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# Benzoisoquinoline-1,3-dione acceptor based red thermally activated delayed fluorescent emitters

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#### Abstract

A strong electron deficient moiety, benzoisoquinoline-1,3-dione, was applied as an electron acceptor of donor-acceptor type thermally activated delayed fluorescent (TADF) emitters. The connection of the benzoisoquinoline-1,3-dione acceptor moiety with a dimethylacridine donor moiety prepared 6-(9,9-dimethylacridin-10(9H)-yl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione and 5-(9,9-dimethylacridin-10(9H)-yl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione as red TADF emitters by strong electron deficiency of the benzoisoquinoline-1,3-dione acceptor. Device optimization of the red TADF emitters based on the delayed fluorescent behaviour of the red TADF emitters could offer high quantum efficiency of 11.2% in the red TADF devices.

Key words : red device, delayed fluorescence, quantum efficiency, benzoisoquinoline-1,3-dione

#### Introduction

The demand for high efficiency organic light-emitting diodes (OLEDs) is getting stronger as the power consumption is one of key issues of OLEDs. Although there have been great advances made in the development of low power OLEDs, the power consumption of the OLEDs is still a challenging issue.

The accomplishment of the low power consumption in the OLEDs was mainly made by high efficiency phosphorescent emitters which show high external quantum efficiency (EQE) close to 30%[1-5]. Red and green phosphorescent emitters already applied in commercial OLED products were main contributors to the development of low power consuming OLEDs[2,5]. However, the high price of the phosphorescent emitters by Ir metal was a hurdle to full utilization of the phosphorescent emitters is to use high efficiency emitters made up of pure organic moieties without any precious metal.

E-type delayed fluorescent emitters which are known as thermally activated delayed fluorescent (TADF) emitters can be a candidate as the pure organic based high efficiency emitters[6-11]. There has been a big progress of EQE of the TADF emitters for the last three years and the best EQE of the TADF device was as high as 30% in the green device[7,12-15]. As a result, the TADF emitters are promising as the organic type high efficiency emitters replacing phosphorescent emitters. However, the EQE of the red TADF device is not as high as that of green or blue devices[6-11,16-18] although high EQE of 17.5% (HAP-3TPA)[11] was known in the red device, which is mostly due to lack of strong electron acceptors for the red TADF emitters. Therefore, new strong electron accepting moieties are needed to reach the EQE level of the green and blue TADF devices.

In this work, an imide type electron deficient moiety, benzoisoquinoline-1,3-dione (BIQ), was used as an electron acceptor of a TADF emitter and was used to synthesize 6-(9,9-dimethylacridin-10(9H)yl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (6AcBIQ) and 5-(9,9-dimethylacridin-10(9H)- yl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (5AcBIQ) as red TADF emitters. Preparation, characterization, and device application of the TADF emitters were comprehensively covered. The 6AcBIQ red TADF emitter exhibited high EQE of 11.2%, red color coordinate of (0.55, 0.44), and peak wavelength of 597 nm.

#### **Experimental**

#### **General information**

4-Bromo-1,8-naphthalic anhydride was purchased from TCI Co. and aniline was supplied from Sigma-Aldrich Co.. 3-Bromo-1,8-naphthalic anhydride and sodium tert-butoxide were products of Alfa Aesar. 9,9-Dimethyl-9,10-dihydroacridine, tri-tert-butylphosphine, tris(dibenzylideneacetone) dipalladium (0), palladium (II) acetate were provided from P&H tech Co.. Molecular sieve, magnesium sulfate, ethanol, toluene, methylene chloride, ethyl acetate, and n-hexane from Duksan Sci. Co. were used without further purification.

The ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra were obtained using Jasco V-730 UV spectrophotometer and Perkin Elmer LS 55 luminescence spectrometer, respectively. Electrochemical analysis was carried out using Ivium Vertex with 0.1 M tetrabutylammonium perchlorate electrolyte in acetonitrile, Ag reference and Pt counter electrodes. Ferrocene was an internal standard material of the electrochemical measurement. Absolute PL quantum yields (PLQYs) of materials were measured using a doped solid film with a Hamamatsu Quantaurus-QY C11347-11 spectrometer.

#### **Synthesis**

Synthetic scheme of 6AcBIQ and 5AcBIQ compounds is described in Scheme 1.

#### 6-Bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione

4-Bromo-1,8-naphthalic anhydride (3.0 g, 10.83 mmol) was dissolved in distilled ethanol (150 mL).

Aniline (1.20 mL, 12.99 mmol) was added to the solution, and then the solution was refluxed overnight under nitrogen. The solution was cooled and the precipitate was filtered with no further purification. The product was an ivory powder (2.8 g, yield 74%)[19,20]. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): $\delta$  8.637-8.590 (m, 2H), 8.363 (d, 1H, J=8.0 Hz), 8.277 (d, 1H, J=8.0 Hz), 8.05 (t, 1H, J=7.75 Hz), 7.533 (t, 2H, J=8.0 Hz), 7.471 (t, 1H, J=7.25 Hz), 7.396 (d, 2H, J=7.0 Hz). MS (m/z): found, 354.0 ([M + H]<sup>+</sup>); Calcd. for C<sub>18</sub>H<sub>10</sub>BrNO<sub>2</sub>, 352.18.

#### 6-(9,9-Dimethylacridin-10(9H)-yl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (6AcBIQ)

6-Bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (0.7 g, 1.99 mmol), 9,9-dimethyl-9,10dihydroacridine (0.46 g, 2.20 mmol), sodium tert-butoxide (0.38 g, 3.95 mmol), and tris(dibenzylideneacetone)dipalladium (0) (0.05 g, 0.05 mmol) were dissolved in toluene (40 ml). Tritert-butylphosphine (0.08 g, 0.40 mmol) was added into the solution, and then the solution was refluxed overnight under nitrogen. The reaction mixture was cooled and extracted with methylene chloride and distilled water. The organic layer was dehydrated with magnesium sulfate and the solvent was evaporated. The crude powder was purified by column chromatography with ethyl acetate and nhexane. An orange powder was obtained as a product after purification (0.62 g, yield 65%)[21,22]. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):δ 8.748 (d, 1H, J=8.0 Hz), 8.556 (d, 1H, J=8.5 Hz), 8.001-7.957 (m, 2H), 7.846 (t, 1H, J=7.75 Hz), 7.635 (d, 2H, J=7.5 Hz), 7.567 (t, 2H, J=7.5 Hz), 7.497 (t, 1H, J=7.25 Hz), 7.445 (d, 2H, J=8.5 Hz), 6.941 (t, 2H, J=8.25 Hz), 6.891 (t, 2H, J=8.5 Hz), 5.909 (d, 2H, J=8.0 Hz), 1.820 (s, 3H), 1.725 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>):δ 163.47, 163.18, 143.09, 139.53, 135.98, 132.29, 131.31, 130.99, 130.25, 129.98, 129.47, 129.32, 129.09, 128.93, 128.53, 128.29, 126.78, 126.37, 124.13, 123.38, 121.06, 113.53, 35.64, 33.06, 32.46. MS (m/z): found, 481.1917 ([FAB+]); Calcd. for C<sub>33</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>, 481.1916.

#### 5-Bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione

5-Bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione was synthesized according to the

synthetic method of 6-bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione except that the reactant was 3-bromo-1,8-naphthalic anhydride (1.0 g, 3.61 mmol). The reaction mixture was extracted with methylene chloride and distilled water, and dehydrated with magnesium sulfate. A white powder was obtained as a product after purification by column chromatography with methylene chloride and n-hexane (0.65 g, yield 51%). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): $\delta$  8.813 (s, 1H), 8.513-8.441 (m, 3H), 7.938 (t, 1H, J=7.8 Hz), 7.551-7.460 (m, 3H), 7.38 (d, 2H, J=8.4 Hz). MS (m/z): found, 354.0 ([M + H]<sup>+</sup>); Calcd. for C<sub>18</sub>H<sub>10</sub>BrNO<sub>2</sub>, 352.18.

#### 5-(9,9-Dimethylacridin-10(9H)-yl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (5AcBIQ) 5-(9,9-dimethylacridin-10(9H)-yl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione was synthesized 6-(9,9-dimethylacridin-10(9H)-yl)-2-phenyl-1Hthe synthetic method of by same benzo[de]isoquinoline-1,3(2H)-dione. 5-Bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (0.65 g, 1.85 mmol) was used instead of 6-bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione palladium (II) acetate (0.02)0.06 mmol) instead and was used of g, tris(dibenzylideneacetone)dipalladium (0). The crude product was purified by column chromatography using methylene chloride instead of ethyl acetate (0.55 g, yield 62%). <sup>1</sup>H NMR (500 MHz, DMSO-

 $d_6$ ):  $\delta$  8.692 (s, 1H), 8.614-8.588 (m, 2H), 8.302 (s, 1H), 8.003 (t, 1H, J=7.75 Hz), 7.572-7.524 (m, 4H), 7.471 (t, 1H, J=8.0 Hz), 7.430 (d, 2H, J=8.5 Hz), 6.999-6.943 (m, 4H), 6.204 (d, 2H, J=9.5 Hz), 1.688 (s, 6H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  163.52, 163.07, 140.06, 139.07, 136.83, 135.92, 134.33, 133.68, 133.09, 131.36, 129.98, 129.06, 128.89, 128.28, 127.99, 127.40, 126.60, 126.36, 125.74, 122.93, 121.10, 113.81, 35.65, 31.34. MS (m/z): found, 481.1910 ([FAB+]); Calcd. for C<sub>33</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>, 481.1916.

#### Device fabrication and measurements

Device structure and device fabrication process of red TADF devices were described below.

ITO/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/ CBP:TPBI:red TADF emitter (25 nm, 5% doping)/TSPO1 (5 nm)/TPBI (40 nm)/LiF (1.5 nm)/Al (200 nm)

ITO represents indium tin oxide, PEDOT:PSS is poly(3,4ethylenedioxythiophene):poly(styrenesulfonate), TAPC is 4,4'-cyclohexylidenebis[N,N-bis(4methyphenyl)benzenamine], mCP is 1,3-bis(N-carbazolyl)benzene, CBP is 4,4'-di(9H-carbazol-9-yl)-1,1'-biphenyl and TPBI is 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene, TSPO1 is diphenyl(4-(triphenylsilyl)phenyl)phosphine oxide. Emitting layer of the TADF devices was 5% 6AcBIQ or 5AcBIQ doped CBP:TPBI. PEDOT:PSS was coated on the ITO substrate by spin coating and other organic layers were layered by vacuum evaporation. Device characterization was performed using CS1000 spectroradiometer and Keithley 2400 source meter.

#### **Results and discussion**

The electron deficient BIQ moiety has two carbonyl units conjugated to a naphthalene backbone structure to allow electron accepting character and low emission energy for red emission. The two carbonyl units are responsible for the strong electron accepting property and the extended conjugation structure is for the long wavelength emission. A strong dimethylacridine donor was combined with the BIQ acceptor for small singlet-triplet energy splitting ( $\Delta E_{ST}$ ) and red-shift of emission wavelength. Two BIQ based acceptors with different substituent positions of 5- and 6- were prepared to investigate the effect of substitution position on the material and device characteristics. Synthesis of the 6AcBIQ and 5AcBIQ started from brominated naphthalic anhydride, which reacted with aniline to synthesize the BIQ core. The brominated BIQ core was modified with dimethylacridine to prepare the final 6AcBIQ and 5AcBIQ products.

The 6AcBIQ and 5AcBIQ were reviewed as TADF emitters by figuring out the molecular orbital represented by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular

orbital (LUMO) in **Figure 1**. B3LYP functional 6-31G basis set embedded in the Gaussian package was used to calculate the molecular orbital. The BIQ electron acceptor and acridine donor isolated the HOMO on the acridine and LUMO on the BIQ. In particular, the perpendicular orientation of the acridine donor to the BIQ acceptor plane by steric hindrance between hydrogen of acridane and BIQ resulted in the isolation of the HOMO and LUMO. The HOMO and LUMO pictures of 6AcBIQ and 5AcBIQ were of little difference.

The similar separation of the HOMO and LUMO from molecular calculation resulted in the similar HOMO and LUMO levels estimated from electrochemical cyclic voltammetry measurements in **Figure 2**. The HOMO/LUMO values of 6AcBIQ and 5AcBIQ were -5.89/-3.89 eV and -5.85/-3.85 eV, respectively. The substitution position of the BIQ acceptor moiety had nothing to do with the HOMO/LUMO levels of the 6AcBIQ and 5AcBIQ. The LUMO level of the BIQ compounds was relatively deep compared to that of other TADF emitters, demonstrating strong electron accepting character of the BIQ acceptor[11, 23, 24]. The calculated HOMO/LUMO level of the BIQ moiety was - 6.47/-2.39 eV.

PL behaviour 6AcBIQ and 5AcBIQ was analysed by recording fluorescence and phosphorescence in **Figure 3**. Fluorescence spectra were collected at room temperature and phosphorescence spectra were gathered at 77k after delay time of 100  $\mu$ s. Broad charge transfer (CT) emission spectra with a peak emission wavelength of 570 nm were commonly observed in the 6AcBIQ and 5AcBIQ emitters. From the onset of the fluorescence spectra, singlet energy values of 2.38 and 2.41 eV in the 6AcBIQ and 5AcBIQ and 5AcBIQ, respectively, were determined. The origin of fluorescence was CT emission in both 6AcBIQ and 5AcBIQ, and that of phosphorescence was also CT emission. This experimental result was coincided with the electronic transition calculation results proposing CT excited state for the lowest triplet excited state. The onset wavelength of the phosphorescent spectra provided triplet energy values of 2.30 and 2.32 eV in the 6AcBIQ and 5AcBIQ emitters.  $\Delta E_{ST}$  values of 6AcBIQ and 5AcBIQ from

the PL data were 0.08 and 0.09 eV, respectively. The  $\Delta E_{ST}$  of the two emitters was less than 0.1 eV, which suggests the potential of 6AcBIQ and 5AcBIQ as up-converting emitting materials.

The up-conversion process from triplet excited state to singlet excited state was analysed by absolute PL quantum yield (PLQY) and delayed fluorescence decay of the emitters doped in the host materials. Absolute PLQYs of 6AcBIQ and 5AcBIQ were 38.9 and 21.5% under nitrogen, while they were 16.8 and 5.2% without nitrogen. The PLQY of 6AcBIQ was higher than that of 5AcBIQ with and without nitrogen, suggesting high radiative transition probability of 6AcBIQ. The 6- position modification of the BIQ backbone was advantageous for light emission by linear orientation of the donor and acceptor unit, while the 5- position modification of the BIQ backbone was disadvantageous by kinked arrangement of the donor and acceptor. Transient PL decay data provided further information about the prompt fluorescence and delayed fluorescence. The transient PL data in **Figure 4** compared PL decay of 6AcBIQ and 5AcBIQ doped in a mixed host of CBP and TPBI. The PL data of the two materials agreed each other, stating similar triplet to singlet up-conversion behaviour through delayed fluorescence. In general, the up-conversion by TADF process relies on the  $\Delta E_{ST}$  of the emitters. In the case of the 6AcBIQ and 5AcBIQ emitters, it seems that the similar  $\Delta E_{ST}$  below 0.1 eV brought about the same TADF behaviour. Excited state lifetime values of the TADF emission was 20.3 and 23.4 µs in the 6AcBIQ and 5AcBIQ emitters. All material related data are summarized in **Table 1**.

The transient PL behaviour of 6AcBIQ was further studied by recording temperature dependent PL decay at different temperatures (**Figure 5**). As the delayed fluorescence of 6AcBIQ TADF emitter is activated by thermal energy, gradual increase of the delayed PL intensity according to temperature was apparent in the PL decay data, confirming that the origin of delayed fluorescence is TADF.

The PL characterization results of 6AcBIQ and 5AcBIQ suggested that they would serve as TADF emitters in the devices. As the peak wavelength of the PL emission of 6AcBIQ and 5AcBIQ was in between 578 nm and 601 nm, they can be regarded as red TADF emitters. Therefore, they were applied as red emitters in the TADF devices by doping in the mixed host of CBP and TPBI. Device data at 5%

doping concentration were used to characterize the device performances of the 6AcBIQ and 5AcBIQ devices. Device data of the 6AcBIQ and 5AcBIQ are displayed in **Figure 6** and **7**. The current density of the two devices was quite similar because the emitters were doped in the same host material at the same doping concentration and had similar HOMO/LUMO levels. However, the luminance was relatively high in the 6AcBIQ device due to better quantum efficiency of the device.

The better exciton generation efficiency of the 6AcBIQ device was confirmed by EQE of the 6AcBIQ and 5AcBIQ devices in **Figure 7**. The maximum EQE of the 6AcBIQ device was 9.5%, which was much higher than 4.6% of the 5AcBIQ device. The EQE was more than doubled just by changing the substitution position of the acridine donor to the BIQ acceptor core. The EQE is closely associated with the PLQY of the emitters, and the relative high EQE of the 6AcBIQ device is also caused by relatively higher PLQY of 6AcBIQ than that of 5AcBIQ.

Electroluminescence (EL) spectra of the 6AcBIQ and 5AcBIQ devices in **Figure 8** demonstrate that the two TADF emitters are red emitters with a peak wavelength around 600 nm. Although the peak wavelength was slightly red-shifted in the 6AcBIQ, the EL spectra were quite similar. The EL emission behaviour was in agreement with the PL emission of the emitters. Color coordinates of the 6AcBIQ and 5AcBIQ were (0.56, 0.44) and (0.54, 0.46), respectively.

The EQE of the 6AcBIQ was further studied by changing the host material from the CBP:TPBI host to a bipolar host material[25]. A bipolar host material reported in the literature, 3-(3-(9H-carbazol-9-yl)phenyl)furo[2,3-b:5,4-b']dipyridine (mCPPFP)[15], was used to enhance the EQE of the 6AcBIQ emitters. The EQE of the mCPPFP:6AcBIQ was 11.2% as shown in **Figure 9**. The EQE was reduced according to doping concentration and maximum EQE was obtained at low doping concentration. Although the EQE was reduced at high doping concentration, the EL spectra moved to long wavelength and color purity was improved. Device characteristics of the red TADF devices are summarized in **Table 2**.

#### Conclusions

In summary, a benzoisoquinoline-1,3-dione based acceptor, BIQ, was developed as a strong electron acceptor for the material design of red TADF emitters. 6AcBIQ and 5AcBIQ emitters derived from the BIQ acceptor functioned as the red TADF emitters by activating delayed fluorescence transition induced by small  $\Delta E_{ST}$ . 6AcBIQ performed better than 5AcBIQ by achieving high EQE of 11.2% as a red TADF emitter. Although the EQE value is not as high as the state of the art red TADF devices, further design and device engineering may improve the EQE further.

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	HOMO/LUMO (eV)	E <sub>S</sub> /E <sub>T</sub> (eV)	$\Delta E_{ST}$ (eV)	PLQY (%) [a]		Excited state
				$N_2$	<b>O</b> <sub>2</sub>	(µs)
6AcBIQ	-5.89/-3.89	2.38/2.30	0.08	38.9	21.5	20.3
5AcBIQ	-5.85/-3.85	2.41/2.32	0.09	16.8	5.2	23.4

### Table 1. Photophysical properties of 6AcBIQ and 5AcBIQ

[a] PLQYs measured in film

	CIE (x,y)	Maximum EQE (%)	Maximum PE (LmW <sup>-1</sup> )	EQE (%) <sup>[a]</sup>	PE (LmW <sup>-1</sup> ) <sup>[b]</sup>
6AcBIQ	0.56, 0.44	9.5	18.7	3.4	3.0
5AcBIQ	0.54, 0.46	4.6	9.9	1.0	0.8
6AcBIQ <sup>[c]</sup>	0.55, 0.44	11.2	23.0	4.4	3.5

Table 2. Device characteristics of 6AcBIQ and 5AcBIQ

[a] External quantum efficiency measured at 1000cdm<sup>-2</sup>
[b] Power efficiency measured at 1000cdm<sup>-2</sup>

[c] Device performances of mCPPFP:6AcBIQ at 3% doping concentration





Figure 1. HOMO and LUMO distribution of (a) 6AcBIQ and (b) 5AcBIQ



Figure 2. CV curves of 6AcBIQ and 5AcBIQ



Figure 3. UV-Vis, fluorescence and phosphorescence spectra of (a) 6AcBIQ and (b) 5AcBIQ



Figure 4. Transient PL curves of 6AcBIQ and 5AcBIQ



Figure 5. Transient PL curves of 6AcBIQ at different temperatures



Figure 6. Current density-voltage-luminance plots of 6AcBIQ and 5AcBIQ at 5% doping concentration



Figure 7. Quantum efficiency plots of 6AcBIQ and 5AcBIQ devices against luminance



Figure 8. EL spectra of 6AcBIQ and 5AcBIQ devices



**Figure 9.** Quantum efficiency-luminance plots of the 6AcBIQ devices with a mCPPFP host according to doping concentration

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- Benzoisoquinoline-1,3-dione as an acceptor of red thermally activated delayed fluorescent emitters
- Combination of benzoisoquinoline-1,3-dione and dimethylacridine in the donoracceptor type molecular design
- High quantum efficiency of 11.2% in red thermally activated delayed fluorescent devices

AND MARINE