



Investigation of a dendrimer-like arrangement of hydrazone fragments for the application as hole transporting materials



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ABSTRACT

A new type of dendrimer-like hydrazone hole transporting materials have been reported and their thermal, optical, electrochemical and photophysical properties are investigated and applicability in construction of hybrid solar cells is evaluated. It was found that hole mobility in these hydrazones reaches respectable $2.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at strong electric fields, which puts them on a par with majority of the best performing amorphous, solution-processed hole transporting materials used today.

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1. Introduction

Electronic and optoelectronic devices using organic materials as active elements, for example, organic light-emitting diodes (OLED), organic photovoltaic devices (OPV), organic field-effect transistors (OFET), organic photoreceptors, organic photorefractive devices, and so forth, have received a great deal of attention from the standpoint of potential technological applications as well as fundamental science.^{1–4} These devices can benefit from such advantages of organic materials as light weight, potentially low cost, and capability of thin-film, large-area, flexible device fabrication. All the devices described above involve charge transport as an essential operation process and hence, require proper charge-transporting materials. Therefore, development of the high-performance, charge-transporting materials is a key issue for the fabrication of high-performance devices.

Realization of organic electronics potential for simple processing requires the ability to form devices by solution deposition methods, preferably using inexpensive, easily purified materials. Thiophene derivatives have demonstrated very good charge mobilities,

solubility, and processability.^{5,6} Their main drawback, however, is a relatively complicated and expensive multi-step synthesis procedure involving organotin, organolithium, or organomagnesium reagents, expensive palladium or nickel catalysts, rigorously anhydrous and oxygen-free conditions.^{6,7} Another large group of hole transporting materials (HTM) are nitrogen-containing triaryl amines. These compounds have long been known as hole transporting materials for the active layer of organic photoreceptors, OLEDs, and organic solar cells. They show very good solubility in common organic solvents, stability towards air and humidity,^{6–8} and adequately high charge-carrier mobilities in vapor deposited,⁹ and spin coated^{10–12} films. Unfortunately, the majority of these HTMs still require use of palladium catalyst and even traces of palladium can significantly affect HTM characteristics and overall device performance.^{6,13} Additional purification, such as costly sublimation, is necessary in order to remove traces of palladium, increasing the cost and synthesis complexity of the HTM. High photosensitivity, good enough charge-transporting properties for technical applications and low cost are the main advantages of aryl aldehyde hydrazones against other classes of charge transporting materials.¹⁴ Combination of these properties and synthetic procedures that do not require palladium catalysis make hydrazone HTMs very appealing candidates for practical applications.

In this publication a new type of arrangement of hydrazone fragments in hole transporting materials is presented. Properties of

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the molecules, containing new type of hydrazone arrangement, are thoroughly investigated and the applicability in construction of hybrid solar cells is evaluated.

2. Results and discussion

2.1. Synthesis

The molecular structures of the investigated hydrazones **HTM1–HTM8** are presented in Fig. 1.

The synthetic procedure of the hole transporting dihydrazones **HTM1–4** is depicted in Scheme 1. Reaction of the aldehydes **1, 2** with phenylhydrazine afforded phenylhydrazones **3, 4**, which were used in arylation reactions (with 4-fluorobenzaldehyde) to obtain aldehydes **5, 6**. Reaction of **5** and **6** with *N*-methyl-*N*-phenyl- and *N,N*-diphenylhydrazines yielded final hydrazones **HTM1, HTM2** and intermediate products **7, 8**. Halogenated dihydrazones **7, 8** were used in substitution reactions with sodium methoxide and hole transporting materials **HTM3, HTM4** were isolated. The above mentioned additional step of halogen substitution with a methoxy

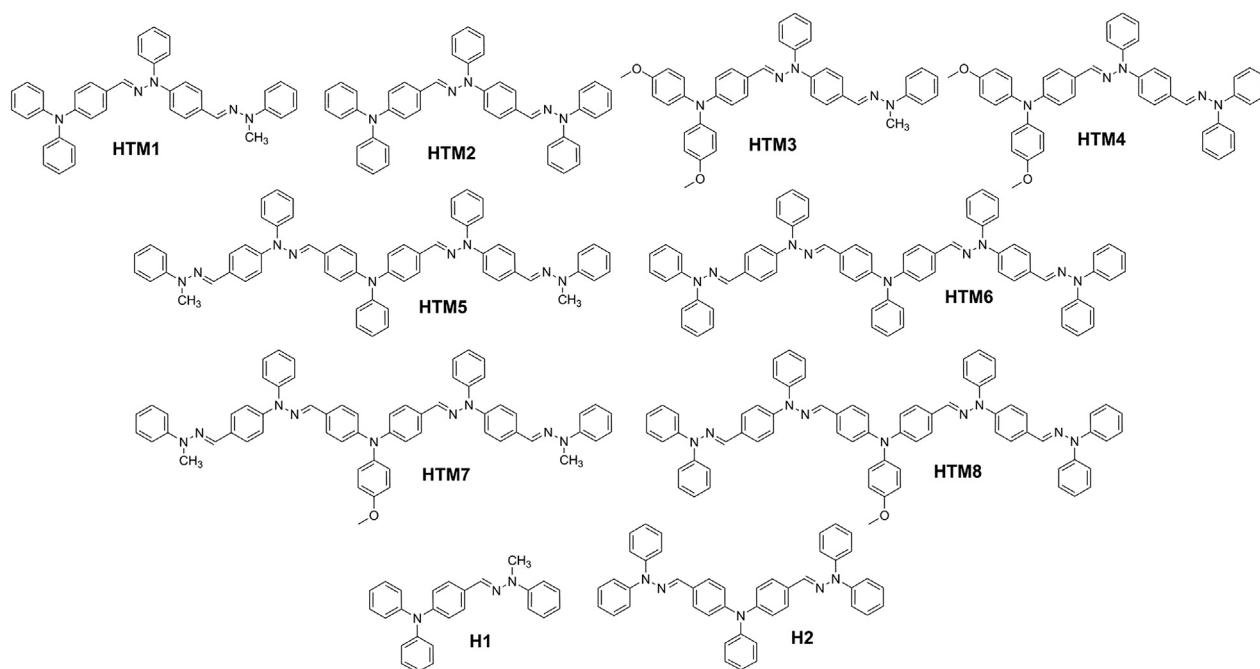
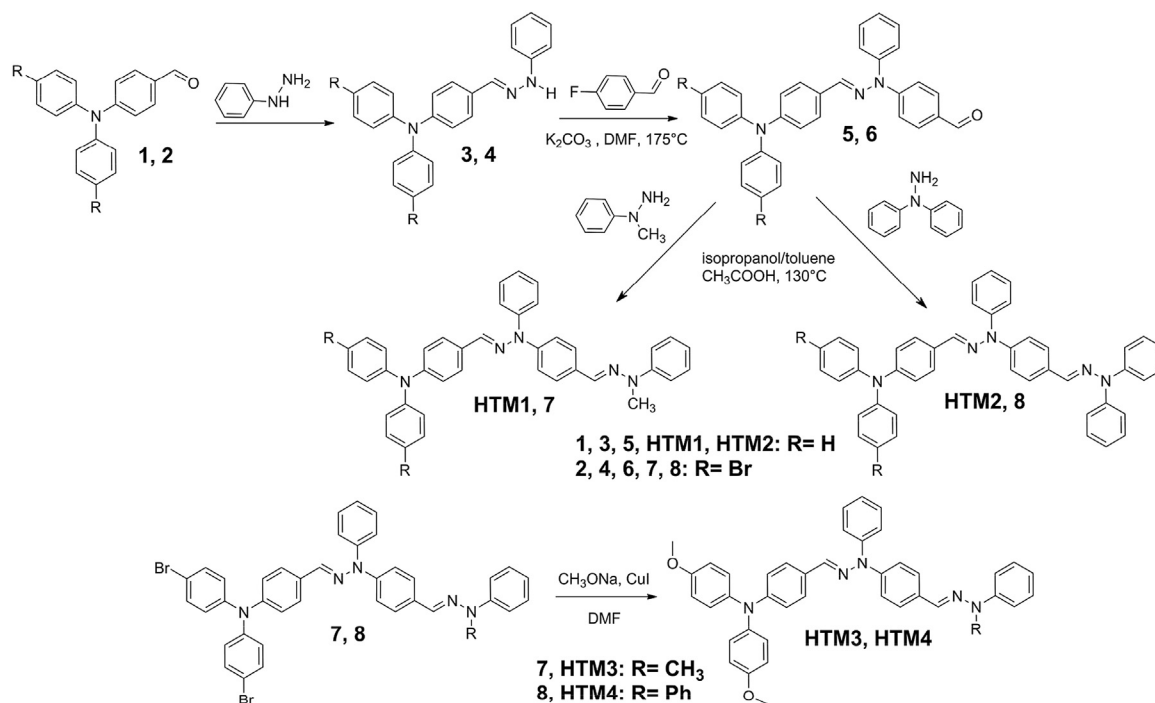


Fig. 1. Structures of the investigated hydrazones **HTM1–8** and reference materials **H1** and **H2**.



Scheme 1. Synthesis of dihydrazones **HTM1–4**.

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