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Amorphous Host Materials Based on Tröger's Base Scaffold for Application in Phosphorescent Organic Light-Emitting Diodes

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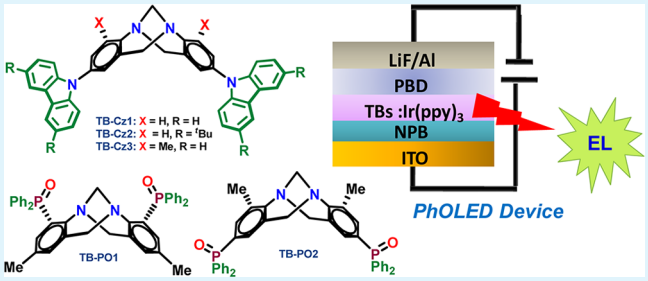
Supporting Information

ABSTRACT: Tröger's bases (**TB**s) functionalized with carbazoles (**TB-Cz**s) and phosphine oxides (**TB-PO**s) were designed and synthesized as host materials for application in phosphorescent organic light-emitting diodes. The **TB** scaffold is shown to impart thermal stability with high T_g values (171−211 °C) as well as high triplet energies in the range of 2.9−3.0 eV. With a limited experimentation of the devices, it is shown that the **TB**s doped with a green phosphor, namely, $Ir(ppy)_3$, permit impressive external efficiencies on the order of ca. 16% with a high brightness of ca. 3000−4000 cd/m^2. Better device performance results are demonstrated by a small structural manipulation of the **TB** scaffold involving substitution of methyl groups in the core scaffold.



KEYWORDS: *Tröger's base, host materials, phosphor, phosphorescence, triplet energy, pholeds*

INTRODUCTION

Research on organic light-emitting diodes (OLEDs) continues to be an exciting enterprise, which is most relevant commercially from the point of view of lighting and display technology. The advantages that OLED-based displays and lighting offer are unmatched by other existing technologies. Thus, the motivation to develop novel functional materials with improved performance of fabricated devices continues unabated.[1−8] Over the past decade, there has been a gradual shift of interest from fluorescence- to phosphorescence-based materials in quest of high efficiencies of light emission by harvesting both singlet and triplet excitons.[9−12] It is now firmly established that the organometallic complexes of certain heavy metals such as Ir, Os, Pt, etc. may allow 100% internal quantum efficiency by means of facile spin−orbit coupling.[13] However, an inevitable shortcoming associated with such phosphorescence-emitting materials in nondoped devices is the quenching due to concentration and triplet−triplet annihilation.[14] These detrimental nonradiative decay mechanisms can be suppressed by dispersing triplet phosphors in a host matrix.[15,16] The design and development of host materials suitable for a certain emitter continue to be a challenge, as the following criteria must be met for a material to be considered as a suitable host for a given guest:[17−19] first, the host material should possess higher triplet energy than the triplet phosphor to prevent reverse energy transfer from the latter back to the host; second, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the host material should be such that the holes and electrons can be injected in a facile manner from adjacent layers; third, the compounds should be thermally and morphologically stable.

The conventional host materials, namely, *m*CP(1,3-bis(*N*-carbazolyl)benzene)[20] and CBP (4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl),[21] suffer from the disadvantage of low glass-transition temperatures (T_g values), which are 60 and 62 °C, respectively. In continuation of our studies based on the de novo design of organic materials for application in OLEDs,[22−26] we surmised that Tröger's Base (**TB**) scaffold, which is V-shaped, rigid, chiral, and C_2-symmetric,[27] can be exploited to impart amorphous property and develop host materials with high T_g values for phosphorescent OLEDs (PhOLEDs). This is based on the knowledge from a just-concluded study in our group that the **TB** scaffold does indeed render the 2,8-substituted derivatives highly amorphous and thermally stable.[28] Accordingly, we designed carbazole- and phosphine oxide-functionalized **TB**s, that is, **TB-Cz1-3** and **TB-PO1-2** in Chart 1, for application as host materials; the functionalities such as carbazole and phosphine oxide appended to the **TB** scaffold have been proven to be excellent for high triplet energy in phosphorescent OLEDs.[29−35] Herein, we report the synthesis, photophysical, electrochemical, and thermal studies of **TB**s functionalized with carbazoles (**TB-Cz**s) and phosphine oxides (**TB-PO**s, Chart 1) and demonstrate the applicability of these materials as host materials in simple PhOLED devices for green emission from the dopant, that is, $Ir(ppy)_3$.

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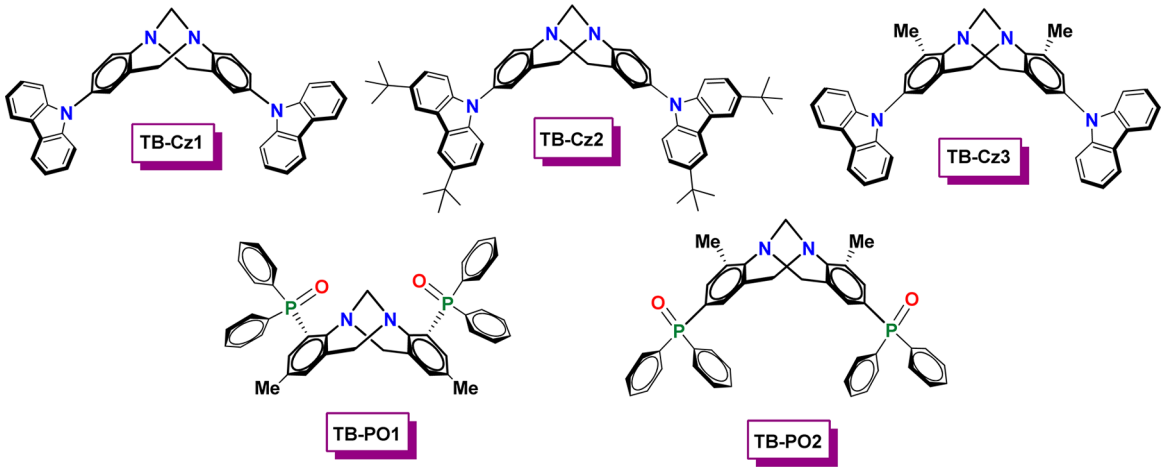
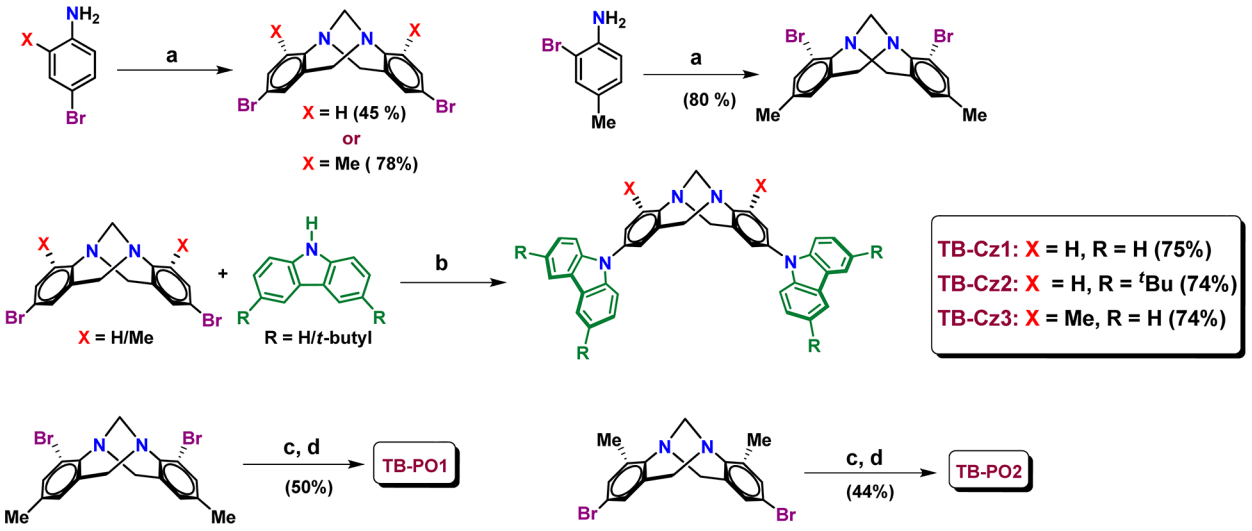
Chart 1. Structures of TBs Functionalized with Carbazole and Phosphine Oxide



Scheme 1. Synthesis of TB-Czs and TB-POs[a]



[a]Reagents and conditions: (a) $(HCHO)_n$, TFA, −20 °C, 48 h; (b) $Pd(OAc)_2$, $P(^tBu)_3$, NaO^tBu, dry toluene, 110 °C, 72 h; (c) ^{n}BuLi, THF, −78 °C, Ph_2PCl, 12 h; (d) H_2O_2, 0 °C, 30 min.

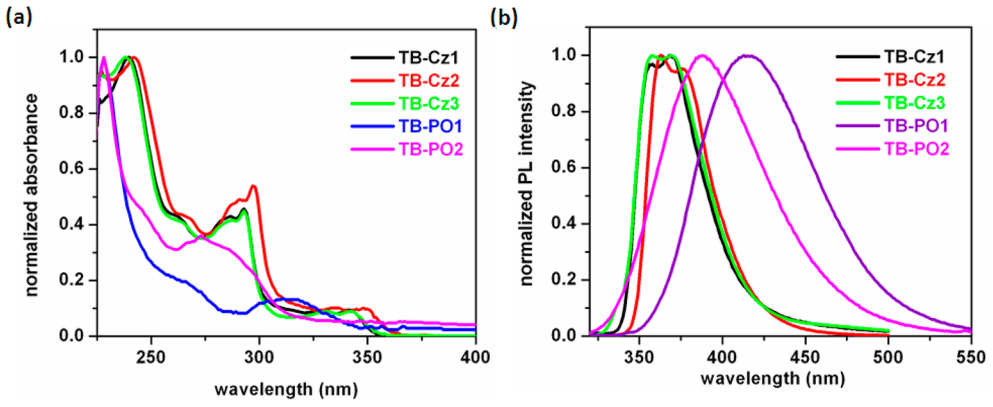


Figure 1. (a) Normalized absorption and (b) emission spectra of **TBs** in dilute DCM solutions.

RESULTS AND DISCUSSION

Synthesis. The 2,8-dibromo-substituted **TBs**, that is, 2,8-dibromo-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]-diazocine, 2,8-dibromo-4,10-dimethyl-6*H*,12*H*-5,11-methanodi-benzo-[*b*,*f*][1,5]-diazocine and 4,10-dibromo-2,8-dimethyl-6*H*,12*H*-5,11-methanodi-benzo[*b*,*f*][1,5]-diazocine, were synthesized by following the literature-reported procedures.[36−38] 2-Fold Buchwald-Hartwig amination of these bromo-substituted **TBs** with carbazole or 3,6-di-*tert*-butylcarbazole afforded three carbazole functionalized **TBs**, that is, **TB-Cz1**, **TB-Cz2**, and

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Table 1. Absorption, Fluorescence, Phosphorescence, Electrochemical, and Thermal Properties of TB-Cz1−3, TB-PO1, and TB-PO2

substrate	λ_{max} (UV)[a] (nm)	band gap[b] (eV)	λ_{max}(PL) sol[a] (nm)	HOMO/LUMO (eV)	E_T (eV)[c]	T_d[d]	T_g[e]
TB-Cz1	240	3.50	368	5.38/1.88	3.03	394	171
TB-Cz2	242	3.42	363	5.44/2.02	2.99	424	211
TB-Cz3	240	3.51	369	5.54/2.03	3.03	405	175
TB-PO1	228	3.60	413	5.42/1.82	3.07	384	196
TB-PO2	228	3.98	388	5.56/1.58	3.0	404	200

[a]Absorption and fluorescence spectra were recorded in DCM solutions (ca. 1×10^{-5} M). [b]Band-gap energies were calculated from red edge absorption onset values. [c]The E_T values were calculated from highest energy peak of phosphorescent spectra recorded in 2-methyltetrahydrofuran at 77 K. [d]From TGA corresponding to 5% weight loss. [e]From DSC.

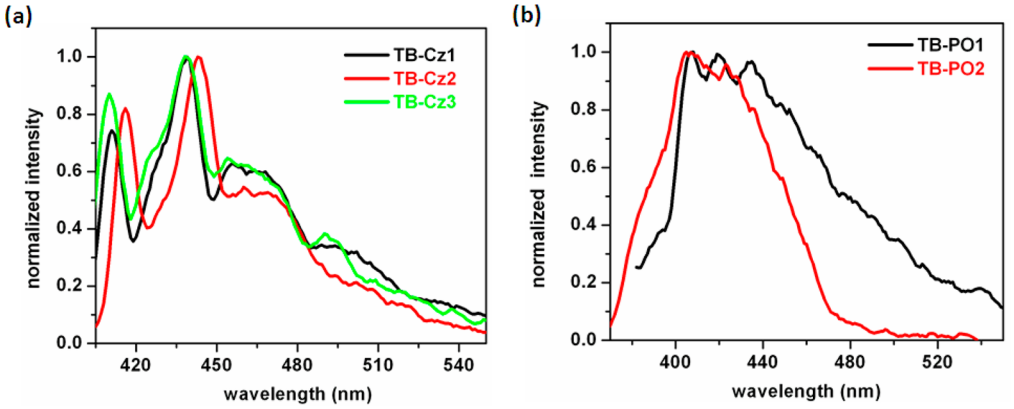

Figure 2. Phosphorescence spectra of **TB-Czs** (a) and **TB-POs** (b) in 2-methyltetrahydrofuran (1×10^{-5} M) at 77 K.

TB-Cz3, in ca. 74−75% isolated yield (Scheme 1). Syntheses of the phosphine oxides involved lithiation of their respective dibromo-**TBs** at low temperature followed by quenching with chlorodiphenylphosphine to yield corresponding phosphines. The latter were subjected to oxidation using H_2O_2 at ambient temperature. The two-step synthesis afforded **TB-PO1** and **TB-PO2** in 44−50% isolated yields (cf. Scheme 1).

Photophysical Properties. UV−vis absorption spectra of all **TBs** were recorded with dilute dichloromethane (DCM) solutions (ca. 1×10^{-5} M). As shown in Figure 1, one observes structured absorption for **TB-Cz1**, **TB-Cz2**, and **TB-Cz3** with the absorption for **TB-Cz2** slightly red-shifted. In contrast, the absorption spectra of both phosphine oxides, that is, **TB-PO1** and **TB-PO2**, are quite different and display primarily two absorption maxima. Although the absorption maximum in the short wavelength region for both **TB-PO1** and **TB-PO2** lies at the same position (ca. 230 nm), the long-wavelength absorption is shifted bathochromically by ∼40 nm for **TB-PO1** when compared to that of **TB-PO2**. Band gaps of all the **TBs** were calculated from their absorption onset values. Phosphine oxide-functionalized **TBs**, that is, **TB-POs**, exhibited comparatively higher band gap energies than their carbazole counterparts (cf. Table 1). In particular, it is noteworthy that the band gap for 2,8-functionalized phosphine oxide, that is, **TB-PO2**, is higher than that for the 4,10 isomer, that is,**TB-PO1.**

Fluorescence spectra of all **TBs** were recorded with dilute DCM solutions (ca. 1×10^{-6} M) for excitation at 300 nm except for **TB-PO2**; for the latter, the fluorescence spectrum was recorded for excitation at 273 nm. Photoluminescence spectral features of all carbazole derivatives, that is, **TB-Czs**, are similar with emission maximum at ca. 363−369 nm; note that the band with emission maximum is closely spaced by another strong emission band within ca. 10−15 nm. Emission maxima for **TB-POs** are quite broad and are bathochromically shifted relative to those of **TB-Czs**. It is noteworthy that the emission maximum of **TB-PO1** is, in particular, red-shifted by ∼25 nm relative to that of **TB-PO2**, which is quite intriguing. One would expect, based on steric inhibition of resonance at *o*-position, that the absorption as well as emission maxima should be red-shifted for the para isomer, that is, **TB-PO2**, relative to the ortho one, that is, **TB-PO1**. Presumably, nitrogen lone pair delocalization into the ring occurs more efficiently in **TB-PO1** due to the assistance by the proximate oxygen of phosphine oxide to account for the observed red shift in the emission as well as absorption maxima of **TB-PO1**; we believe that the oxygen atom of phosphine oxide and nitrogen atom of the **TB** core that undergoes charge delocalization interact effectively.

Triplet energies of all the **TBs** were derived from 0 to 0 transitions in the phosphorescence spectra recorded in dilute 2-methyltetrahydrofuran solution (ca. 1×10^{-6} M) at 77 K (cf. Figure 2). All the compounds were found to possess high triplet energies in the range of 2.9−3.0 eV, which is higher than the triplet energy of the conventional green dopant, namely, $Ir(ppy)_3$ (2.42 eV).[39]

Electrochemical Properties. Electrochemical properties of the **TBs** were investigated by cyclic voltammetry. All the **TB**-substituted carbazoles, that is,**TB-Czs**, exhibited irreversible oxidation in DCM solutions (ca. 1×10^{-3} M) on anodic sweep (cf. Supporting Information). Phosphine oxides, that is, **TB-POs**, exhibited irreversible oxidations similar to carbazole analogues on anodic sweeping of their DCM solutions. The peak corresponding to reduction wave was prominent in case of **TB-PO2**. However, it was not conspicuous for **TB-PO1**. The HOMO energies were calculated from onset oxidation potentials using the equation HOMO = $-e(E_{onset(ox)} - E_{1/2,Fc/Fc+}) - 4.8$ eV. The energies of LUMOs were obtained

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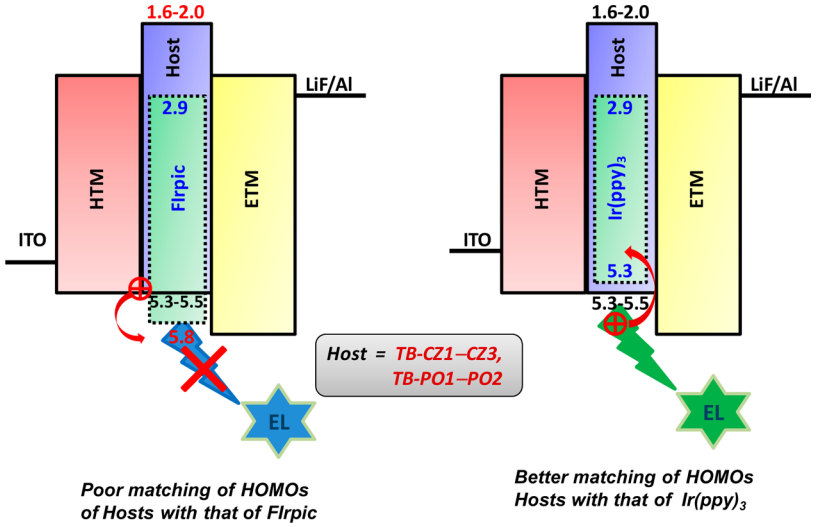

Figure 3. Relative energy-level diagrams of **TB**-based PhOLED devices with FIrpic (left) and $Ir(ppy)_3$ (right) as phosphors.

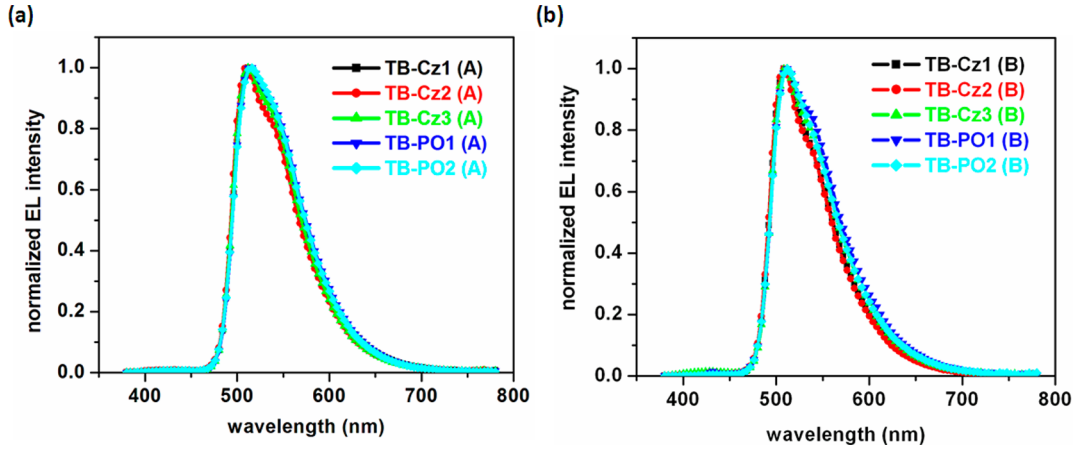

Figure 4. EL spectra recorded from the devices of **TB**s with configuration A (a) and B (b).

by subtracting the band-gap energies from their corresponding HOMO levels.

Thermal Properties. Thermal properties of the **TB**s were examined by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis at a heating rate of 10 °C/min under inert atmosphere. Indeed, all compounds exhibited very high thermal decomposition and T_g values (Table 1), which indicates their ability to endure high thermal stress during vacuum sublimation and joule heating. The excellent thermal properties of **TB**-based materials may be ascribed to the rigidity of the core scaffold and its unique V-shaped geometry, which prevents molecular aggregation leading to stable glass formation. Among carbazole-functionalized **TB**s, the bulky *tert*-butyl groups in **TB-Cz2** contribute to its significantly high thermal stability. The amorphous property of all carbazole-functionalized **TB**s (Chart 1) was additionally confirmed by featureless and broad powder X-ray diffraction patterns (cf. Supporting Information). Unfortunately, phosphine oxide derivatives **TB-PO**s were found to exhibit microcrystallinity in the solid state as revealed by their X-ray diffraction patterns.

Electroluminescent Properties. As mentioned earlier, the triplet energies of all the synthesized **TB**-based hosts fall in the range of ca. 2.9–3.0 eV, which is higher than that of blue emissive dopant, that is, FIrpic (E_T = 2.65 eV).[40] Thus, our initial efforts were focused on examining their applicability for FIrpic as the dopant in PhOLED devices for blue emission. Unfortunately, the results of device performances were disappointing (cf. Supporting Information). Inefficient energy transfer from the hosts to the guests was believed to be the reason for poor efficiency as well as the observed mixed emission emanating from the dopant as well as the host. A careful analysis of the relative energy levels of all materials employed in the devices led us to infer two major impediments for the observed poor results for the devices constructed with FIrpic as the phosphor: first, the LUMO levels of the hosts are very high in energy due to e-rich **TB** scaffold, which presumably decelerates transport of electrons from the electron-transporting TmPyPB layer to the host material, Figure 3. Consequently, population of the electrons injected into the emissive layer is presumably incommensurate to the high population of holes that are accumulated; second, the HOMO levels of the host FIrpic are higher in energy than those of **TB**s, which not only hinders hole transport from the host to FIrpic leading to poor efficiency but also causes accumulation of holes in the host material. Inefficient energy transfer due to incommensurate HOMO−LUMO levels may result in emission from the host itself in addition to concentration quenching (cf. Supporting Information). We therefore surmised that replacement of TmPyPB with a relatively higher LUMO electron-

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Table 2. Device Performance Results for PhOLED Devices Fabricated with TBs as Host Materials

compound	device	V_{on} [a]	η_{ext} [b]	η_p [c]	η_l [d]	λ_{max}^{EL} [e]	L_{max} [f]	CIE (x,y)[g]
TB-Cz1	A	3.5	5.2	10.2	18.1	512	9820	0.31, 0.60
	B	4.5	6.3	9.0	21.0	508	2770	0.29, 0.60
TB-Cz2	A	4.5	4.9	8.02	16.6	512	1450	0.30, 0.60
	B	5.5	15	42.3	24.1	508	312	0.29, 0.59
TB-Cz3	A	4.0	16.0	34.6	54.8	512	4020	0.30, 0.61
	B	4.5	7.40	16.1	23.1	512	2828	0.30, 0.60
TB-PO1	A	4.0	6.9	17.1	23.5	516	2752	0.31, 0.60
	B	4.5	2.7	3.3	8.9	512	359	0.31, 0.58
TB-PO2	A	3.0	8.3	23.8	28.6	516	2860	0.31, 0.60
	B	3.5	7.0	15.6	17.4	512	3100	0.30, 0.60

[a]Turn-on voltage (V). [b]Maximum external quantum efficiency (%). [c]Maximum power efficiency (lm/W). [d]Maximum luminance efficiency (cd/A). [e]λ_{max}^{EL} (nm). [f]Maximum luminance achieved (cd/m^2). [g]1931 chromaticity coordinates.

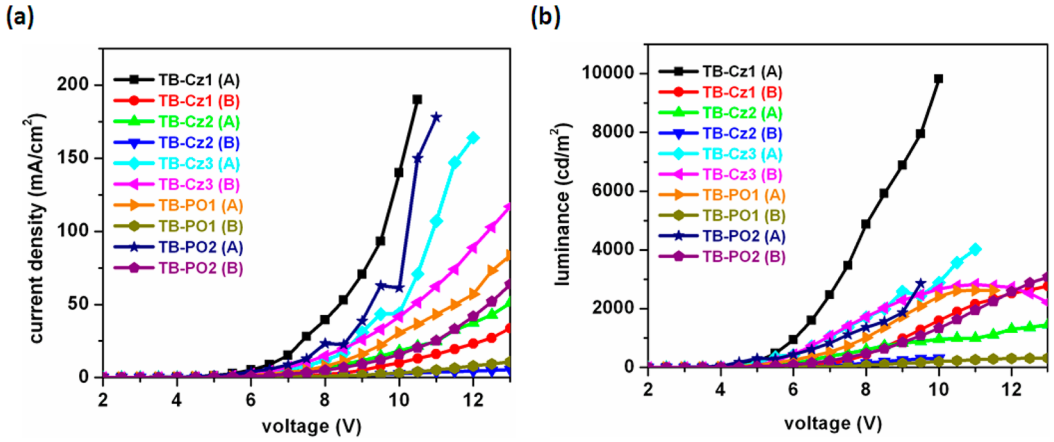

Figure 5. Current density vs voltage (a) and luminance vs voltage (b) profiles for the PhOLED devices constructed for **TB**-based host materials with configurations A and B.

transporting material such as 2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) and that of Firpic with a dopant possessing relatively higher HOMO such as Ir(ppy)$_3$ might improve the device results; note that the LUMO and HOMO for PBD and Ir(ppy)$_3$ are 2.4[12] and 5.3 eV,[41] respectively. Accordingly, two devices of the following configurations were fabricated: configuration A = ITO/NPB (40 nm)/**TB-Czs** or **TB-POs**: Ir(ppy)$_3$(8−9%, 30 nm)/PBD (40 nm)/LiF (2 nm)/Al (150 nm) and configuration B = ITO/NPB (40 nm)/TCTA (10 nm)/**TB-Czs** or **TB-POs**:Ir(ppy)$_3$ (8−9%, 30 nm)/TPBI (40 nm)/LiF (2 nm)/Al (150 nm), where ITO functions as anode, NPB and/or TCTA function as hole-transporting materials, PBD and/or TPBI function as electron-transporting as well as hole-blocking materials, and LiF/Al serves as a composite cathode. Of course, the emissive layer was constructed by coevaporation of **TB**-based host and green-emissive dopant, namely, Ir(ppy)$_3$. Bright green electroluminescence that is characteristic of Ir(ppy)$_3$ was captured from all the devices. Most remarkably, no emission from the host was observed from any of the devices (cf. Figure 4). The results of electroluminescence captured from the two devices for all **TB**s are collected in Table 2, and the corresponding *I*−*V*−*L* characteristics of the devices are shown in Figure 5.

As may be perused from Table 2, all **TB**-based host materials function as hosts for the green emissive phosphor, that is, Ir(ppy)$_3$. Among the carbazole-based derivatives, the performance with **TB-Cz3** is most impressive, followed by that of **TB-Cz1** and **TB-Cz2**. In fact, maximum external quantum efficiency of 16.0%, maximum luminous efficiency of 54.8 cd/A, and maximum power efficiency of 34.6 lm/W were obtained for **TB-Cz3** as the host material in the device configuration A. Although the efficiency parameters for **TB-Cz2** host in the device configuration B are higher, it is noteworthy that the efficiency roll-off is very high, and the maximum brightness is limited to 312 cd/m^2. In fact, the poorer performance exhibited by **TB-Cz2** when compared to other two carbazole derivatives may be a consequence of appended bulky tertiary butyl groups, which appear to function effectively functioning as electrical insulating entities thereby constraining charge transport.[42] The reason why one observes better device performance results with **TB-Cz3** as the host material should be traceable to the influence of the methyl group, which seemingly facilitates better energy transfer; presumably, the host accommodates the dopant in close proximities where the energy transfer is more efficient.

Insofar as the **TB**-based phosphine oxides are concerned, the performance exhibited by **TB-PO2** as the host material is far better than that of its structural isomer **TB-PO1**. A careful analysis of their energy levels (Figure 3) reveals that **TB-PO1** has a higher HOMO level and a low-lying LUMO level when compared to that of **TB-PO2**. Presumably, electron injection is facile in the case of **TB-PO1**, but hole migration from host to dopant is easier in the case of **TB-PO2**. This is further corroborated by the poor device performances noted for FIrpic as the dopant, for which the HOMO energy is much deeper. Thus, it emerges that the substitution of methyl groups in the **TB** skeleton leads to a subtle lowering of the HOMO levels by

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ca. 0.16 eV (**TB-Cz1** vs **TB-Cz3**), which manifests in dramatic improvement of the device performance results.

CONCLUSIONS

Two distinct sets of host materials based on the **TB** scaffold, namely, carbazoles and phosphine oxides, have been designed and synthesized; it is noteworthy that the simple synthetic protocol allows a ready access to these materials. The **TB** scaffold is found to impart amorphous property to all the carbazole and phosphine oxide derivatives with high T_g values, which range from 171 to 211 °C. Although all **TB**s were found to possess large band-gap energy of ca. 2.9−3.0 V, their utility for application as host materials for blue phosphor, that is, FIrPic, was curtailed by poor device performance results. Otherwise, the fact that they function as remarkable host materials for green-emissive $Ir(ppy)_3$ is demonstrated by impressive device performance results. With a limited experimentation with device constructions, external efficiencies on the order of ca. 16% with a high brightness of ca. 3000−4000 cd/m^2 have been observed for both carbazole- and phosphine oxide-functionalized **TB** hosts. It is shown that structural manipulation of the **TB** scaffold by substitution of methyl groups in the core scaffold allows better performance results of the devices when employed as host materials. Thus, utility of the readily accessible V-shaped Tröger's bases, which are known for well over a century and have elicited considerable interest as chiral scaffolds in molecular recognition, is compellingly demonstrated for application in PhOLEDs.

EXPERIMENTAL SECTION

Synthesis of TB-Cz1. An oven-dried pressure tube was cooled under nitrogen gas and charged with 2,8-dibromo-6*H*,12*H*-5,11-methanodi-benzo[*b*,*f*][1,5]-diazocine (0.50 g, 1.31 mmol), carbazole (0.57 g, 3.42 mmol), NaO^{t}Bu (0.60 g, 5.26 mmol), $Pd(OAc)_2$ (0.03 g, 10 mol %), and P(^{t}Bu)$_3$ (32 μL, 0.13 mmol). To the contents was added 10 mL of dry toluene. The pressure tube was sealed under nitrogen and heated at 100 °C for 72 h. After this period, the contents were cooled to room temperature, toluene was removed in vacuo, and the reaction mixture was quenched with water. The organic contents were extracted with chloroform, and the combined extract was dried over anhydrous (anhyd) Na_2SO_4 and filtered. The solvent was removed in vacuo, and the crude product was subjected to neutral alumina column chromatography using ethyl acetate/petroleum ether (20:80) as an eluent to yield pure **TB-Cz1** as a colorless solid material, 0.72 g (75% yield); IR (solid) cm^{-1} 3044, 2944, 1595, 1495, 1451, 1334, 1323, 1308, 1229, 1207; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.35 (d, J = 16.5 Hz, 2H), 4.48 (s, 2H), 4.87 (d, J = 16.5 Hz, 2H), 7.20−7.25 (m, 6H), 7.37−7.40 (m, 12H), 8.11(d, J = 7.35 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 58.6, 66.9, 109.8, 120.0, 120.4, 123.3, 125.4, 126.0, 126.5, 126.7, 129.1, 133.8, 141.0, 146.8; electron impact mass spectrometry (EI-MS$^+$) m/z Calcd for $C_{39}H_{29}N_4$ 553.2392 [M + H]$^+$, found 552.2391.

Synthesis of TB-Cz2. A similar procedure to that described above for the synthesis of **TB-Cz1** was adopted for the synthesis of **TB-Cz2** by employing 2,8-dibromo-4,10-dimethyl-6*H*,12*H*-5,11-methanodi-benzo[*b*,*f*][1,5]-diazocine (0.50 g, 1.31 mmol) and 3,6-di-*tert*-butylcarbazole (0.96 g, 2.6 mmol). The solvent was removed in vacuo, and the crude product was subjected to neutral alumina column chromatography using ethyl acetate/petroleum ether(5:95) as an eluent to yield pure **TB-Cz2** as a colorless powder (0.50 g, 74% yield); IR (film) cm^{-1} 2958, 2865, 1492, 1363, 1262, 1294; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.46 (s, 36H), 4.35 (d, J = 16.5 Hz, 2H), 4.50 (s, 2H), 4.87 (d, J = 16.5 Hz, 2H), 7.19 (s, 2H),7.30−7.45 (m, 12H), 8.13(s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.9, 34.6, 58.5, 66.8, 109.1, 116.1, 123.2, 123.5, 124.9, 126.1, 126.4, 128.8, 134.4, 139.2, 142.8; EI-MS$^+$ m/z Calcd for $C_{55}H_{61}N_4$ 777.4896 [M + H]$^+$, found 777.4891.

Synthesis of TB-Cz3. A similar procedure to that described above for the synthesis of **TB-Cz1** was followed for the synthesis of **TB-Cz3** by employing 2,8-dibromo-4,10-dimethyl-6*H*,12*H*-5,11-methanodi-benzo[*b*,*f*][1,5]-diazocine (0.50 g, 1.22 mmol) and carbazole (0.47 g, 2.3 mmol). The workup followed by neutral alumina column chromatography using ethyl acetate/petroleum ether (10:90) as an eluent led to yield pure **TB-Cz3** as a white powder (0.50 g, 74% yield); IR (KBr) cm^{-1} 3048, 2947, 1597, 1493, 1477, 1452, 1311, 1230, 1209; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.52 (s, 6H), 4.19 (d, J = 17.1 Hz, 2H), 4.49 (s, 2H), 4.77 (d, J = 17.1 Hz, 2H), 7.07 (s, 2H), 7.26−7.29 (m, 6H), 7.41 (brs, 8H), 8.14 (d, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.2, 55.0, 67.5, 109.8, 119.7, 120.2, 122.8, 123.2, 125.8, 127.6, 129.5, 133.3, 135.0, 141.0, 145.3; electrospray ionization mass spectrometry (ESI-MS$^+$) m/z Calcd for $C_{41}H_{33}N_4$ 581.2705 [M + H]$^+$, found 581.2707.

Synthesis of TB-PO1. A solution of 4,10-dibromo-2,8-dimethyl-6*H*,12*H*-5,11-methanodi-benzo[*b*,*f*][1,5]-diazocine (1.0 g, 2.45 mmol) in 50 mL of anhydrous tetrahydrofuran (THF) was cooled to −78 °C under nitrogen gas atmosphere. To this solution was introduced *n*-butyllithium (7.0 mL, 9.8 mmol, 1.4 M in hexane) very slowly under N_2 atmosphere. The contents were allowed to stir at −78 °C for 1 h, and chlorodiphenylphosphine (2.2 mL, 12.2 mmol) was added slowly at −78 °C. The reaction mixture was observed to turn pale yellow and was allowed to warm to room temperature very slowly. The reaction mixture was further stirred for 16 h before the reaction was quenched with water. Subsequently, the reaction mixture was stripped off the THF in vacuo, and the organic contents were extracted with chloroform. The combined extract was dried over anhyd Na_2SO_4 and filtered, and the solvent was removed in vacuo.

The white material obtained from the above operation was dissolved in 25 mL of DCM at 0 °C. To the resultant solution was added 30% aqueous H_2O_2 (0.6 mL), and the solution was stirred for 20 min at room temperature. The reaction mixture was quenched with water, and the organic material was extracted with DCM. The combined extract was dried over anhyd Na_2SO_4 and filtered, and the solvent was removed in vacuo. The crude product was subjected to neutral alumina column chromatography using ethyl acetate/petroleum ether (50:50) as an eluent to yield pure **TB-PO1** as a white powder (0.80 g, 50.3% overall yield); IR (film) cm^{-1} 2963, 2917, 2849, 1435, 1260, 1097, 1020; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 6H), 3.51 (s, 2H), 4.36 (d, J = 18.3 Hz, 2H), 4.72 (d, J = 18.3 Hz, 2H), 6.68 (d, J = 14.05 Hz, 2H), 6.93 (s, 2H), 7.35−7.57 (m, 16H), 7.66−7.70 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 57.8, 65.7, 126.9, 127.8, 127.9, 128.0, 128.1, 128.2, 130.70, 130.78, 131.3, 132.0, 132.2, 132.3, 132.8, 133.4, 133.5, 133.6, 134.5, 135.4; ^{31}P NMR ($CDCl_3$, 500 MHz) δ 28.6; ESI-MS$^+$ m/z Calcd for $C_{41}H_{37}N_2O_2P_2$ 651.2330 [M + H]$^+$, found 651.2332.

Synthesis of TB-PO2. A procedure similar to the one described above for the synthesis of **TB-PO1** was followed for the synthesis of **TB-PO2** using 2,8-dibromo-4,10-dimethyl-6*H*,12*H*-5,11-methanodi-benzo[*b*,*f*][1,5]-diazocine (1.0 g, 2.45 mmol). After the reaction, the crude product was subjected to neutral alumina column chromatography using ethyl acetate/petroleum ether (80:20) as an eluent to yield pure **TB-PO2** as a white powder (0.70 g, 44% overall yield); IR (film) cm^{-1} 3055, 2953, 1590, 1468, 1437, 1178, 1113; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (s, 6H), 3.97 (d, J = 16.5 Hz, 2H), 4.28 (s, 2H),4.54 (d, J = 16.5 Hz, 2H), 7.13 (d, J = 12.2 Hz, 2H), 7.22 (d, J = 12.2 Hz, 2H), 7.43−7.54 (m, 12H), 7.62−7.67 (m, 8H);^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.2, 54.7, 67.1, 126.8, 127.6, 128.2, 128.3, 128.4, 128.5, 128.6, 131.8, 132.0, 132.1, 132.3, 132.4, 132.8, 133.4, 133.5, 149.6 ;^{31}P NMR ($CDCl_3$, 500 MHz) δ 29.5; ESI-MS$^+$$m/z$ Calcd for $C_{41}H_{37}N_2O_2P_2$ 651.2330 [M + H]$^+$, found 651.2339.

ASSOCIATED CONTENT

Supporting Information

Cyclic voltammograms, DSC and TGA profiles, EL spectra, associated plots for the devices constructed, and ^{1}H, ^{13}C, and

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^{31}P NMR spectral reproductions of all the compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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