



Molecular Orientations of Delayed Fluorescent Emitters in a Series of Carbazole-Based Host Materials

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OPEN ACCESS

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Specialty section:

This article was submitted to
Organic Chemistry,
a section of the journal
Frontiers in Chemistry

Received: 27 December 2019

Accepted: 23 April 2020

Published: 25 May 2020

Citation:

Sasabe H, Chikayasu Y, Ohisa S, Arai H, Ohsawa T, Komatsu R, Watanabe Y, Yokoyama D and Kido J (2020) Molecular Orientations of Delayed Fluorescent Emitters in a Series of Carbazole-Based Host Materials. *Front. Chem.* 8:427. doi: 10.3389/fchem.2020.00427

Molecular orientation is one of the most crucial factors to boost the efficiency of organic light-emitting devices. However, active control of molecular orientation of the emitter molecule by the host molecule is rarely realized so far, and the underlying mechanism is under discussion. Here, we systematically investigated the molecular orientations of thermally activated delayed fluorescence (TADF) emitters in a series of carbazole-based host materials. Enhanced horizontal orientation of the TADF emitters was achieved. The degree of enhancement observed was dependent on the host material used. Consequently, our results indicate that π - π stacking, CH/ n ($n = O, N$) weak hydrogen bonds, and multiple CH/ π contacts greatly induce horizontal orientation of the TADF emitters in addition to the molecular shape anisotropy. Finally, we fabricated TADF-based organic light-emitting devices with an external quantum efficiency (η_{ext}) of 26% using an emission layer with horizontal orientation ratio (Θ) of 79%, which is higher than that of an almost randomly oriented emission layer with Θ of 62% ($\eta_{\text{ext}} = 22\%$).

Keywords: delayed fluorescence, molecular orientation, light out-coupling efficiency, carbazoles, weak hydrogen bonds

INTRODUCTION

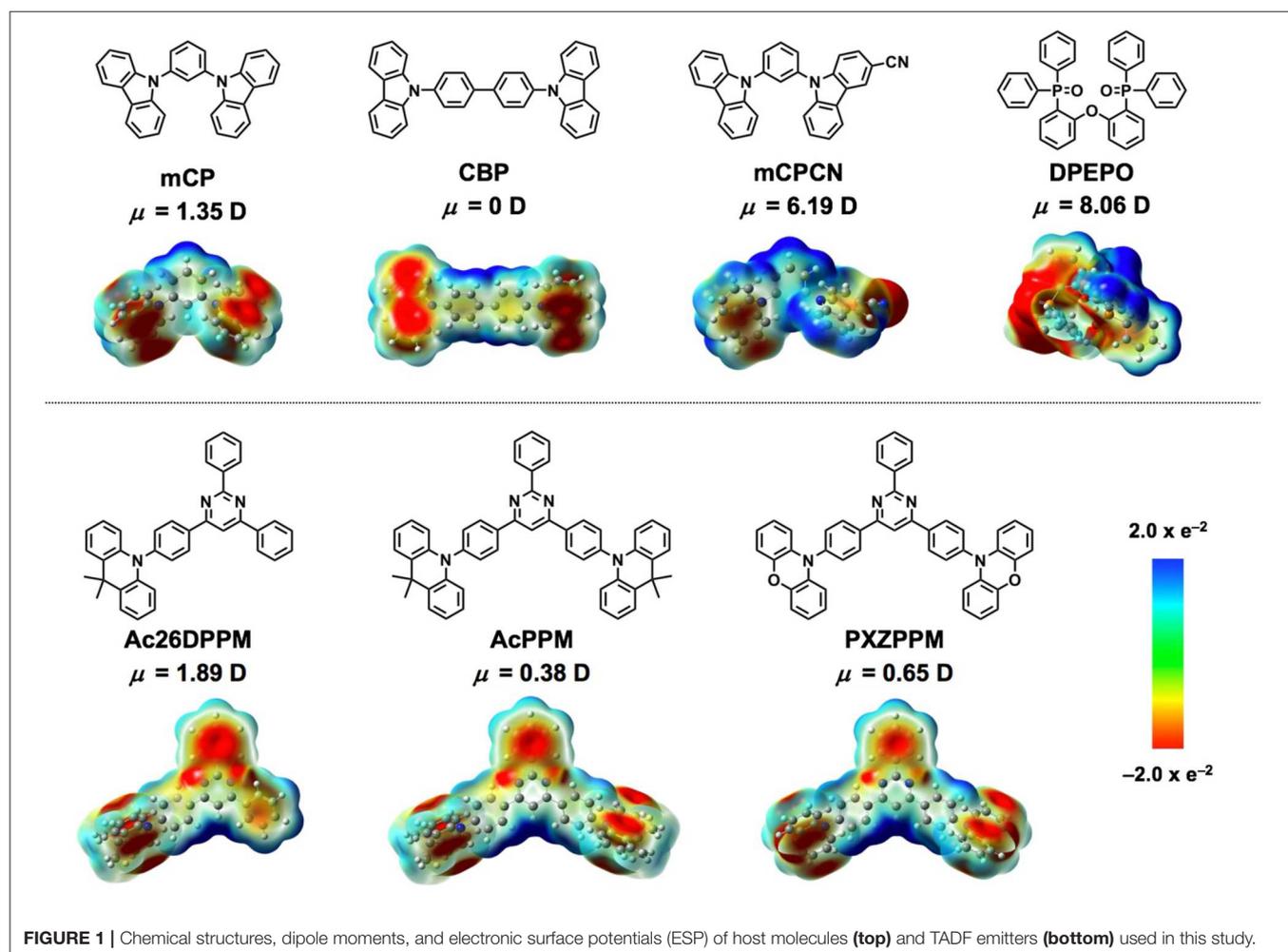
A series of fluorescent emitters exhibiting significant delayed fluorescence, so-called thermally activated delayed fluorescent (TADF) emitters, has attracted much attention due to its potential usefulness in high-performance organic light-emitting devices (OLEDs) that can realize an internal quantum efficiency (η_{int}) of 100% (Uoyama et al., 2012; Sasabe and Kido, 2013; Adachi, 2014; Kaji et al., 2015; Lin et al., 2016; Im et al., 2017; Wong and Zysman-Colman, 2017; Yang et al., 2017; Komatsu et al., 2018). In principle, TADF emitters consist of electron-donor (D) and electron-acceptor (A) moieties realizing efficient intramolecular charge transfer (ICT). The connection between D and A moieties is generally accompanied with a small overlap in the frontier molecular orbital (FMO) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), in other words, a small energy difference between singlet and triplet energies (ΔE_{ST}). Recent rapid development in TADF emitters enables OLEDs to achieve an external quantum efficiency (η_{ext}) over 30% (Kaji et al., 2015; Komino et al., 2016; Lin et al., 2016; Liu et al., 2017; Rajamalli et al., 2017; Wu et al., 2018; Ahn et al., 2019; Kondo et al., 2019). To obtain such a high-performance in OLEDs, horizontal orientation of the emission dipole moment (EDM) is absolutely essential. Perfect horizontal orientation of the EDM has been reported to boost OLED

efficiency up to 150% compared to random EDM orientation (Frischeisen et al., 2011; Yokoyama, 2011; Schmidt et al., 2017; Kim and Kim, 2018; Watanabe et al., 2019b). However, the horizontal orientation ratio (Θ) of most TADF emitters used in OLEDs realizing η_{ext} over 30% is reportedly only around 80%, which is far behind perfect horizontal orientation ($\Theta = 100\%$). In general, a guest TADF emitter is dispersed into a host material to reduce concentration quenching, and to maintain carrier balance in the emission layer (EML). The proportion of guest molecule is commonly much smaller than that of host molecule. Thus, the non-covalent interactions between host and guest molecules should be one of the important factors that controls the molecular orientation.

In an early stage of study on molecular orientation in OLEDs, Yokoyama used variable-angle spectroscopic ellipsometry (VASE) measurements to reveal the anisotropy of the molecular shape, such as in planar and linear structures, is essential to realize horizontal orientation of a series of triphenylamine and carbazole based-fluorescent molecules, even in randomly oriented host molecules (Yokoyama et al., 2009). However, unlike first-generation fluorescent molecules, most TADF molecules do not have a planar structure but instead a winding

chemical structure in needed to realize a small overlap of the frontier molecular orbitals in order to achieve efficient reverse intersystem crossing (RISC). Therefore, in addition to the molecular shape anisotropy, advanced strategies to actively use non-covalent interactions to realize enhanced horizontal orientation are highly desired.

In 2016, Lin and Wong reported three types of sky-blue TADF emitters using triphenyltriazine as an acceptor and substituted acridines as a donor unit (Lin et al., 2016). Among these, **SpiroAc-TRZ** with spirobiphenyl unit showed a photoluminescent quantum yield (η_{PL}) of 100%, and a high Θ value of 83% in **mCPCN** host. They indicated that this high Θ value of **SpiroAc-TRZ** is attributed to the overall planar and balanced/symmetrical structure. The corresponding OLED exhibited an extremely high η_{ext} of nearly 37%. In the same year, Komino and Adachi reported the complete horizontal orientation of a linear-shaped TADF emitter named **Cis-BOX2** in a randomly oriented host matrix at the temperature of 200 K (Komino et al., 2016). The horizontal orientation ratio of **Cis-BOX2** depended on the deposition temperature and the type of host matrix. A **Cis-BOX2**-based OLED showed a very high η_{ext} of 33%.



As mentioned above, although a high Θ value of up to 100% at 200 K has been reported, the underlying mechanism to realize horizontal orientation is still under discussion at this stage (Yokoyama, 2011; Mayr and Brütting, 2015; Moon et al., 2015; Shibata et al., 2015; Friederich et al., 2017; Schmidt et al., 2017; Gujral et al., 2018; Kim and Kim, 2018; Lee et al., 2018; Pal et al., 2018; Watanabe et al., 2019b). In order to deepen insights into the underlying mechanism, we wish to report a systematic investigation on the molecular orientations of TADF molecules in a series of carbazole-based host materials. To reveal the structure–property relationship for horizontal orientation, a series of TADF emitters, which we can systematically change the parameters one by one, should be necessary. In this context, we have already developed a series of pyrimidine-based TADF emitters with different donor group(s) (Figure 1) (Komatsu et al., 2016a,b; Nakao et al., 2017). By comparing these three molecules, we can obtain insight into the effects of two factors: (i) donor number, which reflects the molecular shape anisotropy in these comparisons, and (ii) donor structure. Consequently, we achieved enhanced Θ values of TADF emitters and the degree of enhancement depended on the host material used. Consequently, our results indicate that increased π - π stacking, CH/n ($n = O, N$) weak hydrogen bond (H-bond) interaction, and multiple CH/ π contacts greatly induce horizontal orientation of TADF emitters in addition to the molecular shape anisotropy. Finally, we fabricated a TADF-based OLED with η_{ext} of 26% using an emission layer (EML) with a Θ value of 79%, which is greater than that of an almost randomly oriented EML with a Θ value of 62% ($\eta_{\text{ext}} = 22\%$).

RESULTS AND DISCUSSION

Selection of Carbazole-Based Host Molecules and Phosphine-Oxide Host Molecules

Carbazole derivatives are one of the most popular host materials in OLEDs. Therefore, insights into carbazole-based host materials are considered to be highly valuable. To identify the underlying mechanisms of horizontal orientation, we selected four types of host materials to study and sequentially changed their chemical structures (Figure 1 and Table 1). **mCP** was used as the benchmark material. Extending its π -conjugation, results in **CBP**, which can be used to evaluate the effect of π -conjugation or π - π stacking when compared to **mCP**. The introduction of CN substituent into **mCP** forms **mCPCN** (Lin et al., 2012). Using this molecule, we can validate the effect of CN substituent, such as the dipole/dipole interaction and CH/N weak H-bonds. A phosphine-oxide host material, **DPEPO** (Han et al., 2011) was used to investigate the effect of the dipole moment and CH/O weak H-bonds of P=O substituents (Figure 2). Note that all the host materials used in this study showed random orientation. DFT calculations were performed at B3LYP 6-31G(d) level to evaluate the dipole moment and visualize the electronic surface potential (ESP), as shown in

TABLE 1 | Thermal and optical properties of the host molecules.

Compound	Mw (g/mol)	$T_g^a/T_m^a/T_{d5}^b$ (°C)	$I_p^c/E_g^f/E_a^g/E_T^h$ (eV)	S^i
mCP	408	60/n.d./280	-6.01/3.49/-2.63/3.00	0.08
CBP	485	62/283/413	-5.91/3.44/-2.67/2.60	-0.07
mCPCN	434	97/222/313	-6.08/3.44/-2.64/3.03	0.08
DPEPO	571	n.d./280/322	-6.70/4.00/-2.70/3.30	0.00

^a T_g and T_m were determined using DSC. ^b T_{d5} was determined using TGA. ^c I_p was determined using PYS. ^d E_g was taken as the point where the normalized absorption spectra intersected. ^e E_a was calculated using I_p and E_g . ^f E_T was estimated from the onset of the phosphorescent spectra at 5 K. ^gVASE derived order parameter.

TABLE 2 | Thermal and optical properties of the TADF emitters.

Compound	Mw (g/mol)	$T_g^a/T_m^a/T_{d5}^b$ (°C)	$I_p^c/E_g^f/E_a^g/E_T^h$ (eV)
Ac-26DPPM	516	90/210/383	-5.67/2.90/-2.77/2.80
Ac-PPM	723	n.d./388/442	-5.65/2.80/-2.85/2.65
PXZ-PPM	671	n.d./290/473	-5.65/2.56/-3.09/2.56

^a T_g and T_m were determined using DSC. ^b T_{d5} was determined using TGA. ^c I_p was determined using PYS. ^d E_g was taken as the point where the normalized absorption spectra intersected. ^e E_a was calculated using I_p and E_g . ^f E_T was estimated from the onset of the phosphorescent spectra at 5 K.

Figure 1 and Figure S1 (in supporting information). Among the host materials, **mCP** and **CBP** had small dipole moment <1.5 D, while **mCPCN** with a cyano group and **DPEPO** with phosphine oxide groups possessed a large dipole moment >6.0 D. ESP exhibited strong negative charge (red color) on the π -plane of the carbazole and on the electron-withdrawing groups of CN and P=O. The hydrogen (H) atoms on the aromatic rings had positive charge (blue color).

Selection of TADF Emitters

We selected three types of pyrimidine-based TADF emitters named **Ac26DPPM** (Nakao et al., 2017), **AcPPM** (Komatsu et al., 2016a), and **PXZPPM** (Komatsu et al., 2016b) with different donor group(s) such as dimethylacridine (Ac) and phenoxiazine (PXZ) (Figure 1 and Table 2). By comparing these three molecules, we can obtain insight into the effects of two factors: (i) donor number, which reflects the molecular shape anisotropy in these comparisons, and (ii) donor structure. Note that all the emitter molecules showed random orientation in neat film (Figure S2). Similar to the host molecules, DFT calculations were performed to evaluate the dipole moment and visualize the ESP and the results are shown in Figure 1 and Figure S1. All the emitters have a small dipole moment <2.0 D, especially **AcPPM** ($\mu = 0.38$ D) and **PXZPPM** ($\mu = 0.65$ D). The ESP indicates strong negative charge on the π -plane of position 2 of pyrimidine and on the electron-donating end-cap unit(s) of Ac and PXZ. Similar to the host molecules, H atoms on the aromatic rings had positive charge.

Molecular Orientation of TADF Emitters

First, we investigated the molecular orientations of 10 wt% **Ac26DPPM**-doped host films by using angle dependent PL measurements. Here, a Θ value of 67% indicates random orientation while a value of 100% indicates perfect horizontal orientation. **Ac26DPPM**-doped **mCP** film showed moderate vertical orientation with $\Theta = 53\%$. When **Ac26DPPM** was doped into other host materials (**CBP**, **mCPCN**, and **DPEPO**), all the doped films exhibited almost random orientation with Θ of 62–66% (**Figure 3** and **Figure S3**). Although these films showed random orientation due to the small anisotropy of **Ac26DPPM**, the differences of orientation ratio in the different host materials ($\Delta\Theta$) were 9–13%. These differences are not small but meaningfully significant. Similar results were obtained in the case of **AcPPM** (**Figure 4** and **Figure S4**). When host material was changed from **mCP** to one of the other host materials, a significant enhancement of Θ values up to 22% was observed. Since **AcPPM** has larger molecular shape anisotropy than that of **Ac26PMM**, **AcPPM** showed increased horizontal orientation with Θ of 75–80%. Surprisingly, **PXZPPM** also exhibited similar tendencies as the Ac-end-capped emitters (**Figure 5** and **Figure S5**). When **mCP** was used, the **PXZPPM/mCP** film showed almost random orientation with Θ of 62%, while when **PXZPPM** was doped into the other host materials, all the doped films exhibited significant horizontal orientation with Θ of 74–81%. Among these emitters, it was determined that bulky methyl groups on Ac end-capping groups do not cause a negative effect toward horizontal orientation as the emitter without methyl groups showed very similar Θ values.

Underlying Mechanism for Horizontal Orientation

To validate the underlying mechanisms for horizontal orientation, we compared the chemical structures of the host materials. When host was changed from **mCP** to **CBP**, π -conjugation is expanded from phenyl to a biphenyl linker. Therefore, enhanced π - π stacking can be considered as an additional interaction. Note that the dipole moment of **CBP** is calculated to be 0 D, while that of **mCP** is 1.35 D. Further, the dipole moments of the emitters are smaller than 2.0 D. Thus, dipole/dipole interaction can be ruled out as a major interaction. In the case of **mCPCN**, the difference of chemical structure is only a CN group on the carbazole plane. Since the CN group is a strong electron-withdrawing group, the resulting **mCPCN** has a large dipole moment of 6.19 D. However, as mentioned in the case of **CBP**, the contributions from dipole/dipole interaction can be considered to be small because the emitters used in this study have very small dipole moment <2 D. In fact, the $\Delta\Theta$ of **Ac26DPPM** ($\Delta\Theta = 9\%$) with a larger dipole moment ($\mu = 1.89$ D) was smaller than that of **AcPPM** ($\Delta\Theta = 17\%$) with a smaller dipole moment ($\mu = 0.38$ D). Therefore, it is only CH/N weak H-bond of CN group plays a key role. The binding energy of CH/N weak H-bond is 10–20 kJ/mol (Desiraju and Steiner, 1999). This interaction has been reported to be a key to controlling horizontal orientation of oligopyridine-containing

electron transporters (Sasabe et al., 2011; Yokoyama et al., 2011; Watanabe et al., 2019a,b). **DPEPO** is a frequently used host material in high efficiency TADF OLEDs, and the films using it as the host showed the largest Θ values among the four host materials. **DPEPO** has a large dipole moment of 8.06 D, and therefore the contributions from dipole/dipole interaction are considered to be large. However, similar to the case of **mCPCN**, the contributions from dipole/dipole interaction can be considered to be small because the emitters used in this study have very small dipole moment <2 D. In fact, the $\Delta\Theta$ of **Ac26DPPM** ($\Delta\Theta = 13\%$) with a larger dipole moment ($\mu = 1.89$ D) was smaller than that of **AcPPM** ($\Delta\Theta = 22\%$) with a smaller dipole moment ($\mu = 0.38$ D). Given that **DPEPO** has short conjugation lengths with steric hindrance, π - π interaction is relatively small. Thus, it can be considered that CH/O weak H-bond from P=O and ether linker plays a key role in determining the horizontal orientation when **DPEPO** is used as the host material. Recently, Samuel and Zysman-Colman proposed that the significant number of electronegative sites from P=O and ether linker on the surface of **DPEPO** vacuum-deposited film plays an important role for horizontal molecular orientation (Pal et al., 2018). Further, it has also been reported that the strong acceptor property of P=O forms shorter CH...O H-bond, and the bond length of the CH...O H-bond is relatively shorter than that of CH...N H-bond (Desiraju and Steiner, 1999).

Among the three emitters, **PXZPPM** and **AcPPM** showed similar tendencies for horizontal orientation, even though **AcPPM** has four bulky methyl groups on the acridine end-capping units. One possible reason for this is the contributions from multiple CH/ π contacts between the methyl groups and the π planes. CH/ π contact is a very small interaction, and the binding energy is only 2–3 kJ/mol (Nishio et al., 1998). However, when the molecule has a large number of methyl groups, the contributions would not be negligible in the solid state. In fact, very recently, enhanced horizontal orientation is realized in a series of iridium complexes by introduction of methyl or alkyl groups (Shin et al., 2019). Therefore, we propose that the contributions from multiple CH/ π contacts can collaborate with other strong intermolecular interactions to realize significant horizontal orientation.

OLED Performances

Finally, we fabricated OLEDs using **PXZPPM**/hosts as an emission layer to show the effect of horizontal orientation on the OLED efficiency. Here, we used two types of hosts, **mCP** ($\Theta = 62\%$) and **mCPCN** ($\Theta = 79\%$). Note that we did not use **DPEPO** as a host material because the chemical structure is totally different from **mCP**. The structure of the OLED was [indium tin oxide (ITO) anode (130 nm)/triphenylamine-containing polymer: 4-isopropyl-4'-methylidiphenyliodonium tetrakis(pentafluorophenyl)borate (**PPBI**) (20 nm) (Kido et al., 1997)/di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (**TAPC**) (25 nm)/4,4',4''-tris(N-carbazolyl)triphenylamine (**TCTA**) (5 nm)/10 wt% **PXZPPM**-doped **mCP**, or **mCPCN** (10 nm)/3,3'',5,5'-tetra(3-pyridyl)-1,1',3',3''-terphenyl (**B3PyPB**)

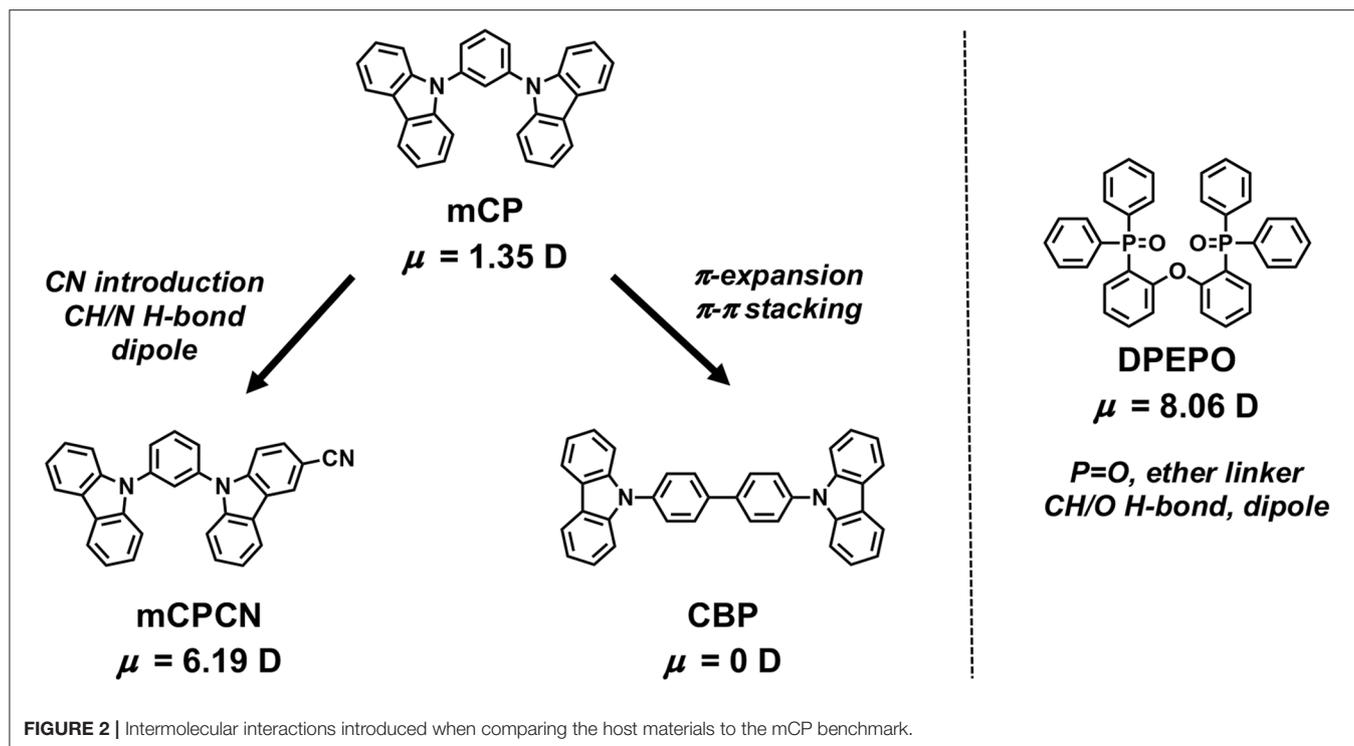


FIGURE 2 | Intermolecular interactions introduced when comparing the host materials to the mCP benchmark.

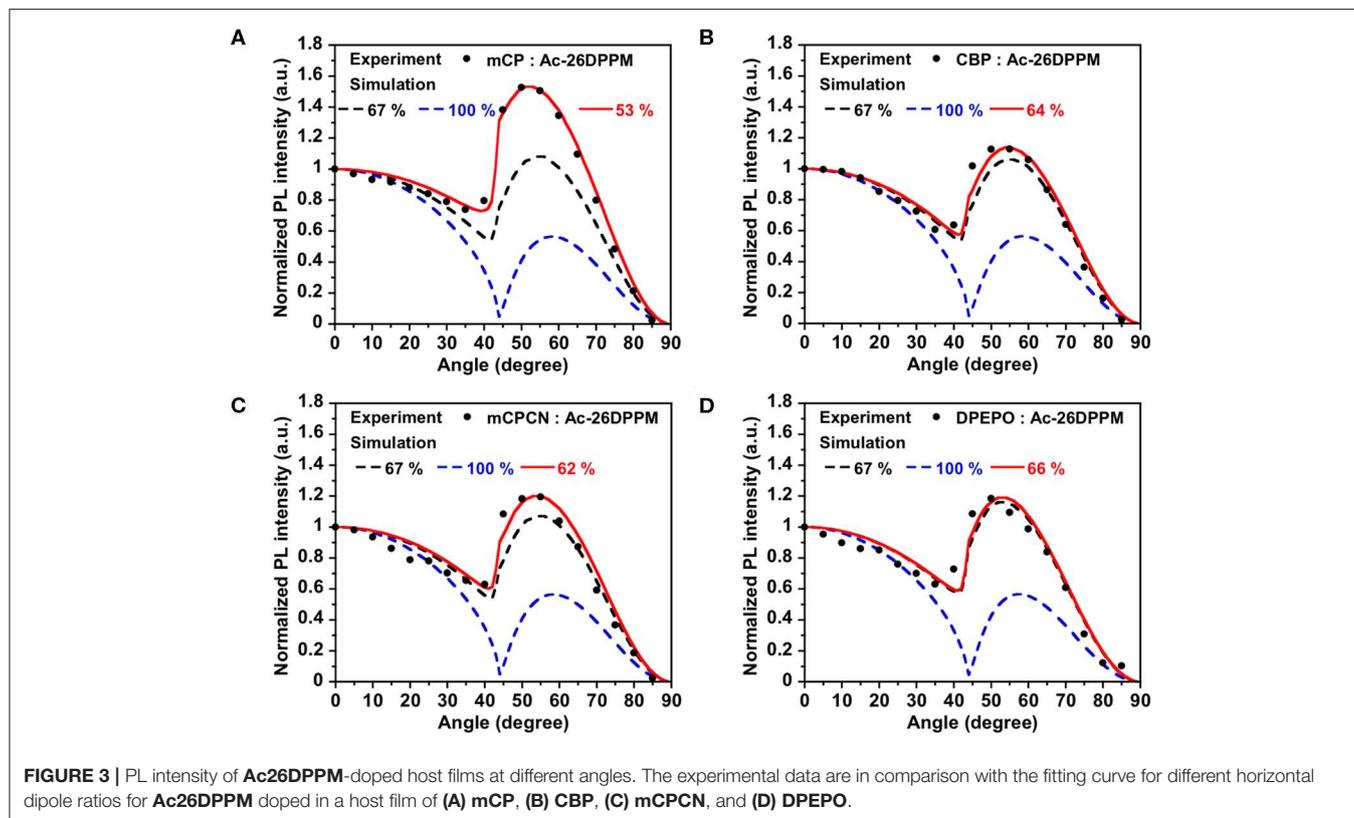


FIGURE 3 | PL intensity of Ac26DPPM-doped host films at different angles. The experimental data are in comparison with the fitting curve for different horizontal dipole ratios for Ac26DPPM doped in a host film of (A) mCP, (B) CBP, (C) mCPCN, and (D) DPEPO.

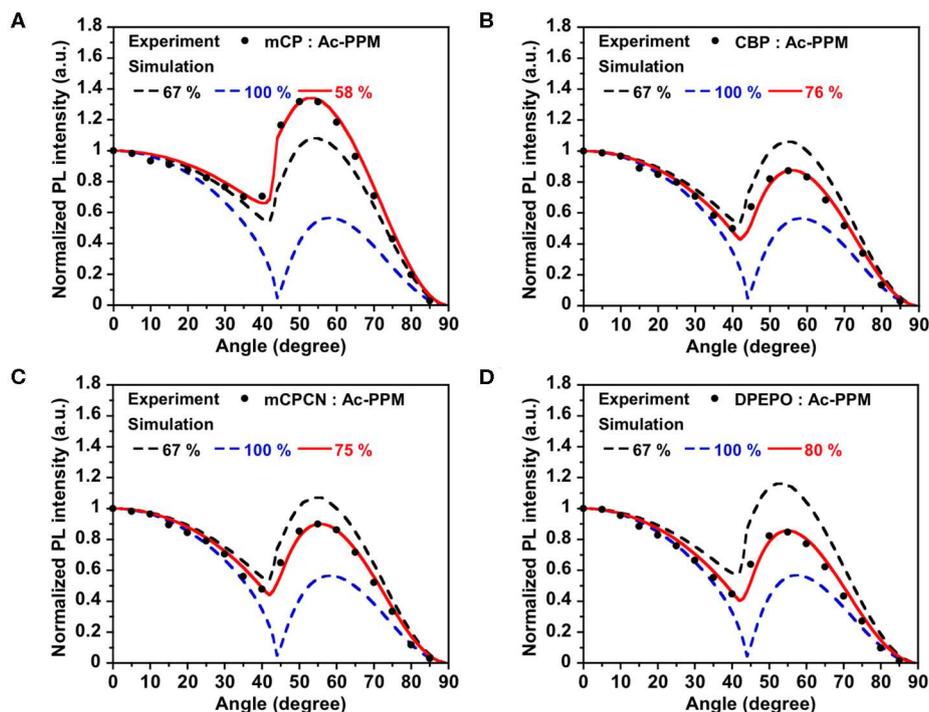


FIGURE 4 | PL intensity of AcPPM-doped in (A) mCP, (B) CBP, (C) mCPCN, and (D) DPEPO host films at different angles. The experimental data are in comparison with the fitting curve for different horizontal dipole ratios.

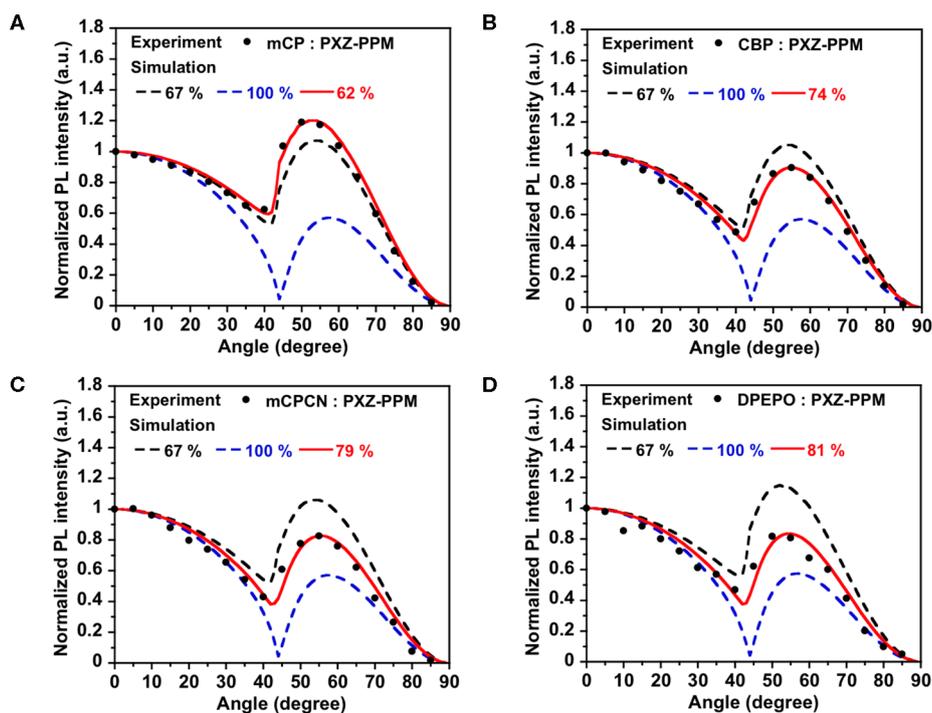


FIGURE 5 | PL intensity of PXZPPM-doped in (A) mCP, (B) CBP, (C) mCPCN, and (D) DPEPO host films at different angles. The experimental data are in comparison with the fitting curve for different horizontal dipole ratios.

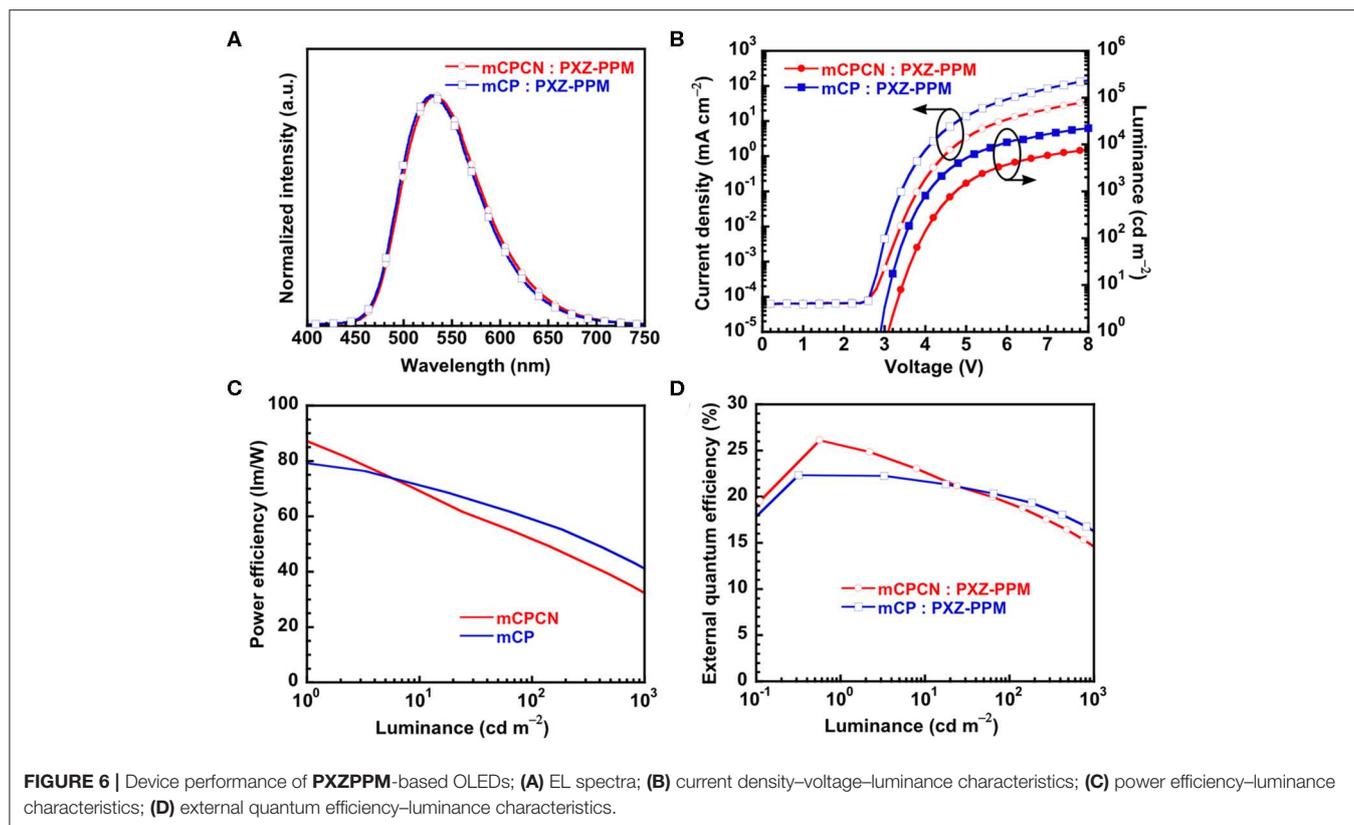


TABLE 3 | Summary of PXZPPM-based OLED performance.

Host	V_{on}^a (V)	$V_{100}/\eta_c, 100/\eta_p, 100/\eta_{ext, 100}^b$ (V/cd A ⁻¹ /lm W ⁻¹ /%)	$V_{1000}/\eta_c, 1000/\eta_p, 1000/\eta_{ext, 1000}^c$ (V/cd A ⁻¹ /lm W ⁻¹ /%)	$\eta_{c, max}/\eta_p, max/\eta_{ext, max}^d$ (cd A ⁻¹ /lm W ⁻¹ /%)
mCP	2.85	3.46/65.7/59.7/20.0	4.07/53.5/41.4/16.3	73.1/82.1/22.3
mCPCN	3.05	3.89/64.8/52.4/19.4	4.74/48.9/32.5/14.6	87.2/91.4/26.1

^aTurn-on voltage at 1 cd m⁻². ^bVoltage (V), current efficiency (η_c), power efficiency (η_p), and external quantum efficiency (η_{ext}) at 100 cd m⁻². ^c V , η_c , η_p , and η_{ext} at 1,000 cd m⁻². ^d η_c , η_p , and η_{ext} at maximum.

(50 nm) (Sasabe et al., 2008)/LiF (0.5 nm)/Al cathode (100 nm)]. TAPC and TCTA were used as the hole transport layers, B3PyPB as the electron transport layer, and LiF as the electron injection layer. The chemical structures of these materials are shown in Figure S6. Figure 6 shows the electroluminescence (EL) spectra, the current density (J)–voltage (V)–luminance (L), and η_{ext} -L characteristics. The electroluminescent characteristics are summarized in Table 3. The EL spectra of both devices showed similar emission with peaks at 529 nm for mCP and at 531 nm for mCPCN host materials. The maximum η_{ext} values were recorded to be 22.3% for mCP and 26.1% for mCPCN. Moreover, the light distribution patterns evaluated by Lambertian factor of these devices were similar, and recorded to be 0.99 for mCP, and 0.97 for mCPCN, as shown in Figure S6. The photoluminescent quantum yields (η_{PL}) of PXZPPM/host films were similar for mCP (71%) and mCPCN (69%) hosts. Given that the carrier balance factor is similar at the peak efficiency, the differences in the maximum η_{ext} values can be attributed to the differences in Θ values of the different host

materials. Note that we also fabricated the devices using CBP and DPEPO as a host material. As a result, higher η_{PL} and Θ values gave superior device performances (Figure S7 and Table S1). Enhancing the horizontal orientation of the emitter apparently increases the light coupling efficiency, thus resulting in a higher η_{ext} value.

CONCLUSION

We performed a systematic investigation on the molecular orientations of TADF emitters in a series of carbazole-based host materials. TADF emitters used in this study have a small dipole moment <2 D. To validate the underlying mechanisms for horizontal orientation, we changed the chemical structure of mCP by: (i) extending the π -conjugation to form CBP, and (ii) the introduction of a CN substituent to form mCPCN. In addition, a phosphine-oxide host material, DPEPO, was used. Although all the emitters and the host materials had random orientation as a neat film, the emitters with larger molecular

shape anisotropy, **AcPPM** and **PXZPPM**, showed enhanced horizontal orientation up to $\Theta \sim 81\%$ in all host films except **mCP**. The third emitter, **Ac26DPPM**, has a smaller molecular shape anisotropy, and subsequently showed vertical orientation in the **mCP** host film ($\Theta = 53\%$). However, when doped into the other host material, **Ac26DPPM** showed random orientation ($\Theta \sim 66\%$). From these results, it can be considered that (i) an increase in the π -conjugation leads to stronger π - π stacking, (ii) the introduction of CN group induces CH/N weak H-bonds, and (iii) the introduction of a strong acceptor P=O and ether groups induces CH/O H-bonds, and all these interactions enhance the horizontal orientation of TADF emitters. In addition, we propose that the contributions from multiple CH/ π contacts can collaborate with other strong intermolecular interactions such as π - π stacking, CH/N and CH/O H-bonds to realize significant horizontal orientation. Finally, we fabricated an **PXZPPM**-based OLED that achieved an η_{ext} of 26% using an EML with Θ of 79%, which is higher than that of an almost randomly oriented EML with Θ of 62% ($\eta_{\text{ext}} = 22\%$). We believe that our results will be beneficial in revealing the underlying mechanism for horizontal orientation leading to superior OLED performances.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/**Supplementary Material**.

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AUTHOR CONTRIBUTIONS

HS and SO conceived the project. HS, YC, SO, and DY interpreted the data and prepared the manuscript and supplementary materials. HS, SO, and JK supervised the project. YC, SO, and DY designed experiments. HA, TO, RK, and YW synthesized and characterized materials. YC, YW, and DY prepared samples, performed variable-angle spectroscopic ellipsometry measurements, and related data analysis. YC, SO, and HA prepared samples and performed angle dependent PL measurements. YC and HA fabricated devices. All authors discussed the results and commented on the manuscript.

ACKNOWLEDGMENTS

We gratefully acknowledge the partial financial support from the Center of Innovation (COI) Program from the Japan Science and Technology Agency, JST. HS acknowledges financial support in part by JSPS KAKENHI (17H03131) from JSPS.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2020.00427/full#supplementary-material>

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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