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Synthesis and characterization of highly stable and efficient star-molecules

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ABSTRACT

A series of well-defined star-shaped molecules have been synthesized by Pd-catalyzed Suzuki cross-coupling starting from very simple reactants with 1,3,5-trisubstituted benzene, 2,4,6-trisubstituted pyridine and trisubstituted phenylcarbazole as the backbones. These star-molecules are all soluble in common organic solvents and electrochemically stable with reversible cyclic voltammographs and high lying HOMOs. They exhibit excellent blue-fluorescence with quantum yield up to 0.87 and high glass transition temperatures. These molecules offer potential as pure blue-light emitting, hole-transport or host materials for optoelectronic applications.

1. Introduction

In the past two decades, organic light-emitting diodes (OLEDs) based on small molecules have received considerable attention primarily due to the ease of fabrication into large-area flat-panel displays and solid-state lighting sources [1–4]. However, as one of the most important components for display and white lighting, the ideal blue light-emitting pixel still remains a great challenge [5–7]. Low efficiency, low thermal stability, low chemical purity, easy crystallization and poor structural uniformity are some of the detrimental factors restricting performance [8]. To improve the performance from a chemical approach, molecules with a rigid structure either star-shaped or dendrite-shaped structure have been designed and effectively used [9–12]. These high-molecular-weight star-molecules or dendrite molecules often include an arylamine or carbazole backbone [13–15].

Compared with linear molecules, star-shaped molecules with well-defined three-dimensional spherical architectures have a site isolation effect and possess the following advantages: (i) high degree of purity, (ii) good solution processability, (iii) good thin film formation, (iv) good thermal stability [16–18]. Molecules with carbazole and arylamine backbones have been extensively studied as blue light-emitting as well as hole and host materials due to their electron-donating property, long conjugation chain, high thermal stability, and high photoluminescence efficiency. These physical properties can be realized through vigorous chemical designs and structure modification [19–22]. Many reports have revealed that the morphological instability of hole-transporting and host materials are responsible for the device lifetime, especially at higher temperature [23–28]. From the synthetic organic chemistry point of view, many hole-transporting and host materials with high glass-transition temperature (T_g) have been synthesized [29–32]. This is very important because such devices not only occasionally need to be operated at high temperature but also need to be operated at high current densities with high luminance in lighting sources. In these circumstances, materials with a high T_g are better, to be able to resist heat. Therefore, materials with a high glass-transition temperature are highly desirable.

In this paper, we have designed a new series of star-shaped molecules containing carbazole/arylamine backbone: **S1–7** (Scheme 1). Their synthesis, thermal stability, UV absorption, electrochemical behavior, and the photoluminescent properties were discussed.

2. Experimental

2.1. Chemicals and instruments

All reactants and solvents, unless otherwise stated, were purchased from commercial sources such as Alfa Aesar and Acros,

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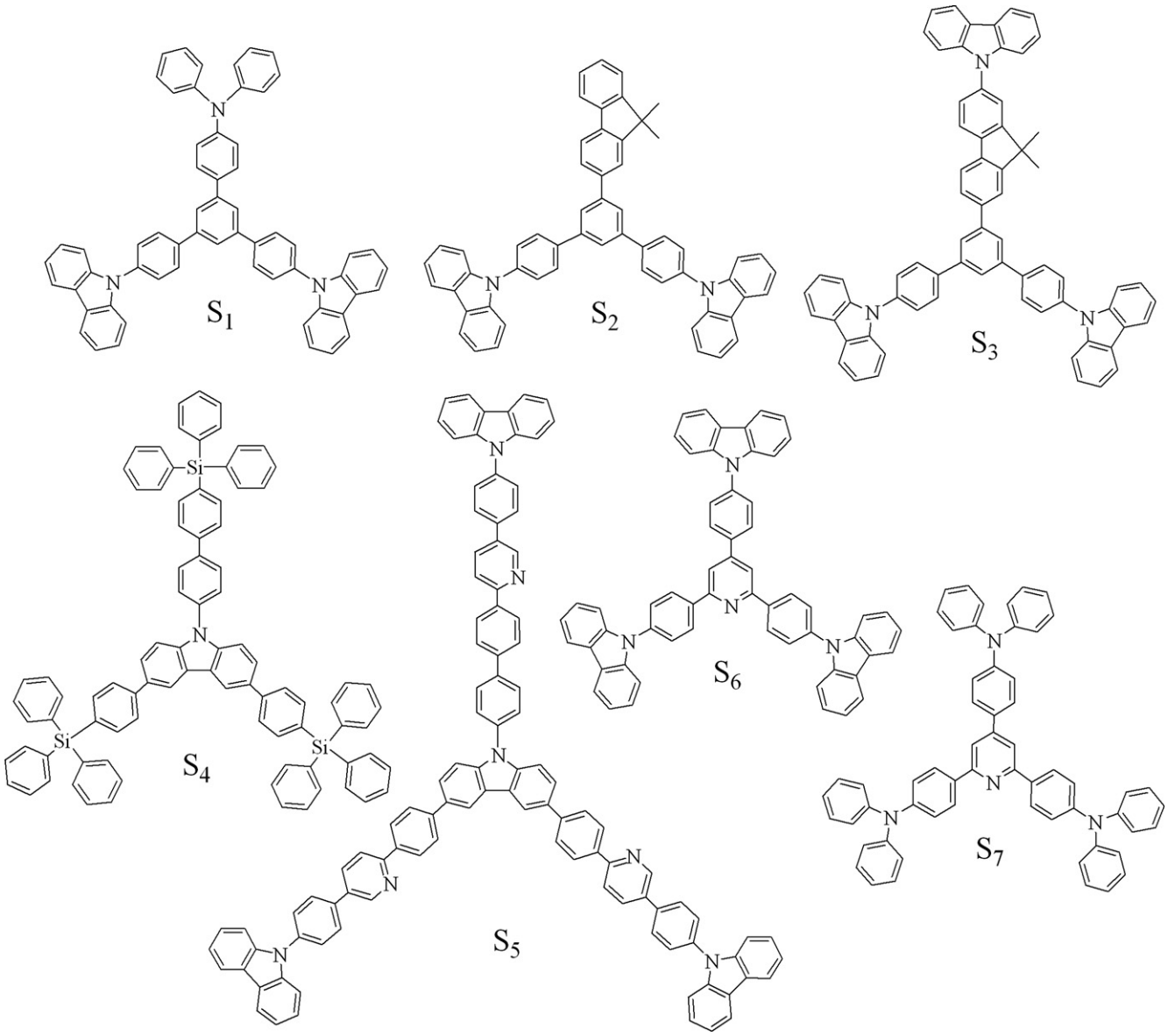

Scheme 1. Chemical structures of the star-shaped molecules $\mathbf{S_{1-7}}$.

and used as received. Melting points were measured on an X-4 microscope electrothermal apparatus (Shanghai Jingmi Instruments). FT-IR data were obtained from a Nicolet 5700. ^{1}H NMR spectra were performed on a Bruker 400 MHz spectrometer. Elemental analysis was carried out on a Vario III elemental analyzer. UV–vis absorption spectra were recorded on a Perkin–Elmer Lambda-35 spectrometer. Photoluminescence (PL) spectra were obtained using a Hitachi F-4500 florescence spectrophotometer. Differential scanning calorimetery (DSC) and thermogravimetric analysis (TGA) were performed on a Perkin–Elmer MAS-5800 instrument with a heating/cooling rate of 10 °C min^{-1} and a nitrogen flow rate of 90 mL min^{-1}. Cyclic voltammetry (CV) was performed on an Autolab Potentiostat 30 with a glassy-carbon electrode in CH_2Cl_2 solutions containing 0.0005 M of compound and 0.10 M $(n\text{-}Bu)_4NBF_4$ against Ag/AgCl, with ferrocene (Fc) as the internal standard. The HOMO energy level can be estimated from the onset potentials through the following equation: $E_{HOMO} = (-4.72 + E_{ref} - E_{ox})$ eV, where E_{ref} is the potential of the Fc reference (positive), E_{ox} is the oxidation potentials of the sample (positive).

2.2. Synthesis

The chemical structure of the star-shaped molecules $\mathbf{S_{1-7}}$ was illustrated in Scheme 1. Suzuki coupling was applied as a key reaction technique to construct the intermediates and the target compounds. Schemes 2–5 outlines the synthetic routes. Our synthetic strategy started from commercially available reagents and intermediates **1**, **2** and **10** were prepared by Ullmann coupling reaction [33–38].

The treatment of **2** with three equiv. of N-bromosuccinimide (NBS) in dichloromethane afforded **16** [39]. Intermediates **3**, **4**, **11**, **12** and **17** were obtained from lithiated **1**, **2**, **8**, **9**, **16** with trimethylborate, respectively [36–41]. Compounds **5**, **8**, **9** were synthesized according to the literature methods [38,42–44]. Intermediates **6, 7, 13–15, 18–20** were synthesized according to reported procedures [38,45,46]. $\mathbf{S_1}$ was obtained by Suzuki cross-