Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Dibenzothiophene-dioxide acceptor based thermally activated delayed fluorescent emitters for color tunable organic light-emitting diodes

Ji Han Kim, Jun Yeob Lee*

School of Chemical Engineering, Sungkyunkwan University, Suwon, Gyeonggi, 446-740, Republic of Korea

ARTICLE INFO

Article history:
Received 7 November 2016
Received in revised form 2 February 2017
Accepted 2 February 2017
Available online xxx

Keywords:
Delayed fluorescence
Dibenzothiophene
Dimethylacridine
Green device

ABSTRACT

2,8-Bis(9,9-dimethylacridin-10(9*H*)-yl)dibenzo[*b*,*d*]thiophene 5,5-dioxide (AcDBTO) was developed as a dibenzothiophene-dioxide acceptor based emitter for use as a thermally activated delayed fluorescent emitter for color tunable organic light-emitting diodes. The dibenzothiophene-dioxide acceptor was modified with two strongly electron donating dimethylacridine donors, which enabled delayed fluorescence behavior in the AcDBTO emitter. The AcDBTO based device demonstrated quantum efficiency of 14.5% as a green delayed fluorescent device and wide emission wavelength from 502 nm to 525 nm with little change of the quantum efficiency.

Introduction

In recent years, a strong need for high efficiency emitters encouraged the development of thermally activated delayed fluorescent (TADF) emitters which can reach 100% electron to photon conversion efficiency [1,2]. Heavy metal based phosphorescent organic light-emitting diodes (OLEDs) have been the dominant technologies for high efficiency OLEDs, but recent demonstration of high efficiency in the TADF OLEDs opened a new way developing high efficiency OLEDs [3–9].

In the design of the TADF emitters, proper selection of donor and acceptor moieties plays a critical role of managing the efficiency of the device dictated by spin up-converting capability of the emitters. As the spin up-conversion process is a function of singlet energy-triplet energy gap, donors and acceptors reducing the singlet energy-triplet energy gap have attracted much attention in the design of TADF emitters.

One of the acceptors used to design the TADF emitters is dibenzothiophene dioxide which has an electron withdrawing sulfone functional group [10,11]. It was included as a building block of TADF emitters in combination with carbazole type donors to meet the basic properties required for TADF characteristics. However, the dibenzothiophene dioxide derived TADF emitters could not fulfill the needs of the TADF emitters possibly due to weak donor character of the carbazole derivatives [12]. Therefore, it is expected that an advanced molecular structure built using a strong donor and dibenzothiophene dioxide may satisfy the singlet energy-triplet energy gap requirements. Moreover, the molecular design having the strong donor may assist tuning the emission color of the TADF devices [13–15].

In this work, a TADF emitter, 2,8-bis(9,9-dimethylacridin-10(9*H*)-yl)dibenzo[*b*,*d*]thiophene 5,5-dioxide (AcDBTO), was developed by connecting two dimethylacridine donors to the dibenzothiophene dioxide acceptor. Synthesis, material characterization and device application were comprehensively described and the AcDBTO TADF device could function as color tunable TADF devices by adjusting the composition of the mixed host while keeping the quantum efficiency irrespective of the emission color of the devices.

Experimental

General information

9,9-Dimethyl-9,10-dihydroacridine (Sun fine global Co.) was used without further purification. Palladium(II) acetate and tri-tert-butyphosphine were purchased from P&H tech Co. Sodium tert-butoxide was supplied from Tokyo chemical industry Co. Toluene and dichloromethane (Duksan Sci. Co.) were used without further purification. Chemical analysis methods of the compound were the same as those of previous work [8].

---

* Corresponding author.
E-mail address: leej17@skku.edu (J.Y. Lee).

http://dx.doi.org/10.1016/j.jiec.2017.02.001
1226-086X/© 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Please cite this article in press as: J.H. Kim, J.Y. Lee, Dibenzothiophene-dioxide acceptor based thermally activated delayed fluorescent emitters for color tunable organic light-emitting diodes, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.02.001

Synthesis

*2,8-Bis(9,9-dimethylacridin-10(9*H*)-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (AcDBTO)*

2,8-Dibromodibenzo[*b,d*]thiophene 5,5-dioxide (0.55 g, 1.47 mmol), 9,9-dimethyl-9,10-dihydroacridine (0.68 g, 3.23 mmol), palladium(II) acetate (0.10 g, 0.44 mmol) and sodium tert-butoxide (0.57 g, 5.88 mmol) were dissolved in toluene (40 mL). The mixture was stirred with a N_2 gas for 15 min. Tri-tert-butylphosphine (0.24 g, 1.17 mmol) was slowly added to the mixture and refluxed for 24 h under a nitrogen atmosphere. The mixtiure was cooled down to room temperature, and was extracted with dichloromethane and distilled water three times. The organic layer was separated and dehydrated with magnesium sulfate. Crude product was obtained after filtration followed by evaporation of solvent. A yellow powder was obtained as a product by further purification with column chromatography with dichloromethane and n-hexane(1:9).

Yield 66% (0.62 g), ^{1}H NMR (500 MHz, DMSO-d^{6}): δ 8.40 (s, 2H), 8.37 (s, 1H), 8.36 (s, 1H), 7.71 (d, 2H, J = 7.6 Hz), 7.49 (d, 4H, J = 7.2 Hz), 7.01–6.97 (t, 4H), 6.93–6.90 (t, 4H), 6.23 (d, 4H, J = 7.2 Hz), 1.61 (s, 12H). ^{13}C NMR (125 MHz, DMSO-d^{6}): δ 146.71, 139.61, 136.72, 134.06, 129.90, 126.67, 125.71, 125.54, 121.10, 113.91, 113.73, 35.58, 31.35. MS (APCI) m/z 557.20 $[(M + H)^{+}]$.

Device fabrication

Green TADF devices were fabricated using the AcDBTO device stack structure of indium tin oxide (ITO, 120 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (60 nm)/4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC) (20 nm)/1,3-di(9H-carbazol-9-yl)benzene (mCP, 10 nm)/mCP: 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBI):AcDBTO (25 nm, 10%)/diphenyl-4-triphenylsilylphenylphosphine oxide (TSPO1) (5 nm)/TPBI (30 nm)/LiF (1.5 nm)/Al (200 nm). All materials were deposited by vacuum thermal evaporation process except for PEDOT:PSS layer which was fabricated using spin coating process. Device performances were characterized using a voltage scanning method at a step of 0.5 V from 0 V. Current density and luminance were gathered using a device characterization system equipped with a Keithley 2635A source measurement unit and CS2000 spectroradiometer.

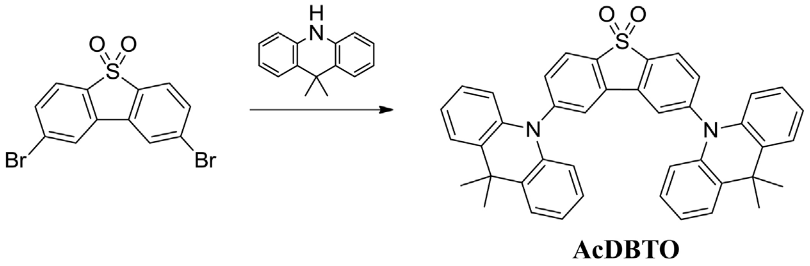
Results and discussion

AcDBTO was constructed to have two strong dimethylacridine donors and a dibenzothiophene dioxide acceptor based on a donor-acceptor-donor platform. Two dimethylacridne donors were included to strengthen charge transfer (CT) character for small singlet energy-triplet energy gap through intensified donor strength and strong intermolecular interaction with electron acceptor based host material. The dibenzothiophene dioxide acceptor was synthesized according to the synthetic steps described in the literature [16] and it was coupled with two dimethylacridine donors by Pd assisted amination procedure as schematized in Scheme 1.

Optimized geometry of AcDBTO was estimated by optimizing the molecular structure using Gaussian 09 program. The dimethylacridine donor was perpendicular to the dibenzothiophene dioxide plane by steric hindrance, which completely separated the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of AcDBTO calculated using B3LYP 6-31G* basis set (Fig. 1).

From the isolated HOMO and LUMO, it can be presumed that the AcDBTO compound may show strong CT properties. As a method of verifying the CT character, solution photoluminescence (PL) analysis of AcDBTO in cyclohexane, toluene, and tetrahydrofuan was carried out as presented in Fig. 2. Stepwise shift of the PL spectrum from short wavelength to long wavelength was noticeable by changing the solvent from non-polar (hexane) to highly polar (tetrahydrofuran) solvent, which corroborated the CT behavior of AcDBTO.

The CT attributes of AcDBTO may assist decreasing singlet energy-triplet energy gap by lowering the singlet energy, which was checked by solid PL measurement results of fluorescence and phosphorescence in Fig. 3. Fluorescence data were obtained from AcDBTO doped polystyrene film and Phosphorescent PL emission data were collected from frozen solid sample at 77 k after removing fluorescence by cutting-off short time PL emission component within 10 μs. Singlet energy-triplet energy gap of AcDBTO was 0.06 eV from singlet energy of 2.53 eV and triplet energy of 2.47 eV. It was relatively smaller than that of other dibenzothiophene dioxide based TADF emitters because of the strong donor strength provided by two dimethylacridine donors. Therefore, the AcDBTO emitter may function as a spin up-converting delayed fluorescent



Scheme 1. Synthetic scheme of AcDBTO.

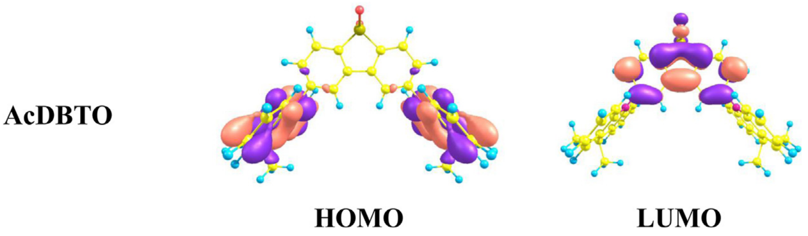


Fig. 1. HOMO and LUMO orbital distribution of AcDBTO.

Please cite this article in press as: J.H. Kim, J.Y. Lee, Dibenzothiophene-dioxide acceptor based thermally activated delayed fluorescent emitters for color tunable organic light-emitting diodes, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.02.001