Carbazole and Benzophenone Based Twisted Donor-Acceptor Systems as Solution Processable Green Thermally Activated Delayed Fluorescence Organic Light Emitters

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New donor-acceptor (D-A) and donor-acceptor-donor (D-A-D) systems with carbazole and benzophenone moieties as donor and acceptor, respectively, have been synthesized. Photoluminescence quantum yields of D-A and D-A-D molecules in thin film were 76 and 73%, respectively. Solution-processed organic light-emitting diodes containing these D-A and D-A-D molecules as emitters showed the maximum external quantum efficiencies of 6.9 and 10.4% with a peak wavelength of 520 and 521 nm, respectively.

Keywords:	Organic light-emitting diode				
	Twisted donor-acceptor				
	Thermally activated delayed fluorescence				

There have been numerous studies of conjugated donoracceptor (D-A) systems and one significant phenomenon of the D-A systems is twisted intramolecular charge transfer (TICT),¹ which is generally related to solvatochromism in fluorescence spectra and thermally activated delayed fluorescence (TADF) in organic light-emitting diodes (OLEDs). Previously, the improvement of efficiency of OLEDs had been achieved by harnessing phosphorescence because electric excitation forms 25% singlet excitons and 75% triplet excitons.² Transition metal-based complexes had been developed as phosphorescence emitters,³ though they are expensive and rare on earth. Recently, a new technology, named TADF, has received much attention,⁴ which can achieve 100% internal quantum efficiency without using any metals by up-converting triplet into singlet excited state.

To develop TADF emitters, it is necessary to reduce the energy difference $\Delta E_{\rm ST}$ between the lowest excited singlet state (S₁) and the lowest triplet state (T₁), and simultaneously to increase the oscillator strength (*f*) between the S₁ and ground state (S₀).⁵ A small $\Delta E_{\rm ST}$ is achieved when the spatial overlap between highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is small, while a large *f* is maintained when the spatial overlap is large.

Considering these two factors, carbazole (CZ) with high electron-donating ability and benzophenone (BP), which emits phosphorescence via intersystem crossing,⁶ are chosen as donor and acceptor, respectively. Although TADF materials composed of CZ or BP moiety have been reported so far,⁷ D-A (**2CZBP**) and D-A-D (**4CZBP**) systems with twisted CZ and BP moieties linked through amino group (Figure 1), have not been investigated yet.

Table 1 shows calculated electronic properties, energy levels of HOMO, LUMO, and HOMO-LUMO energy gap, f, and (ΔE_{ST}) of **2CZBP** and **4CZBP**. The HOMO, LUMO, and HOMO-LUMO energy gap were calculated at the PBE0/6-

31G(d) level of theory, and $\Delta E_{\rm ST}$ was calculated at the TD-PBE0/6-31G(d) level of theory. The energy diagrams are shown in Figure S1. All the quantum chemical calculations were performed using the Gaussian 09 program package.⁸ The HOMO-LUMO gaps of **2CZBP** and **4CZBP** were both 2.6 eV, suggesting that they will emit green fluorescence.

Calculated torsion angles between CZ and BP moieties of **2CZBP** and **4CZBP** are 25° and 31°, respectively (Figure 2). Figure 2 shows HOMO and LUMO distributions of **2CZBP** and **4CZBP**. The HOMOs of **2CZBP** and **4CZBP** are mainly



Figure 1. Chemical structures of 2CZBP, 4CZBP, and 2CZPh.

 Table 1. Calculated electronic properties of 2CZBP and

 4CZBP

	HOMO /eV	LUMO /eV	HOMO- LUMO gap/eV	f^{a}	$\Delta E_{ m ST}^{ m b}$ /eV
2CZBP	-5.2	-2.6	2.6	0.409	0.24
4CZBP	-5.1	-2.5	2.6	0.812	0.29

^aOscillator strength for the $S_0 \rightarrow S_1$ transition. ^bDifference between minimum potential energies of S_1 and T_1 .



Figure 2. HOMOs and LUMOs of 2CZBP and 4CZBP. Electron donating and electron accepting units of 2CZBP and 4CZBP are indicated in red and blue, respectively.

distributed on the CZ moiety and benzene ring of BP moiety covalently linked with amine nitrogen, while the LUMOs are mainly distributed on BP moiety. The moderate HOMO-LUMO spatial separation and overlap leads to the relatively small $\Delta E_{\rm ST}$ (0.24–0.29 eV) and large f (0.409–0.812). The f values of **2CZBP** and **4CZBP** are larger than that of 3-(*N*-carbazolyl)benzophenone (f = 0.36).^{7a} These calculations indicate that **2CZBP** and **4CZBP** are good candidates for green TADF emitters.

Although numerous TADF emitters have been synthesized, many of them have been applied in vacuum-deposition processes. On the other hand, solution processes are simple, and suitable for low-cost mass production of large area OLED displays and lighting. However, reports of solution processable TADF emitter are still rare.⁹ In general, solution processable materials are required to have good solubility in organic solvents, and therefore bulky or long alkyl substituents are usually introduced in aromatic rings, which requires multiple synthetic steps. As we have prepared several carbazole derivatives,¹⁰ we anticipate that *N*-ethylcarbazole derivatives will show enough solubility for solution processing. In this study, we report simple two-step reaction and photophysical properties of **2CZBP** and **4CZBP**. Their applications for solution-processed light emitting layer in OLEDs are also shown.

The synthetic route of **2CZBP** and **4CZBP** are shown in Scheme 1. They were synthesized in moderate yields from commercially available *N*-ethylcarbazole by only two-step reaction. *N*-Ethylcarbazole **1** was iodized with 1,3-diiodo-5,5-dimethylhydantoin to give *N*-ethyl-3-iodocarbazole **2** in 81%. Synthesis of **2CZBP** and **4CZBP**, and their reference **2CZPh**¹¹ (Figure 1) were accomplished in moderate yields using Buchwald-Hartwig amination¹² of **2** with appropriate aminobenzophenone derivatives, **3a** and **3b**, and aniline **3c**, respectively. Isolated **2CZBP** and **4CZBP** are soluble in common organic solvents and applied for solution process. Detailed synthetic procedures and characterization data of these compounds are described in the Supporting Information S2, S3, and S4.

Figure 3 shows the electronic absorption spectra of 2CZBP, 4CZBP, and 2CZPh in CH₂Cl₂. The longest absorption maximum wavelengths (λ_{max} s) of 2CZBP and 4CZBP exhibit bathochromic shift compared with that of 2CZPh and the molar extinction coefficients (ε s) of 2CZBP and 4CZBP at λ_{max} are much larger than that of 2CZPh (Table S5), indicating the charge transfer absorption of 2CZBP and 4CZBP due to the polarized D-A conjugated system. The solvent polarity does not affect 2CZPh, 2CZBP, and 4CZBP in electronic absorption spectra significantly (Figure S6).



Scheme 1. Synthetic route of 2CZBP, 4CZBP, and their reference 2CZPh.



Figure 3. Electronic absorption spectra of 2CZBP, 4CZBP, and 2CZPh in dichloromethane.



Figure 4. PL spectra of (a) 2CZPh, (b) 2CZBP, and (c) 4CZBP in various solvents.

In contrast, solvent effect upon photoluminescence (PL) spectra was observed for **2CZBP** and **4CZBP**, while that upon **2CZPh**, which has no acceptor moiety, was very little (Figure 4). Significant bathochromic shifts and broadening with the increase of polarity of the solvent were observed for **2CZBP** and **4CZBP**. These results indicate that intramolecular charge transfer character exists in **2CZBP** and **4CZBP**, namely, TICT state are induced in the excited states. ΔE_{ST} values of **4CZBP** and **2CZBP** were estimated to be 61 meV and 13 meV from the onset of fluorescence and phosphorescence spectra (Figure S7).

Photoluminescence quantum yields ($\Phi_{PL}s$) and emission peak wavelengths ($\lambda_{PL}s$) of **2CZPh**, **2CZBP**, and **4CZBP** in various solvents are summarized in Table S8.

 Φ_{PL} s of the films for 5 wt% **2CZBP** or **4CZBP** doped in host materials are summarized in Table 2. Among three hosts, 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1), 4,4'bis(*N*-carbazolyl)-1,1'-biphenyl (CBP), and 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl (CDBP), TCz1 gave the highest Φ_{PL} s under nitrogen atmosphere (76% for **2CzBP** and 73% for **4CzBP**). These values were larger than those in oxygen-free toluene (40% for **2CZBP** and 34% for **4CZBP**) due to the restriction of the intra- and inter-molecular nonradiative transition in rigid matrix. The increase of Φ_{PL} of **4CZBP**:TCz1 film

 Table 2.
 PL properties of 5 wt% 2CZBP and 4CZBP doped in host materials

Emitter	Host	$\lambda_{\mathrm{ex}}{}^{\mathrm{a}}$ /nm	$\lambda_{ m PL}$ /nm	$\Phi_{ m PL}$ under N ₂ /%	$arPerta_{ ext{PL}}$ under air $/\%$
2CZBP	TCz1	290	516	76	70
2CZBP	CBP	340	511	70	61
2CZBP	CDBP	290	508	67	56
4CZBP	TCz1	290	504	73	37
4CZBP	CBP	340	517	59	53
4CZBP	CDBP	290	497	52	28

^aExcitation wavelength.



Figure 5. Transient PL decay curves of 5wt% 2CZBP:TCz1 and 5 wt% 4CzBP:TCz1 films at 300 K.

under nitrogen atmosphere compared to that under air suggests that oxygen quenches some T₁ excitons derived from S₁ to T₁ intersystem crossing. As expected from the smaller increase of Φ_{PL} of **2CZBP**:TCz1 film after nitrogen bubbling in Table 2, the delayed fluorescence from a **2CZBP**:TCz1 film is not clear (Figure 5). In contrast, the transient PL decay measurement of a **4CZBP**:TCz1 film shows clear delayed fluorescence in addition to prompt component, confirming the TADF character for **4CZBP**. The result is in accord with large increase of Φ_{PL} after nitrogen bubbling for **4CZBP** systems in Table 2. The delayed PL component of **4CZBP**:TCz1 films increased with increasing temperature as shown in Figure S9, indicating that the delayed PL was thermally activated.

We fabricated OLEDs using 2CZBP:TCz1 or 4CZBP:TCz1 as a solution-processable light emitting layer, indium tin oxide (ITO) as an anode, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as a hole transport layer, 2,2',2"-(1,3,5-benzinetrivl)-tris(1-phenyl-1H-benzimidazole) (TPBi) as an electron transport layer, lithium quinolin-8-olate (Liq) as an electron injection layer, and Al as a cathode. The device structure is ITO (50 nm)/PEDOT:PSS (30-40 nm), /5 wt% 2CZBP or 4CZBP: TCz1/TPBi (50 nm)/Liq (1 nm)/Al (80 nm). The peak wavelengths of the electroluminescence spectra (EL) for 2CZBP and 4CZBP were 520 and 521 nm, respectively. For the devices with doping concentration of 5 wt%, the maximum external quantum efficiencies (η_{EOE} s) of 2CZBP and 4CZBP were 6.9 and 8.5%, respectively (Table S10). A higher η_{EQE} of 10.4% was obtained for **4CZBP** by further optimizing the dopant concentration (15 wt%) and



Figure 6. η_{EQE} -current density characteristics of **2CZBP**- and **4CZBP**-based devices.

the thickness of TPBi (70 nm) (Figure 6). The current density-voltage-luminance characteristics of the fabricated OLEDs are shown in Figure S11.

In summary, we have designed and synthesized twisted D-A and D-A-D molecules, **2CZBP** and **4CZBP**, respectively, containing carbazole and benzophenone moieties, in only twostep reactions from commercially available reagents in moderate yields. Photophysical properties of **2CZBP** and **4CZBP** were examined and the solvent effect upon electronic absorption spectra was little, while that upon PL spectra was observed. From transient PL decay curves and PL spectra under air and nitrogen atmosphere, **4CZBP** showed clear TADF character. Solution-processed OLEDs containing **4CZBP** showed the maximum η_{EQE} of 10.4% with a peak wavelength of 521 nm.

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