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SYNTHESIS AND PROPERTIES OF NOVEL HOLE TRANSPORT MATERIALS FOR ELECTROLUMINESCENT DEVICES

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Abstract: We synthesized low molecular weight triphenyldiamines (TPDs), novel 1,3,5-tris(diarylamino)benzenes (TDABs), polymeric triphenyldiamines and insoluble triphenylamine networks based on tris(4-ethynylphenyl)amine as hole transport materials for electroluminescent displays. The HOMO energy values as determined from cyclic voltammetry measurements for TPDs and TDABs are between -4.97 and -5.16 eV. By using a polymeric TPD as hole transport layer and tris(8-quinolinolato) aluminium as emitter, LEDs with an onset voltage of 3V and a luminance up to 900 cd/m^2 were obtained under ambient conditions.

INTRODUCTION

Recently, a lot of research has been devoted to the development of new organic materials for light emitting devices. In addition to the requirements such as thermal stability, photostability and good film-forming properties, these materials should exhibit electrochemical stability and reversible redox behavior. Triphenylamine derivatives are well

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known hole transport materials with high charge transport mobilities. The low molecular weight triphenyldiamines (TPDs) which are frequently used in light emitting devices (LEDs) have low glass transition temperatures (T_g) and very recently a variety of new derivatives with high T_gs have been developed (Refs. 1-4). For application in organic displays, these materials should not only possess high T_gs and high recrystallization temperatures (or ideally no recrystallization from melt), but also low ionisation potentials (or low HOMO energy values), so that the hole injection barrier from anode can be minimized. The lower the charge injection barrier, the better the long term durability of the device due to a lower joule heat produced at the electrode organic interface (Ref. 5).

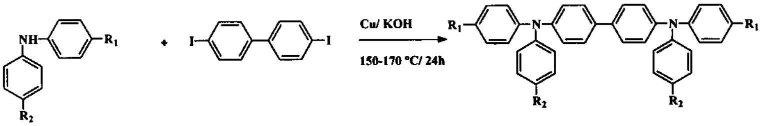
Our aim was to synthesize different triphenylamine derivatives having low ionisation potentials and high T_gs as hole transport and in some cases additionally as emitter materials. In this paper, we report on the synthesis and characterization of low molecular weight triphenyldiamines (TPDs), novel 1,3,5-tris(diarylamino)benzenes (TDABs), polymeric triphenyldiamines (poly-TPDs) and insoluble triphenylamine networks based on tris(4-ethynylphenyl)amine (TEPA).

Cyclic voltammetry (CV) is an important tool to study the electrochemical stability, reversible redox behavior, to get informations on the HOMO and LUMO values of hole and electron transporting materials and to estimate the barriers for charge injection. With the help of an internal redox standard, ferrocene/ ferrocenium (Fc) for each measurement, the HOMO energy levels were calculated from redox potentials (Ref. 6). A knowledge of the energy levels facilitates the tailored fabrication of LEDs with a defined recombination zone for the holes and electrons.

RESULTS AND DISCUSSION

Low molecular weight triphenyldiamines (TPDs) and 1,3,5-tris(diarylamino)benzenes (TDABs)

The following triphenyldiamines (TPD **1-3**), were synthesized according to an Ullmann condensation by reacting the corresponding diarylamines with aromatic diiodides in presence of copper and potassium hydroxide in soltrol at about 170°C under nitrogen atmosphere. The yields for these HTL materials were between 50 to 60% (Scheme 1).



1-3

Scheme 1: Synthesis of Triphenyldiamines **1-3**

Tab. 1. CV and DSC data of TPDs **1-3**

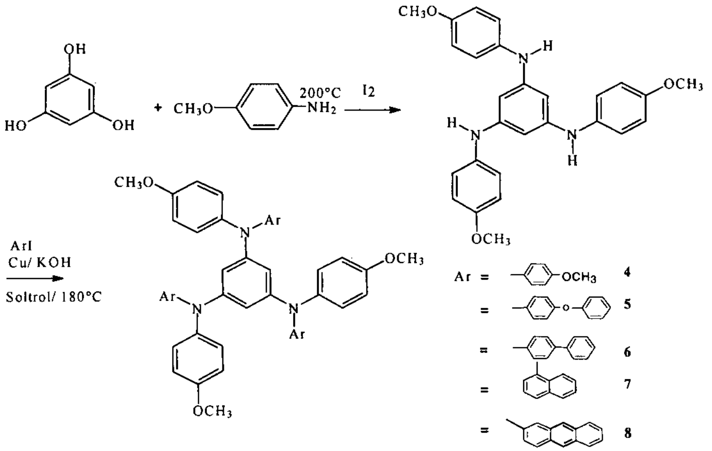
TPDs	R_1	R_2	Tg [°C]	T_m [°C]	E_{ox1} vs.Ag/AgCl [V]	HOMO [eV]
1[a)]	H	H	70	228	0.79	-5.15
2[b)]	H	OCH_3	56	153	0.69	-5.06
3	OCH_3	OCH_3	67	169[b)]	0.59	-4.97

[a)] compound 1 and 2 have been reported in the literature (Ref.5.)

[b)] T_m observed only in the first heating and not present in further heatings (10K/min).

Their thermal (DSC) and electrochemical (cyclic voltammetry, CV) properties were determined. From oxidation potentials obtained from CV, the HOMO values were calculated (Ref. 6). The TPDs possess T_gs in the range of 60-70°C. The HOMO values increase with increasing number of methoxy substitutents and reach value of -4.97 eV in case of **3**.

The TDABs **4-8** were synthesized by Ullmann coupling from aryl iodide and 1,3,5-tris(arylamino)benzene, which was synthesized from phloroglucinol and aromatic amine by Knoevenagel reaction (Scheme 2). In comparison to the known methyl and halogen substituted phenyl derivatives of TDABs (Refs. 7,8), the new aryl derivatives (**7** and **8**) possess higher T_gs. CV measurements show that these compounds have very low HOMO values in the range of -4.98 to -5.16 eV. Compounds **7** and **8** are low molar amorphous triphenylamine derivatives which act both as HTL and emitter.



Scheme 2: Synthesis of 1,3,5-tris(diarylamino)benzenes (TDABs **4-8**)

In order to estimate the charge injection barrier with respect to the anode (ITO) and cathode (eg. Al, Mg/Ag) in LEDs, the HOMO values of the materials were determined by taking the value of -4.8eV as the HOMO level for Fc with respect to zero vacuum level (Ref. 6). The redox potentials were measured at a Pt electrode in millimolar solutions in carefully dried acetonitrile or THF containing 0.1 molar tetrabutylammonium hexafluorophosphate (TBAPF6) versus a Ag/AgCl reference electrode in a three electrode cell configuration. TPDs show two reversible oxidations, whereas TDABs exhibit three oxidations of which at least the first oxidation is reversible. Generally, the oxidation potential values decrease with increasing methoxy substitution.

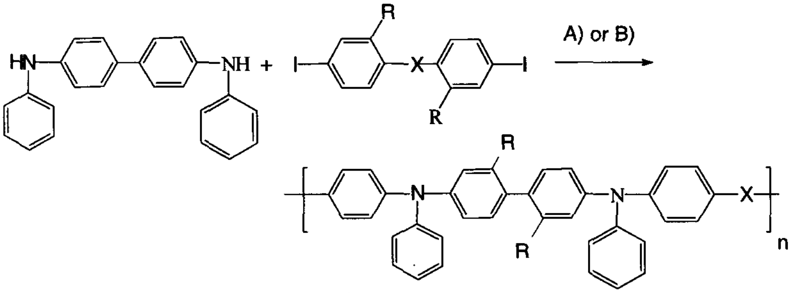
In the TPD series, the tetramethoxy TPD (**3**) has the highest HOMO value of -4.97eV. Also the hexamethoxy substituted TDAB **4** has a HOMO value of -4.98 eV. In the case of TDABs **5-8**, all of them have higher oxidation potentials and the HOMO values are in the range of -5.07 to -5.16 eV. In general all these materials have a low hole injection barrier to ITO. All these compounds have high LUMO values (> -2.4 eV), enabling them to act as good electron blocking materials.

Tab. 2. DSC and CV data of 1,3,5-tris(diarylamino)benzenes

TDABs	**Tg** [°C]	**Trecry.** [°C]	**Tm** [°C]	**ABS λmax** [nm]	**Eoxı** vs.Ag/AgCl [V]	**HOMO** [eV]
4	-	130	182	290	0.64	-4.98
5	54	-	148$^{a)}$	310	0.72	-5.07
6	85	135	200	330	0.76	-5.11
7	88	-	192$^{a)}$	300(360)	0.77	-5.13
8	123	-	$^{b)}$	325(425)	0.72	-5.16

$^{a)}$ T_m observed only in the first heating and not present in further heatings (heating and cooling rate 10 K/min); $^{b)}$ no T_m observed up to 320°C

Polymeric triphenyldiamines (poly-TPDs)



A): Cu/KOH/in Soltrol/170°C/24h

B): Cu/K_2CO_3/18-Crown-6/in o-Dichlorobenzene/170°C/16h

Scheme 3. Synthesis of poly-TPDs **9-11**

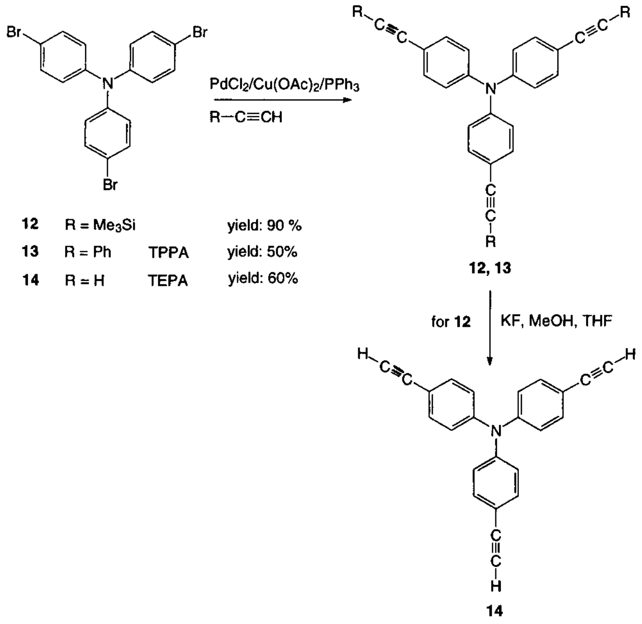
Using a polymer reaction via an Ullmann coupling (route A) between a bis(sec-amine) and diiodide, polymeric TPDs with molecular weights in the oligomeric range were synthesized. By an improved synthetic method (route B), poly-TPDs **11** with a higher molecular weight could be obtained. The poly-TPDs are soluble in THF, cyclohexanone, DMF etc. and form good films by spin-coating from solution. The HOMO values for these materials are between -4.94 and -5.16 eV and they posses high T_gs in the range from 130 to 206°C.

Tab. 3. CV and thermal data of poly-TPDs

Poly-TPDs	X	R	Tg [°C]	M_n [g/mol]	HOMO [eV]
9	-	H	133	1800	-4.94
10	-	CH_3	131	1400	-4.91
11	-O-	H	206	16000	-5.16

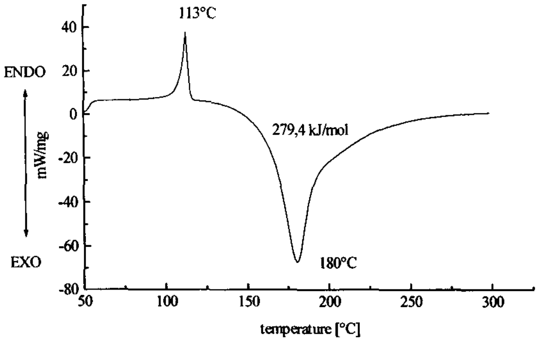
To demonstrate the applicability of these materials in LEDs, we fabricated typical devices , ITO/HTL/Alq3/Al. For example, a device ITO/poly-TPD **11**(80nm)/Alq3(40nm)/ Al(300nm) emits 100 cd/m^2 for a current flow of 16mA/cm^2 and this device had a maximum brightness of 900 cd/m^2 at an applied voltage of 18.5 V(I= 225 mA/cm^2).

Triphenylamine Networks



Scheme 4: Synthesis of tris(4-ethynylphenyl)amine TEPA

A novel hole transporting system, based on thermally curable acetylene-units, the tris(4-ethynyl phenyl)amine [TEPA] was synthesized from tris-(4-bromophenyl)amine via the Pd-catalyzed Heck-Reaction with trimethylsilylacetylene. A similar material containing phenylacetylene-units was also synthesized in the same way (Scheme 4).
TEPA/TPPA-mixture (9:1) could be thermally crosslinked between 160 and 180°C as shown by the DSC-curve (scheme 5) below. The cured films have a high transparency and are stable at temperatures up to 500°C. They are insoluble in common solvents and can be used in multilayer LED devices as hole transporting material.



Scheme 5: Thermal properties of a TEPA/TPPA (9:1)-mixture.

To conclude, triphenyldiamines could be optimized for minimum hole injection barrier with respect to ITO. Novel Tris(diarylamino)benzenes with high T_gs and low HOMO values were synthesized and are found to be good hole transporting materials. We synthesized polymeric TPD with high molecular weight which is soluble in common solvents such as THF, $CHCl_3$. LEDs with an onset voltage of 3 V and a luminance up to 900 cd/m^2 under ambient conditions were obtained. Insoluble triphenylene networks were developed to be used as an insoluble hole transport material allowing the preparation of a second layer by conventional solution casting techniques.

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