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Spiro-fused *N*-phenylcarbazole-based host materials for blue phosphorescent organic light-emitting diodes



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ABSTRACT

Two host materials, SFCA and SFCC, consist of a diphenylamine or carbazole unit linking to spiro-fused phenyl carbazole (SFC) backbone, were designed and synthesized. By choosing the meta linkage way between diphenylamine/carbazole units and SFC ring, higher triplet energies could be easily achieved for the two new materials, which mean that they could be used as effective host material for popular blue phosphorescent material Iridium(III) bis[(4,6-difluorophenyl)pyridinato-N,C²] picolinate (FIrpic, E_T = 2.65). Besides that, the steric SFC structure could guarantee their good thermal stabilities. Their thermal, photophysical and electroluminescent properties were systematically investigated. The blue phosphorescent OLEDs with the two materials as hosts and FIrpic as a dopant exhibited excellent performance with maximum current efficiencies of 33.9 and 40.8 cd/A, respectively.

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1. Introduction

During the last decade, much progress has been made in the field of phosphorescent organic light-emitting diodes (PHOLEDs), because they can effectively harvest electrogenerated singlet and triplet excitons to achieve nearly 100% internal quantum efficiency, which is significantly higher than the 25% upper limit of fluorescence caused by exciton statistics [1–3]. To realize highly efficient PHO-LEDs, a suitable host material is usually employed to disperse the phosphors in emitting layer, and in this way, exciton's triplet-triplet annihilation (TTA) and triplet polaron quenching (TPQ) could thus be suppressed at a low concentration [4,5]. The first principle of designing a

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http://dx.doi.org/10.1016/j.orgel.2015.02.014 1566-1199/© 2015 Published by Elsevier B.V. suitable host material is that the host material should have higher triplet energy level than that of the phosphorescent dopant [6,7]. Besides that, other requirements such as matched frontier molecular level, good carrier mobility and high thermal/morphological stability are also need to meet in molecular design [8–15].

In this regard, the heteroaromatic compounds are considered to be eligible for host materials although there are still several examples for pure hydrocarbon molecules acting as hosts [16–21]. Among these heteroaromatic systems, carbazole-based materials are of particular interest [22–29], because their derivatives can be readily tailored to fulfill the requirements for designing a good host. For example, the first reported host CBP (4,4'-bis(*N*-carbazolyl)-2,2'-biphenyl) molecule is a dimer of *N*-phenylcarbazole moieties. This molecule has concise structure but it always questioned for its detrimental drawbacks in thermal/morphological stabilities. A fused *N*-phenylcar-





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bazole ring is a good alternative to solve this defect, for example, Yang et al. developed a new host material BCBP, which remarkably enhanced glass transition temperature (173 °C) as compared to a low T_g of 62 °C for CBP [30]. However, this design also inherited the low triplet energy (E_T = 2.56 eV) of CBP, which severely limits its application in the most important blue PHOLEDs. Thus, it can be envisaged that if we maintain the fused *N*-phenylcarbazole ring and change the linking ways to reduce the molecular conjugation degree, we can obtain the host materials with high thermal stability and high E_T simultaneously [31–34].

In this paper, two spiro-fused phenyl carbazole type host materials were developed with high triplet energies, which are benefited from the 3D spiro-structure and confined molecular conjugation. Meanwhile, good thermal/morphological stabilities and their physical properties were also investigated. The blue device performances with these materials are 33.9 and 40.8 cd/A for maximum current efficiencies, which are among the highest results in fused *N*-phenylcarbazole systems.

2. Results and discussions

Scheme 1 illustrates the synthetic routes and chemical structures of the two hosts. The fused *N*-phenylcarbazole ring was designed as a core structure, which could be

synthesized by a Friedel–Crafts intramolecular ring-closure in the presence of acid. The final host materials were afforded via a Bulchwald–Hartwig C–N coupling reaction with corresponding arylamine in good yields. The key intermediate 3-BrSFC and final compounds were characterized by ¹H NMR and ¹³C NMR spectroscopies, mass spectrometry and elemental analysis. Furthermore, both of the materials were further purified by vacuum sublimation before device fabrication.

The thermal properties of the compounds were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements in a nitrogen atmosphere at a scanning rate of 10 °C/min (see Table 1). These hosts with fused N-phenylcarbazole ring exhibit high thermal stabilities with decomposition temperatures (T_d , corresponding to 5% weight loss, see Fig. 1) of 361 °C for SFCA and 431 °C for SFCC in thermogravimetric analysis. Their glass transition temperatures (T_{g} , see Fig. 2) were observed at 136 °C for SFCA and 173 °C for SFCC, through differential scanning calorimetry (DSC), which means that the changed the diphenylamine to carbazole unit had much effect on thermal stability. The high T_d and T_g values of the compounds may be mainly ascribed to the spiro-phenylcarbazole structure, and could improve the film morphology and reduce the possibility of phase separation upon heating. Because of the rotation of the



Scheme 1. Synthetic route and chemical structures of the host materials.

Table 1	
Photophysical, electrochemical and thermal properties of	SFCA and SFCC.

	$\lambda_{\max,abs}^{a}(nm)$	$\lambda_{\max,f}^{a}(nm)$	$\lambda_{ph}^{b}(nm)$	$E_T(eV)$	$T_m^{c}(^{\circ}C)$	$T_g^{c}(^{\circ}C)$	T_d^{c} (°C)	HOMO ^d (eV)	LUMO ^d (eV)	E_g^{e} (eV)
SFCA	273, 295, 354	410	456, 487	2.72	263	136	361	-5.70	-2.35	3.35
SFCC	278, 325, 339	372	436, 466	2.84	290	173	431	-5.92	-2.36	3.53

^a Measured in dichloromethane solution at room temperature.

^b Measured in 2-MeTHF glass matrix at 77 K.

^c T_m : melting temperatures, T_g : glass transition temperatures, T_d : decomposition temperatures.

^d HOMO and LUMO were calculated from UPS and the optical band gap from the absorption spectra. respectively.

^e *E*_g: The band gap energies were estimated from the optical absorption edges of UV–Vis absorption spectra.



Fig. 1. TGA thermograms recorded at a heating rate of 10 °C/min.



Fig. 2. DSC traces recorded at a heating rate of 10 °C/min.

phenyl group is limited by the additional bond between the phenyl and carbazole groups, the fused carbazole is more rigid than phenyl carbazole, both of SFCA and SFCC exhibit higher temperature stability than that of our previous reported SAFDPA and SAFCz [32].

Fig. 3 shows absorption and emission spectra of SFCA and SFCC in CH₂Cl₂ solution at room temperature, as well as the phosphorescent (Phos) spectra measured in 2-methyltetrahydrofuran matrix at 77 K. The detailed photo-physical data are summarized in Table 1. The maximum absorption of the two materials differs only by 2 nm. The two absorption bands: one at 273 nm for SFCA and the other at 278 nm for SFCC correspond to the π - π * transition of their conjugated backbones, the energy gaps are estimated from the onset of optical absorption of solution state to be 3.35 eV and 3.53 eV for SFCA and SFCC, respectively. The PL emission peaks of the two compounds are observed at 410 and 372 nm. The PL spectra are strongly red-shifted in the SFCA, because of the aromatic amine unit. Besides, the triplet energies of SFCA and SFCC are determined as 2.72 and 2.84 eV, respectively, which calculated from the highest-energy peaks of the phosphorescence spectra at 77 K.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the



Fig. 3. UV–Vis absorption and PL spectra measured in dichloromethane solution at 10^{-5} M; phosphorescence spectra measured in a frozen 2-methyltetrahydrofuran matrix at 77 K.

SFC-based hosts are probed by UPS (Fig. 4) and UV–Vis absorption. The HOMO levels of SFCA and SFCC are -5.70 and -5.92 eV, respectively. The HOMO level of the SFCA was shifted upward by 0.22 eV, compared to that of the SFCC. As the molecular orbital distribution shows (Fig. 5), they have similar LUMO distributions which are mainly localized at the fluorene moiety. It also explains well why both compounds have nearly the same LUMO levels (-2.35 eV for SFCA and -2.36 eV for SFCC). SFCA's HOMO is localized on the appended aromatic amine. But in SFCC, there are two "carbazole" subunits which form a near-degenerate HOMO. All of the aforementioned characterization data are summarized in Table 1.

The HOMO levels of SFCA and SFCC are significant deeper than those of SAFDPA and SAFCz, these differences are consistent with our previous work [10]. We may forget how surprising it should be that the more planar moiety through the rigid linkage has a much lower HOMO level. To look close at these arylamine blocks and understand how the rigid structure affects the frontier orbitals, we introduce another block, *N*-phenylcarbazole for comparison. As shown in Fig. 6, block B has two factors for rigid



Fig. 4. UPS spectra of SFCA and SFCC.



Fig. 5. HOMO and LUMO distributions of SFCA and SFCC.

planarity while block A and block C have only one factor. The same aspect of A and C is both blocks have a nearly perpendicular phenyl ring attached to the nitrogen atom. It is widely accepted that more planar conjugation help to stabilize molecular frontier orbital. In this case, the change from block C to block B obeys this rule, and hyperconjugation effect from the sp³ hybridized carbon also contributes to increasing the HOMO level. The change from block A to block B. however, provides a lower HOMO level. Although the HOMO of block A was distributed to entirely core, the newly formed biphenyl moiety could pull down the HOMO level. That is because the LUMO of biphenyl ring is significantly lower than that of separated phenyl ring, which could reduce the electron density of central nitrogen. The deeper HOMO of block B can account for the blue shifted fluorescence spectrum of SFCC (see Fig. 3), in which the emission from CT state cannot easily formed.

Since the SFCA and SFCC had high triplet energy for blue phosphorescent emitters, exhibited suitable HOMO/LUMO



Fig. 7. (a) Current density–voltage–luminance characteristics, (b) current efficiency and power efficiency versus current density curves of device SFCA and SFCC.

levels for charge injection, it can be used as host materials in blue phosphorescent devices to evaluate their performances. Blue PHOLEDs based on commonly used FIrpic were fabricated. The devices with configuration as follows



Fig. 6. HOMO distributions and calculated values of A, B and C.

Table 2

Electroluminescence characteristics of the devices.

Device	$V_{\rm on}^{\rm a}$ (V)	$\eta_{\rm c.max}^{\rm b}$ (cd/A)	$\eta_{p,max}^{c}$ (lm/W)	$\eta_{\text{ext.max}}^{\text{d}}$ (%)	CIE $(x, y)^{e}$
SFCA	3.30	33.9	32.2	15.3	0.164, 0.367
SFCC	3.95	40.8	32.5	19.0	0.153, 0.356

^a Turn-on voltages.

^b Maximum current efficiency.

^c Maximum power efficiency.

^d Maximum external quantum efficiency.

^e Commission International de l'Eclairage coordinates measured at 5 mA/cm².



Fig. 8. EQE versus current density of device SFCA and SFCC.



Fig. 9. The corresponding normalized EL spectra of device SFCA and SFCC.

were fabricated, device configuration: ITO/HAT-CN (10 nm)/TAPC (45 nm)/HOST: FIrpic (15 wt%, 20 nm)/ TmPyPB (40 nm)/Liq (2 nm)/Al (100 nm). HAT-CN was used as hole-injection material. TAPC, which has a high E_T and carrier mobility serve as hole transporting layer and electron blocking layer (EBL). TmPyPB and Liq were used to form electron transport layer (ETL) and electron injection layer (EIL). Host for device A1 and device A2 are SFCA and SFCC, respectively. Fig. 7(a) shows the current density as a function of voltage. Fig. 7(b) depicts the current efficiency and power efficiency of the device SFCA and SFCC and Fig. 9 shows the corresponding electroluminescence spectrum. The detailed electroluminescence data are summarized in Table 2. As compared to device SFCC, the device SFCA exhibited lower driving voltage at the same current density. Between the two host devices, device SFCC exhibits a superior performance with maximum current efficiency of 40.8 cd/A and a maximum power efficiency of 32.5 lm/W whilst the device SFCA shows maximum current efficiency of 33.9 cd/A and a maximum power efficiency of 32.2 lm/W. Fig. 8 shows the EQE as a function of current density. The maximum EQE of the device SFCA and SFCC are 15.3% and 19.0%, respectively.

3. Conclusions

In conclusion, two thermally stable high-triplet-energy hosts, based on spiro-fused phenyl carbazole (SFC) core, were synthesized and their morphological stabilities, HOMO/LUMO energy levels have been investigated. The design enhanced the current efficiency of the blue phosphorescent organic light-emitting diodes (PHOLEDs) hosting with FIrpic to 33.9 and 40.8 cd/A, and maximum EQEs are as high as 15.3% and 19.0% for SFCA and SFCC, respectively. These values are among the highest levels in fused *N*-phenylcarbazole systems host material to date, and the building block of fused *N*-phenylcarbazole is a great candidate for the future development of highly promising blue PHOLEDs.

4. Experimental section

4.1. General information

Nuclear magnetic resonance (¹H NMR and ¹³C NMR) spectra were measured on a Bruker-400 spectrometer. Elemental analyses were performed on a Vario EL III microanalyzer. Mass spectra were measured on a Thermo ISQ mass spectrometer using direct exposure probe. Ultraviolet-visible light (UV-Vis) spectra and photoluminescence (PL) spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed using a TA DSC 2010 unit under nitrogen at a heating rate of 10 °C/min from room temperature to 400 °C. 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 from room temperature to 700 °C under nitrogen. Temperature at 5% weight loss was used as decomposition temperature (T_d) .

Ultra-violet photo-emission spectroscopy (UPS) was made by Kratos Analytical A Shimadzu Group Company, consisting of a multiport carousel chamber (base pressure $<5 \times 10^{-10}$ Torr), and an analysis chamber ($<3 \times 10^{-10}$ Torr). Density function theory (DFT) performed using the TD-DFT/B3LYP/6-31G(d) method with Gaussian 09 package.

4.2. OLED fabrication and measurement

1,4,5,8,9,11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN), 1,1-bis[4-[N', N'-di(p-tolyl)amino]phenyl]cyclohexane (TAPC), 1,3,5-tri[(3-pyridyl)phen-3-yl]benzene (TmPyPB), 8-hydroxyquinolinolato-lithium (Liq), bis[3,5-difluoro-2-(2-pyridyl)phenyl]-(2-carboxypyridyl)iridium(III) (FIrpic) were used in the experiments and they were commercially available. The OLED was fabricated by thermal vacuum deposition on preprocessed ITO-coated glass substrates. The substrate was ultrasonically-sequentially cleaned with acetone, ethanol, and deionized water, then dried in an oven, and finally exposed to UV-ozone for about 30 min. HAT-CN was firstly deposited to the ITO substrate, followed by TAPC, emissive layer, and TmPyPB. Finally, a cathode composed of Lig and Al was sequentially deposited onto the substrate through a shadow mask in the vacuum of $2\times 10^{-6}\,\text{Torr.}$ The current density–voltage–luminance (J-V-L) characteristics of the OLEDs were measured by a KEITHLEY 2400 SourceMeter constant current source. The EL spectra and CIE coordinates of the devices were measured with a PHOTO RESEARCH SpectraScan PR 655 photometer at room temperature. The EQE values were values were calculated according to the previously reported methods [35].

4.3. Synthesis of materials

9-(2-Bromophenyl)-9H-carbazole (1) and 3-bromofluorenone (2) were synthesized according to literatures [36]. Other chemicals (from commercial source) were used without further purification. THF was purified by PURE SOLV (Innovative Technology) purification system.

4.3.1. 3-Bromospiro[fluorene-9,8'-indolo[3,2,1-de]acridine] (3-BrSFC)

9-(2-Bromophenyl)-9H-carbazole (1.93 g, 6 mmol) was dissolved in 80 mL THF in a 200 mL Schlenk tube under argon. After the solution was cooled to -78 °C, *n*-butyl lithium (2.63 mL, 6.3 mmol) was added dropwise. The resulting mixture was allowed to stir for 1 h at -78 °C, and then 3-bromofluorenone (1.56 g, 6 mmol) in 50 mL THF was added. After 1 h reaction at -78 °C, the mixture was gradually warmed up to room temperature overnight. 5 mL water was added to the mixture and THF was evaporated under reduced pressure. The resulting solid was dissolved in 80 mL dichloromethane and washed with water (3 × 50 mL). Then the organic layer was separated, dried over Na₂SO₄, filtered and evaporated. The resulting solid was further purified by column chromatography using petroleum ether/dichloromethane (3.5/1, v/v) as elu-

ent to afford 9-(2-(9H-carbazol-9-yl)phenyl)-3-bromo-9H-fluoren-9-ol (2.41 g, 80.2%).

A mixture of 9-(2-(9H-carbazol-9-yl)phenyl)-3-bromo-9H-fluoren-9-ol (1.80 g, 3.58 mmol), acetic acid (40 mL) and hydrochloric acid (4.5 mL) was stirred at 65 °C for 14 h. After cooling to room temperature, filtered and washed with ethanol. The resulting solid was further purified by column chromatography using petroleum ether/ dichloromethane (3/1, v/v) as eluent to afford a white powder (1.63 g, 93.6%). ¹H NMR (CDCl₃, 400 MHz) (δ, ppm): 8.31 (d, J = 8.4 Hz, 1H, Ar-H), 8.26 (d, J = 8.0 Hz, 1H, Ar-H), 8.22 (d, J = 8.0 Hz, 1H, Ar-H), 7.99 (d, J = 2.0 Hz, 1H, Ar-H), 7.91 (d, J = 8.0 Hz, 1H, Ar-H), 7.82 (d, J = 8.0 Hz, 1H, Ar-H), 7.67 (t, J = 8.0 Hz, 1H, Ar-H), 7.46–7.36 (m, 3H, Ar-H), 7.33-7.30 (m, 1H, Ar-H), 7.26-7.17 (m, 2H, Ar-H), 7.11 (t, J = 7.6 Hz, 1H, Ar-H), 7.03 (t, J = 8.0 Hz, 1H, Ar-H), 6.88 (t, *I* = 8.0 Hz, 1H, Ar-H), 6.62 (d, *I* = 8.0 Hz, 1H, Ar-H), 6.53 (d, I = 7.6 Hz, 1H, Ar-H). ¹³C NMR (CDCl₃, 100 MHz) (δ , ppm): 155.59 154.19, 141.68, 138.50, 138.26, 137.02, 136.68, 131.14, 129.20, 129.20, 128.59, 128.10, 128.06, 127.17, 126.71, 126.33, 125.84, 123.73, 123.39, 123.23, 123.10, 122.67, 121.96, 121.27, 121.14, 120.27, 118.27, 114.46, 113.71, 56.63. HRMS (EI): *m*/*z* calcd for: 483.0623, found: 483.0619. Anal. Calcd for C₃₁H₁₈BrN (%): C 76.87 H 3.75, N 2.89; found: C 76.75, H 3.82, N 2.80.

4.3.2. N,N-diphenylspiro[fluorene-9,8'-indolo[3,2,1de]acridine]-3-amine (SFCA)

3-BrSFC (1.22 g, 2.5 mmol), diphenylamine (0.51 g, 3 mmol), palladium acetate (0.011 g, 0.05 mmol), tri-tbutylphosphonium tetrafluoroborate (0.044 g, 0.15 mmol), sodium t-butoxide (0.60 g, 6.25 mmol) were dissolved in toluene under argon. After refluxed for 10 h under stirring, the reaction was cooled to room temperature and 50 mL water was added. The organic layer was separated and the aqueous layer was extracted with 15 mL toluene twice. Then the extracts were combined, dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/dichloromethane (2/1, v/v) as eluent to afford final product. The final product was a white crystalline powder (1.39 g, 97.2%). ¹H NMR (CDCl₃, 400 MHz) (δ, ppm) : 8.25 (d, I = 8.4 Hz, 1H, Ar-H), 8.20 (d, I = 7.6 Hz, 1H, Ar-H), 8.16 (d, J = 7.6 Hz, 1H, Ar-H), 7.87 (m, 1H, Ar-H), 7.64–7.58 (m, 2H, Ar-H), 7.52 (d, J = 2.0 Hz, 1H, Ar-H), 7.40-7.22 (m, 7H, Ar-H), 7.15-7.09 (m, 7H, Ar-H), 7.03-6.97 (m, 3H, Ar-H), 6.90-6.85 (m, 2H, Ar-H), 6.71 (dd, J = 7.6 Hz, 1H, Ar-H), 6.61 (t, J = 7.6 Hz, 1H, Ar-H). ¹³C NMR (CDCl₃, 100 MHz) (δ, ppm): 155.81, 149.69, 147.81, 147.67, 140.67, 139.29, 138.51, 137.01, 136.78, 129.51, 129.26, 128.41, 127.81, 127.69, 126.58, 126.41, 126.09, 125.62, 124.71, 124.27, 124.31, 123.31, 123.17, 122.79 122.60, 122.49, 121.18, 121.02, 120.09, 118.01, 115.21, 114.29, 113.67, 56.41. HRMS (EI): *m*/*z* calcd for: 572.2252, found: 572.2250. Anal. Calcd for C₄₃H₂₈N₂ (%): C 90.18 H 4.93, N 4.89; found: C 90.27, H 4.97, N 4.84.

4.3.3. 3-(9H-carbazol-9-yl)spiro[fluorene-9,8'-indolo[3,2,1de]acridine] (SFCC)

3-BrSFC (1.21 g, 2.5 mmol), carbazole (0.63 g, 3.8 mmol), Pd₂(dba)₃ (0.046 g, 0.05 mmol), *tri-t*-butylphos-

phonium tetrafluoroborate (0.015 g, 0.05 mmol), sodium t-butoxide (0.60 g, 6.25 mmol) were dissolved in toluene under argon. After refluxed for 10 h under stirring, the reaction was cooled to room temperature and 50 mL water was added. The organic layer was separated and the aqueous layer was extracted with 15 mL toluene twice. Then the extracts were combined, dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/dichloromethane (2/1, v/v) as eluent to afford final product. The final product was a white crystalline powder (1.35, 94.4%). ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 8.27-8.32 (m, 2H, Ar-H), 8.20-8.22 (m, 1H, Ar-H), 8.15 (d, J = 7.6 Hz, 2H, Ar-H), 7.99 (t, J = 1.2 Hz, 1H, Ar-H), 7.93 (dd, J = 8.0 Hz, 1H, Ar-H), 7.80 (d, J = 7.6 Hz, 1H, Ar-H), 7.80 (d, J = 7.6 Hz, 1H, Ar-H), 7.62–7.67 (m, 1H, Ar-H), 7.48-7.50 (m, 2H, Ar-H), 7.37-7.41 (m, 5H, Ar-H), 7.24-7.33 (m, 6H, Ar-H), 7.15 (t, J = 7.6 Hz, 1H, Ar-H), 6.92-6.96 (m, 1H, Ar-H), 6.76 (dd, J = 8.0 Hz, 1H, Ar-H), 6.66 (dd, I = 7.6, 1H, Ar-H). ¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 155.50, 154.35, 141.10, 140.93, 139.02, 138.55, 137.46, 137.12, 136.85, 129.27, 129.08, 128.93, 128.14, 128.10, 127.04, 126.72, 126.40, 126.01, 125.93, 124.10, 123.46, 123.35, 123.20, 122.73, 121.31, 120.32, 119.95, 118.61, 118.33, 114.49, 113.78, 109.92, 56.89. HRMS (EI): m/z calcd for: 570.2096, found: 570.2099. Anal. Calcd for C₄₃H₂₆N₂ (%): C 90.50 H 4.59, N 4.91; found: C 90.42, H 4.62, N 4.84.

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References

- M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.
- [2] C.W. Lee, J.Y. Lee, Adv. Mater. 25 (2013) 5450.
- [3] H. Shin, S. Lee, K.-H. Kim, C.-K. Moon, S.-J. Yoo, J.-H. Lee, J.-J. Kim, Adv. Mater. 26 (2014) 4730.

- [4] N.C. Giebink, B.W. D'Andrade, M.S. Weaver, P.B. Mackenzie, J.J. Brown, M.E. Thompson, S.R. Forrest, J. Appl. Phys. 103 (2008) 044509.
- [5] Y. Tao, C. Yang, J. Qin, Chem. Soc. Rev. 40 (2011) 2943.
- [6] L.-S. Cui, S.-C. Dong, Y. Liu, Q. Li, Z.-Q. Jiang, L.-S. Liao, J. Mater. Chem. C 1 (2013) 3967.
- [7] A. Chaskar, H.F. Chen, K.T. Wong, Adv. Mater. 23 (2011) 3876.
- [8] C. Han, Z. Zhang, H. Xu, J. Li, G. Xie, R. Chen, Y. Zhao, W. Huang, Angew. Chem. Int. Ed. 51 (2012) 10104.
- [9] D. Yu, Y. Zhao, H. Xu, C. Han, D. Ma, Z. Deng, S. Gao, P. Yan, Chem. Eur. J. 17 (2011) 2592.
- [10] S.-C. Dong, Y. Liu, Q. Li, L.S. Cui, H. Chen, Z.-Q. Jiang, L.-S. Liao, J. Mater. Chem. C 1 (2013) 6575.
- [11] J. Jin, W. Zhang, B. Wang, G. Mu, P. Xu, L. Wang, H. Huang, J. Chen, D. Ma, Chem. Mater. 26 (2014) 2388.
- [12] K. Brunner, A. van Dijken, H. Börner, J.J.A.M. Bastiaansen, N.M.M. Kiggen, B.M.W. Langeveld, J. Am. Chem. Soc. 126 (2004) 6035.
- [13] J. Li, T. Zhang, Y. Liang, R. Yang, Adv. Funct. Mater. 23 (2012) 619.
- [14] M.-H. Tsai, Y.-H. Hong, C.-H. Chang, H.-C. Su, C.-C. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J.V. Grazulevicius, C.-P. Hsu, Adv. Mater. 19 (2007) 862.
- [15] J. He, H. Liu, Y. Dai, X. Ou, J. Wang, S. Tao, X. Zhang, P. Wang, D. Ma, J. Phys. Chem. C 113 (2009) 6761.
- [16] Z. Jiang, H. Yao, Z. Żhang, C. Yang, Z. Liu, Y. Tao, J. Qin, D. Ma, Org. Lett. 11 (2009) 2607.
- [17] C. Fan, Y. Chen, P. Gan, C. Yang, C. Zhong, J. Qin, D. Ma, Org. Lett. 12 (2010) 5649.
- [18] L.-C. Chi, W.-Y. Hung, H.-C. Chiuband, K.-T. Wong, Chem. Commun. 45 (2009) 3892.
- [19] K.-T. Wong, Y.-L. Liao, Y.-T. Lin, H.-C. Su, C.-C. Wu, Org. Lett. 7 (2005) 5131.
- [20] M. Romain, S. Thiery, A. Shirinskaya, C. Declairieux, D. Tondelier, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel, Angew. Chem. Int. Ed. 54 (2015) 1176–1180.
- [21] S. Thiery, D. Tondelier, C. Declairieux, G. Seo, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel, J. Mater. Chem. C 2 (2014) 4156.
- [22] H.S. Son, J.Y. Lee, Org. Electron. 12 (2011) 1025.
- [23] S.J. Kim, Y.J. Kim, Y.H. Son, J.A. Hur, H.A. Um, J. Shin, T.W. Lee, M.J. Cho, J.K. Kim, S. Joo, J.H. Yang, G.S. Chae, K. Choi, J.H. Kwon, D.H. Choi, Chem. Commun. 49 (2013) 6788.
- [24] X.-D. Yuan, J. Liang, Y.-C. He, Q. Li, C. Zhong, Z.-Q. Jiang, L.-S. Liao, J. Mater. Chem. C 2 (2014) 6387.
- [25] S.-J. Su, C. Cai, J. Kido, Chem. Mater. 23 (2011) 274.
- [26] H. Sasabe, H. Nakanishi, Y. Watanabe, S. Yano, M. Hirasawa, Y.-J. Pu, J. Kido, Adv. Funct. Mater. 23 (2013) 5550.
- [27] D. Yu, F. Zhao, C. Han, H. Xu, J. Li, Z. Zhang, Z. Deng, D. Ma, P. Yan, Adv. Mater. 24 (2012) 509.
- [28] C.-J. Zheng, J. Ye, M.-F. Lo, M.-K. Fung, X.-M. Ou, X.-H. Zhang, C.-S. Lee, Chem. Mater. 24 (2012) 643.
- [29] D. Kim, V. Coropceanu, J.-L. Brédas, J. Am. Chem. Soc. 133 (2011) 17895.
- [30] Z. Jiang, X. Xu, Z. Zhang, C. Yang, Z. Liu, Y. Tao, J. Qin, D. Ma, J. Mater. Chem. 19 (2009) 7661.
- [31] M.H. Tsai, H.W. Lin, H.C. Su, T.H. Ke, C.C. Wu, F.C. Fang, Y.L. Liao, K.T. Wong, C.I. Wu, Adv. Mater. 18 (2006) 1216.
- [32] Y.-X. Zhang, L. Zhang, L.-S. Cui, C.-H. Gao, H. Chen, Q. Li, Z.-Q. Jiang, L.-S. Liao, Org. Lett. 16 (2014) 3748.
- [33] M.S. Park, J.Y. Lee, Chem. Mater. 23 (2011) 4338.
- [34] S.O. Jeon, J.Y. Lee, Tetrahedron 66 (2010) 7295.
- [35] S.R. Forrest, D.D.C. Bradley, M.E. Thompson, Adv. Mater. 15 (2003) 1043.
- [36] L.-S. Cui, S.-C. Dong, Y. Liu, M.-F. Xu, Q. Li, Jiang, Z.-Q. Jiang, L.-S. Liao, Org. Electron. 14 (2013) 1924.