Journal of Materials Chemistry C

COMMUNICATION

Cite this: J. Mater. Chem. C, 2013, 1, 2404

Received 27th December 2012 Accepted 14th February 2013

DOI: 10.1039/c3tc00939d

www.rsc.org/MaterialsC

A host material consisting of a phosphinic amide directly linked donor-acceptor structure for efficient blue phosphorescent organic light-emitting diodest

Atsushi Wada,^{ab} Takuma Yasuda,^{*ac} Qisheng Zhang,^a Yu Seok Yang,^a Isao Takasu,^b Shintaro Enomoto^b and Chihaya Adachi^{*ac}

A host material with a high triplet excited-state energy level and a deep HOMO energy level has been developed by directly linking the donor and acceptor units through a phosphinic amide. Phosphorescent organic light-emitting diodes containing this material and a deep-blue dopant achieved an external quantum efficiency of 19.7%.

Phosphorescent organic light-emitting diodes (PHOLEDs) have been studied intensively because they can achieve an internal quantum efficiency of nearly 100%, corresponding to an external quantum efficiency (EQE) of 20%, by harvesting both singlet and triplet excitons.¹ To date, high efficiency green, red, and sky-blue PHOLEDs have been reported.² However, high efficiency deep-blue PHOLEDs, which are indispensable in fullcolor displays and white lighting applications with high color rendering index values, have not been realized.³

Recently, to realize high efficiency deep-blue PHOLEDs, research has been in progress in the following areas: (i) single emitting layer using donor–acceptor host materials having bipolar properties, with a high triplet excited-state (T_1) energy level and/or a deep HOMO energy level;^{3e,4} (ii) double emitting layers using hole-transporting host materials and electron-transporting host materials with high T_1 energy levels.⁵ We have focused on donor–acceptor host materials with a high T_1 energy level and a deep HOMO energy level because these materials can confine the high triplet excitons of the deep-blue dopants to suppress quenching of the emission by the host materials.⁶ In

addition, these donor-acceptor host materials can promote hole injection into the HOMO of the dopant and lead to direct charge recombination in the dopant, which is more efficient for the formation of excitons than host-to-dopant energy transfer,⁷ and can also improve the recombination probability because hole-electron recombination and exciton formation occur at the center of the emitting layer and not at the interface.⁸ In this communication, we report that the use of donor-acceptor host materials with a high T_1 energy level and a deep HOMO energy level has improved the efficiency of PHOLEDs with a deep-blue dopant.

A donor-acceptor host material with a phenylene spacer, N-(4-diphenylphosphoryl phenyl)carbazole (3, Fig. 1), was previously reported.⁹ Compound 3 has a high T_1 energy level. However, 3 also has a shallow HOMO energy level, because the phenylene spacer weakens the electron-withdrawing characteristic of the diphenylphosphine oxide moiety.¹⁰ To obtain donor-acceptor host materials with both a high T_1 energy level and a deep HOMO energy level, we have designed two compounds, 3,6-di-*tert*-butyl-N-(4-diphenylphosphoryl)carbazole (1) and N-(4-diphenylphosphoryl)carbazole (2), by directly linking the donor and acceptor units through the phosphinic amide (Fig. 1). Compounds 1 and 2 without the phenylene spacer are expected to have deeper HOMO levels than compound 3 with the spacer, because the directly linked diphenylphosphine oxide moiety stabilizes the HOMO energy level more strongly.

Compound **1** was synthesized from 3,6-di-*tert*-butylcarbazole by treatment with *n*-butyllithium, followed by chlorodiphenylphosphine to give the corresponding phosphine product. Afterwards, oxidation of the phosphine precursor with H_2O_2 produced **1** with an overall yield of 75% (see ESI for details[†]). Compounds **1–3** were then purified by temperaturegradient sublimation under vacuum conditions before measurements and device fabrication processes.

The molecular structure of **1** was revealed by single-crystal X-ray analysis, and an ORTEP drawing of **1** is displayed in Fig. 2a. The O1–P1–N1, O1–P1–C1, and O1–P1–C2 bond angles are 111.41°, 112.38° and 112.47°, respectively, indicating that

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^aCenter for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan. E-mail: yasuda@cstf.kyushu-u.ac.jp; adachi@cstf.kyushu-u.ac.jp; Fax: +81-92-802-6921; Tel: +81-92-802-6920

^bCorporate Research & Development Center, Toshiba Corp. 1, Komukai-Toshiba, Saiwai, Kawasaki, 212-8582, Japan. E-mail: atsushi1.wada@toshiba.co.jp; Fax: +81-44-520-1255; Tel: +81-44-549-2195

International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

[†] Electronic supplementary information (ESI) available. CCDC 894700. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3tc00939d



Fig. 1 Schematic drawings (top) and molecular structures (bottom) of host materials 1–3.



Fig. 2 (a) ORTEP drawing of **1**. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–O1 1.472(2), P1–N1 1.690(3), P1–C1 1.793(4), P1–C2 1.787(3), O1–P1–N1 111.41(11), O1–P1–C1 112.38(11), O1–P1–C2 112.47(12). (b) HOMO and LUMO distributions of **1**, derived from DFT calculations at B3LYP/6-31G(d).

the phosphine center forms a slightly distorted tetrahedral geometry (the ideal value for the tetrahedral geometry is 109.5°). This configuration should be favorable for the suppression of donor-acceptor electronic interactions. The HOMO and LUMO distributions for **1** have been studied *via* density-functional theory (DFT) calculations (Fig. 2b). The HOMO is localized on the carbazole unit, whereas the LUMO is mainly distributed on the diphenylphosphine oxide moiety. The clear spatial separation of the HOMO and the LUMO suggests a disruption of the π -conjugation *via* the phosphinic amide linkage, which is

preferable to maintain the high T_1 energy level of the donor-acceptor materials.

The thermal properties of compounds 1–3 are summarized in Table 1 (see also the ESI[†]). The decomposition temperature $(T_d, \text{ corresponding to 5% weight loss})$ is observed at 312 °C for 1, at 296 °C for 2, and at 375 °C for 3. The glass transition temperature (T_g) is observed distinctly at 68 °C for 1, at 33 °C for 2, and at 72 °C for 3. The T_g of compound 1 is much higher than that of 2, indicating that the introduction of the *tert*-butyl substituents into the carbazole unit significantly enhances the thermal stability of the phosphinic amide derivatives. The phosphinic amide 1 has a higher T_g than commonly used host materials such as mCP (60 °C) and CBP (62 °C),¹¹ and would form thermally and morphologically stable amorphous thin films. Smooth surface morphologies were observed for deposited thin films of 1 and 3 (see ESI[†]), implying that these materials can serve as host materials in PHOLEDs.

The absorption and photoluminescence (PL) spectra of compounds 1-3 in tetrahydrofuran (THF) solutions are shown in Fig. 3a, and the photophysical data are listed in Table 1. Compounds 1-3 exhibit a couple of characteristic absorption peaks in the range of 280-340 nm, which can be assigned to the π - π^* and n- π^* transitions of the carbazole unit.¹² Structured fluorescence emission peaks are observed at 340-370 nm in the solutions at room temperature. The phosphorescence spectra of 1-3 were measured in 2-methyltetrahydrofuran at 77 K (those of 1–3 are shown in the inset of Fig. 3a). The T_1 energy levels in the solutions were determined to be 2.99 eV for 1, 3.02 eV for 2, and 3.02 eV for 3 from the highest energy peak of the phosphorescence spectra. Fig. 3b depicts the absorption and PL spectra of compounds 1-3 in thin films. The fluorescence emission peaks are observed at 385 nm for 1, 367 nm for 2, and 384 nm for 3 in the thin films, which overlap well with the metal-to-ligand charge-transfer absorption peak of iridium(III)bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate (FIr6) acting as a phosphorescent deep-blue dopant emitter.7 This suggests that effective energy transfer from these host materials to FIr6 would occur.1 The phosphorescence spectra of 1 and 3 in thin films were measured at 77 K (inset of Fig. 3b). The T_1 energy levels in the thin films were estimated to be 3.10 eV for 1 and 2.79 eV for 3. Compound 1 shows a higher T_1 energy level than compound 3 in the thin films, although 1 shows a lower T_1 energy level than 3 in the solutions. This is probably because the tert-butyl

Table 1 Thermal and photophysical properties of compounds 1, 2, and 3										
					Solution			Film		
	$T_{\rm g}/T_{\rm d}^{\ a} [{\rm eV}]$	$HOMO^{b}$ [eV]	$LUMO^{c} [eV]$	E_{g}^{d} [eV]	$\lambda_{max,abs} [nm]$	λ _{max,em} [nm]	$T_1^e [eV]$	$\lambda_{\max,abs} \left[nm \right]$	$\lambda_{\max,em} \left[nm \right]$	$T_1^e [eV]$
1	68/312	6.20	2.52	3.68	293, 312, 324	353, 368	2.99	293, 312, 324	385	3.10
2	33/296	5.44	1.65	3.79	288, 306, 318	344, 361	3.02	290, 308, 320	367	f
3	72/375	6.04	2.53	3.51	292, 311, 323(sh), 337	345, 360	3.02	296, 318, 326, 340	384	2.79

^{*a*} Glass transition temperature (T_g) determined by DSC measurement and decomposition temperature (T_d) obtained from TGA analysis. ^{*b*} Determined using photoelectron yield spectrometry (AC-3). ^{*c*} Estimated from the HOMO and E_g . ^{*d*} Estimated from the absorption onset of thin films. ^{*e*} Estimated from the highest energy peak of the phosphorescence spectra at 77 K. ^{*f*} Not observed.



Fig. 3 UV/Vis absorption and PL spectra of **1–3** in (a) THF solutions and (b) thin films at room temperature (insets: phosphorescence spectra taken at 77 K).

substituents of 1 suppress the intermolecular electronic interactions which reduce the T_1 energy levels.¹³ Because both values in the thin films are higher than that of FIr6 $(T_1 =$ 2.72 eV),⁷ the triplet excitons can thus be effectively confined in FIr6 by using 1 and 3 as the host materials. To verify this notion, the transient PL decay behavior of 10 wt% FIr6-doped thin films of 1 and 3 was examined under excitation at 337 nm at room temperature (see ESI⁺). A single exponential decay curve was observed in both co-deposited films, indicating that the triplet excitons are indeed confined in FIr6. The PL quantum efficiencies of the FIr6:1 and FIr6:3 thin films excited at 337 nm were 87 \pm 1% and 86 \pm 1%, respectively. The FIr6:1 and FIr6:3 thin films exhibited PL quantum efficiencies of 97 \pm 2% when the dopant was directly excited at 360 nm, and thus intrinsically high PL efficiencies could be obtained in these systems.14 It was also found that the HOMO energy level became deeper, in the order of 3 (6.04 eV) \leq FIr6 (6.1 eV) \leq 1 (6.20 eV),⁷ from the results of photoemission spectroscopy studies (see Table 1).

As shown schematically in Fig. 4a, PHOLEDs were fabricated with the following device structure: ITO/TAPC (40 nm)/mCP (10 nm)/10 wt% FIr6:1 (device A) or 3 (device B) (20 nm)/DPEPO (40 nm)/LiF (0.7 nm)/Al (100 nm), where ITO is indium tin oxide, TAPC is 1,1-bis{4-[N,N-di(p-tolyl)amino]phenyl}cyclohexane, mCP is 1,3-bis(carbazol-9-yl)benzene, and DPEPO is bis {2-[di(phenyl)phosphino]-phenyl}ether oxide. TAPC ($T_1 = 2.87$ eV) was used as a hole transport layer, mCP ($T_1 = 3.00$ eV) was used



Fig. 4 (a) Energy-level diagrams of devices A and B (top) and the molecular structures of the materials (bottom) used in the OLEDs. (b) *J*–*V*–*L* characteristics for devices A and B. (c) EQE dependence on current density for devices A and B (inset: EL spectra of the devices).

as an electron transport layer.¹⁵ All these materials have higher T_1 energy levels than that of FIr6 (2.72 eV).⁷ The current densityvoltage-brightness (*J*–*V*–*L*) characteristics and EQE *versus* current density characteristics of the devices are shown in Fig. 4b and c, respectively. Both devices exhibited emission from FIr6 (inset of Fig. 4c).¹⁵ The *Commission Internationale de L'Eclairage* (CIE) coordinates of devices A and B are (0.16, 0.31) and (0.16, 0.29), respectively. These values are outside the deepblue region because the emission peak at 489 nm is enhanced by the microcavity effect.¹⁶ The turn-on voltages (defined as the voltage at L > 1 cd m⁻²) of devices A and B are 4.7 and 4.5 V, respectively (see Fig. 4b). The maximum EQE reaches 19.7 \pm 0.4% in device A, while device B shows a maximum EQE of 14.3 \pm 0.2% (Fig. 4c). This noticeable electroluminescence (EL) efficiency enhancement in device A compared to device B can be explained by the difference in the emission mechanisms governed by the difference between the HOMO energy levels of 1 and 3. There are two primary mechanisms of exciton formation and emission in OLEDs, i.e., host-to-dopant energy transfer and direct charge recombination on the dopant molecules.7 Direct charge recombination will be a more effective way to achieve high efficiency in blue PHOLEDs, because energy losses during the host-dopant energy transfer process can be avoided. In device A, because the HOMO energy level of FIr6 is shallower than that of 1 as the host (Fig. 4a), FIr6 can emit predominantly through direct charge recombination. On the other hand, in device B, FIr6 possibly emits through host-to-dopant energy transfer as a result of the HOMO energy level of FIr6 being deeper than that of 3. The resulting higher turn-on voltage observed in device A supports this explanation.

In conclusion, we have used an effective molecular design strategy for host materials featuring directly linked donoracceptor structures through phosphinic amides. The newly developed host material **1**, having a sufficiently high T_1 energy level, a deep HOMO energy level and morphological stability, is suitable as a host material for PHOLEDs with a deep-blue dopant. The PHOLEDs using FIr6 and **1** have demonstrated high performance levels, with an EQE of approximately 20%.

Acknowledgements

This research was supported by the Japan Society for the Promotion of Science (JSPS) through its "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)". The authors would like to thank Dr Taisuke Matsumoto for technical support in X-ray crystallographic analysis, and also gratefully acknowledge the support of the International Institute for Carbon Neutral Energy Research (WPI-I2CNER), sponsored by the MEXT, Japan.

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