A New Class of High Mobility Hole Transport Materials

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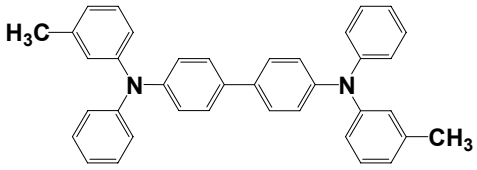
Abstract

We present a new class of Hole Transport Materials. After the discussion of the design concepts of hole transport materials with enhanced hole mobility, we will report on the physical properties of selected candidates, hole mobilities as well as the electrophotographic performance of the materials in two layer organic photoreceptors

Introduction

Polyarylamines like TTA, TPD and Stilbene derivatives (see figure 1) are the mostly used Hole transport materials in negative charged two layer organic photoconductors.



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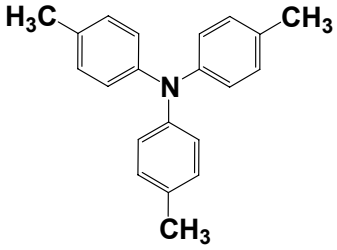
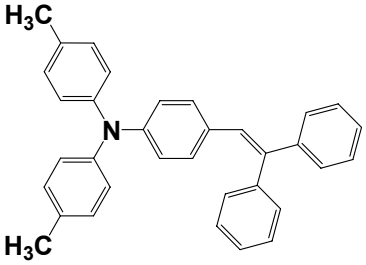


TTA Sensient ST 1093



Stilbene Sensient ST 1374

Figure1: *Common Hole Transport Materials*

Their properties such as redox potential (see table 1) – to be in the range of the most common Charge Generation Material TiOPc (Titanyl Phthalocyanine), their solubility in solvents suitable for the industrial production of polycarbonate layers, and the possibility to provide nearly trap-free high purity materials are the main reasons for the success of these materials.

Table 1: Properties of Hole Transport Materials

	$E_{1/2}$ [V]	Hole Mobility [cm²/Vs	Reference
TTA	0.85	1*10-6	[1]
TPD	0.78	9*10-6	[1]
Stilbene	0.82	1*10-5	[2]

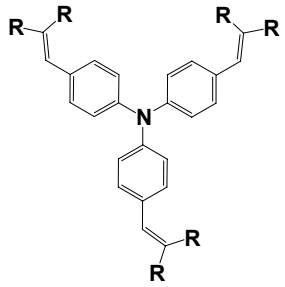
For a long time the range of charge carrier mobilities was in compliance with the needs of the printer and copier industry. With the development of faster and smaller commercial printing devices, the electrophotographic cycle time has come down significantly

In order to achieve this shorter cycle time Hole Transport Materials should have hole mobilities clearly higher than 10^{-5} cm²/Vs.

The objective of our investigations was to find new Hole Transport Materials on the base of our main products TPD and TTA.

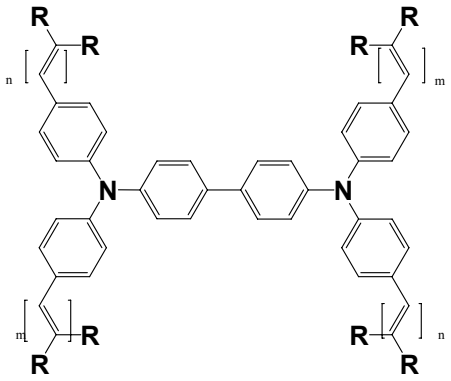
The comparison of the structure of TTA, TPD and Stilbene with their hole mobilities and the resultsof a literature and patent analysis [1, 3, 4] lead us to the hypothesis that an increase of the delocalized pi-electron systems of the hole transport materials should improve their hole transport properties. The unexpected high mobility of Stilbene lead us to the decision to achieve this by incorporation of styryl groups into the common Hole Transport Materials.

We started our screening experiments with the modification of TTA and TPD (Fig. 3, 4):



n...1,2 R... Aryl

Figure2: *Concept 1 based on TTA*



R...H, branched Alkyl Aryl, substituted Aryl
n...0,1,2
m...1,2

Figure3: *Concept 2 based on TPD*

Later on we broadened our focus by introducing structural units which cause planarization along the π electron chain and hence increase hole mobility and enhance the layer forming properties (**Concept 3,** for details see reference [5]).

Experimental

Synthesis of the Hole Transport Materials

The improved Hole Transport Materials were synthezised by a modified Horner-Wadsworth-Emmons Olefination [6] (see figure 4).

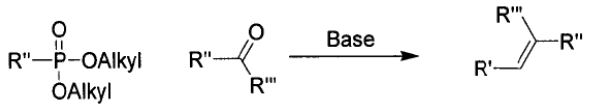


Figure4: *Standard Synthetic Route*

Especially for Concept 1 and Concept 2 compounds it is difficult to provide the intermediate aldehydes. Therefore, we use for these compounds a proprietary synthesis route via ketal intermediates (see figure 5, for details see reference [7]).

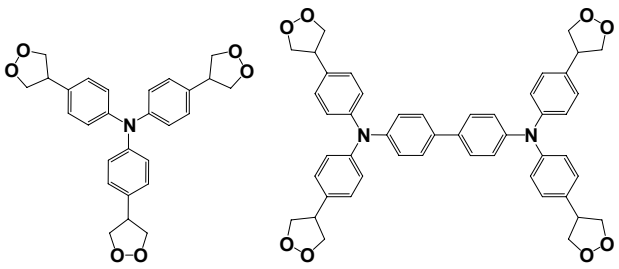


Figure5: *Ketal Intermediates for alternative Synthetic Route*

Electrophotographic Properties

All samples of the concepts 1, 2 and 3 were tested against several criteria like solubility in solvents used in OPC layer production and their performance? in the OC device.

In table 2 the electrophotographic results of he best candidates of the three concepts are listed.

The electrophotographic characteristics of the new materials were tested in a double layer system as described in the following:. An aluminized polyester film with a polyamide blocking layer was coated with a Titanyl Phthalocyanine/PVB layer. Subsequently, this Charge Generation Layer was coated with the Hole Transport Layer containing the new materials to be tested in a polycarbonate binder. For reasons of solubility, the test materials were employed as 70:30 a blend with Stilbene.

The electrophotographic performance was analyzed as follows: The dark decay is monitored for 3 s. The residual potential is determined at a light intensity of 4.5 μJ/cm², and we use the Energy required for a 50% drop of the initial voltage as a measure for the sensitivity.

Table 2: Electrophotographic Test Results

	Charge Accept. [-V]	Dark Decay [V]	Residual Potential [-V]	$E_{0.5}$ [μJ/cm²]
TPD	675	33	<10	0.100
Stilbene	840	40	<10	0.110
C1 +Stilbene	830	50	<10	0.113
C2 +Stilbene	730	60	<10	0.112
C3 +Stilbene	750	58	<10	0.123

Hole Transport Properties

The Hole mobility was measured by the Xerograpic Time of Flight method (XTOF) [8] with a proprietary XTOF measurement device. The Hole Mobility was measured at a charge potential of 24V/μ

Table 3: Hole Mobility Results [9]

	Layer Thickness [μm]	Hole Mobility 10 e^{-6} [cm²/Vs]
TPD	26.7	9.3
TPD+Stilbene	27.4	13.1
C1+Stilbene	26.4	46.4
C2+Stilbene	30.7	31.3
C3+Stilbene	31.0	88.1

Results and Discussion

We have found that there are in all concepts candidates with a good electrophotographic performance. Best mobility results in combination with an excellent electrophotographic performance were found by introducing of above mentioned planarization principle (Concept 3).

Samples of high mobility Hole Tranport Materials following Concept 3 can be obtained from the authors upon request.

References

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