



Relationship between room temperature phosphorescence and deuteration position in a purely aromatic compound



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ARTICLE INFO

Article history:

Received 11 September 2013

6 November 2013

In final form 12 November 2013

Available online 19 November 2013

ABSTRACT

The development of organometallic and purely organic compounds showing room temperature phosphorescence (RTP) has several promising applications. We report a relationship between the phosphorescence characteristics and deuteration position in a purely organic aromatic compound. Hydrogen–deuterium exchange at the carbons where the lowest unoccupied molecular orbital is located is the most effective method to enhance the RTP lifetime and quantum yield. The increase in RTP lifetime comes from a decrease in the Franck–Condon factor while the enhancement of RTP yield is caused by an increase in intersystem crossing from the lowest singlet excited state to the lowest triplet excited state.

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1. Introduction

Materials with a high triplet exciton yield at room temperature (RT) can create new opportunities in the development of sensitizers for photopolymerization [1], photodynamic therapy [2,3], optical limiters [4,5], organic light emitting diodes (OLEDs) [6–8], and high-resolution sensing probes for tumor imaging [9]. For these applications, the control of triplet excitons is necessary to enhance their properties. The key to controlling triplet excited states lies in controlling the radiative and nonradiative decay rates of the lowest triplet excited state (T_1) and the generation of triplet excitons. An increase in spin–orbital coupling based on the heavy atom effect [10] for species such as metals and halogens enhances the triplet yield and the radiative rate at T_1 , resulting in an enhancement in RT phosphorescence (RTP) yield [11]. However, the triplet excitons of purely organic (metal- and halogen-free) compounds have not been well controlled.

In the 1960s, theoretical considerations of the nonradiative process revealed that the high-energy C–H stretching vibration in aromatic hydrocarbons strongly increases the Franck–Condon factor and this accelerates nonradiative deactivation at T_1 in purely organic aromatic carbons [11,12]. From these considerations, a decrease in the C–H stretching vibration energy by deuteration around aromatic hydrocarbons reduces the nonradiative process at T_1 , resulting in an enhancement of the triplet lifetime and the phosphorescence quantum yield at liquid nitrogen temperature. This is well known as the isotope effect. In 2010, the isotope effect of iridium complexes as emitters with RT phosphorescence (RTP)

was investigated because they potentially provide an improvement in the efficiency and lifetime of phosphorescent OLEDs [13]. Although a decrease in nonradiative deactivation from T_1 was observed, a significant enhancement of the RTP characteristics after deuteration was not observed because the radiative process is much faster than the nonradiative process in T_1 . Purely organic materials with a RTP yield higher than 10% have recently been reported [14,15]. The radiative process is not faster than the nonradiative process in T_1 for purely organic aromatic hydrocarbons, which is different to the behavior of organometallic RTP compounds. In this report, the suppression of nonradiative deactivation by deuteration is considered to be the reason for the enhancement in RTP yield and lifetime [14]. However, a further investigation into the deuteration effect is required to characterize the highly efficient RTP behavior of purely organic materials. Additionally, fully deuterated aromatic compounds are synthesized from expensive deuterated precursors that are typically prepared using a palladium catalyst and deuterium water. If important deuterated positions that enhance RTP characteristics are revealed, the use of deuterated precursors to obtain efficient purely organic RTP can be minimized.

Here, we investigate the enhancement of RTP characteristics upon deuteration by considering the influence of deuteration position in an aromatic hydrocarbon on the RTP characteristics. We selected N,N'-diphenyl-N,N'-(3-methyl phenyl)-1,1'-biphenyl-4,4'-diamine (TPD), which is a well-known hole transport material that provides blue fluorescence in OLEDs [16]. Deuteration of the hydrogens directly connected to the carbons within the lowest unoccupied molecular orbital (LUMO) at T_1 was found to be most effective at enhancing the RTP lifetime. On the other hand, deuteration of the hydrogens directly connected to the carbons

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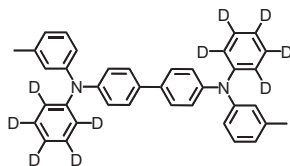
within the LUMO at the lowest singlet excited state (S_1) effectively accelerates the intersystem crossing (ISC) from S_1 to T_1 , leading to an enhancement in RTP yield. This report provides important findings for the development of low cost purely organic molecules with efficient RTP characteristics.

2. Materials and methods

2.1. Synthesis of compounds

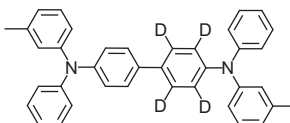
TPD (**a**) is commercially available from the Tokyo Chemical Corporation, and the other TPD derivatives (**b–e**) shown in **Figure 1** were synthesized by the Buchwald–Hartwig reaction [17]. ^1H and ^{13}C NMR spectra were recorded with an ECX-400 spectrometer (JEOL Ltd., Tokyo, Japan) operating at 400 MHz for ^1H and 100 MHz for ^{13}C NMR. The chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS; $\delta = 0$) as an internal reference. Mass spectra were collected on a JMS-700 spectrometer (JEOL Ltd., Tokyo, Japan) by fast atom bombardment. The ^1H and ^{13}C NMR results and the mass spectra data are as follows:

b:



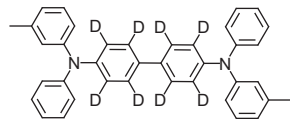
^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.44 (*d*, $J = 8.7$ Hz, 4H), 7.17–7.08 (*m*, 6H), 6.95–6.91 (*m*, 4H), 6.84 (*d*, $J = 7.3$ Hz, 2H), 2.27 (*s*, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 147.74, 146.90, 139.21, 134.68, 129.14, 127.31, 125.18, 124.10, 123.91, 121.74; HRMS-El(*m/z*): [M] $^+$ calcd for $\text{C}_{38}\text{H}_{22}\text{D}_{10}\text{N}_2$, 526.319; found, 526.310. The yield of the deuteration positions shown in **Figure 1** was nearly 100%.

c:



^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.44 (*d*, $J = 8.7$ Hz, 2H), 7.25 (*t*, $J = 7.9$ Hz, 4H), 7.17–7.10 (*m*, 8H), 7.01 (*t*, $J = 7.3$ Hz, 2H), 6.95–6.91 (*m*, 4H), 6.84 (*d*, $J = 7.5$ Hz, 2H), 2.27 (*s*, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 147.90, 147.73, 146.88, 146.75, 139.22, 134.62, 129.27, 129.14, 127.29, 125.19, 124.12, 123.90, 122.71, 121.74; HRMS-El(*m/z*): [M] $^+$ calcd for $\text{C}_{38}\text{H}_{28}\text{D}_4\text{N}_2$, 520.282; found, 520.271. The yield of the deuteration positions shown in **Figure 1** was nearly 100%.

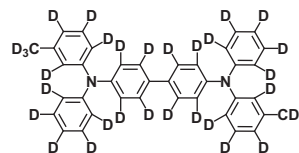
d:



^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.25 (*t*, $J = 7.9$ Hz, 4H), 7.15 (*t*, $J = 7.9$ Hz, 2H), 7.11 (*d*, $J = 7.9$ Hz, 4H), 7.01 (*t*, $J = 9.3$ Hz, 2H), 6.95–6.01 (*m*, 4H), 6.84 (*d*, $J = 7.3$ Hz, 2H), 2.27 (*s*, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 147.90, 147.73, 146.75, 139.22, 134.42, 129.27, 129.15, 125.19, 124.28, 123.91, 122.71, 121.74; HRMS-El(*m/z*): [M] $^+$ calcd. for $\text{C}_{38}\text{H}_{24}\text{D}_8\text{N}_2$, 524.307; found, 524.301. The

yield of the deuteration positions shown in **Figure 1** was nearly 100%.

e:



a (100 mg) was treated with 10% Pd on active carbon (75 mg, 0.1 mmol Pd) and D_2O (15 g) in a 30-mL Teflon-lined autoclave at 240 °C for 12 h. The internal pressure reached 4–5 MPa. After slow cooling to RT, ethyl acetate (100 mL) was added. The D_2O phase of the reaction was washed three times with ethyl acetate (50 mL each time). After filtration through silica gel the filtrate was dried over Na_2SO_4 , and then filtered. Evaporation of the solvent gave the crude deuterated product. The crude material was purified by column chromatography (silica gel; eluent = 30% dichloromethane/hexane) to give **e** as a white powder (41.2 mg, 39%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.43 (*d*, $J = 8.7$ Hz, 0.74H), 7.24 (*t*, $J = 8.0$ Hz, 0.10H), 7.17–7.09 (*m*, 0.94H), 7.00 (*t*, $J = 7.3$ Hz, 0.12H), 6.94–6.91 (*m*, 0.57H), 6.84 (*d*, $J = 7.9$ Hz, 0.12H), 2.27 (*s*, 0.39H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 147.90, 147.73, 146.89, 139.22, 134.68, 129.27, 129.14, 127.31, 125.19, 124.28, 124.10, 123.91, 122.71, 121.74; HRMS-El(*m/z*): [M] $^+$ calcd for $\text{C}_{40}\text{D}_{35}\text{N}_2$, 548.457; found, 546.451. The deuteration yield calculated using the molecular weights determined before and after deuteration was 94%. The deuteration yield was also determined by comparing the peak areas in the ^1H NMR spectra using the method shown in Ref. [14] and was found to be 91%.

2.2. Molecular property calculations

All calculations were performed using the GAUSSIAN 09 program package [18]. The optimized structures of S_1 and T_1 was determined by density functional theory (DFT) calculations. Further calculations of their properties were performed at the time-dependent DFT level. Both the ground and excited state calculations were performed using the B3LYP functional [19] and the 6-31G * basis [20] sets.

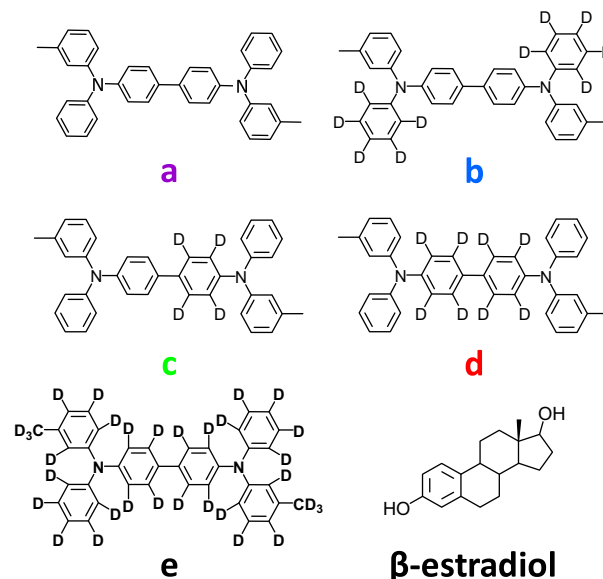


Figure 1. Chemical structures of **a–e** as guests and β -estradiol as a host.

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