About the Influence of the Molecular Structure of selected classes of small molecules on their thermal behavior

Dr. Andreas M. Richter, Dr. Volker Lischewski, M. Felicetti

Sensient Imaging Technologies GmbH, Chemiepark Bitterfeld-Wolfen, Areal A, Emil-Fischer-Straße 3

Abstract

The molecular structure influences the thermal behavior of HTM. For OLED the glass transition temperature and evaporation temperature are critical. We report how changes in structure cause changes on both parameters. The results may be of interest for chemists when they design new molecule structures for OLED.

1. Introduction

It is well known, that materials for organic light emitting diodes (OLED) and other photoelectronic applications, often suffer from the drawback, that the desired amorphous state of the layers is not sufficiently stable and limits the life-time of the devices. The reason is that the material undergoes micro-recrystallization, especially when the operation temperature of the device is higher than the glass transition temperature, T_g, of the layer material. The result is decreasing luminance, lower luminous efficiency, dark spots and the devices finally die. It is known that the morphological behavior is strongly influenced by the molecular structure of the components used [7].
It is one of the goals chemists have when they design OLED compounds to reduce recrystallisation by increasing the glass transition temperature [5, 6]. That can be done by the introduction and variation of specific substituents as described below.
In case of SM-OLED (Small Molecule ODED) the devices are made by vacuum deposition. For this process the evaporation behavior and the thermal stability of compounds are critical parameters one should draw on conclusion when designing new molecules.

2. Changing the Glass Transition Temperature

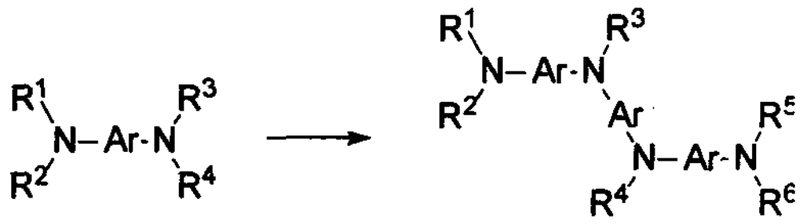
HTM (Hole Transport Materials) mostly are built of triarylamine units. The glass transition temperature, and therefore in many cases the stability of their glass state as well, can be improved by relatively simple structural changes:

- "Oligomerisation" of the triarylamines (2 … 5 triarylamine units per molecule)
- Symmetric or asymmetric introduction of bulky substituents into the molecule
- Introduction of bridges into the molecule in order to make the structure more rigid

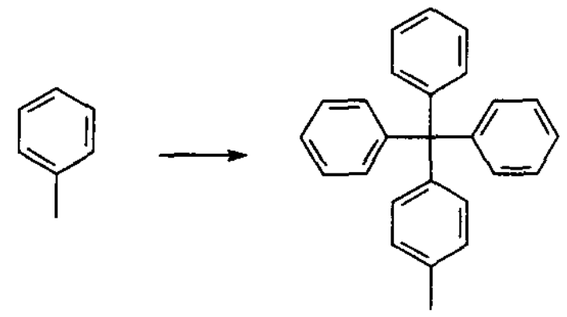
2.1. Selected Molecular changes

In order to investigate the influence of changes in the molecular structure of some selected HTM we have carried out the following types of modifications and studied their effects on the glass transition temperature:

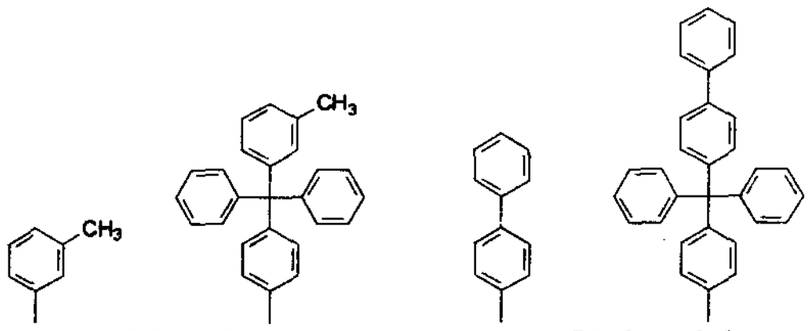
- transition from triarylamine dimeres to tetrameres:



- replacement of phenyl by trityl phenyl:

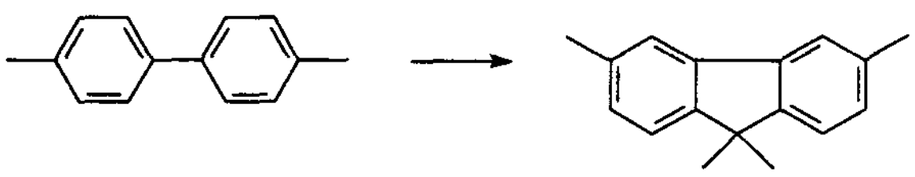


- introduction of additional substituents:



m-Methyl *Biphenylyl*

- bridging of the biphenylen unit:



Some examples of the various molecules synthesized and characterized are summarized in Tables 1 - 5.

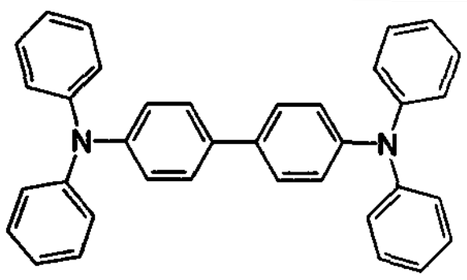
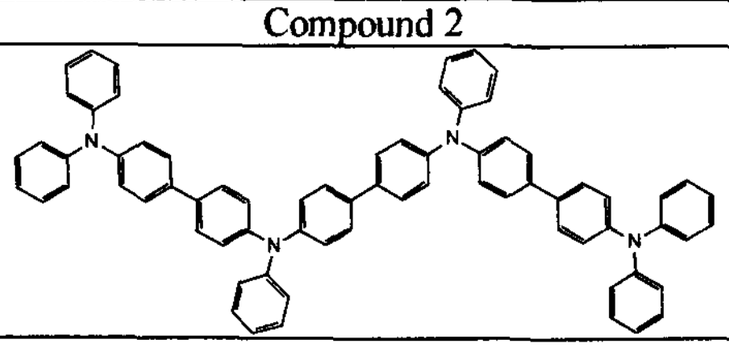
Table 1: Transition from Dimers to Tetrameres				
Compound 1	T_g	Compound 2	T_g	T_g - shift
	74		144	70

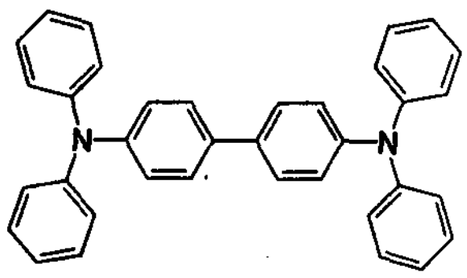
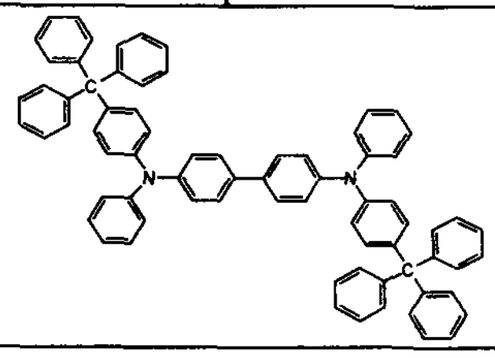
Table 2: Introduction of the Trityl-phenyl-group				
Compound 1	T_g	Compound 2	T_g	T_g - shift
	74		144	+ 70

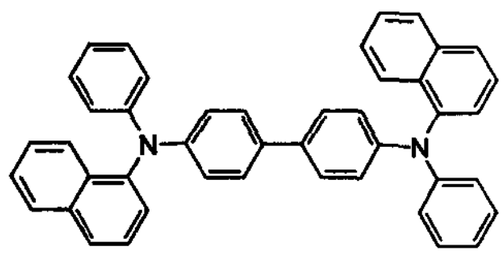
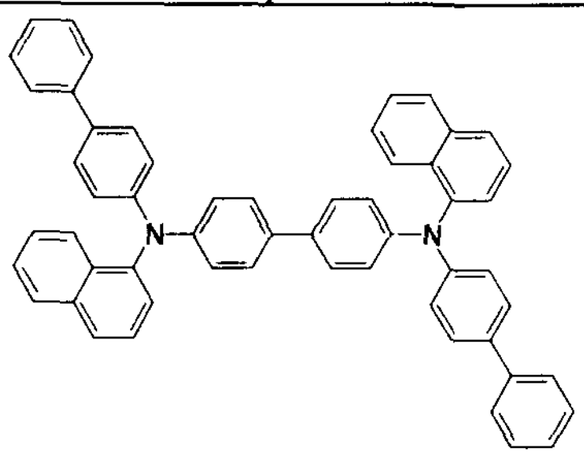
Table 3: Introduction of substituents: Biphenylyl				
Compound 1	T_g	Compound 2	T_g	T_g - shift
	100		136	+ 36

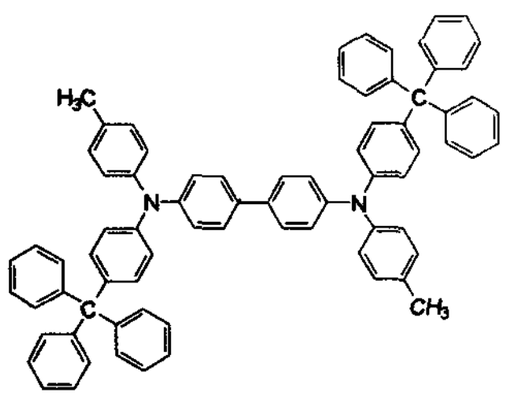
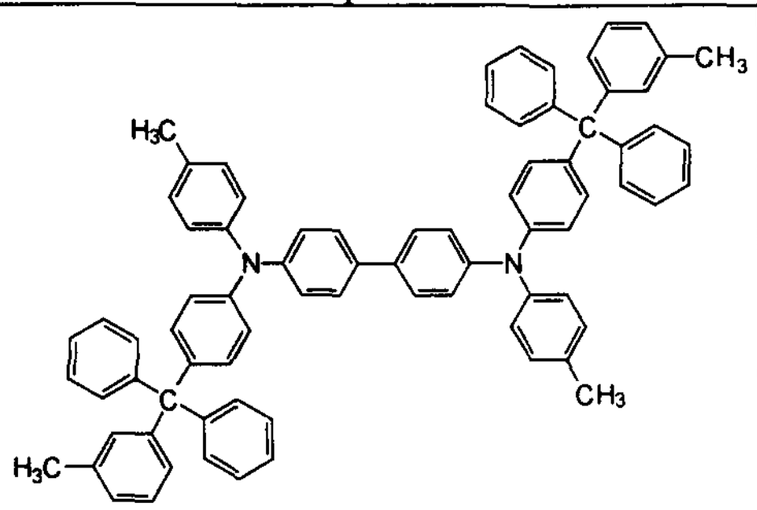
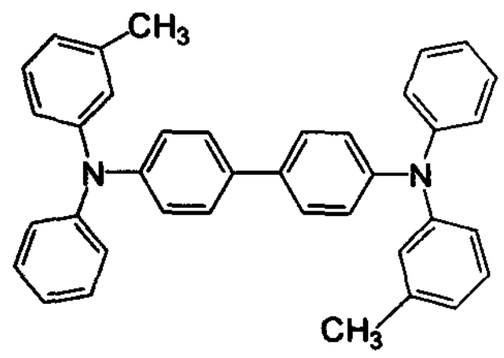
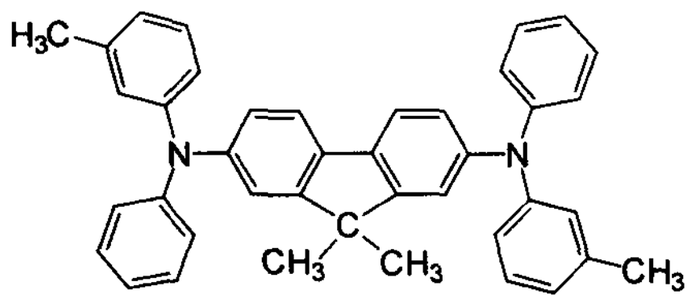
Table 4: Introduction of substituents: Methyl				
Compound 1	T_g	Compound 2	T_g	T_g - shift
	148		128	- 20

Table 5: Bridging of biphenylene center unit				
Compound 1	T_g	Compound 2	T_g	T_g - shift
	62		78	+ 16

2.2 Influences on the Glass Transition Temperature

The examples in Tables 1 - 5 show already that the structural modifications have an influence on the T_g value. The more detailed discussion will show that the structural changes influence the glass transition temperature in a qualitatively foreseeable manner. The introduction of bulky spacefilling structures (Trityl-, Biphenylyl-; see tables 2 and 3) causes a strong increase in T_g. Also it is possible to increase the glass transition temperature by introduction of bridging groups that increase the rigidity of the molecules or just making the molecules bigger by a formal "dimerization" (table 1).
On the other hand - small molecular units, like methyl groups, cause an „internal plasticizer effect" which results in a decrease of T_g.
Surveying our results closer, you can find, that the T_g shift caused by a certain structural change is not a constant value but varying within a quite broad range (table 6).

Table 6: Structural Changes and T_g Shift

Structural change	T_g-shift
Introduction of Trityl phenyl group	+ 55 ... +74
Introduction of Biphenylyle group	+ 3 ... + 36
Transition Dimere → Tetramere	+ 55 ... + 70
Bridging	+ 4 ... +16
Introduction of the Methyl group	- 9 ... - 20

These results show that our original idea to create an incremental model failed. There is no simple correlation where the shift values of T_g could be simply added. The extent of T_g shift in general depends on the basic molecular structure of the molecule which undergoes the mentioned structural change. This means, the contribution to T_g shift caused by any structural change, depends on the original level of the glass transition temperature before the introduction of the change.
We qualitatively found that the values of T_g are converging to a maximum value T_g^{max}.

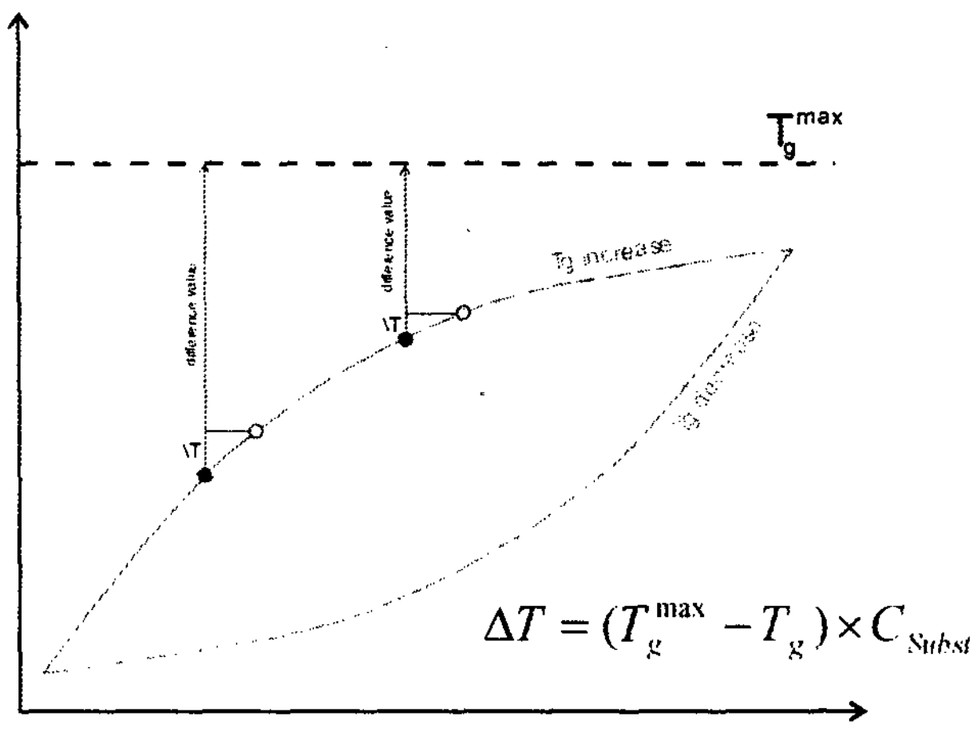


Figure 1: Structural T_g shift and T_g^{max} (schematically)

The averaged increase in T_g caused by a certain structural change, will be the smaller, the higher the T_g-value is without the structural change. This means, that a structure which is already distorted to large extent can be further distorted only by heavy means.
Contrary to this are the effects of methyl groups. They cause a plasticising of the glassy structure and therefore a decrease in T_g. The higher the original T_g is, e. g. the more rigid the structure without methyl groups, the larger is the extent of the decrease in T_g caused by the introduction of a methyl group.

3. Correlations Between Structure and Evaporation Temperature

We investigated the evaporation behavior of selected OLED materials in order to find if there is a correlation to their molecular parameters.
The experiments were carried out as thermogravimetric measurements under high vacuum conditions. A sample of about one milligram was enclosed in a thermogravimetric cell, then the pressure was reduced to 10^{-6} Torr and during a linear temperature rise up to 500°C the mass loss was recorded.
As a result we obtained graphs like the following:

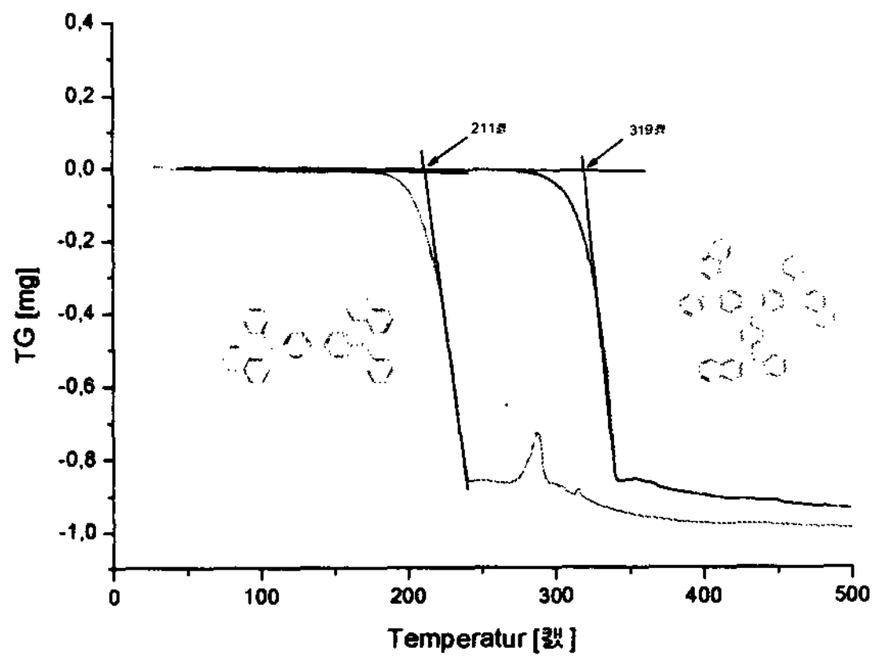


Figure 2: High vacuum thermogravimetric plot

We found that – in a first approximation – the temperatures of the beginning vaporization clearly depends on the molecular mass of the samples. Structural properties seems to have a minor influence.

The measurements have been carried out in mg-scale. Bulk-effects should be negligible under these conditions but for sublimation in preparative scale or evaporation within the device production process this should be drawn in conclusion. Indeed, under our conditions we found a quite constant difference of 60-80°C between the "micro-sublimation" in TGA and preparative sublimation (up to 1-kg-quantity). This has to be drawn in conclusion when designing new molecules.

There are different strategies to increase the T_g value. They can lead to bigger molecules. The bigger the molecule the higher the evaporation temperature will be and – as a negative side effect – also evaporation speed is reduced which may have a bad impact on productivity of the device manufacturing.

We have sublimed many members of different compounds classes. Figure 3 shows that in first order evaporation temperature and molecular weight correlate in most of the cases.

But there is a certain temperature limit of approx. 500°C which is reached when the molecular weight of a molecule exceeds 1500 au. That has to be drawn in conclusion when thinking about new structures for SM-OLED.

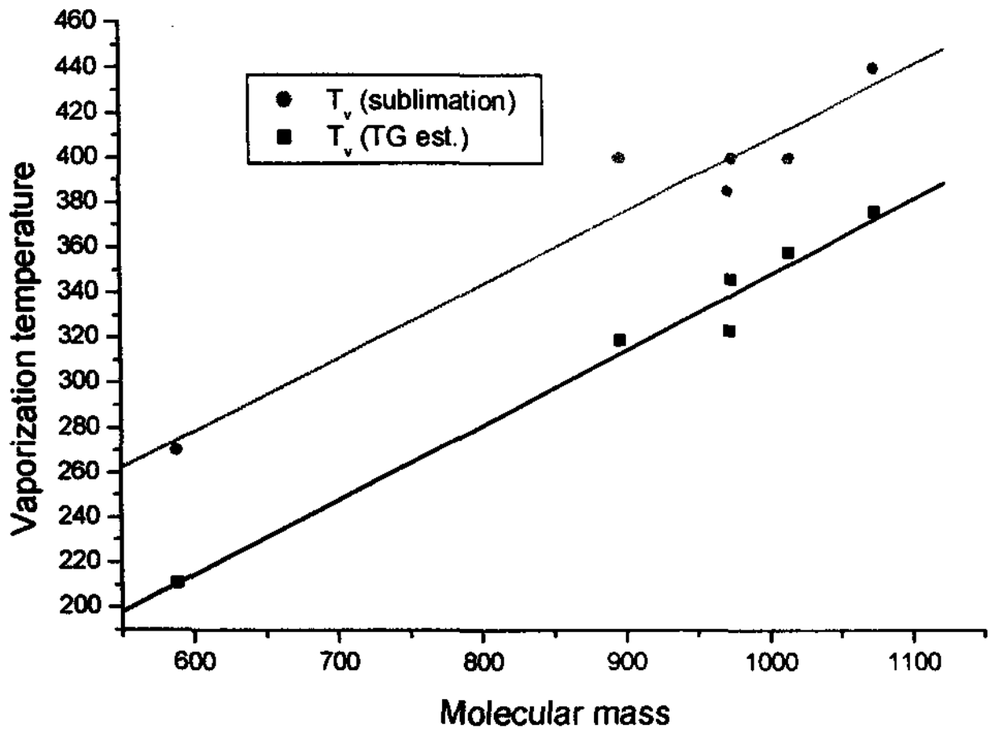


Figure 3: Vaporization temperature of CTL substances vs. molecular mass

It should be interesting to investigate if there is any influence of the polarity of the molecule onto its vaporization temperature. In the future we plan experiments to determine the dipole characteristics of our samples and after this it should be possible to come to conclusions which are more detailed concerning the influences onto the vaporization temperature.

4. Acknowledgement

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5. References

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