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Molecular design approach of increasing the triplet energy of host materials using pyrrole as a core structure†

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Received 28th August 2015 Accepted 15th November 2015 We developed and synthesized 9,9'-(1-phenyl-1*H*-pyrrole-2,5-diyl)bis(9*H*-carbazole) (PPyCz2) as a hole transport type high triplet energy host material for blue phosphorescent organic light emitting diodes. We approached the molecular design by inserting a pyrrole moiety to prevent extension of conjugation of molecule and achieved a high triplet energy of 2.99 eV in the PPyCz2 host. Furthermore, the PPyCz2 host showed a high external quantum efficiency of 14.8% in blue phosphorescent organic light emitting diodes.

Introduction

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Phosphorescent organic light emitting diodes (OLEDs) have emerged as high performance OLEDs because of their high external quantum efficiency (EQE) in recent years.¹⁻⁶ Phosphorescent emitting materials are key components of the high efficiency phosphorescent OLEDs and they were generally added to the host material, which called a host–guest system.⁷⁻¹⁰ In this system, the host material can prevent the concentration quenching of dopant material, efficiently transfer energy to dopant, and eventually improve device performances. For these reasons, a main focus of OLED research is to develop a host material having high triplet energy to archive high performances in OLEDs.

High triplet energy host materials have been developed for their distinct purpose to prevent back energy transfer from host to dopant for high efficiency in OLEDs. Especially, it is important to apply the high triplet energy host material in blue phosphorescent devices compared to red or green devices because blue phosphorescent dopants have a high triplet energy.

To design the high triplet host materials, it is necessary to use a high triplet energy core structure. There are several hole transport type cores having the high triplet energy such as carbazole¹¹⁻¹⁷ acridine,^{18,19} and dibenzothiophene.²⁰⁻²² Although all of them have high triplet energy, the host materials derived from the cores possessed lower triplet energy than the cores because of extension of conjugation by the substituents of the cores. Therefore, molecular design studies limiting the extension of conjugation have been conducted, which were introduction of tetrahedral geometry based silane,^{23,24} phosphine oxide^{25,26} or sp³ carbon,^{27,28} control of connecting position in aromatic rings,²⁹ and distortion of the backbone structure by steric hindrance.³⁰ These methods could maintain the triplet energy of the core structures, but the tetrahedral geometry weakens the chemical bond between the cores and substituents. Therefore, a molecular design approach to increase the triplet energy of the molecular structure without tetrahedral linkage would be desirable to develop the high triplet energy host materials.

Herein, we approached the design of high triplet energy host material by introducing a pyrrole core between carbazoles and investigated blue phosphorescent OLEDs fabrication using the new hole transport type pyrrole based host material. We demonstrated a high triplet energy of 2.99 eV and EQE of 14.8% in blue phosphorescent OLEDs using a 9,9'-(1-phenyl-1*H*-pyrrole-2,5-diyl)bis(9*H*-carbazole) (PPyCz2) host material without any tetrahedral geometry based linkage.

Experimental

General information

1-Phenylpyrrole, *n*-bromosuccinimide, carbazole, (\pm) -*trans*-1,2diaminocyclohexane, and copper iodide (CuI) were purchased from Sigma Aldrich. Co., and potassium phosphate (K₃PO₄), 1,4-dioxane, and tetrahydro furan (THF) were obtained from Duksan Sci. Co.

Synthesis

2,5-Dibromo-1-phenyl-1*H***-pyrrole**. 1-Phenylpyrrole (0.50 g, 3.49 mmol) was dissolved in THF (20 ml) and the solution was cooled at -78 °C. After 30 min, *n*-bromosuccinimide (1.24 g, 6.98 mmol) was added to the solution and the solution was stirred for 30 min. The color of the solution was turned into green and the

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temperature of the solution was raised up to -10 °C. After stirring for 10 h, the solution was extracted with methylene chloride and distilled water. The methylene chloride was evaporated, and a residual solid was purified by column chromatography with hexane. The product was obtained as a solid (0.95 g, yield 91%). ¹H NMR (400 MHz, DMSO): δ 7.58–7.53 (m, 3H), 7.31–7.27 (m, 2H), 6.44 (s, 2H). MS *m*/*z* 302 [(M + H)⁺].

9,9'-(1-Phenyl-1*H*-pyrrole-2,5-diyl)bis(9*H*-carbazole) (PPyCz2). 2,5-Dibromo-1-phenyl-1*H*-pyrrole (0.80 g, 2.66 mmol), 9*H*-carbazole (1.02 g, 6.11 mmol), K₃PO₄ (2.82 g, 13.29 mmol), and CuI (0.30 g, 1.56 mmol) were dissolved in 1,4-dioxane (30 ml). And (\pm) -trans-1,2-diaminocyclohexane (0.18 g, 1.56 mmol) was added in the solution, and the solution was refluxed overnight. The solution was filtered, extracted with ethyl acetate, and purified by column chromatography. The final product was further purified by sublimation and was obtained as a white powder (0.24 g, 19%). ¹H NMR (400 MHz, DMSO): δ 8.10 (d, 2H, *J* = 7.2 Hz), 7.49–7.42 (m, 8H), 7.24 (t, 4H, *J* = 16 Hz), 6.91 (d, 2H, *J* = 7.2 Hz), 6.78–7.72 (m, 5H). ¹³C NMR (100 MHz, DMSO): δ 142.0, 134.6, 128.4, 128.2, 127.6, 126.4, 125.8, 124.2, 122.4, 120.3, 110.2, 107.5. MS *m/z* 474 [(M + H)⁺].

Device fabrication

Hole and electron only device structures of PPyCz2 were indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, 60 nm)/1,1-bis[(di-4-tolylamino)phenyl] cyclohexane (TAPC, 20 nm)/*N*,*N*'-dicarbazolyl-3,5-benzene (mCP, 10 nm)/PPyCz2 (25 nm)/TAPC (5 nm)/Al (200 nm) and ITO/ PEDOT:PSS (60 nm)/diphenyl-4-triphenylsilylphenyl-phosphine oxide (TSPO1, 10 nm)/PPyCz2 (25 nm)/TSPO1 (5 nm)/1,3,5tris(*N*-phenylbenzimidizol-2-yl)benzene (TPBi, 30 nm)/LiF (1 nm)/Al (200 nm), respectively. ITO/PEDOT:PSS/TAPC/mCP/ PPyCz2:FIrpic (bis[2-(4,6-difluorophenyl)pyridinato-C2,*N*](picolinato)iridium(m))/TSPO1/TPBi/LIF/Al was the blue device configuration.

Measurements

The ultraviolet-visible (UV-vis) spectra were measured by SCINCO S-3100 UV-vis spectrophotometer and photoluminescence (PL) spectra were analyzed by HITACHI F-7000 fluorescence spectrometer. The cyclic voltammetry (CV) data were measured by IVIUM B09054. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded by JEOL JNM-LA400 spectrometer. Fabricated devices were electrically analyzed by Keithley 2400 source measurement unit and light emission performances were measured by CS2000 spectroradiometer.

Results and discussion

The molecular design of the high triplet energy material was carried out using a pyrrole moiety. The feasibility of the pyrrole moiety as the core of the high triplet energy material was estimated by calculated Gaussian data of phenylpyrrole (PPy) and phenylcarbazole (PCz) in Fig. 1. A basic set of B3LYP/G-31G* of Gaussian 09 software was used for the calculation. The calculated triplet energy of PPy was 3.58 eV and was much higher



Fig. 1 The calculated Gaussian data of phenyl pyrrole and phenyl carbazole.

than 3.18 eV of PCz, proposing that the PPy core is appropriate as the core of the high triplet energy material. As can be easily predicted from the chemical structure, the absence of two phenyl units dispersing the aromatic character of carbazole increased the triplet energy of PPy.

The carbazole modified target molecule, PPyCz2, was also compared with carbazole modified carbazole compounds, 9'-phenyl-9'*H*-9,2':7',9"-tercarbazole (27PTCz), and 9'-phenyl-9'*H*-9,3':6',9"-tercarbazole (36PTCz), by molecular calculation



Fig. 2 The calculated Gaussian data of PPyCz2, 27PTCz, and 36PTCz.

summarized in Fig. 2. The calculated triplet energy of PPyCz2 (3.18 eV) was much higher than that of 27PTCz (2.89 eV) and 36PTCz (3.06 eV). The replacement of the PCz core of 27PTCz and 36PTCz with the PPy core increased the triplet energy by more than 0.1 eV by limiting the expansion of the conjugated structure using the PPy core. Although two carbazole moieties were directly attached to the PPy core without any tetrahedral linkage or intentional distortion, calculated triplet energy of PPyCz2 was higher than that of 27PTCz and 36PTCz.

The molecular orbital of PPyCz2 was further studied for deep understanding of the triplet energy calculation results in Fig. 2. Geometrical structure and the highest occupied molecular orbital (HOMO)/the lowest unoccupied molecular orbital (LUMO) distribution in Fig. 3 can give hints about the origin of the high triplet energy of PPvCz2. One main reason is the dihedral angle (79°) between pyrrole and carbazole suppressing the conjugation between the two moieties. The substitution of two carbazole moieties at 2,5-positions of PPy renders the carbazole moieties and phenyl unit of PPy to repel each other because of steric hindrance by hydrogen of carbazole and phenyl unit of PPy. Therefore, the triplet energy of PPyCz2 was increased due to the limitation of conjugation. The little HOMO and LUMO dispersion on the PPy is also an output of the disconnected conjugation. Both the HOMO and LUMO were mostly located on carbazole due to the good electron donating and accepting nature of the carbazole moiety by aromatic character of carbazole. From the molecular calculation results, it can be predicted that the HOMO and LUMO levels of the PPyCz2 would be similar to those of common carbazole compounds. Therefore, the PPyCz2 may have higher triplet energy than common carbazole



Fig. 3 Molecular orbital distribution and dihedral angle of PPyCz2.



Scheme 1 Synthetic scheme of PPyCz2



Fig. 4 UV and PL spectra of PPyCz2.

type host materials while keeping the HOMO and LUMO levels of the carbazole compounds.

Scheme 1 shows synthetic scheme of PPyCz2. The compound was easily synthesized by electrophilic halogenation and Ullmann coupling reaction as the high selectivity of electrophilic bromination in PPy at 2,5-positions caused high yield of 91%. Chemical identification results by NMR and mass analysis are presented in Experimental section.

Material characterization results of PPyCz2 by UV-vis absorption and PL emission are presented in Fig. 4. The π - π * transition of PPyCz2 contributes to UV-vis absorption peaks below 300 nm and n- π * transition of carbazole is involved in the absorption peaks above 300 nm. The calculated edge energy of the UV-vis spectra is 3.51 eV which can be an estimated UVgap of PPyCz2. Triplet energy of PPyCz2 from phosphorescent emission peak by low temperature PL spectra is 2.99 eV, which is higher than that of other carbazole type host materials without any tetrahedral linkage or substituents for steric hindrance. Peak position of the solution PL spectrum in toluene was 364 nm.



Fig. 5 CV measurement data of PPyCz2.



Fig. 6 Hole and electron only device performance of PPyCz2.

CV was used to calculate the ionization potential (IP) and electron affinity (EA) of PPyCz2 through onset point of oxidation and reduction scans (Fig. 5). Oxidation and reduction potentials of PPyCz2 were 1.28 V and -2.42 V through the CV scan. The calculated IP and EA of PPyCz2 were -6.08 eV and -2.38 eV, which were similar to those of common carbazole type host materials. The CV results agree with the HOMO and LUMO calculation results presented in Fig. 3. In the case of thermal properties, differential scanning calorimeter scan of PPyCz2 was carried out, but glass transition temperature was not observed as is presented in ESI.†

Hole and electron only device performances of PPyCz2 are shown in Fig. 6. The hole current density of PPyCz2 was higher than electron current density due to hole transport type characteristic of PPyCz2. As the PPyCz2 host is composed of PPy and carbazole which have hole carrying property, hole current density of PPyCz2 was higher than electron current density.

The blue phosphorescent OLED fabrication was performed using PPyCz2 as a host and FIrpic as a dopant with different doing concentrations of 3%, 5%, and 10%. The device structure can be schematized as shown in Fig. 7. The ITO as electrode, PEDOT:PSS as a hole injection layer (60 nm), TAPC as a hole transport layer (20 nm), FIrpic doped PPyCz2 as an emission layer (30 nm), mCP (10 nm) and TSPO1 (5 nm) as exciton blocking layers, TPBi as an electron transport layer (30 nm), LIF as an electron injection layer (1 nm), and Al as an electrode (200 nm) were used for the blue device configuration. The hole injection might be efficient because of similar HOMO level of



Fig. 7 Blue device structure of PPyCz2 device.



Fig. 8 Current density, voltage, and luminance curves of PPyCz2 devices.



Fig. 9 EQE-luminance data of PPyCz2:Flrpic device.

PPyCz2 and mCP and hole transport type character of PPyCz2. Electron injection might also be efficient as there is an energy barrier of only 0.12 eV for electron injection from TSPO1 to PPyCz2.

Fig. 8 shows current density, voltage, and luminance curves of the PPyCz2 blue devices. At high doping concentration, the current density was increased because of electron hopping behavior by FIrpic dopant as proved in other work. The shallow LUMO levels of PPyCz2 induced electron trapping by the FIrpic dopant, and the electron transport is assisted by electron hopping phenomenon at high FIrpic concentration, resulting in high current density at high doping concentration.

The current density data can be correlated with EQEluminance data in Fig. 9. The maximum EQE of the PPyCz2 devices was 13.9, 14.8, and 12.9% at 3%, 5% and 10% doping concentrations, respectively. The high doping of FIrpic caused concentration quenching of dopant and decreased the EQE at 10% doping. The moderate 5% doping was better than 10% doping in terms of concentration quenching effect and was better than 3% doping in terms of charge balance by better electron transport. In particular, the high triplet energy of PPyCz2 (2.99 eV) could be matched with that of FIrpic (2.65 eV) for energy transfer and contributed to the EQE. However, relatively low EQE compared to other EQE of FIrpic devices was caused by low quantum yield of FIrpic doped PPyCz2. The measured PL quantum yields of the FIrpic doped PPyCz2 films were 0.21, 0.27 and 0.19 at 3%, 5% and 10% doping

Doping concentration	EQE^{a} (%)		$\operatorname{CE}^{b}(\operatorname{cd} \operatorname{A}^{-1})$		PE^{c} (lm W ⁻¹)		
	[1000 cd]	Max	[1000 cd]	Max	[1000 cd]	Max	Color coordinate
3%	8.9	13.9	16.3	25.1	5.1	16.4	(0.15, 0.28)
5%	11.1	14.8	20.8	27.6	7.2	17.0	(0.15, 0.29)
10%	10.6	12.9	20.5	24.8	7.0	17.1	(0.15, 0.31)

^a EQE, external quantum efficiency. ^b CE, current efficiency. ^c PE, power efficiency.



Fig. 10 Electroluminescence spectrum of PPyCz2.

concentrations, respectively, which can explain the doping concentration dependency of EQE. The current efficiency and power efficiency data of the PPyCz2 devices were presented in ESI.† The current efficiency and power efficiency data were also optimized at 5% doping concentration. Detailed device performance data are summarized in Table 1.

Electroluminescence (EL) spectra of blue devices are presented in Fig. 10. The color coordinates of PPyCz2 devices were (0.15, 0.28), (0.15, 0.29), and (0.15, 0.31) at 3, 5, and 10% doping concentrations, respectively. Furthermore, the energy transfer from host to dopant might be efficient because other peaks are not observed in EL spectra.

Conclusions

A PPy based high triplet host material, PPyCz2, was designed and synthesized using high triplet energy pyrrole core and carbazole substituents. The high triplet energy of the PPy core and distortion of the carbazole unit in PPyCz2 allowed high triplet energy of 2.99 eV and high external quantum efficiency of 14.8% in blue phosphorescent OLEDs. Therefore, proper modification of the pyrrole core can increase triplet energy of the host material for blue phosphorescent OLEDs.

References

- 1 C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.*, 2001, **90**, 5048.
- 2 C.-H. Chen, L.-C. Hsu, P. Rajamalli, Y.-W. Chang, F.-I. Wu, C.-Y. Liao, M.-J. Chiu, P.-Y. Chou, M.-J. Huang, L.-K. Chu and C.-H. Cheng, *J. Mater. Chem. C*, 2014, 2, 6183.

- 3 S.-Y. Kim, W.-I. Jeong, C. Mayr, Y.-S. Park, K.-H. Kim, J.-H. Lee, C.-K. Moon, W. Brütting and J.-J. Kim, *Adv. Funct. Mater.*, 2013, 23, 3896.
- 4 S. O. Jeon, S. E. Jang, H. S. Son and J. Y. Lee, *Adv. Mater.*, 2011, 23, 1436.
- 5 C. W. Lee and J. Y. Lee, Adv. Mater., 2013, 25, 5450.
- 6 M. Kim and J. Y. Lee, Adv. Funct. Mater., 2014, 24, 4164.
- 7 R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li and M. E. Thompson, *Appl. Phys. Lett.*, 2003, 83, 3818.
- 8 Y. Divayana and X. W. Sun, Phys. Rev. Lett., 2007, 99, 143003.
- 9 W. S. Jeon, T. J. Park, S. Y. Kim, R. Pode, J. Jang and J. H. Kwon, *Org. Electron.*, 2009, **10**, 240.
- S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, 459, 234.
- 11 S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki and F. Sato, *Appl. Phys. Lett.*, 2003, **83**, 569.
- 12 D. R. Whang, Y. You, S. H. Kim, W.-I. Jeong, Y.-S. Park, J.-J. Kim and S. Y. Park, *Appl. Phys. Lett.*, 2007, **91**, 233501.
- M. H. Tsai, H. W. Lin, H. C. Su, T. H. Ke, C. C. Wu, F. C. Fang,
 Y. L. Liao, K. T. Wong and C. I. Wu, *Adv. Mater.*, 2006, 18, 1216.
- M. H. Tsai, Y. H. Hong, C. H. Chang, H. C. Su, C. C. Wu,
 A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius,
 J. V. Grazulevicius and C. P. Hsu, *Adv. Mater.*, 2007, 19, 862.
- 15 Y. Tao, J. Xiao, C. Zheng, Z. Zhang, M. Yan, R. Chen, X. Zhou, H. Li, Z. An, Z. Wang, H. Xu and W. Huang, *Angew. Chem.*, *Int. Ed.*, 2013, 52, 10491.
- 16 C. Han, Z. Zhang, H. Xu, J. Li, G. Xie, R. Chen, Y. Zhao and W. Huang, *Angew. Chem., Int. Ed.*, 2012, **51**, 10104.
- 17 D. Yu, F. Zhao, C. Han, H. Xu, J. Li, Z. Zhang, Z. Deng, D. Ma and P. Yan, *Adv. Mater.*, 2012, **24**, 509.
- 18 M. S. Park and J. Y. Lee, Chem. Mater., 2011, 23, 4338.
- M. Romain, D. Tondelier, B. Geffroy, A. Shirinskaya,
 O. Jeannin, J. Rault-Berthelot and C. Poriel, *Chem. Commun.*, 2015, 51, 1313.
- 20 S. H. Jeong and J. Y. Lee, J. Mater. Chem., 2011, 21, 14604.
- 21 W.-C. Lin, W.-C. Huang, M.-H. Huang, C.-C. Fan, H.-W. Lin, L.-Y. Chen, Y.-W. Liu, J.-S. Lin, T.-C. Chao and M.-R. Tseng, *J. Mater. Chem. C*, 2013, 1, 6835.
- 22 C. Han, Z. Zhang, H. Xu, S. Yue, J. Li, P. Yan, Z. Deng, Y. Zhao, P. Yan and S. Liu, *J. Am. Chem. Soc.*, 2012, 134, 19179.
- 23 J. J. Lin, W. S. Liao, H. J. Huang, F. I. Wu and C. H. Cheng, *Adv. Funct. Mater.*, 2008, 18, 485.

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- 24 S. L. Gong, Y. H. Chen, J. J. Luo, C. L. Yang, C. Zhong, J. G. Qin and D. G. Ma, *Adv. Funct. Mater.*, 2011, **21**, 1168.
- 25 J. Q. Ding, Q. Wang, L. Zhao, D. G. Ma, L. X. Wang, X. B. Jing and F. S. Wang, *J. Mater. Chem.*, 2010, **20**, 8126.
- 26 H. H. Chou and C. H. Cheng, Adv. Mater., 2010, 22, 2468.
- 27 S. H. Ye, Y. Q. Liu, K. Lu, W. P. Wu, C. Y. Du, Y. Liu, H. T. Liu,
- T. Wu and G. Yu, Adv. Funct. Mater., 2010, 20, 3125.
- 28 S. C. Dong, Y. Liu, Q. Li, L. S. Cui, H. Chen, Z. Q. Jiang and L. S. Liao, *J. Mater. Chem. C*, 2013, **1**, 6575.
- 29 Y. Suzuri, T. Oshiyama, H. Ito, K. Hiyama and H. Kita, *Sci. Technol. Adv. Mater.*, 2014, **15**, 054202.
- 30 M. Kim, S. K. Jeon, S.-H. Hwang and J. Y. Lee, *Phys. Chem. Chem. Phys.*, 2015, **17**, 13553.