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# Meta-linked CBP-derivatives as host materials for a blue iridium carbene complex

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# ABSTRACT

We present four derivatives of 4,4'-bis(9-carbazolyl)biphenyl (CBP) for the use as host materials in blue phosphorescent organic light emitting diodes. By replacing the *para*-link-age by a *meta*-linkage of the carbazole substituents at the central biphenyl unit materials with improved thermal and optical properties are obtained. The triplet energy of the *meta*-linked host materials is significantly increased to more than 2.90 eV compared to 2.58 eV for the *para*-linked CBP. Moreover, selective methyl substitution of the basic *meta*-CBP structure leads to materials with high glass transition temperatures up to 120 °C and electrochemical stability of the oxidised species against dimerisation. The high triplet energy allows the use of the *meta*-CBP derivatives as host materials for the carbene emitter *mer*-tris(*N*-dibenzofuranyl-*N'*-methylimidazole)iridium (III) (Ir(dbfmi)) with a pure blue emission at 450 nm.

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# 1. Introduction

The presentation of OLEDs based on the electrophosphorescence was a breakthrough in device performance. With the introduction of phosphorescent emitters both the electrogenerated singlet and triplet excitons contribute to the emission of light. The fast intersystem crossing efficiently converts singlet excitons to the triplet state leading to a theoretical internal quantum efficiency of 100% [1-3]. The most frequently used blue phosphorescent emitter is the greenish blue phosphor FIrpic with an emission maximum  $(\lambda_{em})$  at ~470 nm. For white OLEDs, however, a saturated blue emission with a  $\lambda_{em}$  at 450 nm would be beneficial. A number of blue phosphors has been reported in the last years and recently been reviewed by Sasabe and Kido [4]. Carbene type emitters such as mer-tris(N-dibenzofuranyl-N'-methylimidazole)iridium (III) (Ir(dbfmi)) [5] are attractive candidates for a saturated blue emission.

To avoid self-quenching the emitter has to be doped into an appropriate host material [6]. For an efficient exothermic energy transfer from the host to the guest molecules, the triplet energy of the host must be higher compared to the emitter. In the case of blue emitters the host's energy gap between the singlet ground state ( $S_0$ ) and the first excited triplet state ( $T_1$ ) has to be at least 2.8 eV. To obtain high triplet energies for the host materials the conjugation of the materials must be limited. This requirement makes the development of host material for blue triplet emitters particularly challenging because lowering the conjugation, i.e. increasing the singlet and triplet energies may negatively affect the charge transport properties [7].

Many organic compounds used as host materials for phosphorescent emitters are based on carbazole [8–11]. One reason is the high intrinsic triplet energy of carbazole of 3.0 eV [12]. The most prominent example for a carbazole based host material is 4,4'-bis(9-carbazolyl)-biphenyl (CBP) where the N-atoms of the carbazole units are connected with a biphenyl unit at the 4,4'-positions. The molecular



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structure allows for an extended conjugation of the carbazole units over the biphenyl structure leading to a decrease in triplet energy to around 2.56 eV [13]. If the conjugation between the constituting units in carbazole derivatives is minimised the triplet energy can be maintained at a high level. Many approaches to confine the conjugated system in carbazole derivatives have been described in literature. One way to minimise the conjugation in carbazole based host materials introduced by Tokito et al. is to attach two methyl groups in the 2,2'-positions of the central biphenyl in CBP leading to the host material 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl (CDBP) [14,15]. Due to the steric hindrance the biphenyl is forced into a tilted conformation which reduces the conjugation in the molecule and concomitantly enlarges the triplet energy to 2.79 eV. We recently reported a series of CBP-based materials with high triplet energies using a similar concept by introducing methyl and trifluoromethyl substituents in the 2,2'-positions of the central biphenyl unit [16,17]. Another design concept is to choose different linkers between the carbazole units such as a single phenyl ring instead of biphenyl in N,N'-dicarbazolyl-3,5-benzene (mCP) [18,13] or non-conjugated units as, for example, an aliphatic cyclohexyl ring, an oxygen-bridge [19] or a diphenylsilane linker [20]. In mCP another effect reduces the conjugation: instead of the para-connection, the two carbazole moieties are metalinked over the phenyl ring [21,22]. A major drawback of mCP however is its high crystallinity. Matrix materials with carbazole units linked to a biphenyl in the 3,3'-positions have been described in a patent of Adachi and Forrest [23] and a number of following patents. In the scientific literature meta-linked CBP derivatives are to the best of our knowledge only reported in a theoretical study about heterofluorene linker groups between the two carbazoles as alternatives to biphenyl [24]. Besides the high triplet energy a host material has to reveal a stable amorphous phase at device operating temperatures [25]. This ensures homogeneous mixing of the emitter within the matrix material and minimises the effects of concentration quenching. In addition the use of organic glasses in OLEDs helps to avoid



Fig. 1. Chemical structures and synthetic routes to (a) *meta*-linked CBP derivatives 1 and 2 and (b) twisted *meta*-linked CBP derivatives 3 and 4. Reagents and conditions: (i) Cu(OAc)<sub>2</sub>, DMF, 100 °C, 90 min; (ii) I<sub>2</sub>, HIO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, CCI<sub>4</sub>, acetic acid, 80 °C, 18 h; (iii) Cu, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, *o*-dichlorobenzene, reflux, 24 h.

grain boundaries which may act as trap states [26,27]. Organic glasses can be obtained by avoiding strong intermolecular forces like hydrogen bonding or  $\pi$ - $\pi$  stacking between the molecules. A very common design concept for molecular glasses is the space-filling star-shaped topology, as in the well-known hole transporting organic glass 4,4',4"-tris(carbazol-9-yl)triphenylamine (TCTA) [28]. Furthermore, the introduction of bulky substituents leads to a larger intermolecular distance and a hindrance in packing and therefore to amorphous behaviour. For example, in 9-(4-tert-butylphenyl)-3,6-bis(triphenylsilyl)-carbazole (CzSi) [29] and 3,5-di(N-carbazolyl)-tetra-phenylsilane (SimCP) [30] packing of the molecules is avoided by introducing bulky triphenylsily groups. However, the separation of the conducting units usually leads to a decrease in charge carrier mobility.

In this work we describe the preparation, the thermal and optical characterisation of four *meta*-linked CBP-derivatives. Materials revealing high triplet energies and amorphous behaviour with high glass transition temperatures are achieved by attaching the carbazole units at the *meta*-position of the phenyl rings of the biphenyl moiety in combination with a selective methyl substitution at the *meta*-CBP structure. The high triplet energy allows the use as host materials for the pure blue carbene emitter *mer*tris(*N*-dibenzofuranyl-*N*'-methylimidazole)iridium (III) (Ir (dbfmi)). The molecular structures of the host materials **1–4** are depicted in Fig. 1.

# 2. Experimental

#### 2.1. Materials

All chemicals and reagents were used as received from commercial sources without further purification. The solvents for reactions and purification were all distilled before use.

#### 2.2. Characterisation

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AC 300 (300, 75 MHz) and CDCl<sub>3</sub> as solvent. All data are given as chemical shifts  $\delta$  (ppm) downfield from Si(CH<sub>3</sub>)<sub>4</sub>. For optical measurements, 10<sup>-5</sup> M cyclohexane (Ultrasolv<sup>®</sup>) solutions of the materials as well as thin films on quartz substrates were prepared by spincoating. The UV/Vis spectra were measured in solution and on neat films with a Hitachi U-3000 spectrometer. Fluorescence spectra in solution were obtained from a Shimadzu spectrofluorophotometer RF-5301PC using excitation at 300 nm. Phosphorescence spectra of thin films have been measured at 5 K (Helium cryostat Optistat CF from Oxford Instruments) applying the technique of time-gated spectroscopy (with fluorescence and phosphorescence lifetime spectrometer FLSP 920 from Edinburgh Instruments). For differential scanning calorimetry measurements (DSC) a Diamond DSC apparatus from Perkin Elmer was used (heating/cooling rate 10 K min<sup>-1</sup>, nitrogen). Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA815e machine at a heating rate of 10 K/min under nitrogen. Cyclic voltammetry measurements were carried out in absolute solvents measuring at a platinum working electrode versus a Ag/AgNO<sub>3</sub> reference electrode. Each measurement was calibrated against an internal standard (ferrocene/ferrocenium redox system). The purity of the target compounds was checked with a Waters size exclusion chromatography system (SEC) for oligomers (analytical columns: cross-linked polystyrene gel (Polymer Laboratories), length:  $2 \times 60$  cm, width: 0.8 cm, particle size: 5 µm, pore size 100 Å, eluent THF (0.5 mL/min, 80 bar), polystyrene standard).

#### 2.3. Computational methods

The transport levels of the materials used were determined via density functional calculations. For the ionisation potential and the electron affinity first the geometry of the neutral as well as the charged states were optimised using the BP86-functional [31,32] in combination with a split-valence basis set (SV(P)) including polarisation functions on all heavy atoms [33]. For iridium an effective core potential was employed [34]. For the energetics we performed single point calculations at the optimised geometries using the same functional in combination with a TZVP-basis set [35]. To account for dielectric solid state effects a UPS/IEPS-calibrated version of the conductor like screening model (COSMO) [36] was used in conjunction with these single point calculations. All calculations were carried out with the turbomole program package [37].

# 2.4. Synthetic procedures

The synthesis of tris[(3-phenyl-1*H*-benzimidazol-1-yl-2 (3H)-yliden-1,2-phenylene]-irdidium (DPBIC) [38], 2,8-bis (triphenylsilyl)-dibenzofuran (DBFSi) [39], *mer*-tris(*N*-dibenzofuranyl-*N*'-methylimidazole)-iridium (III) (Ir(dbfmi)) [5,39] and 3,6-dimethyl-carbazole [16] is described in literature.

3,3'-Dibromobiphenyl was synthesized according to a procedure reported by Demir et al. [40] Yield: 43%. EI-MS *m/z*: 312 (100, M<sup>+</sup>), 232 (5), 152 (95). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.70 (dd, 2H), 7.52–7.46 (m, 4H), 7.31 (dd, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 142.11, 131.16, 130.74, 130.50, 126.09, 123.33.

5,5'-Diiodo-2,2'-dimethylbiphenyl: 2,2'-Dimethylbiphenyl (9.9 g, 54 mmol) in 120 mL of acetic acid and 5.5 mL of water were heated to 90 °C to get a clear solution. After the addition of iodine (10.9 g, 43 mmol), iodic acid (5.7 g, 32 mmol), 5.5 mL of sulphuric acid and 5.5 mL of tetrachloromethane the solution was stirred at 80 °C for 18 h. The excess of iodine was removed by adding a solution of sodium hydrogen sulphide. The product was extracted with dichloromethane and washed several times with water. After drying the organic layer over anhydrous sodium sulphate, the solvent was recrystallised from ethyl acetate to yield 6.9 g (16 mmol, 30%) of a white solid. EI-MS *m/z*: 434 (100, M+), 180 (50), 165 (47). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.58 (dd, 2H), 7.42 (ds, 2H), 7.00 (d, 2H). 1.99 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>), *δ* (ppm): 142.30, 137.65, 136.56, 135.48, 131.83, 90.41, 19.38.

# 2.5. General procedure for the Ullmann- type reaction

Dihalogenobiphenyl (2.3 mmol), carbazole (5.06 mmol), potassium carbonate (2.5 g, 18.4 mmol), copper powder (0.58 g, 9.2 mmol) and 18-crown-6 (0.12 mg, 0.46 mmol) were refluxed in 15 mL of *o*-dichlorobenzene in an argon atmosphere for 24 h. Copper and inorganic salts were filtered off and the solvent was evaporated. Column chromatography on silica gel with mixtures of hexane/tetrahy-drofurane as eluent yielded the products **1–4** as white solids.

3,3'-Bis(carbazolyl)biphenyl (1): Yield: 47%. EI-MS *m*/z: 484 (100, M+), 316 (10), 234 (39). <sup>1</sup>H NMR (300 MHz, CDCl3),  $\delta$  (ppm): 8.17 (d, 4 H), 7.88 (m, 2H), 7.75 (dt, 2H), 7.70 (dd, 2 H), 7.60 (dt, 2H), 7.51 (d, 4H), 7.43 (dt, 4H), 7.31 (dt, 4H). (<sup>13</sup>C NMR (75 MHz, CDCl3),  $\delta$  (ppm): 142.42, 141.19, 138.82, 130.84, 126.80, 126.52, 126.39, 126.10, 123.79, 120.71, 120.40, 110.08.

3,3'-Bis(3,6-dimethylcarbazolyl)biphenyl (**2**): Yield: 55%. EI-MS *m/z*: 540 (100, M+), 345 (5), 270 (24). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.92 (m, 4H), 7.86 (m, 2H), 7.70 (dt, 2H), 7.66 (dd, 2H), 7.57 (dt, 2H), 7.38 (d, 4H), 7.24 (dd, 4H), 2.56 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 142.38, 139.63, 139.24, 130.70, 129.55, 127.52, 126.41, 126.05, 125.76, 123.84, 120.56, 109.75, 21.74.

3,3'-Bis(carbazolyl)-6,6'-dimethylbiphenyl (**3**): Yield: 50%. EI-MS *m/z*: 512 (100, M<sup>+</sup>), 329 (8), 257 (17), 166 (12). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.15 (d, 4H), 7.55–7.39 (m, 14H), 7.32–7.26 (m, 4H), 2.33 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 142.51 141.25 135.65, 135.46, 131.85, 127.96 126.45, 126.26, 123.67, 120.65, 120.20, 110.09, 20.11.

3,3'-Bis(3,6-dimethylcarbazolyl)-6,6'-dimethylbiphenyl (**4**): Yield: 55%. EI-MS *m/z*: 568 (100, M<sup>+</sup>), 358 (15), 284 (29), 192 (24). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.90 (s, 4H), 7.52–7.45 (m, 4H), 7.41–7.38 (m, 4H), 7.33 (d, 4H), 7.21(d, 4H), 2.55 (s, 12H), 2.30 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 142.47, 139.72, 136.06, 134.98, 131.70, 129.30, 127.69, 127.39, 126.10, 123.70, 120.49, 109.74, 21.73, 20.06.

#### 2.6. OLED fabrication

The organic layers were deposited by thermal evaporation in high vacuum ( $<10^{-6}$  mbar) onto indium-tin-oxide (ITO, 10 ohm/square) precoated glass substrates. Prior to use the ITO glass was degreased using organic solvents and cleaned using an UV-ozon oven for 30 min. The organic layers and the metal cathode were evaporated without breaking the vacuum. The current density–luminance– voltage (J–L–V) characteristics of the OLEDs were measured by a Keithley source meter 2400 and a Konica Minolta CS-200, respectively. EL spectra were taken by a CCD spectral analyser by Zeiss. EQEs were calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution.

#### 3. Results and discussion

# 3.1. Synthesis

In Fig. 1a the synthetic route to the *meta*-linked CBP derivatives **1** and **2** is depicted. In a copper-mediated homocoupling reaction 3-bromophenylboronic acid reacts to 3,3'-dibromobiphenyl [40]. An Ullmann-type reaction of dibromobiphenyl with carbazole or 3,6-dimethylcarbazole [16] yields the host materials.

To obtain the twisted *meta*-linked CBP-derivatives **3** and **4**, first, 5,5'-diiodo-2,2'-dimethyl-biphenyl was prepared by direct iodination [41] of 2,2'-dimethylbiphenyl with iodine and iodic acid in acetic acid (Fig. 1b). Via 2D <sup>1</sup>H NMR experiments (see Supporting Information) the selective iodination at the 5- and 5'-positions of the biphenyl could be confirmed. Here, the inductive effect of the methyl groups in the 2- and 2'-positions of the biphenyl increases the electron density in the 5- and 5'-positions and favours the electrophilic attack of I<sup>+</sup>. We consider this 5,5'diiodo-2,2'-dimethylbiphenyl unit as a versatile building block for the synthesis of materials with confined conjugation which, to the best of our knowledge, has not been described in the literature before. The tilted *meta*-linked CBP derivatives **3** and **4** were prepared via the Ullmann-type reaction of 5,5'-diiodo-2,2'-dimethylbiphenyl with carbazole or 3,6-dimethylcarbazole [16].

Mass spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy were used to identify the materials. The data are given in the experimental part. All materials were purified by repeated zone sublimation.

# 3.2. Thermal properties

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We examined the thermal properties of the *meta*-linked CBP derivatives **1–4** by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in nitrogen atmosphere at a scanning rate of 10 K min<sup>-1</sup>. All results are summarised in Table 1.

Both the *para*-linked CBP and the *meta*-linked **1** show crystalline behaviour in the DSC experiment. For the *meta*-derivative **1** the melting and the crystallisation are observed at around 10 °C lower temperatures than for CBP. Methyl substitution at the pendant carbazoles in **2** leads to a material with a much lower tendency to crystal-

able I			
Thermal properties	of CBP and the	meta-linked ho	st materials 1-4.

	$T_{\rm g}(^{\circ}{\rm C})$	$T_{\rm m}$ (°C)	$T_{\rm cr}$ (°C)	$T_{id}^{a}$ (°C)
CBP	-	283	205 <sup>b</sup>	365
1	-	271	191 <sup>b</sup>	315
2	107	270	184 <sup>c</sup>	349
3	108	237	176 <sup>c</sup>	319
4	120	212	-	319

 $T_{g:}$  glass-transition temperature,  $T_{m:}$  melting temperature,  $T_{cr:}$  crystallisation temperature and  $T_{id:}$  initial decomposition temperature.

<sup>a</sup>  $T_{id}$  is the temperature at which an initial mass loss was observed in a thermogravimetric experiment with a heating rate of 10 K min<sup>-1</sup> in a nitrogen atmosphere.

<sup>b</sup> Observed during cooling scan.

<sup>c</sup> Observed only during the heating scan.

lise. The glass transition of **2** is observed at 107 °C and the recrystallisation is observed at a high temperature of 184 °C. In compound **3** the introduction of methyl groups only at the central biphenyl unit leads to nearly the same glass transition temperature of 109 °C and nearly the same recrystallisation temperature of 176 °C. The biphenyl substitution in combination with the methyl substitution at the carbazoles increases the  $T_{\rm g}$  even to 120 °C for compound 4. Moreover, for compound 4 crystallisation is observed neither in the cooling nor in the heating cycle which renders 4 the derivative of the series with the highest tendency to form a molecular glass. This thermal investigation shows that the introduction of additional methyl groups at the central biphenyl and/or the adjacent carbazole moieties of the meta-linked molecular structure has beneficial effects on the thermal properties, i.e. amorphous materials with high  $T_{g}$ s in the range of 107–120 °C are obtained.

#### 3.3. Optical properties

The room temperature UV/Vis absorption and fluorescence spectra of  $10^{-5}$  M cyclohexane solutions of **1–4** are depicted on top of Fig. 2. Compounds **1** and **3** as well as compounds **2** and **4** show very similar spectra. In each compound the absorption and photoluminescence behaviour is dominated by optical transitions localised on the carbazole units. Since the chromophore in compounds **1** 



**Fig. 2.** Top: absorption and fluorescence spectra of **1–4** taken in  $10^{-5}$  M solutions in cyclohexane at 300 K. Bottom: normalised phosphorescence spectra of CBP and **1–4** measured in 2 wt.% solid solution of the compounds in PMMA at 5 K.

and **3** and in compounds **2** and **4** are identical it is not surprising that these two pairs of materials show nearly the same absorption and fluorescence spectra. For compound **2** and **4** the additional methyl substituents on the chromophore 3,6-dimethylcarbazole cause a bathochromic shift of 13 nm in the absorption and emission spectra compared to compounds **1** and **3**.

As a prerequisite for the application of **1–4** as host materials, their triplet energy has to be higher compared to that of the blue phosphorescent emitter. By measuring phosphorescence at low temperatures the triplet energies can be experimentally determined as the highest energy peak of luminescence.

In order to understand how the meta-linkage of the carbazole units affects the triplet energy we compare the phosphorescence spectra of the para-linked CBP and the *meta*-linked derivative **1–4**. The most striking difference in the normalised spectra (see Fig. 2, bottom) is the remarkable blue shift in phosphorescence of 1-4 compared with CPB. The emission of 1, for example, is shifted to lower wavelengths by 65 nm compared with CBP, corresponding to triplet energies ( $\Delta E(T_1 - S_0)$ ) of 2.98 eV for **1** and 2.58 eV for CBP. This is a proof of the design concept of meta-connection to achieve high triplet energies. In fact, the methyl substitution at the central biphenyl moiety is expected to lead to even higher triplet energies by introducing torsion between the phenyl rings of the biphenyl unit as is well known from CDBP. However, in the case of the meta-linked host materials the additional twisted molecular structure has only minor effects on the emission characteristics. Similar to the emission at room temperature, compounds 1 and 3 and compounds 2 and 4 reveal the highest energy peaks at the same wavelength, while the shape of the phosphorescence spectra is different. In the case of the twisted methyl substituted biphenyl containing compounds 3 and 4 the 0-0 transition is more pronounced and the width of the spectra is smaller than for 1 and 2. As an effect of the methyl substitution at the 3- and 6-positon of the carbazole units we observe again a small bathochromic shift of ca. 10 nm for compounds 2 and 4 compared to 1 and 3.

All results of the photo physical investigations of CBP and the *meta*-linked matrix materials **1–4** are summarised in Table 2.

#### 3.4. Cyclic voltammetry

The electrochemical behaviour of **1–4** was investigated by cyclic voltammetry in a conventional three-electrode setup using a platinum working electrode, a platinum wire as counter electrode, and a Ag/AgNO<sub>3</sub> reference electrode. Particularly, the oxidation behaviour of **1–4** in dichloromethane solutions was studied. From the half-wave potential of the first oxidation relative to ferrocene the HOMO value of the compounds can be deduced. By adding the optical band gap to the HOMO value the LUMO value can be estimated. As the cyclic voltammetry is measured in solution and not in the solid state the values of HOMO and LUMO may differ from the solid state values in an OLED. Both the experimentally received and the calculated values for the energy levels of CBP and of **1–4** are listed in

# Table 2

Optical	properties and	energy	levels	of CBP	and t	he	meta-linked	host	materials	1-4	4
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	Solution	Film	Solution	Film	Film	Calculated	Calculated		Experimental	
	$\lambda_{\mathrm{EA}}^{\mathrm{a}}\left(\mathrm{nm}\right)$	$\lambda_{\mathrm{EA}}^{\mathbf{b}}(\mathrm{nm})$	$\lambda^{RT}_{em}c(nm)$	$\lambda^{5K}_{em}{}^{d}(nm)$	$\lambda^{5K}_{em}^{e}(nm)$	HOMO (eV)	LUMO (eV)	HOMO <sup>g</sup> (eV)	LUMO <sup>h</sup> (eV)	
CBP	350	357	356, 374	484	477	-5.58	-1.78	-5.63	-2.16	
1	344	354	340, 357	421	415	-5.71	-1.77	-5.65	-2.15	
2	357	365	353, 370	452 <sup>f</sup>	421	-5.48	-1.71	-5.56	-2.17	
3	346	354	342, 359	423	415	-5.64	-1.51	-5.65	-2.16	
4	358	369	355, 373	431	421	-5.44	-1.47	-5.53	-2.17	

<sup>a</sup> Absorption edge measured in 10<sup>-5</sup> M cyclohexane solutions at room temperature.

<sup>b</sup> Absorption edge measured on neat films at room temperature.

<sup>c</sup> Wavelengths of the intensity maxima of the fluorescence at 300 nm excitation of 10<sup>-5</sup> M cyclohexane solutions at room temperature.

<sup>d</sup> Measured on film samples (100%) at 5 K.

<sup>e</sup> Measured in 2 wt.% PMMA at 5 K.

<sup>f</sup> No 0-0 transition is observed.

<sup>g</sup> Estimated from the half-wave potential of the first oxidation in the cyclic voltammetry experiment.

<sup>h</sup> Estimated from the HOMO values and the optical band gap (determined from the UV/Vis absorption onset of neat films).

Table 2. The *meta*-linked compounds **1** and **3** with unsubstituted carbazole units reveal almost the same energy levels as for CBP. In contrast, **2** and **4** show ca. 10 mV higher HOMO levels which can be attributed to the inductive effect of the additional methyl groups in the 3- and 6-positons of the carbazole units. The cyclic voltammetry experiments show that the behaviour upon oxidation is clearly dominated by the molecules' site with the highest electron density, i.e. the carbazole moieties. Contrary to the theoretical expectations, the substitution on the central biphenyl unit does not affect the HOMO levels and fairly no effects of the different substitution pattern on the LUMO levels are observed.

Charge transport processes in organic semiconductors involve the formation of radical anions and cations. Thus, investigations of the electrochemical stability can give information about the stability of the materials in OLED devices. To evaluate the electrochemical stability of the materials we carried out multicycle experiments. The cyclic voltammograms showing five repeated oxidation cycles of **1** and **2** in  $2 \times 10^{-3}$  M dichloromethane solutions are given as Supporting Information. In the case of 1, the oxidation cycles are not reproducible. After the first reduction into the uncharged molecule at 0.88 V an additional reduction at around 0.59 V is observed. The latter can be attributed to new oligomeric species formed during dimerisation reactions at the active 3- and 6-positions of the carbazole units after the first oxidation of the molecule [42.43]. As the oligomeric species is oxidised more easily the corresponding oxidation process takes place at a lower voltage of around 0.70 V. In contrast, 2 reveals a fully reversible oxidation behaviour. The methyl substitution at the adjacent carbazole units blocks the electroactive 3- and 6-positions and renders the oxidised species stable against dimerisation in solution. The same stability of the radical cations was also found for compound 4 in contrast to 3.

#### 3.5. Blue phosphorescent organic light-emitting diodes

Common blue phosphors as for example FIrpic and FIr6 show blue emission tailing to the green region with emission maxima at 472 nm (CIE colour coordinates x = 0.17,

y = 0.34) [14] and 458 nm (CIE colour coordinates x = 0.16, y = 0.26) [44], respectively. For solid state lighting, phosphors with a more saturated blue emission would be beneficial. Due to the high triplet energy of more than 2.9 eV the host materials **1–4** should be suitable for saturated blue emitters. Thus, we have tested the host materials with the pure blue carbene emitter Ir(dbfmi) with a  $\lambda_{em} = 450$  nm and CIE colour coordinates of x = 0.16, y = 0.18.



**Fig. 3.** Top: energy level diagram of the OLED device with the configuration ITO/PEDOT:PSS/MoO<sub>3</sub>-doped DPBIC (10 nm)/DPBIC (10 nm)/1: Ir(dbfmi) (5 %, 20 nm)/1 (10 nm)/Cs<sub>2</sub>CO<sub>3</sub>-doped BCP (20 nm)/Cs<sub>2</sub>CO<sub>3</sub> (1 nm)/Al (100 nm) employing **1** as host for Ir(dbfmi); ionisation potentials and electron affinities obtained from calculations are indicated. The grey dotted lines represent the levels of the emitter Ir(dbfmi). Bottom: luminance-voltage plot (filled symbols) and current density–voltage characteristic (open symbols).

The first OLED device setup is shown in Fig. 3. On top of the ITO glass substrate poly(3,4-ethylene-dioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) was applied by spin coating as hole injection layer followed by 10 nm DPBIC p-doped with molybdenum(VI) oxide as hole transporting layer. An additional 10 nm thick layer of DPBIC followed as exciton and electron blocker. The 20 nm emission layer consisted of 5% Ir(dbfmi) doped into the *meta*-linked CBP host materials. Ten nanometer of the host material were deposited as hole and exciton blocking layer followed by 20 nm of caesium carbonate doped 2,9-dimethyl-4,7diphenyl-1,10-phenanthroline (BCP) as electron transporting layer. As cathode 1 nm Cs<sub>2</sub>CO<sub>3</sub> and 100 nm aluminium were deposited.

The turn-on voltage at 1 cd  $m^{-2}$  of 4.5 V is quite high and luminances of 100 and 1000 cd  $m^{-2}$  are achieved at voltages of 5.6 and 6.8 V, respectively. In some cases we



**Fig. 4.** Top: energy level diagram of the optimised OLED device with the configuration ITO/PEDOT:PSS/MoO<sub>3</sub>-doped DPBIC (10 nm)/DPBIC (10 nm)/1: DPBIC:Irt(dbfmi) (75:20:5, 20 nm)/DBFSi (5 nm)/BCP (5 nm)/Cs<sub>2</sub>CO<sub>3</sub>-doped BCP (40 nm)/Cs<sub>2</sub>CO<sub>3</sub> (1 nm)/Al (100 nm) employing **1** as host for Ir(dbfmi) with chemical structures of the materials used; lonisation potentials and electron affinities obtained from calculations are indicated. The grey dotted lines represent the levels of the emitter Ir(dbfmi). Bottom: electroluminescence spectrum of the devices with **1** as host material for Ir(dbfmi) at 4.25 V. CIE coordinates: x = 0.16, y = 0.18.

observed a small contribution of the hole transporting material DPBIC to the emission. This indicates that the exciton formation is shifted towards the hole conducting layer. We attribute this to the high energy barrier for hole injection from the DPBIC into the emission layer causing as well the high turn-on voltage. In contrast, electrons do not have to overcome major energy barriers.

To improve the hole injection into the emission layer we coevaporated the hole transporting DPBIC into the emission layer providing a barrier free path for holes. The optimised device setup and the molecular structures of the materials used are shown on top of Fig. 4. Ten nanometer molybdenum(VI) oxide doped DPBIC as hole transporting layer and an additional 10 nm thick layer of DPBIC were used as exciton and electron blocker. The 20 nm thick emission layer comprises a mixed matrix system of the carbazole containing host materials **1–4** with DPBIC and the blue emitter Ir(dbfmi) in the ratio 75:20:5. 2,8-Bis (triphenylsilyl)-dibenzofuran (DBFSi) (5 nm) was used as exciton and hole blocking material followed by 5 nm BCP and 40 nm BCP n-doped with Cs<sub>2</sub>CO<sub>3</sub>. As cathode 1 nm Cs<sub>2</sub>CO<sub>3</sub> and 100 nm aluminium were deposited.

In the electroluminescence spectrum of the optimised device setup the pure emission of the phosphor Ir(dbfmi) can be observed with CIE-coordinates of x = 0.16 and y = 0.18 (Fig. 4, bottom). The CIE-coordinates do not change within the voltage range between 4.2 and 8.2 V. By decreasing the hole injection barrier in the mixed matrix



**Fig. 5.** Top: luminance-voltage curves (black filled symbols) and current density-voltage characteristics (grey open symbols) of the optimised device setup. Bottom: external quantum efficiency-luminance curves of the devices with **1–4** as host material for Ir(dbfmi).

# Table 3

Performance data at 100 cd m <sup>-2</sup> a	and 1000 cd m <sup>-2</sup> using 1	1–4 as host materials for t	he blue emitter Ir(dbfmi).
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	At 100 cd $m^{-2}$			At 1000 cd m <sup>-2</sup>				
	Voltage (V)	$\eta_{\rm C}  ({ m cd}  { m A}^{-1})$	$\eta_{ m P}({ m lm}{ m W}^{-1})$	$\eta_{\rm ext}$ (%)	Voltage (V)	$\eta_{\rm C}  ({ m cd}  { m A}^{-1})$	$\eta_{ m P}~({ m Im}~{ m W}^{-1})$	$\eta_{\mathrm{ext}}$ (%)
1	3.5	11.5	10.2	8.2	4.4	5.7	4.1	4.1
2	4.9	0.9	0.6	0.5	6.6	0.6	0.3	0.4
3	3.7	12.2	10.2	8.7	4.4	8.5	6.0	6.1
4	4.3	4.5	3.3	2.6	5.3	3.1	1.9	1.8

 $\eta_{\rm C}$ : Current efficiency;  $\eta_{\rm P}$ : power efficiency;  $\eta_{\rm ext}$ : external quantum efficiency.

system the exciton formation zone could be successfully separated from the hole transporting layer. Moreover, the applied voltages at 100 and 1000 cd  $m^{-2}$  could be significantly lowered, to 3.5 and 4.4 V, respectively, in the case of host **1** (see Fig. 5).

Peak luminances are 5300 cd  $m^{-2}$  for 1, 5000 cd  $m^{-2}$  for **2**, 10,800 cd m<sup>-2</sup> for **3** and 9300 cd m<sup>-2</sup> for **4**. For hosts **1** and **3** higher luminances are reached at lower voltages than for 2 and 4. Comparing the efficiencies of the four meta-linked CBP-derivatives 1-4, the compounds 2 and 4 with methyl substituents at the 3- and 6-positions of the carbazole units show significantly lower efficiencies than **1** and **3**. As evident from the current density-voltage-plot in Fig. 5, higher operation voltages are needed in the devices employing the host materials 2 and 4. One possibility might be that the transport properties of 2 and 4 with methyl substituents at the carbazole units are worse compared to 1 and 3 with unsubstituted carbazole units. In contrast, **1** and **3** give similar performances with slightly better values for 3 at higher luminances. The highest efficiency was achieved for 3 with an external quantum efficiency of 8.7% and a power efficiency of 10.2 lm W<sup>-1</sup> at 100 cd m<sup>-2</sup> and 6.1% and 6.0 lm W<sup>-1</sup> at 1000 cd m<sup>-2</sup>. These efficiencies are comparable to those of Ir(dbfmi) in the phosphine oxide based host material PO9 recently reported by Sasabe et al. [5] At a brightness of 1000 cd m<sup>-2</sup> they reported an external quantum efficiency of 6.2% which compares well with the external quantum efficiency of 6.1% we found for the host material **3**. All performance data are summarised in Table 3.

The large differences in device performance as evident from Table 3 are quite surprising as the chemical structures of all hosts **1–4** are very similar. These findings show that each combination of emitter and host needs to be chosen very carefully as the host-emitter-system is very sensitive to even small structural variations which may change the charge-carrier balance in the device or the chemical compatibility of host and emitter. Both effects in conjunction with the relatively long triplet lifetime of Ir(dbfmi) of ~20  $\mu$ s [5] could negatively influence the device performance.

# 4. Conclusions

We have described a series of CBP derivatives with a *meta*-linkage of the carbazole moieties to the central biphenyl unit. By selective methyl substitution at two sites of the basic *meta*-CBP structure, the 3- and 6-position of the pendant carbazoles and at the 6- and 6'-position of

the biphenyl unit, the tendency to crystallise could be lowered. Glass transition temperatures in the range of 107-120 °C were achieved. The meta-linkage reduces the conjugation of the molecules effectively, leading to high triplet energies in the range of 2.93-2.98 eV compared with 2.58 eV for CBP. Here, the additional twist by the methyl substitution at the biphenyl unit does not increase the triplet energy any further, but narrows the phosphorescence spectra of 3 and 4 compared with 1 and 2. Introducing methyl groups at the 3- and 6-position of the pendant carbazole units in the matrix materials 2 and 4 leads to electrochemical stability of the oxidised species in cyclic voltammetry. First results from OLED tests show that meta-linked CPB-derivatives are suited host materials for blue emitters, e.g., Ir(dbfmi), with pure blue emission at 450 nm. The highest efficiencies were achieved with the twisted *meta*-linked derivative **3** giving external quantum efficiencies of 8.7% and 6.1% and power efficiencies of 10.2 and 6.0  $\text{Im W}^{-1}$  at 100 and 1000 cd  $\text{m}^{-2}$ , respectively.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2011. 08.012.

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