Chemical Physics Letters 666 (2016) 7–12

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Triptycences as thermally activated delayed fluorescence materials: Effect of π-conjugation length and donors

Ying Gao [a], Tan Su [b], Yong Wu [c], Yun Geng [d,*], Min Zhang [d], Zhong-Min Su [a,d,*]

[a] College of Chemistry, Jilin University, Changchun 130012, PR China
[b] Institute of Theoretical Chemistry, Jilin University, Changchun 130021, PR China
[c] School of Pharmaceutical Sciences, Changchun University of Chinese Medicine, 1035 Boshuo Road, Changchun 130117, PR China
[d] Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, PR China

ARTICLE INFO

Article history:
Received 30 August 2016
In final form 26 October 2016
Available online 27 October 2016

Keywords:
Thermally activated delayed fluorescence
Singlet-triplet energy splitting
Radiative decay rate

ABSTRACT

Based on a thermally activated delayed fluorescence (TADF) triptycene compound **1**, compounds **2**–**7** were designed by varying electron-donating units (**2**–**5**) and increasing π-conjugation length (**6** and **7**). The results indicate that singlet-triplet energy splitting (ΔE_{ST}) of compounds **2**–**5** is reduced largely, but their improvement of radiative decay rate (k_r) is slightly small. However, the compound **6** not only reduces the ΔE_{ST} but also enhances k_r. For compound **7**, the k_r value is comparable with compound **6**, but ΔE_{ST} value is quite large. Therefore, possessing an appropriate π-conjugation length might be helpful to improve TADF performances for the materials investigated here.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted significant interest because of their potential applications in flat-panel displays and light sources, which mainly comprise two types of materials: fluorescent and phosphorescent materials [1–4]. In the past two decades, numerous efforts have been devoted to the first generation fluorescence-based OLEDs and the second generation phosphorescence-based OLEDs. According to the spin statistics, the singlet and triplet excitons are generated in a rate of 1:3 during electroluminescent process. For conventional fluorescent material, only singlet excitons can be used with internal quantum efficiency (IQE) at almost 25% in OLEDs. The phosphorescent materials containing Ir (III), Pt (II) and Os (II) exhibit very high IQE, originating from enhanced intersystem crossing (ISC) by heavy atoms. The IQE approaches to 100% [5–7]. However, the phosphorescent OLEDs have some disadvantages, such as expensive and unsustainable rare metals and efficiency roll-off at high current density [8].

In 2009, a new conceptual mechanism for OLEDs was discovered: thermally activated delayed fluorescence (TADF) based on conventional organic aromatic compounds [8–15]. In TADF devices, the triplet excitons can be converted into singlet excitons via thermally activated reverse intersystem crossing (RISC) from triplet excited state (T_1) to singlet excited state (S_1). Thus, both singlet and triplet excitons can be used for light emission. The 100% IQE can be theoretically obtained [16]. Compared to the conventional fluorescent and phosphorescent materials, the TADF materials show many advantages. For instance, the upper limit of the internal electroluminescent quantum efficiency of the TADF emitter can be improved due to high photoluminescence quantum yield. Simultaneously, a short TADF lifetime is able to reduce the singlet-triplet annihilation, triplet-polaron annihilation and triplet-triplet annihilation [17,18].

It is also necessary for a TADF molecule to possess a small singlet-triplet energy splitting (ΔE_{ST}) for effective RISC from T_1 to S_1, which is easy to be overcome by thermal energy. While, a small ΔE_{ST} value generally indicates that a small overlap between the ground and excited states wave functions of a luminescent molecule [19]. Therefore, a TADF molecule generally composes of electron donor (D) and electron acceptor (A) units. Meanwhile, the molecule is a twisted structure for achieving a small HOMO-LUMO overlap [20–23]. Based on the D-A model, a large number of highly efficient TADF materials with various colors have been studied and successfully applied in fluorescent OLEDs [23–32]. Recently, two three-dimensional TADF molecules with donor and acceptor on different fins of a tripycene scaffold, have been synthesized and characterized. The separation and weak coupling between their HOMOs and LUMOs, which mainly localized on different arms of the triptycene, result in a small ΔE_{ST} [33].

---

* Corresponding authors at: Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, PR China (Z.-M. Su).
E-mail addresses: gengyun575@nenu.edu.cn (Y. Geng), zmsu@nenu.edu.cn (Z.-M. Su).

http://dx.doi.org/10.1016/j.cplett.2016.10.069
0009-2614/© 2016 Elsevier B.V. All rights reserved.

In this work, based on the structure of three-dimensional triptycene TADF molecule, we intend to further design efficient TADF material with smaller ΔE_{ST} via considering increasing the π-conjugation length and selecting a proper combination of electron donor and electron acceptor. Therefore, compounds **2**–**7** were designed (Fig. 1). By employing density functional theory/time-dependent density functional theory (DFT/TD-DFT), we have studied a series of optoelectronic properties to estimate their performances in OLEDs with the aim of selecting excellent material for organic optoelectronic devices.

2. Computational details

All calculations were performed with the Gaussian 09 program [34]. A series of calculations on compound **1** were performed with four functionals (B3LYP, CAM-B3LY, M062X and PBE0). The optimized parameters and experimental values are summarized in Table S1 of Supporting Information. The geometric parameters at the optimized ground state (S_0) obtained with B3LYP agree well with experimental values. In addition, the HOMO and LUMO levels evaluated by B3LYP are the closest to the experimental values. Therefore, B3LYP is chosen to optimize the structures of compounds **1**–**7**. The TD-B3LYP method was used to optimize the lowest singlet excited state (S_1) geometries. The UV–vis absorption spectra of compounds **1**–**7** were stimulated using B3LYP with the polarized continuum model (PCM) [35] in cyclohexane media. Furthermore, the vertical ionization potential (IP_V), vertical electron affinity (EA_V) and hole and electron reorganization energy ($\lambda_{h/e}$) were estimated at the B3LYP level. In all of the calculations, the cc-pVDZ basis set was employed for all atoms. TD-DFT calculation

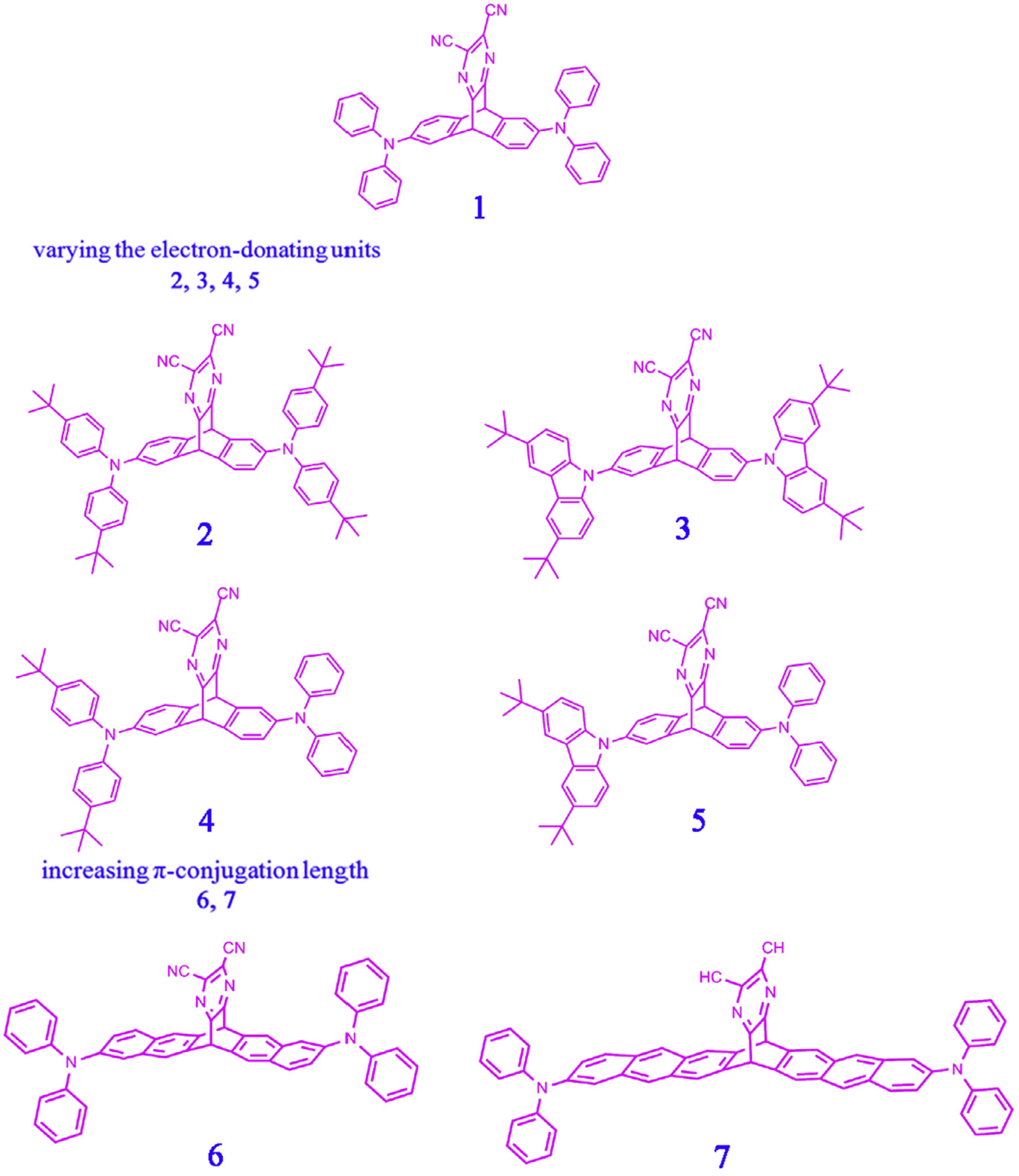

Fig. 1. Molecular structures of compounds **1**–**7**.