An electron-transporting host material compatible with diverse triplet emitters used for highly efficient red- and green-electrophosphorescent devices†

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A bifluorene analogue, T2N, containing a pyridyl moiety serves as both a host and an efficient electron-transporting material that is compatible with various heavy metal-containing red (Ir, Ru, Os, and Pt) and green (Ir) phosphors for highly efficient phosphorescent OLEDs possessing simple device architectures.

Dispersing transition metal-containing phosphors into suitable host materials can reduce the quenching processes associated with the relatively long lifetimes and triplet–triplet annihilations of triplet excited states. Using this approach, both singlet and triplet excitons can be harvested efficiently, making it possible to prepare organic light-emitting devices (OLEDs) exhibiting 100% internal efficiency.[1] Most of the efficient host materials reported were hole-transporting (HT) compounds—in particular, carbazole-based organoaryls;[2] electron-transporting (ET) host materials are relatively rare.[3] Electrophosphorescent devices incorporating HT-type host materials normally require sophisticated configurations, incorporating various functional materials, including transporting and blocking layers, to facilitate efficient exciton confinement on the phosphors. Such devices are not sufficiently cost-effective to compete with other contemporary flat-panel display technologies. In contrast, ET-type host materials are capable of being fabricated into efficient OLEDs with simplified device structures. Thus, the development of efficient ET-type host materials is in high demand for providing extra flexibility in designing device configurations. In previous studies, we used spiro-configured bifluorenes as hosts for red electrophosphorescent devices;[4] the maximum electroluminescence (EL) quantum efficiencies observed were substantially higher than that obtained when using the carbazole-based host

4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP).[2a,3a] We suspected that if we implanted a π-electron-deficient heteroarene into the bifluorene backbone, the resulting molecule would have a relatively higher electron affinity, which would facilitate injection and transport of electrons from the cathode. In this paper, we report a new 4-azafluorene-based host, **T2N** (Scheme 1), in which a nitrogen atom has been implanted into the backbone of a bifluorene unit, exhibiting modified electronic properties. This new material serves as a suitable ET host for a range of distinctive green and red emitters possessing wide structural features, giving electrophosphorescent devices with low turn-on voltages and remarkable efficiencies.

Scheme 1 depicts our synthetic pathway toward **T2N**. Suzuki coupling of the pyridine-containing amide **1** and the fluorene boronic ester **2** afforded the amide **3** in 68% isolated yield. The azafluorenone **4** was obtained in 77% yield through intramolecular cyclization upon treating **3** with LDA. The Grignard reaction of **4** with *p*-tolylmagnesium bromide and subsequent Friedel–Crafts alkylation provided **T2N** in 42% yield.
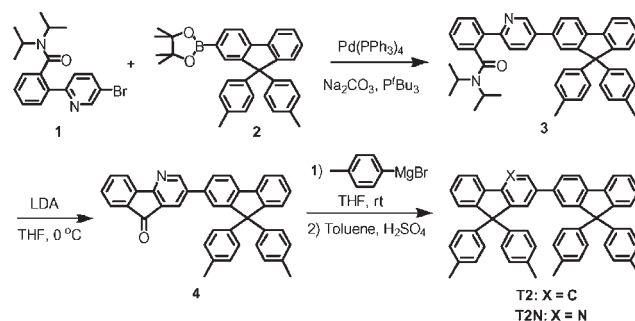
Scheme 1 Synthesis of **T2N**.

The introduction of a pyridyl moiety as a constituent of the π-conjugated backbone had an interesting effect on the physical properties of **T2N** relative to those of its pure-hydrocarbon counterpart, **T2**.[5] The fluorescence and absorption spectra of **T2N** in CH_2Cl_2 solution (Fig. 1) exhibited limited red shifting relative to those of the parent bifluorene **T2**. The phosphorescence of **T2N** was also measured at 77 K (in EtOH). The difference between the fluorescence (377 nm) and phosphorescence (506 nm) spectra corresponds to an exchange energy of *ca.* 1.2 eV between the singlet and triplet states of **T2N**. The triplet energy of 2.45 eV (defined as the 0–0 transition in the

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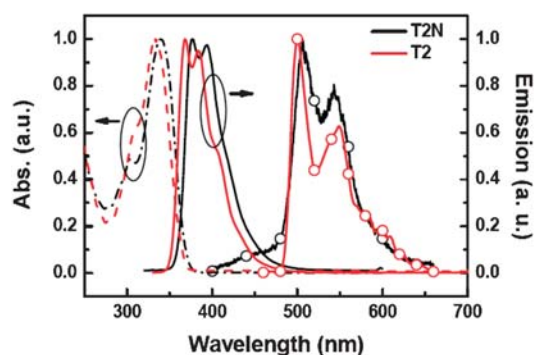
Fig. 1 UV-Vis, fluorescence (room temperature in CH_2Cl_2 solution), and phosphorescence (77 K, EtOH) spectra of **T2N** (black) and **T2** (red).

Scheme 2 Structures of the heavy metal complexes used in this study.

phosphorescent spectrum) of **T2N** is similar to that of **T2** (2.48 eV).[4] These results indicate that the photophysical properties are slightly altered upon introducing the pyridyl moiety onto the conjugated chromophore.

The highest occupied molecular orbital (HOMO) energy level (-5.75 eV) of **T2N**, taken from ultraviolet photoelectron spectroscopy (UPS) measurements (Fig. S-1, ESI†), and the corresponding lowest unoccupied molecular orbital (LUMO) energy (-2.50 eV) derived by subtracting the HOMO energy from the UV-Vis absorption edge (3.25 eV). The energy band diagrams of **T2** and **T2N** can be obtained from the UPS data (ESI†). The main features of occupied molecular orbitals of **T2N** at 4.6 eV, 7 eV, and 9 eV below the Fermi level all shift toward lower binding energy with respect to that of **T2**. The data indicate that the energy level of HOMO, as well as LUMO, of the **T2N** is lower than those of **T2** (HOMO: -5.65 eV, LUMO: -2.35 eV). Thus, the electronic structure of the parent bifluorene **T2** was perturbed after embedding the nitrogen atom into the parent hydrocarbon backbone. This modification decreased both the HOMO and LUMO energy levels; in particular, the low LUMO energy level of **T2N** is a crucial feature for reducing the energy barrier for electron injection from the cathode. In addition, the presence of the C9 *p*-tolyl substituents provided high thermal and morphological stability to the thin films of **T2N**, as indicated by their high decomposition (5% weight loss) temperatures (T_d = 340 °C) and moderately high glass transition temperatures (T_g = 144 °C). The relatively high triplet energy of **T2N** suggests that it might be a suitable host material for yellow to red phosphors. We employed a relatively simple configuration for fabricating OLED devices: ITO/polyethylenedioxythiophene/
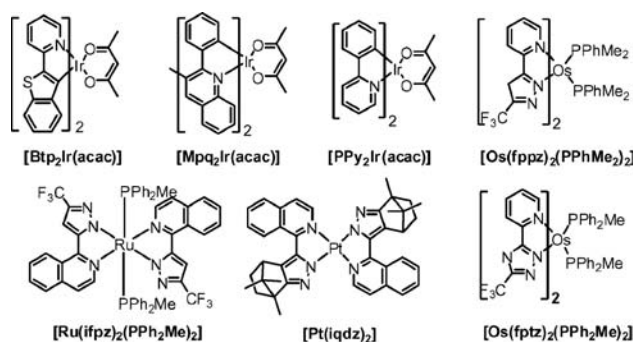
polystyrene sulfonate (PEDOT:PSS, 30 nm)/4,4′,4″-tri(*N*-carbazolyl)triphenylamine (TCTA, 40 nm)/**T2N**:dopant (25 nm)/**T2N** (35 nm)/LiF (0.5 nm)/Al; TCTA functioned as the HT layer, while **T2N** functioned as both host and ET materials. The low barrier between the HOMO energy levels of TCTA (-5.6 eV) and **T2N** (-5.75 eV) allowed direct hole injection from TCTA into **T2N**. The electrons injected from the **T2N** layer were trapped by the dopants dispersed within it, recombining with the holes to generate excitons directly, allowing efficient confinement of the emissive excitons within the emissive layer. We used the heavy metal complexes[6] (Scheme 2) Os(fptz)$_2$(PPh$_2$Me)$_2$, Os(fppz)$_2$(PPhMe$_2$)$_2$, Btp$_2$Ir-(acac), Mpq$_2$Ir(acac), Pt(iqdz)$_2$, and Ru(ifpz)$_2$(PPh$_2$Me)$_2$ as red dopants and PPy$_2$Ir(acac) as a green dopant for the **T2N** layer. Table 1 summarizes the electroluminescence characteristics of the resulting devices.

As indicated in Fig. 2(a), these devices turned on at low voltages (2.9–5.7 V at a brightness of 0.1 cd m^{-2}), probably because the HOMO and LUMO energy levels of **T2N** matched well with those of TCTA and cathode, leading devices to have high current density (Fig. 2(b)). All of the devices exhibited high external quantum efficiencies ($\eta_{ext} > 10\%$; Fig. 3(a)), and the EL spectra revealed pure dopant emissions (Fig. 3(b)). These results suggest that our present device structure, incorporating **T2N** as an ET-type host, generally provides high-efficiency OLEDs for red phosphors featuring diverse metal centres, and **T2N** can also accommodate a green emitter [PPy$_2$Ir(acac)] efficiently.

Among these devices, the highest external quantum efficiency (15.5% at 0.1 mA cm^{-2}) and highest brightness (29 700 cd m^{-2} at 19 V) with saturated red emission of CIE1931 coordinates (0.68, 0.32) were obtained when using 9 wt% Os(fptz)$_2$(PPh$_2$Me)$_2$ as the dopant. To the best of our knowledge, this is the highest efficiency reported for a red

Table 1 Electroluminescence characteristics of devices incorporating various red and green dopants

| Dopant (wt%)	$V_{on}{}^a$/V	L_{max}/cd m^{-2}	I_{max}/mA cm^{-2}	$\eta_{ext\ max}$ (%, cd A^{-1})	$\eta_{p\ max}$/lm W^{-1}	CIE (x,y)
Btp$_2$Ir(acac) (5%)	3.2	8600 (18 V)	1330	10.4, 8.1	6.8	0.68; 0.32
Mpq$_2$Ir(acac) (9%)	4.7	23 300 (19.5 V)	1180	13.7, 13.3	9.3	0.66; 0.34
Os(fptz)$_2$(PPh$_2$Me)$_2$ (9%)	5.5	29 700 (19 V)	1150	15.5, 11.4	6.9	0.68; 0.32
Os(fppz)$_2$(PPhMe$_2$)$_2$ (9%)	5.7	22 000 (19.5 V)	1250	13, 9.7	6.8	0.68; 0.32
Pt(iqdz)$_2$ (9%)	3.8	15 000 (19.5 V)	1200	10.2, 12.3	9.4	0.64; 0.36
Ru(ifpz)$_2$(PPh$_2$Me)$_2$ (6%)	5.6	4200 (19.5 V)	800	11.2, 7.9	6.3	0.68; 0.32
PPy$_2$Ir(acac) (10%)	2.9	69 000 (17 V)	1600	12.3, 45	38	0.48; 0.52

^{a} At a brightness of 0.1 cd m^{-2}.
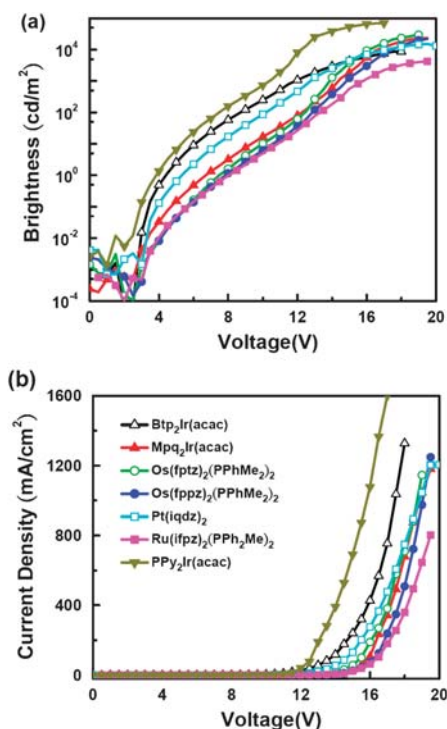
Fig. 2 (a) Brightness *vs.* voltage and (b) current density *vs.* voltage characteristics of devices having an identical structure but incorporating different dopants.
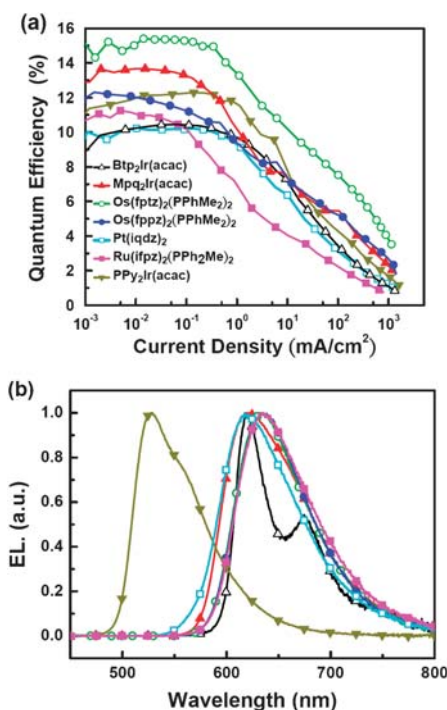

Fig. 3 (a) External quantum efficiencies (EQEs) and (b) EL spectra of devices incorporating various dopants.

phosphorescent OLED employing an ET-type host material. We note that although the efficiency dropped upon increasing the brightness,[7] this device retained its high efficiency (10% at 18 mA cm^{-2}) at a brightness of 1000 cd m^{-2}.

In summary, we have synthesized a novel host material, **T2N**, featuring an electron-deficient pyridyl moiety embedded into a bifluorene backbone. The electronic behaviour of this chromophore was modulated significantly relative to that of its parent compound, rendering **T2N** suitable for use as an electron-transporting host material compatible with various heavy metal-containing red and green phosphors. Most importantly, taking advantage of the dual functions of **T2N**, high-efficiency red- and green-phosphorescent OLEDs possessing simple device architectures can be fabricated.

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