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## FULL PAPERS

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## Effective Host Materials for Blue/White Organic Light Emitting Diodes by Utilizing Conjugation Twisted Structure in 10-Phenyl-9,10-Dihydroacridine Block

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Dedication ((optional))

Abstract: Two new 10-phenyl-9,10dihydroacridine derivatives attached by dibenzothiophene (DBT) and dibenzofuran (DBF) are synthesized. The influence of the substituents of these materials is studied by theoretical calculations (DFT calculation) and experimental measurements. Thanks to the twisted N-phenyl ring, both molecules possess sufficiently high triplet energies and are suitable for

## Introduction

Organic light-emitting diodes (OLEDs) with unique structure and favorable properties (such as ultra-thin, light weight, low drive voltage, low power consumption, high brightness, full-color emission, rapid response, and flexibility, etc.) have been rapidly developed into next-generation display and solid-state lighting technology.<sup>1</sup> Since the ratio of electron-generated singlet and triplet excitons formed in device is approximately 1:3, the efficiency of conventional fluorescent OLEDs are limited within 25% in internal quantum efficiency (IQE) while the efficiency of phosphorescent OLEDs (PHOLEDs) can, in theory, achieve nearly 100% IQE by utilizing both excitons.<sup>1c,1d,2</sup> To get highly efficient PHOLEDs, a host/dopant system is important to disperse triplet emitters. Up to now, the red and green PHOLEDs has already been achieved the 20% theoretical external quantum efficiency, and various host and high efficiency dopant materials have been developed to realize the high efficiency red and green PHOLEDs. However, compared to red and green PHOLEDs, highly efficient blue PHOLEDs are hard to obtain due to the large energy gaps of blue phosphors, and the

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hosts for phosphorescent organic lightemitting diodes. To evaluate the electroluminescent (EL) performance of these materials, FIrpic based blue PHOLEDs and two-color white PHOLEDs (FIrpic and PO-01 as the dopants) were fabricated using the common device structures. High external quantum efficiencies (EQE) of 21.1% and 20.9% for FIrpic based blue PHOLEDs were achieved by FPhAc

and TPhAc, respectively. The white device based on host FPhAc was achieved higher performance with maximum EQE of 24.7% than used TPhAc as host material.

**Keywords:** Dibenzothiophene • Dibenzofuran • Host material • Twisted • Blue phosphorescent organic light-emitting diode •

selection of host materials is very important for the high efficient blue PHOLEDs.<sup>2f-2h</sup> In recent years, high external quantum efficiency blue PHOLEDs were achieved based on new device structures, phosphor emitters or host materials.<sup>3</sup> In this regard, most of the host materials in PHOLEDs rely on the aromatic amine derivatives,<sup>3,4</sup> e.g. the common used triphenylamine (TPA) and 9phenyl-9H-carbazole (PhCz). Bin et al. reported a FIrpic-based OLED with an high external quantum efficiency of 29% by using a PhCz-based host material SitCz.3a Lee et al. also reported the high external quantum efficiency of 30% for FIrpic-based devices hosted by PhCz derivatives.<sup>3b-3d</sup> The former (TPA) has a free fan-like configuration and the latter (PhCz) can be viewed as a rigidified TPA via direct C-C linkage between 2, 2'-positions. This tiny change in structure leads to many different properties, such as conjugation degree, distributions of frontier molecular orbitals and derivation ways in chemical modifications.<sup>1i,4g</sup> Both TPA and PhCz blocks are widely studied but another triphenylamine derivative, named 10-phenyl-9,10-dihydroacridine (PhAc), is less reported up to now. From the view of structure, PhAc is also a rigid TPA with 2, 2'- positions connected by a nonconjugated  $sp^3$  carbon atom. This carbon has neither donating nor accepting attribute, thus we can predict that it has little effect on original frontier molecular orbitals of TPA. The N-phenyl ring, similar to that of PhCz, will possess nearly perpendicular configuration to the backbone.<sup>4g-4i</sup> Even though, PhAc is more like TPA than PhCz because PhCz can also act as electron-rich biphenyl in some cases.41,4m Additionally, the bridgehead carbon atom on PhAc can be further modified for functional materials. In this way, Lee et. al. prepared a series of hole-transport materials with high triplet energies based on PhAc core.<sup>5,6</sup> Our group combined PhAc with fluorene in spiro-structure

to develop blue host materials, in which the fluorene precursor was elaborately selected to control the conjugation degree.<sup>4g-4i</sup> However, the work about derivation on the N-phenyl ring of PhAc is rarely reported. As aforementioned, this phenyl ring has little effect on the coplanar 9,10-dihydroacridine because of the twisted configuration, which is crucial to control molecular conjugation. That will be another effective way to design high-triplet-energy hosts. The high-triplet-energy hosts are vital important to achieve highly efficient blue or white PHOLEDs, which are widely acknowledged as the most difficult issue in this research area. The structures of three building blocks TPA, PhCz and PhAc are described in Scheme 1.



Scheme 1. Molecular structures of triphenylamine (TPA), 9-phenyl-9H-carbazole (PhCz), and 10-phenyl-9,10-dihydroacridine (PhAc).

Recently, the other heterocyclic structures similar to carbazole were applied to building the new host materials,<sup>7.9</sup> e.g. dibenzofuran (DBF)<sup>7.9</sup> and dibenzothiophene (DBT).<sup>7c,8,9</sup> The structures of carbazole, DBF and DBT are shown in Scheme 2. Compared to carbazole, DBF and DBT also possess high triplet energies of 3.04 and 3.10 eV, respectively. However, the electron-donating ability of DBF and DBT might be less than carbazole.<sup>9</sup> The possible reason is the stronger electronegativity of the O atom in DBF and it will be limited the electron donating ability of DBF. Due to the S atom has a much lower electronegativity that makes DBT has a much stronger aromaticity compared to DBF or carbazole and it also reduces the ability of electron donating for DBT.<sup>9</sup> These properties will make DBF and DBT more neutral than carbazole.



Scheme 2. Molecular structures of carbazole, dibenzofuran (DBF), and

## dibenzothiophene (DBT)

By combining PhAc with another two heterocyclic blocks dibenzofuran (DBF) and dibenzothiophene (DBT), two novel host materials, FPhAc and TPhAc, were designed and synthesized by incorporating PhAc with DBF and DBT units. DBF and DBT also possess high triplet energies of 3.04 and 3.10 eV, respectively; and they are positioned as meta-substituents of PhAc to reduce molecular conjugation degree. On the other hand, DBF and DBT are relatively neutral blocks as compared to nitrogen heterocycles, which could modulate the properties of PhAc-based blocks. Their thermal behaviour, electrochemical properties, the chargetransporting abilities, and the devices performances were investigated. In electroluminescent evaluations, both host materials present high efficiencies in blue and white PhOLEDs with common device structures. High efficiencies of 46.5 cd A<sup>-1</sup>, 38.9 lm W<sup>-1</sup> and 21.1% and 45.5 cd  $A^{\text{-1}},\ 35.9\ \text{lm}\ W^{\text{-1}}$  and 20.9% for current efficiency (CE), power efficiency (PE) and external quantum efficiency (EQE) for FIrpic based blue PHOLEDs were achieved by FPhAc and TPhAc, respectively. Finally, to further assess the performance of these materials, two-color white PHOLEDs were fabricated using FIrpic and PO-01 as the dopants. The device based on host FPhAc was achieved higher performance with maximum efficiencies of 67.0 cd  $A^{-1}$ , 53.8 lm  $W^{-1}$ , and 24.7%. The white PHOLEDs also showed low drive voltages of 4.11 and 4.28 V at 1000 cd  $m^{-2}$  for the devices based on FPhAc and TPhAc, respectively.

## **Results and Discussion**

#### Synthesis and Structural Characterization

Although there are some work were studied the properties of PhAc derivatives served as hole-transporting materials for OLEDs,<sup>4,5</sup> however, they used the synthetic method (Scheme 3), which will be limited the position of the substituents and the possibility of derivative work on the nitrogen atom of acridine. In this work, we take the new synthetic strategy (Scheme 3) and can be getting the different derivative on the nitrogen atom. The synthetic routes to obtain the target materials are outlined in Scheme 3. The key intermediate of 10-(3-bromophenyl)-9,9-diphenyl-9,10-dihydroacridine was readily afforded through the classic Buchwald-Hartwig C-N coupling reaction between 1-bromo-3-iodobenzene and 9,9-diphenyl-9,10-dihydroacridine in moderate yield. At last, the final products can be obtained via Pd-catalyzed Suzuki-Miyaura coupling reaction between 10-(3-bromophenyl)-9,9-diphenyl-9,10dihydroacridine and the corresponding boronic acid of dibenzofuran (DBF) and dibenzothiophene (DBT) in good yields.



 Pd(OAC)<sub>2</sub>, t-Bu<sub>3</sub>PBF<sub>4</sub>, t-BuONa, toluene, ref ii) n-BuLi, THF, -78 °C; HOAc, HCl, reflux.



i) Cu, K<sub>2</sub>CO<sub>3</sub>, o-DCB; ii) THF, 0 °C; HOAc, HCl, 110 °C; iii) Pd<sub>2</sub>(dba)<sub>3</sub>, S-Phos, t-BuONa, toluene, 80 °C.



Scheme 3. Synthetic routes and chemical structures of the materials.

## **Thermal Properties**

The thermal properties of FPhAc and TPhAc were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), both materials exhibited good thermal stabilities. The glass transition temperature ( $T_g$ , Figure 1) was measured as 100 °C for FPhAc, whilst TPhAc showed slightly higher  $T_g$  of 105 °C. The thermal decomposition temperatures ( $T_d$ , corresponding to 5% weight loss, Figure 1) of FPhAc and TPhAc are 394 and 408 °C, respectively, which exhibited similar trend to  $T_g$ . These data show slight difference, indicating that it is the PhAc core other than the DBF or DBT appending groups determines thermal stabilities. It is worth noting that both molecular FPhAc and TPhAc present  $T_g$  are obvious higher than those of classical host materials for blue PHOLEDs, such as mCP or CBP.<sup>4q,4r</sup> Therefore both of these compounds could be used as potential stable organic host materials for PHOLEDs under vacuum evaporation due to the high  $T_g$  and  $T_d$ .



Figure 1. DSC and TGA (inset) curves of FPhAc and TPhAc.

## **Photophysical Properties**

Figure 2 shows the UV-vis absorption and photoluminescence (PL) spectra of FPhAc and TPhAc at room temperature in toluene solution and the phosphorescence spectra measured in 2-MeTHF solution at 77 K. The data of photophysical properties of FPhAc and TPhAc are summarized in Table 1. In the absorption spectra, the maximum absorption wavelengths (Abs  $\lambda_{max}$ ) are 300 and 297 nm for FPhAc and TPhAc, respectively, and the absorption onset of TPhAc is red-shifted by 11 nm as compared to FPhAc. As a result, the optical band gap  $(E_s)$  of TPhAc (3.50 eV) is smaller than that of FPhAc (3.61 eV). On the other hand, the PL spectra of FPhAc and TPhAc are almost identical to each other with the maximum emission wavelengths (PL  $\lambda_{max}$ ) at 410 and 408 nm, respectively. The highest vibronic bands of phosphorescence spectra at 77 K for FPhAc and TPhAc are at 451 and 463 nm, then the triplet energies  $(E_{\rm T})$  are calculated as 2.75 and 2.68 eV for FPhAc and TPhAc, respectively.

## **DFT Simulation**

To better understand the electronic distributions of FPhAc and TPhAc, DFT calculations were utilized to simulate their FMO spatial distributions at a B3LYP/6-31G(d) level. As Figure S7 illustrates, these materials have similar highest occupied molecular

orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distributions. The HOMOs of FPhAc and TPhAc are localized at the electron-rich acridine centers, and the LUMOs are distributed on the DBF and DBT units with N-phenyl ring acts as separation group. Both materials have similar HOMO levels because of the same distributions, which means the heterocyclic structure of DBF and DBT are almost no contribution for the HOMO energy levels. But the DBF/DBT moiety in FPhAc/TPhAc can remarkably reduce the LUMO by 0.74 and 0.83 eV, respectively. It is recognized that due to the S atom has a much lower electronegativity and the involvement of an S atom in the conjugation make DBT has a much stronger aromaticity than DBF.9 Based on the optimize of the molecular structure, we found, the angle between the two planes of the phenyl and the 9,10-dihydroacridine is near 90° (about 84°), which means this phenyl ring has little effect on the acridine core. FPhAc and TPhAc have shown the similar results. However, the dihedral angles between phenyl plane and the ring compound plane are 37° and 47° for FPhAc and TPhAc, respectively. The possible reason of this phenomenon is the S atom has much larger size in DBT than O atom in DBF, so that the interaction between the phenyl and the DBT is stronger and the dihedral angle between these two planes is bigger.



Figure 2. UV-vis absorption and PL spectra of FPhAc and TPhAc in toluene solution at 10<sup>-5</sup> M; phosphorescence spectra measured in a frozen 2-MeTHF matrix at 77 K.

## **Electrochemical Properties**

The electrochemical behavior of FPhAc and TPhAc was measured by cyclic voltammetry (CV) method using typically tri-electrode configuration with ferrocene as the internal standard in dichloromethane solution (Figure 3). Based on these results, the HOMO levels of these materials are calculated as 5.54 eV from the onset of the first oxidation waves. These values are almost the same, indicating that the nature of the DBF and DBT ring has almost no influence on the HOMO energy levels. In other word, the DBF and DBT ring are almost no contribution for the HOMOs. These experimental results are in conformity with DFT calculation result. And the LUMO energy levels can be calculated from the HOMOs and the optical  $E_{gs}$ , which are 2.01 and 2.11 eV of FPhAc and TPhAc, respectively.

In order to get more reliable energy levels, ultraviolet photoemission spectroscopy (UPS) was used to determine the

HOMO levels (Figure 4). The HOMO levels of FPhAc and TPhAc are 5.72 and 5.78 eV, respectively. And the LUMO levels of these materials are 2.19 and 2.36 eV, respectively. The UPS schematic diagram shows the HOMO levels can be gained via this equation  $E_{\rm HOMO} = hv - E_{\rm k}$ , hv is the light energy of the light source and normally we used He I as the light source (hv = 21.2 eV);  $E_{\rm k}$  is the kinetic energy distribution of the photo-electrons. The LUMO energies levels can be calculated by  $E_{\rm LUMO} = E_{\rm g} - E_{\rm HOMO}$ ,  $E_{\rm g}$  is the optical energy gap at film state (Figure S8). These results are consistent with the CV results DFT calculation.



Figure 3. Cyclic voltammetry (CV) curves of FPhAc and TPhAc.







Figure 4. UPS schematic diagram and UPS spectra of FPhAc and TPhAc.

To evaluate the electroluminescent (EL) properties of FPhAc and TPhAc as host materials, bis(4,6-(difluorophenyl)pyrudinato-N,C')picolinate iridium(III) (FIrpic) based blue phosphorescent OLEDs were fabricated using this simple device structure (Figure S8): ITO/HAT-CN (10 nm)/TAPC (40 nm)/Host: 15% FIrpic (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al (120 nm). FPhAc (B1) and TPhAc (B2) were doped with 15% FIrpic as the emitting layer (EML). In order to prevent the spread of the triplet excitons and to confine it in the EML, 1,1-bis[4-[N',N'-di(p-tolyl)amino]phenyl] cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)phen-3-yl]benzene (TmPyPB), which have a high triplet energies  $(E_T)$  and good hole and electron transporting mobility, served as hole transporting layer (HTL)/electron blocking layer (EBL) and electron transporting layer (ETL)/hole blocking layer (HBL), respectively. And to make sure the efficient of carrier injection, dipyrazino[2,3-f:2',3'h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) and 8hydroxyquinolinolatolithium (Liq) were utilized as the hole injection (HIL) and electron injection layers (EIL), respectively.

Figure 5 shows current density-voltage-luminance characteristic curves (a, b) and external quantum efficiency, current efficiency and power efficiency versus luminance curves (c, d) for devices B1-2 and W1-2. The detailed electroluminescence characteristics data are summarized in Table 2. The blue and white devices shows relatively lower drive voltages of 4.52/4.67 V and 4.62/4.49 V at 1000 cd m<sup>-2</sup> for FPhAc and TPhAc based devices, respectively. The EL spectra of these devices show relatively greenish blue emission with CIE coordinates of (0.17, 0.39) for device B1 and (0.16, 0.39) for device B2 compared to the typical FIrpic based devices (Figure S12), which means that only the FIrpic emission peak was observed without any emission from the hosts of FPhAc and TPhAc. Such finding strongly indicated that the process of excitons formed under holes and electrons recombination and the excitons emission process were efficiently confined inside the emitting layer, which could be attributed to the high E<sub>T</sub>s and appropriate HOMO/LUMO energy levels for the hosts. The CIE coordinates for W1 and W2 are (0.33, 0.46) and (0.36, 0.48), respectively.

Figure 5c illustrates the efficiencies of the blue phosphorescent devices. High efficiencies were achieved by these blue devices. The maximum efficiency of device using FPhAc as host material (B1) reached 46.5 cd  $A^{-1}$  for the current efficiency (CE), 38.9 lm  $W^{-1}$  for the power efficiency (PE), and 21.1% for the external quantum efficiency (EQE). The device based on host TPhAc (B2) shows similar performance, with slightly lowered maximum efficiency of 45.5 cd  $A^{-1}$ , 35.9 lm  $W^{-1}$ , and 20.9% for CE, PE, and EQE, respectively.

In order to further evaluate the performance of FPhAc and TPhAc, we also fabricated the two-color white phosphorescent OLEDs using FIrpic and bis(4-phenylthieno[3,2-c]pyridinato-N,C<sup>2+</sup>)acetylacetonateiridium(III) (PO-01) as blue and yellow dopants, respectively. The device structure is similar to the blue devices: ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA (10 nm)/Host: 15% FIrpic: 0.5% PO-01 (15 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al (120 nm). Figure 5d illustrates the efficiencies of the white phosphorescent devices. The detailed EL performance data are summarized in Table 2. Similar to the blue devices, high efficiencies were achieved by white devices based on FPhAc and TPhAc. The maximum efficiency of the devices based on FPhAc (W1) reached 67.0 cd A<sup>-1</sup> for the current efficiency (CE), 53.8 lm W<sup>-1</sup> for the power efficiency (PE) and 24.7% for the external quantum efficiency (EQE). The devices based on TPhAc (W2) shows similar performance, with slightly lowered maximum CE, PE and EQE for 55.0 cd A<sup>-1</sup>, 44.0 lm W<sup>-1</sup> and 19.4%, respectively.

Table 1. Physical Properties of FPhAc and TPhAc.

Host	Abs $\lambda_{max}{}^{[a]}$	$PL\lambda_{max}{}^{[a]}$	$T_{\rm g}^{\rm [b]/o}{ m C}$	$T_{\rm d}^{\rm [c]/o}{\rm C}$	$E_{ m g}^{[d]}/ m eV$	$E_{\mathrm{T}}^{\mathrm{[e]}}/\mathrm{eV}$	HOMO <sup>[f]</sup> /eV	LUMO <sup>[g]</sup> /eV
	/nm	/nm						
FPhAc	300	410	100	394	3.61/3.53	2.75	-5.72	-2.19
TPhAc	297	408	105	408	3.50/3.42	2.68	-5.78	-2.36

[a] Measured in toluene solution at room temperature. [b] Tg: Glass transition temperature. [c] Td: Decomposition temperature. [d] Eg: Band gaps, calculated from the corresponding absorption onset at solution/film state. [e] E<sub>T</sub>: Measured in 2-MeTHF glass matrix at 77 K. [f] HOMO levels, calculated from UPS data. [g] LUMO levels, calculated from the HOMO and  $E_g$  at film state.





Figure 5. Current density-voltage-luminance characteristic curves and external quantum efficiency (EQE), current efficiency (CE) and power efficiency (PE) versus luminance

## Conclusion

curves for devices B1-2 (a, c) and W1-2 (b, d).

In conclusion, two novel host materials, FPhAc and TPhAc, were synthesized and fully characterized. High efficiencies were achieved of PHOLEDs using these new host materials. The best performances of blue and white devices based on TPhAc were 21.1% and 24.7% for EQE, respectively. These results demonstrate the potential of 10-phenyl-9,10-dihydroacridine (PhAc) block, when it is intendedly

modified from the nitrogen atom, it can form new materials with separated HOMO/LUMO and thus lead to high triplet host materials for highly efficient blue and white PHOLEDs.

Table 2. Electroluminescence characteristics of the devices.

Device <sup>[a]</sup>	11	$V^{[b]}$	$\Box \eta_{ ext{CE}}{}^{[c]}$	$\Box \eta_{ ext{PE}}^{[c]}$	EQE <sup>[c]</sup>	$CIE^{[d]}$
	HOST	[V]	[cd A <sup>-1</sup> ]	[lm W <sup>-1</sup> ]	[%]	[x, y]
B1	FPhAc	4.52	46.5, 42.3, 33.5	38.9, 29.3, 18.0	21.1, 19.3, 15.3	0.17, 0.39
B2	TPhAc	4.67	45.5, 40.0, 29.8	35.9, 26.9, 15.2	20.9, 18.5, 13.8	0.16, 0.39
W1	FPhAc	4.62	67.0, 62.2, 55.7	53.8, 42.4, 28.3	24.7, 22.9, 20.5	0.33, 0.46
W2	TPhAc	4.49	55.0, 52.5, 47.1	44.3, 36.9, 24.6	19.4, 18.6, 16.4	0.36, 0.48

[a] The notation 1 and 2 in devices B1 and B2 indicates the corresponding devices fabricated with FPhAc and TPhAc as the host respectively. Device configuration: B1 and B2: ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA (10 nm)/Host:15% FIrpic (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/A1 (120 nm); W1 and W2: ITO/HAT-CN (10 nm)/TAPC (45 nm)/Host: 15 wt% FIrpic: 0.5% PO-01 (15 nm)/TmPyPB (40 nm)/Liq (2 nm)/A1 (120 nm). [b] Voltages at 1000 cd m<sup>-2</sup>. [c] Efficiencies in the order of the maxima, at 1000 cd m<sup>-2</sup> and at 5000 cd m<sup>-2</sup>. [d] CIE coordinates measured at 5 mA cm<sup>-2</sup>.

#### **Experimental Section**

#### **General Information**

All chemicals and reagents were used as received from commercial sources without further purification. THF was purified by PURE SOLV (Innovative Technology) purification system. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 spectrometer at room temperature. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. The glass transition temperatures  $(T_g)$  were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature ( $T_d$ ). Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature. Deaerated dichloromethane was used as solvent for oxidation scan with tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) as the supporting electrolyte. The cyclic voltammograms were obtained at scan rate of 0.1 V s<sup>-1</sup>. Ultra-Violet Photoemission Spectroscopy (UPS) analysis were carried out with an unfiltered He I (21.2 eV) gas discharge lamp and a hemispherical analyzer, which made by KRATOS ANALYTICAL SHIMADZU GROUP COMPANY. DFT calculations were performed using B3LYP/6-31g(d) basis set using Gaussian 09.

## Synthesis and Characterization

1-bromo-3-iodobenzene, dibenzofuran-4-boronic acid and dibenzothiophene-4-boronic acid were commercially available. THF was purified by PURE SOLV (Innovative Technology) purification system. Other reactants or reagents were used as received.

#### Preparation of 9,9-diphenylacridane

Methyl anthranilate (20 g, 132 mmol), iodobenzene (26.9 g, 132 mmol), K<sub>2</sub>CO<sub>3</sub> (36.4 g, 264 mmol), and copper powder (0.17 g, 2.64 mmol) was scattered in 1,2-dichlorobenzene (*o*-DCB) and stirred for 10 hours at 180 °C under argon. After the reaction cooling to room temperature, filtered and washed with dichloromethane (DCM). Remove the solvent under reduced pressure and the crude product was purified by column chromatography using petroleum ether/dichloromethane (2/1, v/v) to afford the pure product as a colourless oil (23 g). This product was used in the next step needn't to further purification.

77% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.89 (s, 3H), 6.66-6.78 (m, 1H), 7.06-7.10 (t, J = 7.6, 7.2 Hz, 1H), 7.23-7.25 (m, 3H), 7.28-7.35 (m, 3H), 7.94-7.97 (m, 1H), 7.47 (s, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.95, 147.97, 140.79, 134.12, 131.65, 129.39, 123.58, 122.54, 117.12, 114.04, 111.92, 51.79 ppm. MS m/z: 227.10. Anal. calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub> (%): C 73.99, H 5.77, N 6.16; found: C 73.78, H 5.88, N 6.32.

The colourless oil (10 g, 44 mmol) was dissolved in 180 mL tetrahydrofuran (THF) in a 500 mL Schlenk tube under argon and cooled to 0 °C, and then phenylmagnesium chloride (PhMgCl, 2 M in THF, 66 mL, 132 mmol) was added dropwise under stirred.

After 1 h reaction at 0 °C, the mixture was gradually warmed up to room temperature overnight. The reaction was quenched by water (5 mL). Put the mixture into 50 mL water, the product was extracted with EtOAc ( $3\times50$  mL), the combined organic layers were washed with brine and dried over anhydrous sodium sulfate (NaSO<sub>4</sub>). Filtrated and evaporated under reduce pressure to afford a yellow oil or yellow soild (14 g), which was directly used in the next reaction without further purification. The crude product was dissolved in 100 mL acetic acid (HOAc) under 70 °C and 10 mL hydrochloric acid (HCl) was added dropwise under stirred. The mixture was reaction overnight at 70 °C. After the reaction cooling to room temperature, filtered and washed with absolute ethyl alcohol, and dried under vacuum to give 9,9-diphenylacridane as white power (12 g). 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.25 (s, 1H), 6.86 (m, 9H), 7.16 (m, 8H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  30.1, 56.7, 120.2, 125.6, 126.2, 127.1, 127.4, 127.6, 127.6, 127.9, 128.5, 130.0, 130.2, 130.2, 139.7, 146.0, 149.3 ppm. <sup>10</sup> MS m/z: 334.16. Anal. calcd for C<sub>25</sub>H<sub>19</sub>N (%): C 90.06, H 5.74, N 4.20; found: C 90.05, H 5.68, N 4.32.

## Preparation of 10-(3-bromophenyl)-9,9-diphenyl-9,10-dihydroacridine

9,9-diphenylacridane (10 g, 30 mmol), 1-bromo-3-iodobenzene (12.7 g, 45 mmol), tris(dibenzylidene-acetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>, 0.27 g, 0.3 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos, 0.37 g, 0.9 mmol), sodium t-butoxide (*t*-BuONa, 5.76 g, 60 mmol) were dissolved in toluene under argon and heated to 110 °C. After 20 h reaction under stirring, the reaction was cooled to room temperature and 200 mL water was added. The product was extracted with dichloromethane (DCM, 3×100 mL), the combined organic layers were washed with brine and dried over anhydrous sodium sulfate (NaSO<sub>4</sub>). Filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/dichloromethane (2/1, v/v) to give 10-(3-bromophenyl)-9,9-diphenyl-9,10-dihydroacridine as a white crystalline power (12.45 g).

85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.39-6.41 (d, J = 8.4 Hz, 2H), 6.86-6.92 (m, 4H), 6.96-6.98 (m, 4H), 6.96-7.00 (m, 4H), 7.01-7.09 (m, 3H), 7.20-7.26 (m, 8H), 7.36-7.40 (t, J = 8.0 Hz, 1H), 7.56-7.59 (m, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  114.03, 120.50, 123.58, 126.38, 126.97, 127.70, 129.79, 130.15, 130.40, 131.54, 131.75, 134.53, 141.86, 142.20, 146.33 ppm. MS m/z: 488.40. Anal. calcd for C<sub>31</sub>H<sub>22</sub>BrN (%): C 76.23, H 4.54, N 2.87; found: C 76.28, H 4.68, N 2.92.

Preparation of 10-(3-(dibenzo[b,d]furan-4-yl)phenyl)-9,9-diphenyl-9,10-dihydroacrid-ine

10-(3-bromophenyl)-9,9-diphenyl-9,10-dihydroacridine (3 g, 6.1 mmol), dibenzofuran-4-boronic acid (1.6 g, 7.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.35 g, 0.3 mmol) were dissolved in THF under argon, and then 2 M K<sub>2</sub>CO<sub>3</sub> (THF/Water = 5/1, v/v) was added. The resulting solution was heated at 70 °C overnight. After cooled to room temperature, the mixture was evaporated to remove solvents. The residue was washed with water and extracted with dichloromethane for 3 times. The organic layer was collected and evaporated. The crude product was purified by chromatography on silica gel using petroleum ether as eluent to afford of 10-(3-(dibenzo[b,d]furan-4-yl)phenyl)-9,9-diphenyl-9,10-dihydroacridine (FPhAc) as a white powder (3.0 g).

86% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.64-6.66 (m, 2H), 6.87-6.94 (m, 4H), 7.02-7.11 (m, 7H), 7.19-7.28 (m, 7H), 7.32-7.47 (m, 3H), 7.53-7.57 (m, 2H), 7.63-7.67 (t, *J* = 8.0, 7.6 Hz, 1H), 7.71 (m, 1H), 7.91-7.97 (m, 2H), 8.04-8.07 (m, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  111.85, 114.28, 120.11, 120.18, 120.67, 122.84, 123.21, 124.00,

124.62, 125.06, 126.23, 126.55, 126.87, 127.60, 128.47, 129.70, 129.96, 130.27, 130.43, 131.55 ppm. MS m/z: 575.70. Anal. calcd for  $C_{43}H_{29}NO$  (%): C 89.71, H 5.08, N 2.43; found: C 89.78, H 5.26, N 2.52.

 $\label{eq:preparation} Preparation ~of ~10-(3-(dibenzo[b,d]thiophen-4-yl)phenyl)-9,9-diphenyl-9,10-dihydro-acridine$ 

 $10\mbox{-}(dibenzo[b,d]thiophen-4\mbox{-}yl)penyl)\mbox{-}9,9\mbox{-}diphenyl\mbox{-}9,10\mbox{-}dihydroacridine (TPhAc) was prepared in a similar manner with FPhAc. The result to afford a white power.$ 

80% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.59-6.61 (d, J = 8.0 Hz, 2H), 6.87-6.93 (m, 4H), 7.00-7.03 (m, 4H), 7.07-7.43 (m, 3H), 7.18-7.27 (m, 7H), 7.44-7.57 (m, 5H), 7.63-7.67 (t, J = 8.0, 7.6 Hz, 1H), 7.81-7.85 (m, 2H), 8.13-8.18 (m, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  111.85, 114.28, 120.11, 120.18, 120.67, 122.84, 123.21, 124.00, 126.23, 127.60, 128.47, 129.70, 129.96, 130.27, 130.76, 131.55, 138.64, 141.08, 142.24, 146.46, 153.20, 156.06 ppm. MS m/z: 591.70. Anal. calcd for C<sub>43</sub>H<sub>29</sub>NS (%): C 87.27, H 4.94, N 2.37; found: C 87.20, H 4.98, N 2.42.

## **Device Fabrication and Testing**

Bis(4,6-(difluorophenyl)pyrudinato-N,C')picolinateiridium(III) (FIrpic), 1,1-bis[4-[N',N'-di(p-tolyl)amino]-phenyl]cyclohexane (TAPC), 1,3,5-tri](3-pyridyl)phen-3yl]benzene (TmPyPB), dipyrazino[2,3-f:2',3'-h]-quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN), 8-hydroxyquinolinolatolithium (Liq) and bis(4-phenylthieno[3,2c]pyridinato-N,C<sup>2</sup>)acetylacetonateiridium(III) (PO-01) were commercially available. The OLEDs were fabricated on the indium-tin oxide (ITO) coated transparent glass substrates, the ITO conductive layer having a thickness of ca. 100 nm and a sheet resistance of ca. 30  $\Omega$  per square. The substrates was cleaned with ethanol, acetone and deionized water, and then dried in an oven, finally exposed to UV ozone for 30 min. All of the organic materials and metal layers under a vacuum of ca. 10<sup>-6</sup> Torr. Four identical OLED devices were formed on each of the substrates and the emission area of 0.09 cm<sup>-2</sup> for each unit. The EL performances of the blue and white devices were measured with a PHOTO RESEARCH SpectraScan PR 655 PHOTOMETER and a KEITHLEY 2400 SourceMeter constant current source at room-temperature.

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## Entry for the Table of Contents (Please choose one layout only)

Layout 2:

## **Catch Phrase**

Effective Host Materials for Blue/White Organic Light Emitting Diodes by Utilizing Conjugation Twisted Structure in 10-Phenyl-9,10-Dihydroacridine Block



Two new 10-phenyl-9,10dihydroacridine derivatives attached by dibenzothiophene (DBT) and dibenzofuran (DBF) are synthesized. Thanks to the twisted N-phenyl ring, both molecules possess sufficiently high triplet energies and are suitable for hosts for phosphorescent organic light-emitting diodes with maximum efficiency of 24.7% achieved.