SINGLET OXYGEN AND ORGANIC LIGHT-EMITTING DIODES
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ABSTRACT
The preparation of light emitting diodes employing a new class of materials, 5,10-dihetera-5,10-dihydro-indeno[3,2b]indenenes, as hole transport agents is described. These materials have been found to be more resistant to degradation by singlet oxygen than a poly(p-phenylene vinylene) (PPV) derivative.

KEY WORDS: Organic light-emitting diode, PPV, singlet oxygen

1. INTRODUCTION
Three prerequisites of materials to be used in organic light-emitting diodes (LEDs) are solid-state fluorescence, good charge mobility, and resistance to oxidative degradation. Poly(p-phenylene vinylene) (PPV) certainly meets the first two requirements, but physical and chemical studies in these labs and elsewhere have highlighted decomposition of PPV-type materials as a potential failure mechanism in organic LEDs. Recent work has shown that singlet oxygen (\(1^0_2\)) is an intermediate in this process in the case of BCHA-PPV, a cholestanoxy-substituted PPV, and in fact that BCHA-PPV is a good sensitizer for \(1^0_2\). With these observations, study of the factors involved in \(1^0_2\) sensitization and design of electroluminescent molecules and materials that resist oxidative degradation have become important problems.

In this study, two members of the general class of 5,10-dihetera-5,10-dihydroindeno[3,2b]indenenes, potential hole-transporting replacements for PPV, have been examined. Specifically, these materials are indoloindole 1a and thianaphthindole 2a, which may satisfy all three prerequisites mentioned above. Each of these materials contains a stilbene chromophore, but one that is incorporated into and possibly stabilized against oxidative degradation by an aromatic ring system. It has been observed experimentally that environmentally stable nitrogen-centered radical cations are formed in N,N'-dimethylindolo[3,2b]indole 1b, supporting the potential hole-transporting properties of this class of compounds. In fact, the hole-transport properties of 2a have been studied previously, and 2a is a good hole transporting material. Compound 1b is known to be...
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highly fluorescent in solution,\textsuperscript{3} and we have found that 1a and 1b are also fluorescent in the solid state.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{structure}
\caption{Structures of compounds 1a and 1b.}
\end{figure}

2. EXPERIMENTAL SECTION

5,10-dihydroindolo[3,2-b]indole (1a) was prepared by the method of Dougherty.\textsuperscript{5}

Thianaphthindole (2a) Ethyl acetoacetate (12 g, 92 mmol) was added slowly via pipette to a mixture of thiosalicylic acid (10 g, 65 mmol) and sulfuric acid (65 ml) contained in an Erlenmeyer flask. When addition was complete, the mixture was heated to 45 °C for two hours and then allowed to cool to room temperature. The mixture was poured onto ice and the yellow-brown solid that was formed was filtered and steam distilled. A slightly pink solid collected in the receiver and was immediately mixed with excess phenylhydrazine in acetic acid. After standing overnight, a precipitate had formed. The solid was collected by filtration, washed with acetic acid and then with water, recrystallized from ethanol, and sublimed to yield 2a, 2.7 g, 19% yield (mp 250-1 °C, lit.\textsuperscript{6} 251-2 °C).

Physical Measurements Amorphous thin films of 1a and 2a were prepared by resistive heating in a bell-jar evaporator with a base pressure <5x10\textsuperscript{-5} torr. For photoluminescence measurements, films were prepared on fused silica substrates, while for measurements of the photoconductivity of 1a, thin films were deposited on ITO coated glass and aluminum electrodes were then deposited by evaporation. Photoluminescence measurements were conducted such that >99% of the incident light was absorbed, and emission was measured with an integrating sphere. Photoconductivity was measured by a time-of-flight technique that has been described elsewhere.\textsuperscript{7}

3. RESULTS AND DISCUSSION

3.1 Synthesis A facile synthesis of compounds 1a based on Pd-catalyzed coupling of 1-iodo-2-nitrobenzene (Scheme 1) has recently been reported.\textsuperscript{5} Compound 2a can be prepared by modification of a much older synthesis described by McClelland (Scheme 2).\textsuperscript{6} Steam distillation is essential to the isolation of the intermediate benzothiophen-3-one, which is then condensed in a Fischer indole synthesis with phenylhydrazine in acetic acid.

3.2 Photoluminescence The solid state photoluminescence efficiencies of compounds 1a and 2a have been measured for evaporated thin films with a thickness of approximately 3000 Å. The quantum yield of fluorescence for 1a, 8.7%, is comparable to that observed in our laboratory for both PPV (8%) and tris(8-hydroxyquinoline)aluminum (Alq) (12%),
SCHEME 1

\[
\begin{align*}
&\text{NO}_2 &\text{I} + \equiv \text{TMS} &\xrightarrow{\text{Pd(II), Cul, Et}_3\text{N}} &\text{NO}_2 \equiv \text{TMS} \xrightarrow{\text{KOH, MeOH}} &\text{NO}_2 \\
&\text{NO}_2 &\text{I} + \equiv \text{Ph} &\xrightarrow{\text{Pd(II), Cul, Et}_3\text{N}} &\text{NO}_2 \equiv \text{Ph} \xrightarrow{\text{KMnO}_4, \text{CH}_2\text{Cl}_2} &\text{O} \text{O}_2 \\
&\text{NO}_2 &\text{O}_2 \equiv \text{O} &\xrightarrow{\text{SnCl}_4, \text{AcOH, HCl}} &\text{N} \text{N} \text{N} &\xrightarrow{\text{NaH, THF, RI}} &\text{R} \text{R}
\end{align*}
\]

SCHEME 2

\[
\begin{align*}
&\text{COOH} &\text{COOH} &\xrightarrow{\text{H}_2\text{SO}_4} &\text{COOH} + \text{PhNHNH}_2 \xrightarrow{\text{AcOH}} \\
&\text{SH} &\text{COOH} &\xrightarrow{\text{H}_2\text{SO}_4} &\text{COOH} + \text{PhNHNH}_2 \xrightarrow{\text{AcOH}} \\
&\text{S} &\text{N} &\xrightarrow{\text{NaH, THF, RI}} &\text{R} \text{R}
\end{align*}
\]
while that for 2a is 2.7%. The difference between the values for 1a and 2a can be attributed to a heavy atom effect.

3.3 Photoconductivity The photoconductivity of 1a has been measured in an evaporated thin film sandwiched between ITO and aluminum electrodes. The value of the hole mobility, $1 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a field of $1 \times 10^5 \text{ V cm}^{-1}$, shows that holes are easily transported in this material. Good hole mobility in 2a has been demonstrated previously.$^4$

3.4 Singlet oxygen chemistry The relative stabilities of these materials under steady-state irradiation in the presence of oxygen reveal that they are substantially less sensitive to degradation by photooxidation than BCHA-PPV in both Rose Bengal-sensitized and self-sensitized experiments. The overall bleaching rate constants for 1a and 2a are one to two orders of magnitude lower than for BCHA-PPV. The enhanced stability is attributed in part to the amine function, as amines are good physical quenchers of $^1\text{O}_2$. Absolute kinetic studies are underway.

3.5 Electroluminescence Heterostructure devices have been made using 1a as the hole transporting layer, with Alq as the electron transporting layer, an ITO anode and Mg cathode. The electroluminescence spectra of these devices indicate that the observed light is due to Alq emission, and the intensity of the observed light in our first set of devices shows brightness of 600 cd m$^{-2}$ at a current density of 60 mA cm$^{-2}$. We expect to increase the efficiency through improvements in our device fabrication process.

4. CONCLUSIONS

Two members of a class of compounds capable of functioning as hole-transporting agents in organic LEDs have been synthesized, and experiments show that they are more resistant to photooxidative degradation than BCHA-PPV. The structure/property relationships that govern oxidative degradation are important to extending the lifetimes of organic LEDs to a useful regime. Further studies in this area are underway and will be reported in due course.

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