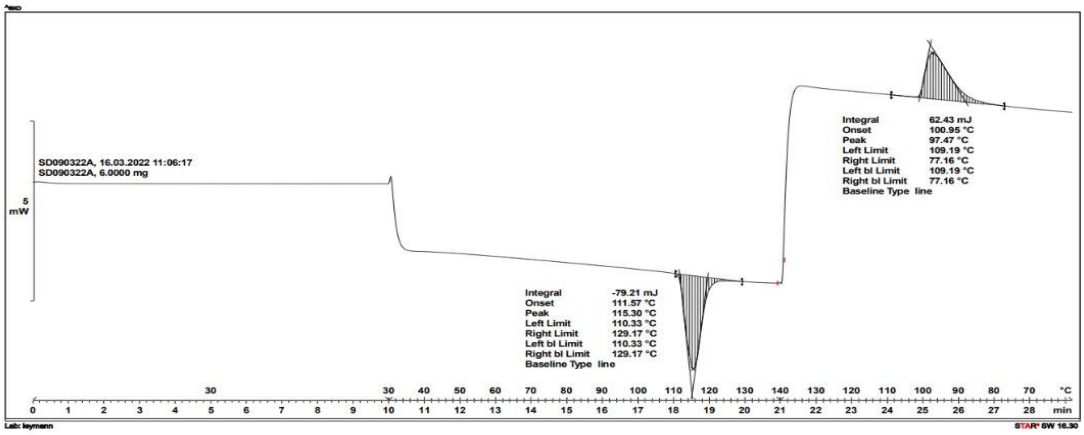


Figure 6: Two-step DSC diagram of compound **7**.

In addition, the conductivity was measured in different electron transport materials (Alq3, BPhen, CET-1, MH250, fullerene) with different loadings. Very promising conductivity values were obtained (see Table 2). Compound **8** was furthermore tested by Heliatek GmbH. However, it turned out that the conductivity of this material is too high. High conductivity of the n-side can lead to processing problems, particularly in patterning of the solar film. A lower conductivity by changing the substituents at the amino groups through more electron withdrawing candidates could solve this problem.

ETM	wt%	Conductivity [S/cm]
Alq3	5.0%	3.0E-07
Alq3	10.0%	2.3E-07
BPhen	5.0%	1.6E-07
BPhen	10.0%	4.8E-07
CET-1	5.0%	5.9E-05
CET-1	10.0%	8.8E-06
MH250	5.0%	4.3E-04
MH250	10.0%	6.8E-04
C_{60}	10%	1.6E+01

Table 2: Conductivity tests of **7** on different ETMs with different loading.

For the decomposition tests, we used **8** as a model compound. The sublimation temperature of **8** is 180 °C. The decomposition temperature is approx. 240 °C (determined by TGA). 240°C decomposition temperature is remarkably high for an extremely electron-rich n-dopant and holds promise for further derivatives. To assess the stability towards oxygen, **8** was exposed to air for 15 min. UV/vis spectroscopy before and after exposure (Figure 7) showed that no significant change, indicating that **8** is stable in air for brief periods of time. Furthermore, for the thermal stress tests, four samples of this material were sealed in ampules in the absence of air and were exposed at different temperatures (190, 210, 230 and 250 °C) for 5 days each. Decomposition of compound **8** was determined assessed via DSC or UV/vis. The UV/vis spectra were measured in toluene. Heating of **8** to 190 or 210 °C for 5 days did not cause significant change in the respective DSC traces and the UV/vis spectra were essentially identical before and after heating (see Figures 8–11).

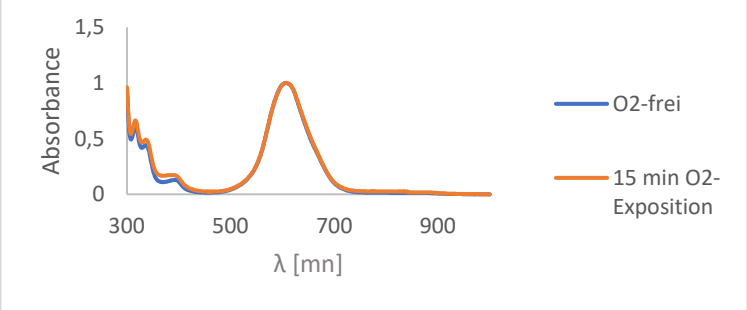


Figure 7: UV/vis spectra of untreated **8** (blue) and the same material exposed to oxygen for 15 min (orange).

Figure 8: Ampules filled with compound **8**: a) before (left) and after (right) 5 days at 190 °C; b) before (left) and after (right) 5 days at 210 °C.

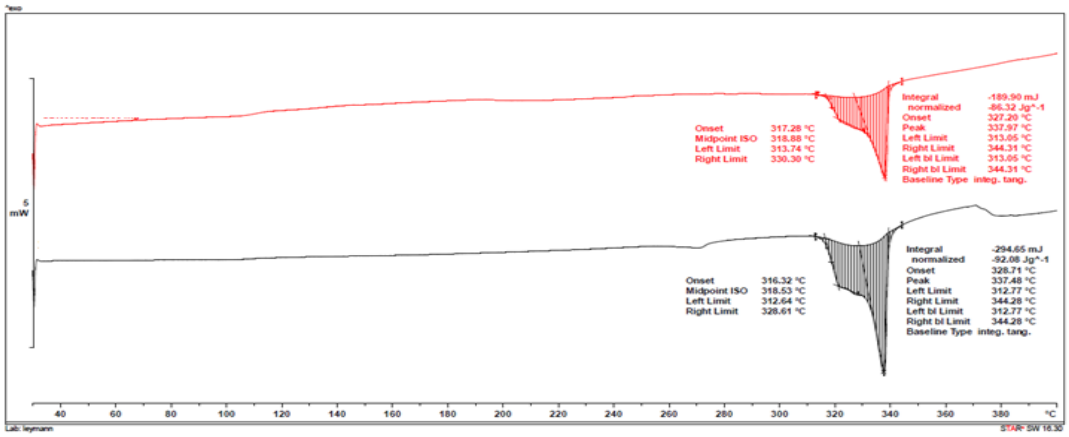


Figure 9: DSC traces of compound **8**: before (top) and after (bottom) heating to 190 °C for 5 days.

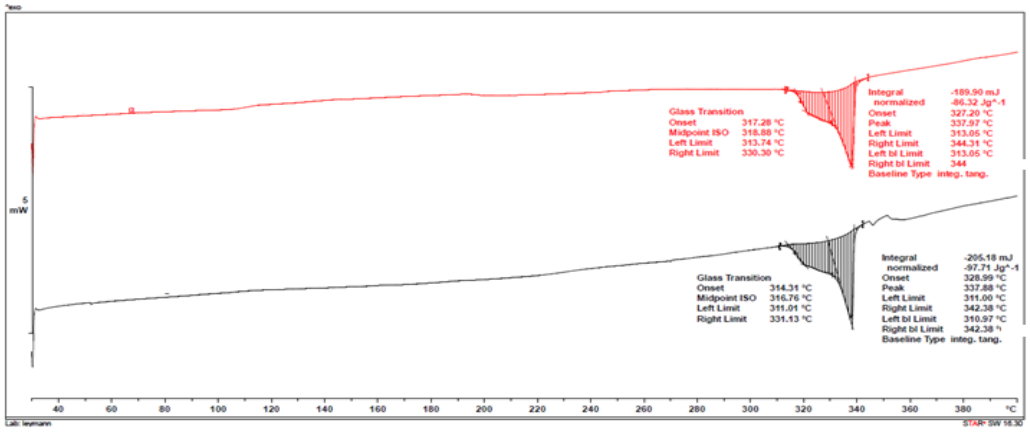


Figure 10: DSC traces of compound **8**: before (top) and after (bottom) heating to 210 C for 5 days.

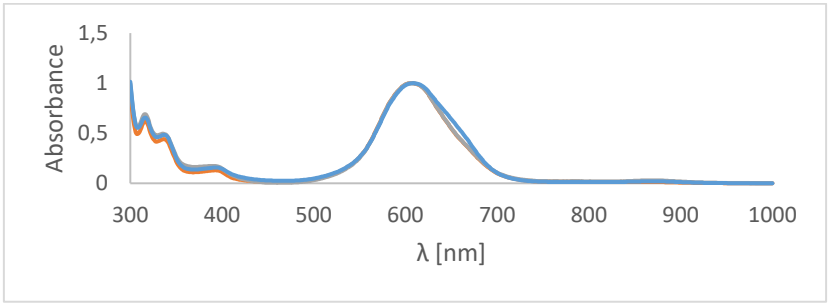


Figure 11: UV/vis spectra of compound **8**; untreated (orange); after 5 days at 190 °C (grey) and 210 °C (blue).

However, heating **8** to 230 or even 250 °C for 5 days led to decomposition judging its DSC traces, while the UV/vis spectrum of that sample which was treated at 230 °C showed no significant differences (Figures 12–15). No UV/vis spectrum of the sample heated to 250 °C could be measured as the material was not soluble in toluene anymore.

Figure 12: Ampules filled with compound **8**: a) before (left) and after (right) 5 days at 230 °C; b) before (left) and after (right) 5 days at 250 °C.

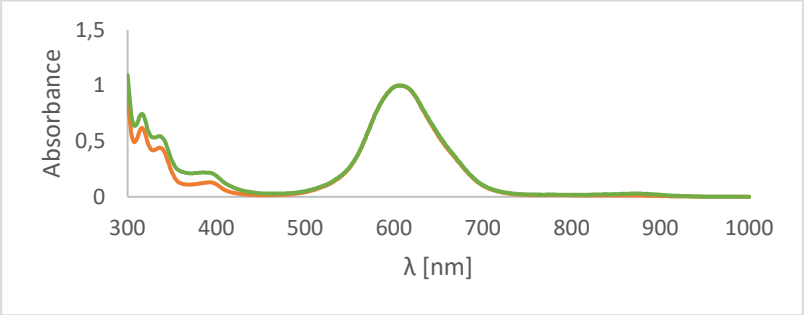


Figure 13: UV/vis spectrum of compound **8**; untreated (orange) and after 5 days at 230 °C (green).

The DSC trace of the sample that was heated to 230 °C for 5 days, a slight shift of the onset of approximately 10 °C was observed (see Figure 14). After heating compound **8** to 250 °C for 5 days, the DSC trace changed completely and no melting point was observed (Figure 15).

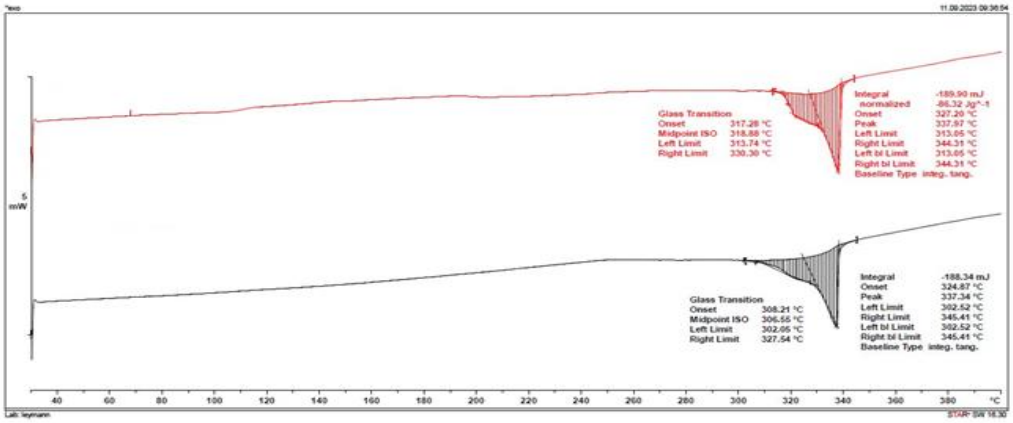


Figure 14: DSC trace of compound **8**: before (top) and after (bottom) 5 days at 230 °C.

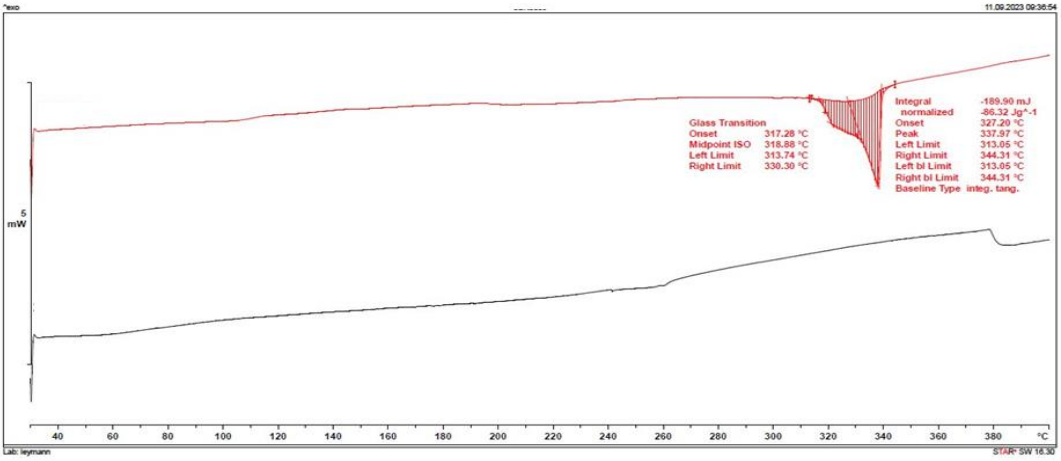


Figure 15: DSC trace of compound **8**: before (top) and after (bottom) 5 days at 250 °C.

Bibliography

/Gompper1988/ R. Gompper et al., Angew. Chem. 1988, 100, 875-878.

/Nollau2000/ A. Nollau et al., Appl. Phys. 2000, 87, 4340-4343

/Schwarze2018/ M. Schwarze et al., ACS Appl. Mater. Interfaces 2018, 10, 1340-1346.

/Tietze2013/ M. Tietze et al., Phys. Rev. B 2013, 88, 085119.

/Tietze2015/ M. Tietze et al., Adv. Funct. Mat. 2015, 25, 2701-2707.

/Tietze2018/ M. Tietze et al., Nat. Commun. 2018, 9,1182.

/Walzer2007/ K. Walzer et al., Chem. Rev. 2007, 107 (4), 1233–1271.

4 Published Project Results

So far, no results were published. However, we expect that our work will soon lead to scientific publications.