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SPIRO LINKED COMPOUNDS FOR USE AS ACTIVE MATERIALS IN ORGANIC LIGHT EMITTING DIODES

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Abstract: Spiro-linkage of low molecular weight entities as a new structural concept for the design of new active materials for electroluminescent applications is presented. These spiro linked compounds result in nonpolymeric organic glasses with high thermal stability as can be derived from their high glass transition temperatures (T_g), and characterized by differential scanning calorimetry. Blue emitters based on spiro linked oligophenyles are presented. These compounds are soluble in common organic solvents and show high photoluminescence quantum efficiency in the solid state and high morphologic stability with glass transition temperatures up to 250°C. Charge transport materials based on spiro linked versions of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) for electron transport, and spiro linked versions of triphenyldiamin derivatives (TPD) for hole transport show improved morphologic properties with nearly unchanged electronic properties compared to the parent compounds.

High quality amorphous films can be prepared with the spiro compounds by vapor deposition as well as by simple spin coating.

INTRODUCTION

In recent years, there has been an interest in exploring organic materials for electroluminescent applications in view of the versatility in molecular systems accessible through design and synthesis. For the fabrication of organic electroluminescence (EL) devices, both single crystals (Ref.1) and glasses (Ref.2) have been attempted to avoid problems associated with grain

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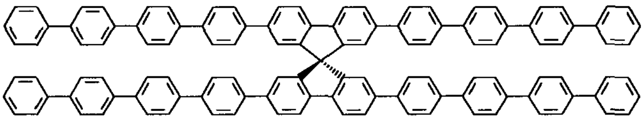
boundaries present in polycrystalline materials. Since it is easier and less expensive to prepare glasses than single crystals the recent interest is focused on glassy materials. One approach is to use conjugated polymers (Ref. 3) or to incorporate requisite moieties as part of polymer structures that readily form glasses (Ref. 4). An alternative approach is to design structures of relatively low molecular weights that possess glass-forming abilities. Although the glass-forming property of polymeric systems is well known, the formation of stable glasses is an exception in low molar mass systems, especially if high glass transition temperatures (T_g) are required. o-Terphenyl (Ref. 5) and 1,3,5-tris(naphthyl)benzenes (Ref. 6) are rare examples of low-molecular weight organic compounds that form stable glassy states above room temperature. Recently, Shirota and co-workers synthesized novel 'starburst' shaped molecules with high T_g (Ref. 7). Amorphous or quasi-amorphous films of several organic compounds used in EL devices can be formed by vapour deposition onto a cooled substrate, but usually they suffer from low morphologic stability. Recent studies have focused on improving the durability of EL devices and several studies have shown that the degradation of the EL devices is attributable to morphological changes resulting from the thermal instability of the amorphous organic layers used in the EL devices (Ref. 8). This morphological change will be promoted by the movement of molecules due to rapid molecular motion near the glass transition temperature (T_g). Therefore, beside the imperative optical and electronic properties of a low-molecular organic material used in an EL device, a high T_g is required to have a long lifetime.

RESULTS AND DISCUSSION

A surprisingly variable concept for the design of amorphous electroluminescent materials with high T_g is based on the specific introduction of spiro centers into defined low molecular, oligomeric and polymeric structures. The basic idea is to use known structures which already have the desired electronic properties and to modify their steric demand in such a way that their processability and morphologic stability is improved while their electronic properties are retained. A very promising structural concept is to use only one additional carbon atom to connect two molecular entities with the desired electronic properties by a spiro-junction (Ref. 9). This concept has several benefits; the steric demand of the resulting rigid structure results on one hand in a higher solubility leading to solution processable materials; on the other hand the unwieldy structure also surpresses very effective excimer formation frequently observed in the solid state (Ref. 10), therefore the light emitting properties should be stabilized.

Blue Light Emitting Materials

Using this concept, we synthesized blue light emitting materials in form of symmetrically spiro-linked oligo-phenyls up to spiro-linked deciphenyls (Spiro-10Φ **1**). The two molecular halves of the spiro compound are orthogonally arranged due to the sp^3 spiro-carbon atom (Ref. 11).



1 (Spiro-10Φ)

p-Deciphenyl, the parent compound of Spiro-10Φ is not described in literature, but is expected to be completely insoluble in common organic solvents. Therefore it is surprising that the spiro-linkage of two of such chains by one additional carbon atom results in a material which is solution processable, despite the fact, that the molecular weight is doubled. The solubility of **1** in chloroform at room temperature is about 10 g/l, and even higher at elevated temperatures. This high solubility which is found for all spiro linked *p*-oligophenyls, and which is several orders of magnitude higher than the solubility of the parent *p*-oligophenyls, is a result of the steric demand of these structures. The spiro linked *p*-oligophenyls are colorless with strong emission in the blue range of the visible spectrum.

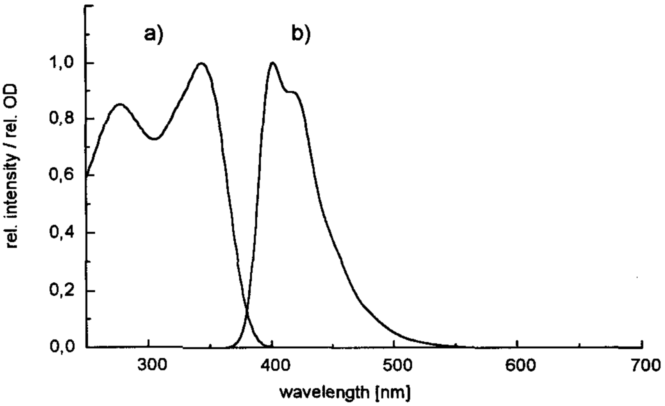
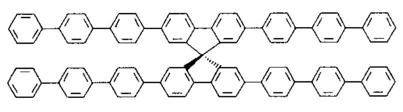
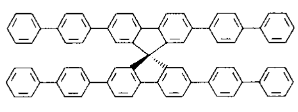


Fig. 1: Absorption and photoluminescence spectrum of **1** (Spiro-10Φ) in dichloromethane a) absorption spectrum; b) photoluminescence spectrum ($c<10^{-6}$ M, excit. 350 nm)

The absorption and photoluminescence spectra of **1** (spiro-10Φ) in dichloromethane are given as an example in figure 1. The absorption is dominated by two strong peaks at 278 nm and 344 nm, the emission spectrum shows a peak at 402 nm with a shoulder at 420 nm. With this spiro-linked oligophenyls, transparent colorless films can be fabricated by a simple spin coating process or by vapor deposition showing blue photoluminescence with a high quantum yield. In figure 2 the photoluminescence spectra of spiro-8Φ **2** and spiro-6Φ **3** in dilute solution and in solid state are shown.



2 (Spiro-8Φ)



3 (Spiro-6Φ)

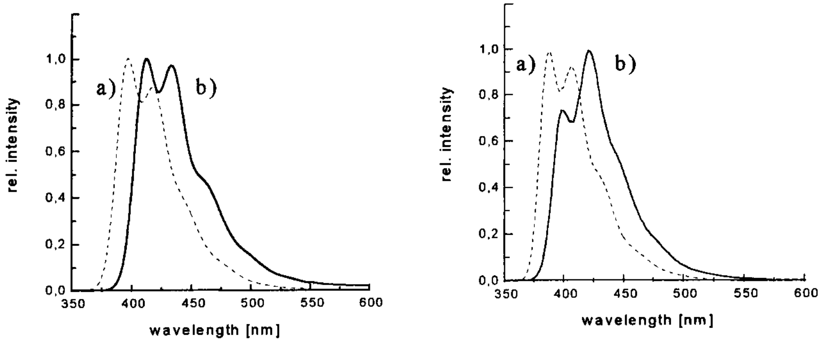


Fig 2: Photoluminescence spectra of **2** (Spiro-8Φ) and **3** (Spiro-6Φ)
a) dilute solution in dichloromethane, $c<10^{-6}$ M;
b) solid film on quartz (prepared by spin coating).

Photoluminescence quantum yield of **1** (spiro-10Φ), **2** (Spiro-8Φ) and **3** (Spiro-6Φ) in dilute solution is 0.95 and no concentration quenching effects could be observed. The photoluminescence spectrum of the solid film on quartz is comparable to the spectrum in dilute solution. The amorphous nature of a spin-coated thin film of **3** (spiro-6Φ) has been proven by e-beam diffraction. For a morphologic stability of these films under thermal stress a high glass transition temperature is required for the materials.

Figure 3 shows differential scanning calorimety (DSC) thermograms of **3** (Spiro-6Φ). A crystalline sample shows a sharp melting point, peaking at 408°C. An amorphous sample with crystalline parts shows a glass transition at 212°C followed by an exothermal signal peaking at 271°C due to the recrystallization of the amorphous part of spiro-6Φ, induced by the crystalline part. If the sample has been melted completely at 450°C it only shows a glass transition at 212 °C on subsequent cooling or heating cycles without recrystallization.

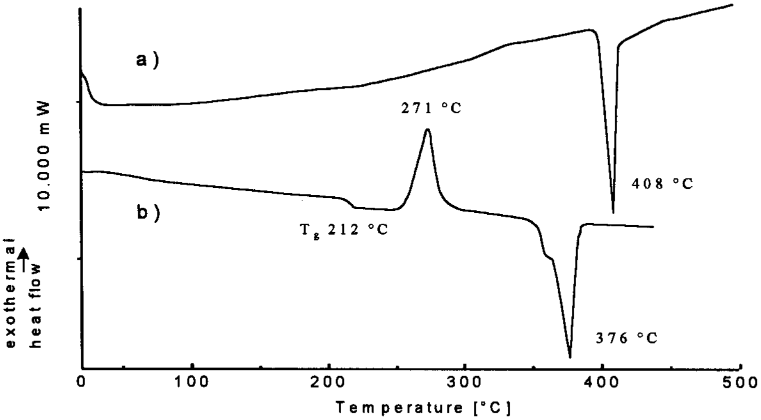


Fig. 3: Differential scanning calorimetry of **3** (spiro-6Φ) , heating rate 5°C min^{-1}
a) crystalline sample; b) amorphous sample with crystalline parts.

The same behavior was found for **2** (spiro-8Φ), if the sample was first heated to melt at 500°C (melting signal peaking at 440°C). When the melt sample is cooled down with 10°C/min it spontaneously forms a supercooled liquid state, and then changes into an amorphous glassy state. When the amorphous glassy sample obtained by cooling down to room temperature with 10°C/min is again heated, a glass-transition phenomenon is observed at 243°C, where the specific heat and other physical properties change. No exothermic peak due to crystallization is observed up to 500°C. Only the glass transition phenomenon is observed when the cycle of cooling and heating is repeated. For this high melting temperatures also a high thermochemical stability is required. The high thermochemical stability of the spiro linked *p*-oligophenyls is demonstrated with the thermogravimetric analysis of **2** (spiro-8Φ) as shown in figure 4. The thermal decomposition under a stream of nitrogen starts above 550°C and the temperature for 5% weight loss is 585°C at a heating rate of 10°C/min.

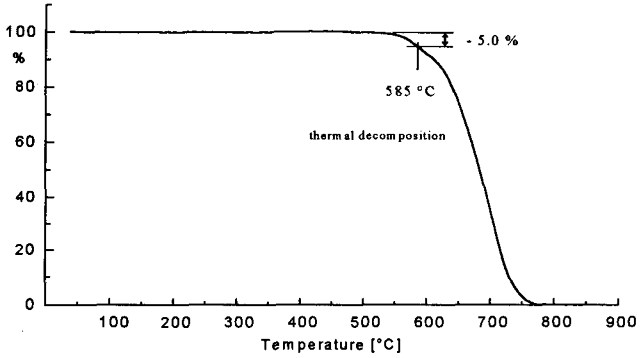
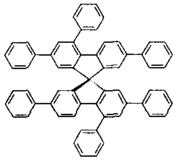


Fig. 4: Thermogravimetric analysis of **2** (spiro-8Φ); heating rate 10 °C/min, under nitrogen.

Naito and Miura reported relations between thermodynamic parameters and amorphous properties of nonpolymeric organic dye glasses and suggested, that molecules preferably used for amorphous films should have a symmetric globular structure with a large molecular weight and small intermolecular cohesion (Ref. 12). According to this, globular spiro-linked oligophenyls have been synthesized as shown with the structures **4, 5** and **6.**



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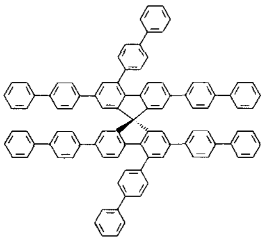

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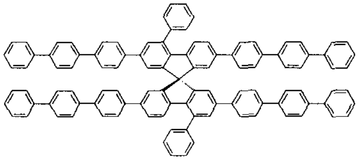


6

In contrast to phenyl substituted *p*-oligophenyls, where the additional phenyl substituents induce a twisting and therefore disturb the conjugation along the main chain, the additional two phenyl or biphenyl units in **4, 5** and **6** can not disturb the conjugation along the two *p*-oligophenyl chains. The reason is that the central two phenyl rings in each chain are fixed planar by the spiro-carbon. Therefore the electronic properties of the globular molecules **4, 5** and **6** can be compared with their spiro linked *p*-oligophenyl counterparts. The absorption and photoluminescence spectra of **6** in dichloromethane is given as an example in figure 5.

The absorption spectrum shows two peaks centered at 277 nm and 348 nm, and the emission spectrum shows a peak at 401 nm with a shoulder at 421 nm.

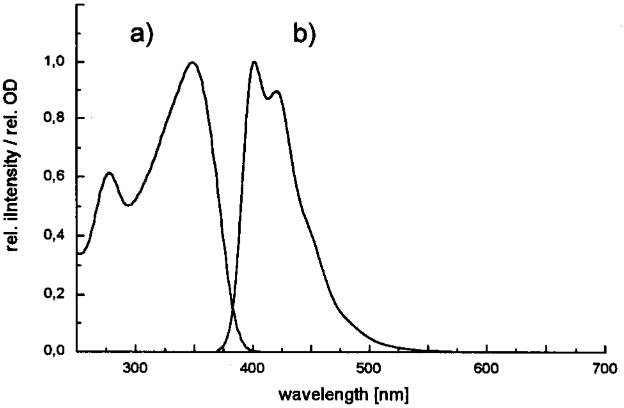


Fig. 5: Absorption and photoluminescence spectrum of **6** in dichloromethane

a) absorption spectrum; b) photoluminescence spectrum (c<10^{-6} M, excit. 350 nm)

The higher steric demand of this globular compounds results in a higher solubility compared to the spiro linked *p*-oligophenyls. As in the case of the spiro-linked *p*-oligophenyls, transparent colorless films can be fabricated with these compounds by a simple spin coating process or by vapor deposition, showing blue photoluminescence with a high quantum yield.

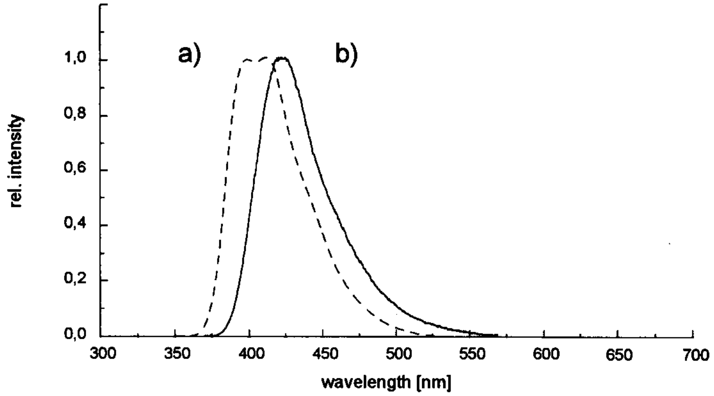


Fig.6: Photoluminescence spectra of **5**;

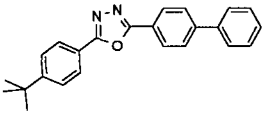
a) dilute solution in dichloromethane, c < 10^{-5} M;

b) solid film on quartz (prepared by spincoating).

In figure 6 the photoluminescence spectra of 5 in dilute solution and in solid state are shown. Transparent colorless films can be prepared with **5** and the glass transition temperature is determined at 236°C. The photoluminescence quantum yield in the amorphous state is 0.48 and shows even after thermal annealing neither a decrease in fluorescence intensity nor any detectable excimer emission. This results shows that by usig the spiro-concept not only the glass transition temperature can be increased, thereby stabilizing the amorphous glassy state, but also the luminescent properties in the solid state can be influenced positively.

Electron transport material

The spiro-concept has also been extended to materials with explicit charge transport properties. Based on the well known electron transport material 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) 7 (Ref. 13), with compound **8** (spiro-PBD) we designed a spiro-linked version with nearly unchanged electronic, but improved morphologic properties.



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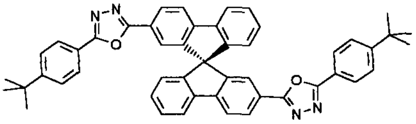

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As presented in figure 7, the spiro-PBD **8** shows a glass transition at 163°C, whereas the parent compound PBD 7 melts already at 138°C. The reason for his higher morphologic stability of the amorphous state of **8** (spiro-PBD) compared to 7 (PBD) is on one hand the steric demand of the spiro-molecule and on the other hand the higher melting point of **8** (spiro-PBD, melting signal peaking at 337 °C) due to the higher molecular weight. This means that in this case the spiro-linkage leads to a glass transition temperature even higher than the melting point of the parent PBD compound. The electronic properties are nearly unchanged by the spiro-linkage as demonstrated with the cyclic voltammogram of the reduction of spiro-PBD **8** in THF/(0.1M)TBAHFP shown on the right hand of figure 7. Spiro-PBD **8** can reversibly accept four electrons. The first voltammetric wave at -2.46 V vs. ferrocene/ferricinium corresponds to the reversible uptake of two electrons resulting in a stable bis(radikal anion) as proved by spectroelectrochemistry, and differs only by 20 mV from the first reduction potential of PBD 7 under the same conditions. In figure 8 the absorption and the photoluminescence spectrum of **8** is shown and compared with the photoluminescence spectrum of 7.

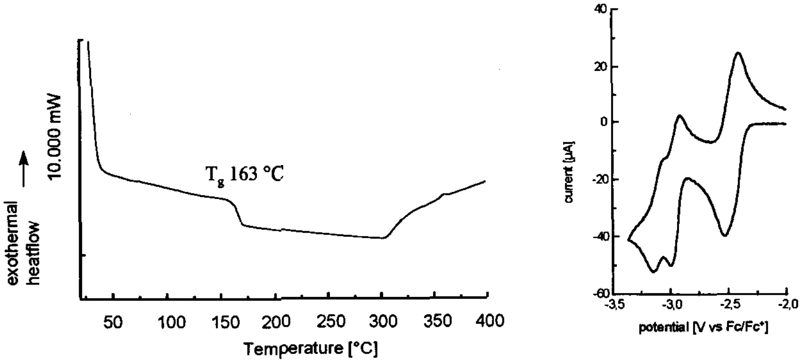


Fig. 7: left: DSC thermogram with glass transition of 7 (spiro-PBD); heating rate 10°C/min, after melting the sample at 400°C and rapid cooling down
right: cyclic voltammogram of 7 in THF/TBAHFP 0.1M

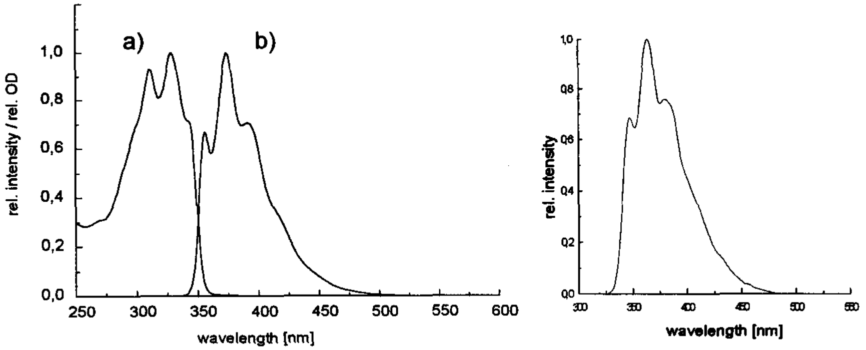
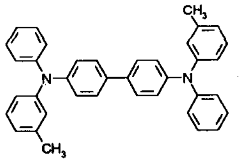


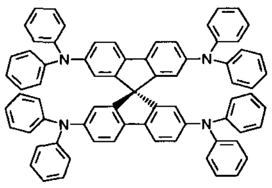
Fig. 8: left: Absorption and photoluminescence spectrum of **8** (spiro-PBD) in dichloro methane; a) absorption spectrum; b) photoluminescence spectrum
right: photoluminescence spectrum of 7 (PBD) in dichloromethane

Hole transport material

A charge transport material often used as hole transport material is N,N'-Diphenyl-N,N'-(*m*-tolyl)benzidine **9** (TPD) (Ref. 14) but this material suffers from the very low morphologic stability of the amorphous films due to the low T_g (60°C) of this material (Ref. 8). Analogous to PBD 7 and spiro-PBD **8** we synthesized spiro-linked versions of structures similar to TPD. Compounds **10** is given as example.



9 (TPD)



10

The spiro-linkage again results in an increased T_g. Figure 9 shows a differential scanning calorimety (DSC) thermogram of **10**. The sample was first heated to melt at 300°C. When the melt sample is cooled down with 20°C/min it spontaneously forms a supercooled liquid state, and then changes into an amorphous glassy state. When the amorphous glassy sample obtained by cooling down to room temperature is heated again, a glass-transition phenomenon is abserved at 133°C. Then an exothermic peak due to crystallization is observed starting at 185°C, followed by an endothermic peak due to melting peaking at 275°C. This is a similar exothermic pattern corresponding to the crystallization as observed in starburst triarylamin molecules (Ref. 15). Compared to TPD which shows a glass transition at 60°C the glass transition of **10** occurs at a temperature more than 70°C higher and thus demonstrates the higher morphologic stability of **10**.

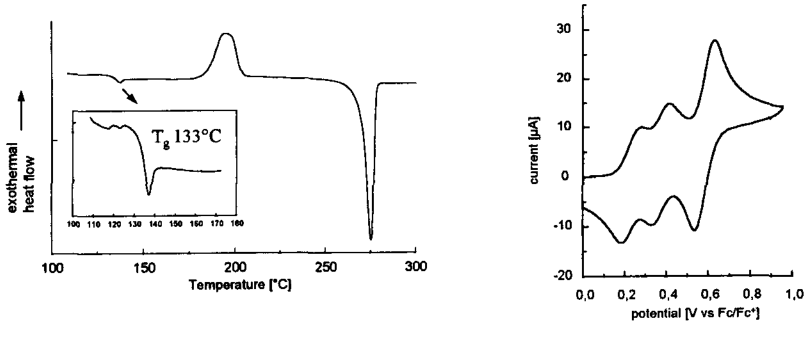


Fig. 9: left: DSC thermogram with glass transition of **10**, heating rate 20°C/min, after melting the sample at 300°C and cooling down to room temperature.
right: cyclic voltammogram of **10** in dichloromethane/TBAHFP 0.1M;

On the right of figure 9, the cyclic voltammogram of the reversible oxidation of **10** in dichloromethane/(0.1M)TBAHFP is shown. The molecule can be oxidized reversibly to the tetracation. The first two signals correspond to the oxidation to the radical cation and the bis(radical cation) with $E_{1/2}$ at 0.230 V and 0.370 V vs. ferrocen/ferricinium. Three cation and tetra cation formation are merged in the third wave at 0.585 V. The first oxidation of **10** occurs about 0.110 V more positive than the first oxidation of TPD **9**. This can be explained by a more effective conjugation along the central biphenyl unit due to the planarization caused by the spiro carbon. If used as hole transport layer in contact with an ITO electrode the barrier hight of **10** should be 110 mV lower than with TPD **9**.

CONCLUSION

Based on the spiro linkage of low molecular weight compounds new blue light emitting materials with high quantum efficiency in the solid state have been synthesized. Charge transport materials based on spiro linked well-known compounds result in new materials with nearly unchanged electronic but improved morphologic properties. The spiro compounds presented form stable nonpolymeric organic glasses with high glass transition temperatures, usually associated with amorphous polymers. High quality amorphous films of these luminescent or charge transport materials can be prepared by conventional spin coating as well as by vapor deposition. These novel materials are now tested as emitting layers and as charge injection and charge transport layers in organic light emitting devices. We will report on these measurements in the near future.

ACKNOWLEDGEMENT

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