Controlling singlet–triplet splitting in carbazole–oxadiazole based bipolar phosphorescent host materials

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A rational molecular design strategy for carbazole–oxadiazole based bipolar host materials was developed to improve the device efficiency of blue phosphorescent organic light-emitting diodes (PHOLED). Steric effects of strategically placed methyl groups led to an increase of triplet energies (o-2MPCzPOXD: 2.66 eV and o-3MPCzPOXD: 2.73 eV versus the initial host material o-PCzPOXD: 2.62 eV) while less pronouncedly affecting singlet energies and, therefore, retaining low driving voltages, high power efficiencies and remarkably low efficiency roll-offs in PHOLEDs. The maximum quantum efficiencies (EQE) for blue devices (FIrpic) were significantly raised for o-2MPCzPOXD (13.6%) and o-3MPCzPOXD (11.5%) versus o-PCzPOXD (9.0%) although yielding comparable values for green devices (Ir(ppy) 3; 12.9% and 15.4% versus 13.2%). Supported by theoretical calculations a structure–property relationship was established from photo-physical properties, PHOLED performance measurements and structural characterization from single crystal data.

1. Introduction

Organic Light Emitting Diodes (OLEDs) received great attention during the last two decades due to potential applications in flat panel displays and solid state lighting [1–10]. The introduction of phosphorescent emitters by Forrest et al. in 1998 [11,12] significantly enhanced the efficiency of OLEDs due to the fact that phosphorescent transition metal emitters harvest singlet and triplet excitons simultaneously. Thus, phosphorescent OLEDs (PHOLEDs) can theoretically achieve 100% internal quantum efficiency [13,14].

In fact, triplet emitters have to be dispersed in an organic host matrix to avoid concentration quenching [15,16]. Bipolar host materials proved to be especially useful due to balanced charge transport properties resulting in simplified device structure and broader recombination zones [7,17,18]. To efficiently confine triplet excitons on the dopant higher triplet energies (E_T) of the host materials compared to the phosphorescent dopant are required [19–21]. However, the combination of p- and n-type moieties in a molecule significantly decreases the triplet energy of host materials [7,17].

Therefore, the molecular design of bipolar host materials focuses on the interruption of the conjugated π-system to reduce the donor–acceptor interaction [7,10,17]. While aiming for increased triplet energies of host materials, the enhancement of singlet energies should be limited in order to achieve the desired device performances. Thus,
methodologies to independently tune singlet and triplet energies are highly desirable.

Recently, we reported on the concept of planarizing triarylamine (TAA) donor structures in TAA–oxadiazole–TAA based materials significantly enhancing the ortho-linkage effect [22]. Utilizing phenylcarbazole (PCz) resulted in o-PCzPOXD as an efficient bipolar host material for green [Ir(ppy)3] PHOLEDs with a remarkably low efficiency roll off. However, lower efficiencies were observed in blue (FIRpic) devices as a consequence of a slightly lower $E_T$ value (o-PCzPOXD = 2.62 eV) compared to FIRpic (=2.65 eV [7]).

The objective of this work is to increase the $E_T$ values of o-PCzPOXD while retaining low driving voltages and high power efficiencies in the device by elevating the singlet energy ($E_S$) less pronounced. This task is being tackled by sterically induced torsion introducing methyl groups at specific sites of the PCz core (Scheme 1) in order to reduce the overall electronic conjugation. Hence, due to the widespread applications of TAA donor structures in many fields of material science the strategy is of general interest for the design of novel donor–acceptor scaffolds. In addition, a distinct correlation between the molecular structures and the observed material properties is revealed.

2. Materials and methods

2.1. General information

All reagents and solvents were purchased from commercial suppliers and used without further purification. Anhydrous solvents were prepared by filtration through drying columns. Column chromatography was performed on silica 60 (Merk, 40–63 µm). NMR spectra were recorded on a Bruker Avance DRX-400 Spectrometer or a Bruker Avance 200 Spectrometer. High resolution mass spectra (HRMS) were obtained from a Thermo Scientific LTQ Orbitrap XL hybrid FTMS (Fourier Transform Mass Spectrometer) and Thermo Scientific MALDI LTQ Orbitrap interface; α-cyano-4-hydroxycinnamic acid was used as matrix. Thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements were carried out with a heating rate of 5 K/min in a flowing argon atmosphere (25 ml/min). For the TG measurements, a Netzsch TG 209 F9 Tarsus system with open aluminum oxide crucibles was used. For the DSC measurements, a Netzsch DSC 200 F3 Maia, working with aluminum pans with pierced lids, was employed. UV/VIS absorption and fluorescence emission spectra were recorded in DCM solutions (5 µM) with a Perkin Elmer Lambda 750 spectrometer and an Edinburgh FLS920, respectively. Time resolved experiments were obtained using a Quantel Brilliant tripled Nd-YAG laser (355 nm, 20 Hz repetition rate, pulse width ~5 ns). Spectra were measured using a SPEX 270 monochromator equipped with both photomultiplier and CCD. This set-up is controlled using a home-built Labview-based program which allows using different instruments such as photon counting, oscilloscope, and additional mechanical shutters. For the measurement of the triplet emission, a mechanical shutter was triggered by the pulsed laser. A pretrigger period of 0.5 ms was followed by a 1 ms aperture and a rest time of 300–500 ms allowed obtaining the measurements shown in the Supplementary Material. The slit of the monochromator was also opened further (up to 0.5 mm) to measure the triplet emission. Cyclic voltammetry was performed using a three electrode configuration consisting of a Pt working electrode, a Pt counter electrode and an Ag/AgCl reference electrode and a PGSTAT128 N, ADC164, DAC164, External, DIO48 potentiostat provided by Metrohm Autolab B.V. Measurements were carried out in a 0.5 mM solution in anhydrous DCM with Bu4NBF4 (0.1 M) as supporting electrolyte. The solutions were purged with nitrogen for 15 min prior to measurement. HOMO energy levels were calculated from the onset of the oxidation peaks. The onset potential was determined by the intersection of two tangents drawn at the background and the rising of the oxidation peaks.

2.2. Synthetic details

9-(4-Bromo-3-methyl-phenyl)-9H-carbazole (1) [23] and 2,5-bis(2-bromophenyl)-1,3,4-oxadiazole (8) [24] were synthesized according to previously published procedures whereas 1-fluoro-2-methyl-4-nitrobenzene (3) was
purchased by Apollo Scientific and used without further purification.

2.2.1. 9-[3-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-9H-carbazole (2)

The synthesis of 2 was accomplished analogously to published procedures [25]. To a solution of 9-(4-bromo-3-methylphenyl)-9H-carbazole (1) (4.37 g, 13.0 mmol, 1.00 eq.) in anhydrous THF (45 ml) under argon atmosphere n-BuLi (6.24 ml, 15.6 mmol, 1.20 eq., 2.5 M in hexanes) was added dropwise at −78 °C. Subsequently the reaction mixture was stirred at −80 °C for 1 h before Pinbop® (2.90 g, 15.6 mmol, 1.20 eq.) was added and the reaction was allowed to warm to room temperature slowly. After stirring overnight the solvent was removed under reduced pressure and the residue was partitioned between aqueous HCl (1N) and DCM. The aqueous phase was extracted with DCM, the combined organic layers were washed with H2O, dried over anhydrous Na2SO4, and concentrated under reduced pressure. The crude product was purified by column chromatography (light petroleum:DCM 70:30 → 50:50) yielding 5 (6.07 g, 22.3 mmol, 76%) as orange solid. 1H NMR (200 MHz, CD2Cl2): δ = 8.17 (d, J = 7.6, 1.2, 0.8 Hz, 2H), 7.41 (d, J = 8.1, 7.2, 1.3 Hz, 2H), 7.27 (d, J = 7.6, 7.2, 1.2 Hz, 2H), 7.13–7.05 (m, 3H), 6.76–6.66 (m, 2H), 3.90 (bs, 2H), 1.83 (s, 3H) ppm. 13C NMR (50 MHz, CD2Cl2): δ = 147.8 (s), 142.2 (s), 138.8 (s), 130.5 (d), 126.6 (s), 126.3 (d), 123.3 (s), 120.7 (d), 119.8 (d), 117.5 (d), 113.9 (d), 110.3 (d), 17.8 (q) ppm. Calculated: m/z 272.13080 [M]+, 273.13862 [M+H]+. Found: MS (MALDI): m/z 272.13162 [M]+, 273.13845 [M+H]+.

2.2.2. 9-(2-Methyl-4-nitrophenyl)-9H-carbazole (4)

The synthesis of 4 was done analogously to a published procedure [26]. Carbazole (8.36 g, 50.0 mmol, 1.00 eq.) and K2CO3 (7.60 g, 55.0 mmol, 1.10 eq.) were suspended in anhydrous DMAc (100 ml) and cyclohexane (38 ml) in a 250-ml three necked flask equipped a Dean–Stark trap. The mixture was heated to 100 °C for 3.5 h under argon atmosphere. After complete removal of water, the residual cyclohexane was distilled off and 1-fluoro-2-methyl-4-nitrobenzene (3) (8.53 g, 55.0 mmol, 1.10 eq.) was added. Then the mixture was heated to reflux for 2.5 h before hydrochloric acid (180 ml, 1 M) was added, leading to the formation of a yellow precipitate. The reaction mixture was filtered and the crude product was purified by crystallization of a yellow precipitate. The reaction mixture was stirred at 80 °C for 3.5 h under argon atmosphere. After stirring overnight the solvent was removed under reduced pressure and the residue was partitioned between aqueous Na2SO4 solution, dried over anhydrous Na2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography (light petroleum:DCM 70:30 → 50:50) yielding 6 (3.43 g, 9.0 mmol, 44%) was obtained after column chromatography (light petroleum:DCM 100:0 → 98:2) followed by crystallization from EtOH as white solid. 1H NMR (200 MHz, CD2Cl2): δ = 8.18 (d, J = 7.5, 1.1, 0.8 Hz, 2H), 7.89 (d, 1.8 Hz, 1H), 7.62 (d, J = 8.2, 2.0 Hz, 1H), 7.42 (d, J = 8.0, 7.3, 1.1 Hz, 2H), 7.30 (d, J = 7.5, 7.3, 1.0 Hz, 2H), 7.13 (d, J = 8.2, 1.8 Hz, 1H), 7.05 (d, J = 8.0, 1.0, 0.8 Hz, 2H), 1.93 (s, 3H) ppm. 13C NMR (50 MHz, CD2Cl2): δ = 141.4 (s), 141.1 (d), 140.4 (s), 137.1 (d), 136.5 (s), 131.6 (d), 126.6 (d), 123.6 (s), 120.8 (d), 120.3 (d), 110.2 (d), 94.7 (s), 17.6 (q) ppm. Calculated: m/z 383.01654 [M]+. Found: MS (MALDI): m/z 383.01771 [M]+.

2.2.3. 9-(2-Methyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-9H-carbazole (7)

Compound 7 was synthesized analogously to 2. Starting from 6 (3.09 g, 8.0 mmol, 1.00 eq.), n-BuLi (3.84 ml, 9.6 mmol, 1.20 eq.) and Pinbop® (1.79 g, 9.6 mmol, 1.20 eq.) 7 (2.07 g, 5.4 mmol, 67%) was isolated as white crystals after crystallization from EtOH. 1H NMR (200 MHz, CD2Cl2): δ = 8.17 (d, J = 7.5, 1.2, 0.8 Hz, 2H), 7.92 (d, J = 0.8 Hz, 1H), 7.81 (d, J = 7.7, 0.8 Hz, 1H), 7.45–7.33 (m, 3H), 7.27 (d, J = 7.5, 7.4, 0.9 Hz, 2H), 7.03 (d, J = 8.0, 0.9, 0.8 Hz, 2H), 1.98 (s, 3H), 1.39 (s, 12H) ppm. 13C NMR (50 MHz, CD2Cl2): δ = 141.5 (s), 139.2 (s), 138.6 (d), 137.0 (s), 134.1 (d), 129.0 (d), 126.5 (d), 123.6 (s), 120.8 (d), 120.1 (d), 110.3 (d), 84.6 (s), 25.3 (q), 17.8 (q) ppm (C-B was not detected). Calculated: m/z 383.02511 [M]+. Found: MS (MALDI): m/z 383.02614 [M]+.
2.2.5. 9,9’-[(1,3,4-Oxadiazole-2,5-diylbis[2-methyl-1,1’-biphenyl]-2,4-diyl][bis[9H-carbazole]} (o-2MPCzPOXD)

o-2MPCzPOXD was synthesized using standard Suzuki cross-coupling conditions [29]. Dibromide 8 (0.76 g, 2.0 mmol, 1.00 eq.), 2 (1.92 g, 5.0 mmol, 2.50 eq.), K₂CO₃ (5 ml, 2 M aqueous solution) and Pd(PPh₃)₄ (0.12 g, 0.1 mmol, 0.05 eq.) were added to degased THF (40 ml) under argon counterflow. The mixture was heated to reflux under argon atmosphere until full conversion (TLC), poured on H₂O and repeatedly extracted with DCM. The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo after filtration. o-2MPCzPOXD (0.70 g, 1.0 mmol, 48%) was isolated after column chromatography (light petroleum:DCM 70:30) as white solid. 

H NMR (400 MHz, CD₂Cl₂): δ = 8.16 (d, J = 7.8 Hz, 4H), 7.88–7.83 (m, 2H), 7.66–7.61 (m, 2H), 7.47–7.27 (m, 22H), 2.10–2.09 (m, 6H) ppm. 

13C NMR (100 MHz, CD₂Cl₂): δ = 165.1 (s), 165.0 (s), 141.4 (s), 141.1(9) (s), 141.1(5) (s), 140.3(2) (s), 140.2(5) (s), 138.6 (s), 138.5 (s), 137.5 (s), 131.9 (d), 131.8(7) (d), 131.8(3) (d), 131.3 (d), 131.1 (d), 129.7 (d), 129.6 (d), 128.7 (d), 128.5(5) (d), 128.5(0) (d), 126.5 (d), 124.6 (d), 124.5 (d), 123.8(2) (s), 123.8(1) (s), 123.7(8) (s), 120.7 (d), 120.4 (d), 110.4(2) (d), 110.3(7) (d), 20.5 (q), 20.4 (q) ppm (due to high rotational barriers induced by the methyl groups, signals from two conformational isomers were detected). 

Calculated: m/z 732.28836 [M⁺], 732.29619 [M⁺]+[Na⁺]. Found: MS (MALDI): m/z 732.28880 [M⁺]⁺, 732.29514 [M⁺]+[Na⁺].

2.2.6. 9,9’-[(1,3,4-Oxadiazole-2,5-diylbis[3-methyl-1,1’-biphenyl]-2,4-diyl][bis[9H-carbazole]} (o-3MPCzPOXD)

o-3MPCzPOXD was synthesized analogously to o-2MPCzPOXD. Starting from 8 (0.65 g, 1.7 mmol, 1.00 eq.), 7 (1.63 g, 4.25 mmol, 2.50 eq.), K₂CO₃ (4.25 ml, 2 M aqueous solution) and Pd(PPh₃)₄ (0.10 g, 0.1 mmol, 0.05 eq.) o-3MPCzPOXD (1.02 g, 1.4 mmol, 82%) was isolated after column chromatography (light petroleum:DCM 50:50) as white solid. 

H NMR (400 MHz, CD₂Cl₂): δ = 8.14 (d, J = 7.9 Hz, 4H), 7.98 (d, J = 7.6 Hz, 2H), 7.76 (dd, J = 7.6, 7.6, 2H), 7.63–7.58 (m, 4H), 7.32–7.24 (m, 12H), 7.17 (dd, J = 8.0, 1.6 Hz, 2H), 6.78 (d, J = 7.9 Hz, 4H), 1.86 (s, 6H) ppm. 

13C NMR (100 MHz, CD₂Cl₂): δ = 165.7 (s), 141.9 (s), 141.5(8) (s), 141.5(7) (s), 137.6 (s), 135.8 (s), 132.4 (d), 132.1 (d), 131.5 (d), 130.6 (d), 129.3 (d), 128.8 (d), 128.4 (d), 126.6 (d), 123.5 (s), 123.4 (s), 120.8 (d), 120.1 (d), 110.1 (d), 178 (q) ppm. Calculated: m/z 732.28836 [M⁺], 733.29619 [M⁺]+[Na⁺], 755.27813 [M⁺]+[Na⁺]. Found: MS (MALDI): m/z 732.28983 [M⁺]⁺, 733.29548 [M⁺]+[Na⁺], 755.27905 [M⁺]+[Na⁺].

2.3. Computational details

All (TD)DFT computations were performed using the Gaussian 09 package, revision D.01 [30]. Density functional theory (DFT) and time-dependent (TD)DFT calculations were performed using the Becke three parameters hybrid functional with Lee–Yang–Perdew correlation (B3LYP) [31,32], in combination with Pople basis sets (6-31G*, 6-31+G*) [33]. Geometry optimizations were performed in gas phase and without symmetry constraints. For the calculation of HOMO/LUMO levels, ground state (S₀) geometries were optimized applying the 6-31+G* basis set. The determination of triplet energy (Eₜ) was achieved by the calculation of the T₁ excitation energy applying TDDFT level and the 6-31+G* basis set to a S₀ geometry optimized at DFT level using the 6-31G* basis set. To calculate the contribution of the molecular subunits to HOMO and LUMO levels, wavefunctions of the optimized geometries were decomposed to atomic level (using Hirshfeld partition by percentage) [34] and then summed up according to relevant functional structure moieties. Orbital plots were generated using GaussView [35].

2.4. Single crystal diffraction

Crystals of 2, 4, 7, o-2MPCzPOXD and o-3MPCzPOXD suitable for single crystal diffraction were selected under a polarizing microscope, embedded in perfluorinated oil and attached to Kapton™ mounts. Intensity data were collected in a dry stream of nitrogen at 100 K on a Bruker KAPPA APEX II diffractometer system. Data were reduced using SMART-Plus [36] and an empirical absorption correction using the multi-scan approach implemented in SADABS [36] was applied. The crystal structures were solved by charge-flipping implemented in SUPERFLIP [37] and refined against F with the JANA2006 [38] software package. The non-H atoms were refined with anisotropic displacement parameters (ADPs). The H atoms were placed at calculated positions and refined as riding on the parent C atoms. Both methyl groups in o-2MPCzPOXD and o-3MPCzPOXD were modeled as disordered around two different positions. The lengths of the C–C bonds connecting the disordered methyl groups to the remaining molecule were restrained to 1.510(1) Å. The atoms of one carbazole and the connected benzene in o-2MPCzPOXD featured highly anisotropic displacement parameters indicating disorder. Nevertheless the atoms could not be resolved into distinct positions. Instead, the atoms of the carbazole were refined with anharmonic ADPs leading to distinctly improved residuals.

2.5. Device fabrication and measurement

All the devices were fabricated on glass substrates pre-coated with 180 nm indium tin oxide (ITO) with a sheet resistance of 10 Ω per square. The ITO substrates were degreased in an ultrasonic solvent bath and then dried at 120 °C for 30 min. Before loaded into the deposition chamber, the ITO surface was treated with UV–ozone for 15 min. All layers were grown in succession by thermal evaporation without breaking the vacuum (<5 × 10⁻⁴ Pa). The device structures were described in the text. The organic materials and metal oxide were evaporated at the rate in a range of 1–2 Å/s, and the metals were evaporated at the rate of 8–10 Å/s. The overlap between ITO and Al electrodes was 4 mm × 4 mm which is the active emissive area of the devices. Current–voltage–brightness characteristics were measured by using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured by a Spectrascan PR650 spectrophotometer. EQEs were...
calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution. All the measurements were carried out in ambient atmosphere.

3. Results and discussion

3.1. Molecular design

The concept of introducing sterically demanding groups in order to tune intramolecular torsion angles to achieve high $E_T$-values was applied to uni- and bipolar host materials [21,39–43]. However, the modification of torsion angles inevitably influences not only triplet but also singlet states and thus may lead to undesirably increased singlet–triplet splitting due to reorganization of the molecular orbitals [39]. Recently, Monkman et al. showed that by thoughtful and selective placement of sterically demanding groups this effect can be limited [44]. In this work we aim to increase the $E_T$ while retaining reasonably low singlet energy values by the introduction of methyl groups to the molecular scaffold of o-PCzPOXD. Based on theoretical calculations we chose to attach the methyl groups to the phenyl ring of the phenylcarbazole fragment (Scheme 1). Due to the placement of the methyl groups between the carbazole donor and the oxadiazole acceptor the overall conjugation should be decreased while the location of HOMO and LUMO levels should remain on the respective molecular subunit in order to preserve the original electronic structure.

3.2. Synthesis

The synthetic approach toward target host materials o-2MPCzPOXD and o-3MPCzPOXD, which relies on Pd-catalyzed Suzuki cross-coupling reactions as key step, is outlined in Scheme 2. Whereas a synthetic protocol toward bromide 1 is available, 6 was synthesized starting from commercially available 1-fluoro-2-methyl-4-nitrobenzene (3). Conversion of 3 with carbazole yielded the corresponding nitro compound 4, which was subsequently reduced to amine 5. Iodo-compound 6 was obtained by diazotization of 5 and treatment of the diazonium intermediate with KI. Lithiation of 1 and 6 and conversion of the organo-lithium-intermediates with isopropyl pinacol borate yielded the corresponding pinacol boronic esters 2 and 7. In the final step the boronic esters were reacted with dibromide 8 in a Suzuki cross-coupling reaction giving target molecules o-2MPCzPOXD and o-3MPCzPOXD in 48% and 82% yield.

Scheme 2. Synthesis of o-2MPCzPOXD and o-3MPCzPOXD: (i) (a) THF, –78 °C, n-BuLi (1.2 eq.), (b) isopropyl pinacol borate (1.2 eq.); (ii) (a) DMAC/cyclohexane (5:2), carbazole (1.0 eq.), K$_2$CO$_3$ (1.1 eq.), reflux; (b) 3 (1.1 eq.) reflux; (iii) EtOH, SnCl$_2$·2H$_2$O (3.5 eq.), reflux; (iv) (a) H$_2$O, HCl, NaNO$_2$ (1.05 eq.), –5 °C, (b) KI (1.1 eq.); (v) boronic acid ester 2/7 (2.5 eq.), K$_2$CO$_3$ (5.0 eq., 2 M aq.), Pd(PPh$_3$)$_2$I$_2$ (5 mol%), THF, reflux.
yields, respectively. The steric demand of the methyl group next to the reaction center hampers the formation of o-2MPCzPOXD resulting in distinctly lower yields. The molecular structure of all newly synthesized compounds was confirmed by $^1$H and $^{13}$C NMR measurements and high resolution mass spectroscopy. Unexpectedly two signals for the methyl group in o-2MPCzPOXD were observed in $^1$H NMR spectra. Moreover, two distinct signals were found for a majority of the carbon atoms in $^{13}$C NMR measurements indicating that the interconversion of both possible conformational diastereomers with the methyl-groups cis or trans with respect to the plane of the POXD core is significantly hindered. Furthermore, aromatic $^1$H NMR spectra of the host materials (Fig. 1) was determined from single crystal data. Although single crystals feature packing effects, the results can be extrapolated to amorphous materials and even solutions.

As already described for o-PCzPOXD [50] the PCz moieties are located cis relative to the POXD cores for all compounds. Different conformational isomers of o-2MPCzPOXD as well as o-3MPCzPOXD were observed in the difference Fourier maps and, therefore, the methyl groups were modeled as disordered around two different positions. The two possible positions of the methyl groups (C21 and C28 respectively) are unequally occupied. In single crystals of o-3MPCzPOXD atomic sites C21 (94.8(3)%), C28 (87.7(5)%), which are located cis with respect to the plane of the POXD core, are preferably occupied compared to C21' (5.2(3)%) and C28' (12.3(5)%). This finding can be explained by the close vicinity of C21 and C28' within the molecular structure leading to unfavorable interactions. Furthermore, the incorporation of not only the conformational cis-isomer but also of the trans-isomers can be concluded from the diverging site occupancies of C21 and C28. Similar observations were made for o-2MPCzPOXD crystals in which C21 (77.5(5)%), C28 (79.5(5)%) are more frequently occupied compared to C21' (22.5(5)%), C28' (20.5(5)%). However, the diverging occupancies are within the error of measurement. A difference of 2% of a carbon atom corresponds to approximately 0.1 electrons and the presence of the trans-isomer of o-2MPCzPOXD can thus not be concluded from the obtained data.

In case of o-3MPCzPOXD the torsion angles $\Phi^1$ of the least squares planes of the carbazole moieties and the PCz-benzenes are significantly increased (79.34(4)°/82.35(4)°) compared to o-PCzPOXD (57.68(5)°/56.38(5)°) as result of the methyl groups next to the carbazoles. In contrast, the variation of $\Phi^1$ for o-2MPCzPOXD (58.69(8)°/58.26(15)°) is negligible compare to o-PCzPOXD. The inverse situation is observed for $\Phi^2$, which is enlarged in o-2MPCzPOXD (64.44(11)°/66.97(12)°) versus o-PCzPOXD (54.12(6)°/53.49(6)°), whereas no change was observed for o-3MPCzPOXD (54.18(5)°/51.85(5)°). Moreover, altered torsion angles $\Phi^3$ were found for o-2MPCzPOXD, whereupon one is smaller (19.48(12)°) and one larger (43.83(12)°) compared to o-PCzPOXD (32.44(8)°/33.63(8)°) and o-3MPCzPOXD (38.36(6)°/32.34(6)°). The increased respective torsion angles of the aromatic moieties next to the methyl-groups in o-2MPCzPOXD and o-3MPCzPOXD significantly reduce the overall conjugation of the $\pi$-system and, in particular, the conjugation between the carbazole donors and the POXD acceptors. Therefore, decreased intramolecular charge transfer and, as a result, higher triplet energies are expected for the methyl-modified host materials.

### 3.3. Molecular structures

The influence of additional methyl-groups on the torsion angles $\Phi^1$, $\Phi^2$ and $\Phi^3$ (Scheme 3, Table 1) in the molecular structure of the host materials (Fig. 1) was determined from single crystal data. Although single crystals feature packing effects, the results can be extrapolated to amorphous materials and even solutions.

As already described for o-PCzPOXD [50] the PCz moieties are located cis relative to the POXD cores for all compounds. Different conformational isomers of o-2MPCzPOXD as well as o-3MPCzPOXD were observed in the difference Fourier maps and, therefore, the methyl groups were modeled as disordered around two different positions. The two possible positions of the methyl groups (C21 and C28 respectively) are unequally occupied. In single crystals of o-3MPCzPOXD atomic sites C21 (94.8(3)%), C28 (87.7(5)%), which are located cis with respect to the plane of the POXD core, are preferably occupied compared to C21' (5.2(3)%) and C28' (12.3(5)%). This finding can be explained by the close vicinity of C21 and C28' within the molecular structure leading to unfavorable interactions. Furthermore, the incorporation of not only the conformational cis-isomer but also of the trans-isomers can be concluded from the diverging site occupancies of C21 and C28. Similar observations were made for o-2MPCzPOXD crystals in which C21 (77.5(5)%), C28 (79.5(5)%) are more frequently occupied compared to C21' (22.5(5)%), C28' (20.5(5)%). However, the diverging occupancies are within the error of measurement. A difference of 2% of a carbon atom corresponds to approximately 0.1 electrons and the presence of the trans-isomer of o-2MPCzPOXD can thus not be concluded from the obtained data.

In case of o-3MPCzPOXD the torsion angles $\Phi^1$ of the least squares planes of the carbazole moieties and the PCz-benzenes are significantly increased (79.34(4)°/82.35(4)°) compared to o-PCzPOXD (57.68(5)°/56.38(5)°) as result of the methyl groups next to the carbazoles. In contrast, the variation of $\Phi^1$ for o-2MPCzPOXD (58.69(8)°/58.26(15)°) is negligible compare to o-PCzPOXD. The inverse situation is observed for $\Phi^2$, which is enlarged in o-2MPCzPOXD (64.44(11)°/66.97(12)°) versus o-PCzPOXD (54.12(6)°/53.49(6)°), whereas no change was observed for o-3MPCzPOXD (54.18(5)°/51.85(5)°). Moreover, altered torsion angles $\Phi^3$ were found for o-2MPCzPOXD, whereupon one is smaller (19.48(12)°) and one larger (43.83(12)°) compared to o-PCzPOXD (32.44(8)°/33.63(8)°) and o-3MPCzPOXD (38.36(6)°/32.34(6)°). The increased respective torsion angles of the aromatic moieties next to the methyl-groups in o-2MPCzPOXD and o-3MPCzPOXD significantly reduce the overall conjugation of the $\pi$-system and, in particular, the conjugation between the carbazole donors and the POXD acceptors. Therefore, decreased intramolecular charge transfer and, as a result, higher triplet energies are expected for the methyl-modified host materials.

### 3.4. Theoretical calculations

To gain insight on the electronic properties of the materials on the molecular level, studies applying density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed. According to the DFT calculations, absolute HOMO/LUMO values are in a small range of 5.50–5.55/2.02–2.04 eV, which correlates well with the experimental data (Table 3). Contour plots for o-PCzPOXD, o-2MPCzPOXD and o-3MPCzPOXD, comparing the HOMO.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characteristic torsion angles of host materials.</th>
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<tbody>
<tr>
<td>$\Phi^1$</td>
<td>o-PCzPOXD</td>
</tr>
<tr>
<td></td>
<td>57.68(5)°/56.38(5)°</td>
</tr>
<tr>
<td>$\Phi^2$</td>
<td>54.12(6)°/53.49(6)°</td>
</tr>
<tr>
<td>$\Phi^3$</td>
<td>32.44(8)°/33.63(8)°</td>
</tr>
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</table>

* Inexact because the benzene and carbazole moieties are disordered.
and LUMO distributions, are depicted in Fig. 2. As expected, HOMO levels are mainly located at one of the carbazole (Cz) moieties and the adjacent benzene (P) linker, whereas LUMOs reside at the POXD core. The spatial separation of the frontier orbitals was found to be more efficiently realized in the methyl substituted derivatives. To get a better quantitative description of this separation, the contribution of the different structural elements (Cz, P, POXD, P’, Cz’) to the HOMO and LUMO was calculated. The results are given in Table 2. Comparing o-2MPCzPOXD to o-PCzPOXD the HOMO distribution is nearly unchanged. For both compounds approximately 89% of the electron density is located at one carbazole moiety and 10–11% are situated at the benzene linker. In contrast the LUMO distribution is modified by the additional methyl group and is distinctly better confined at the POXD motive (PCz: 89%; 2MPCz: 95%). Notably these findings directly correlate to the increased torsion angle $\Phi^2$ of o-2MPCzPOXD. Whereas the phenylcarbazole subunit and thus the HOMO distribution is essentially unaffected by the methyl group the torsion angle $\Phi^2$ between the phenylcarbazole donor and POXD acceptor is increased, confining the LUMO to the POXD core. Analogously, the LUMO distribution is nearly unchanged in o-3MPCzPOXD compared to o-PCzPOXD, whereas the HOMO is basically restricted to the carbazole moiety (PCz: 89%; 3MPCz: 95 %) owing to the increased torsion angle $\Phi^1$. Therefore, the additional methyl groups do not cause a reorganization of the molecular orbitals but the enhanced torsion angles lead to a better confinement of the HOMO and LUMO distribution to the corresponding molecular subunit. Due to the better spatial resolution higher $E_T$ are expected for o-2MPCzPOXD and o-3MPCzPOXD and indeed the calculated $E_T$ values increase from o-PCzPOXD (2.83 eV) to o-3MPCzPOXD (2.91 eV) and o-2MPCzPOXD (2.92 eV).

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>HOMO (%)</th>
<th>LUMO (%)</th>
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<tbody>
<tr>
<td></td>
<td>PCz 2MPCz 3MPCz</td>
<td>PCz 2MPCz 3MPCz</td>
</tr>
<tr>
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<td>89</td>
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</tr>
<tr>
<td>Cz’</td>
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</table>

### Table 3

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<tr>
<th></th>
<th>Tg/Tm/Td (°C)</th>
<th>opt. BG (eV)$^{bc}$</th>
<th>$\lambda_{PL,max}$ (nm)$^c$</th>
<th>HOMO/LUMO (eV)</th>
<th>$E_T$ (eV)</th>
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<tr>
<td></td>
<td>Exp.$^d$</td>
<td>Cal.$^e$</td>
<td>Exp.$^f$</td>
<td>Cal.$^g$</td>
<td></td>
</tr>
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<td>o-PCzPOXD [22]</td>
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<td>428</td>
<td>-5.64/-2.12</td>
<td>-5.55/-2.04</td>
</tr>
<tr>
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<td>128/238/401</td>
<td>3.53</td>
<td>427</td>
<td>-5.60/-2.07</td>
<td>-5.50/-2.02</td>
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<tr>
<td>o-3MPCzPOXD</td>
<td>n.o.$^h$</td>
<td>3.57</td>
<td>420</td>
<td>-5.66/-2.09</td>
<td>-5.55/-2.02</td>
</tr>
</tbody>
</table>

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* Determined from DSC/TGA analysis.
* Determined from the absorption onset.
* Measured in DCM (5 μM) at r.t.
* HOMO levels were calculated from the onset of the oxidation peak. CV-measurements were carried out in a 0.5 mM solution in anhydrous DCM with Bu$_4$NBF$_4$ (0.1 M) as supporting electrolyte; LUMO levels were calculated from HOMO levels and the optical band gap.
* Exp.$^d$ determined applying density functional theory level (B3LYP/6-311+G*).
* Cal.$^e$ estimated from the highest energy vibronic transition in toluene at 77 K.
* Cal.$^f$ calculated applying time-dependent density functional theory level (B3LYP/6-311+G*).
* Not observed.
3.5. Photo-physical properties

In order to investigate the impact of the additional methyl groups in o-2MPCzPOXD and o-3MPCzPOXD on the photo-physical properties UV/VIS absorption as well as fluorescence and phosphorescence emission spectra have been recorded (Fig. 3). Absorption spectra of the methyl substituted materials and o-PCzPOXD are highly similar. All compounds show a sharp absorption peak at 290 nm which can be attributed to transitions of the carbazole moiety \(\varepsilon/(1 \text{ mol}^{-1} \text{ cm}^{-1}) = \approx 57,000 \) (o-PCzPOXD), \(\approx 50,000 \) (o-2MPCzPOXD), \(\approx 43,000 \) (o-3MPCzPOXD). Longer wavelength absorption results from charge transfer transition from electron-rich carbazole to electron-withdrawing oxadiazole [52]. For o-2MPCzPOXD and o-3MPCzPOXD the intensity of this transition is distinctly decreased compared to o-PCzPOXD indicating a decreased degree of charge transfer. The absorption onset of the newly developed materials is slightly blue shifted from o-PCzPOXD (353 nm) to o-2MPCzPOXD (351 nm) and o-3MPCzPOXD (347 nm), corresponding to an optical band gap of 3.51, 3.53 and 3.57 eV.

Due to the slight electron-donating nature of the methyl group, methyl substituted phenylcarbazoles are expected to be stronger electron-donors compared to plain phenylcarbazole. Therefore, applying the new MPCz donors to the oxadiazole acceptor, slightly red shifted emission may be expected. However, this effect is overcompensated by the increased molecular torsion induced by the steric demand of the methyl substituents leading to slightly blue shifted emission maxima of o-2MPCzPOXD (427 nm) and o-3MPCzPOXD (420 nm) compared to o-PCzPOXD (428 nm).

Strikingly, this effect is much more pronounced in phosphorescent emission spectra of methyl-substituted host materials and the highest vibronic sub-bands are blue shifted from o-PCzPOXD (473 nm) to o-2MPCzPOXD (466 nm) and o-3MPCzPOXD (454 nm), corresponding to \(E_T\) of 2.62, 2.66 and 2.73 eV. Therefore, the \(E_T\) of the newly developed materials was raised by 0.11 eV, whereas the HOMO-LUMO gap was increased by only 0.06 eV and thus the singlet–triplet splitting even slightly reduced by 0.05 eV. Notably the increase of \(E_T\) from o-PCzPOXD to o-2MPCzPOXD and o-3MPCzPOXD correlates with the increased torsion angles as discussed in the crystallographic section. These results suggest that the methyl substituted...
host materials are distinctly better suited for light blue emitting FIrpic, since the $E_g$ of the target materials is raised over the crucial value of 2.65 eV, allowing for an exothermic energy transfer from the host to the dopant. Accordingly, the effect on driving voltages of the PHOLED devices is expected to be negligible, due to the low overall increase of the HOMO–LUMO gap. All photo-physical characteristics are summarized in Table 3.

3.6. Thermal properties

The thermal and morphological stability (Table 3) of o-2MPCzPOXD and o-3MPCzPOXD were investigated by DSC and TGA (Supplementary Material Figs. S 15 and 16). The decomposition temperatures ($T_d$ – corresponding to the temperatures of 5% mass loss) of o-2MPCzPOXD and o-3MPCzPOXD are 401 °C and 415 °C and therefore slightly higher compared to o-PCzPOXD (395 °C) [22]. The glass transition temperature ($T_g$) of o-2MPCzPOXD (128 °C) was found to be similar to that of o-PCzPOXD (125 °C) [22]; no glass transition was detected for o-3MPCzPOXD but exothermic crystallization was observed at 212 °C during cooling.

3.7. Electro-chemical properties

The electrochemical properties (Table 3) of the newly developed materials were studied by cyclic voltammetry (CV). Both materials exhibit irreversible oxidation (Fig. 4) typically for 3,6-unprotected carbazole materials [53]. The HOMO levels were calculated from the onset of the oxidation waves relative to ferrocene and are located at −5.60 and −5.66 eV for o-2MPCzPOXD and o-3MPCzPOXD, respectively. These values indicate no significant injection barrier for holes from the adjacent layers and are in a characteristic range for oxadiazole/carbazole-based bipolar materials [44,52]. Upon cathodic scans no reduction peaks were observed. Thus, the LUMO levels were calculated from the HOMOs and the onset of absorption and are located at −2.07 and −2.09 eV for o-2MPCzPOXD and o-3MPCzPOXD. These values deviate only slightly from the HOMO (−5.64 eV) and LUMO (−2.12 eV) of o-PcPOXD [22] revealing negligible influence of the additional methyl groups on the absolute location of the levels, as predicted by the theoretical calculations.

3.8. Electroluminescent properties

To investigate the bipolarity of the materials, hole-only devices (HODs; structure: ITO/MoO$_3$ (10 nm)/TCTA (20 nm)/POXD (40 nm)/TCTA (20 nm)/MoO$_3$ (10 nm)/Al) and electron-only devices (EODs; structure: ITO/LiF (1 nm)/TPBI (20 nm)/POXD (40 nm)/TPBI (20 nm)/LiF (1 nm)/Al) were fabricated. Current–voltage curves are given in Fig. 5. o-PcPOXD featured highly balanced charge carrier density. Despite similar charge carrier injection barriers the charge transport properties were distinctly less balanced for o-2MPCzPOXD and o-3MPCzPOXD. Hole current densities were slightly higher in HODs of o-2MPCzPOXD and o-3MPCzPOXD compared to o-PcPOXD. In contrast electron current densities in EODs decreased in the order o-PcPOXD > o-2MPCzPOXD > o-3MPCzPOXD.

The significantly lower electron current densities of o-2MPCzPOXD and o-3MPCzPOXD may be attributed to the additional methyl groups which are located in close vicinity above and below the POXD plane as can be seen in Fig. 1. The steric demand of these methyl groups may impede the intermolecular overlap of LUMO orbitals located on the POXD core and thus decrease the electron current density. However, more complex factors influencing the molecular arrangements and therefore charge transport properties of the molecules in film cannot be rule out.

In order to evaluate the applicability of o-2MPCzPOXD and o-3MPCzPOXD in comparison to o-PcPOXD as host materials in red, green and blue PHOLEDs, devices with the architecture of ITO/MoO$_3$/NPB (70 nm)/TCTA (5 nm)/ EML (10 nm)/TPBI (35 nm)/LiF/Al have been fabricated. The emissive layers consist of coevaporated hosts o-PcPOXD (I), o-2MPCzPOXD (II) or o-3MPCzPOXD (III) and red (R – 6% Ir(MDQ)$_2$acac), green (G – 8% Ir(ppy)$_3$) or blue (B – 12% FIrpic) guest emitter. NPB is used as hole transporting layer while TPBI is applied as electron transporting and hole blocking layer due to its low lying HOMO level [54–57]. Additionally a thin TCTA layer is inserted between the hole transporting and emitting layer in order to confine triplet excitons more effectively in the EML as result of a larger triplet energy of TCTA compared to NPB [55]. All
devices exhibited low turn-on voltages between 2.8 and 3.4 V. Current density–voltage–luminance and current efficiency–luminance–power efficiency charts are depicted in Fig. 6 and the key EL parameters of all devices are summarized in Table 4.

Among green devices GI-III exhibited the best performance with a maximum current efficiency (CE) of 54.0 cd A$^{-1}$, a maximum power efficiency (PE) of 47.8 lm W$^{-1}$ and a maximum external quantum efficiency (EQE) of 15.4%, whereas GI and GII showed comparable but slightly lower efficiency values. Most notably, the efficiency roll-off in GI-III was extremely low as already observed for other oxadiazole based bipolar host materials employing planarized arylamine donors [22]. At a practical brightness of 1000 cd m$^{-2}$ GI-III featured CE of 44.5–52.7 cd A$^{-1}$ corresponding to efficiency roll-offs of 0.7–2.4%. Even at a brightness of 5000 cd m$^{-2}$ the CE values were still as high as 41.3–46.5 cd A$^{-1}$ (roll-off: 7.8–13.9%). Devices RI-III displayed similar performance with CE_max of 20.3–15.9 cd A$^{-1}$, PE_max of 15.3–11.2 lm W$^{-1}$ and EQE_max of 12.8–11.4% whereupon the best results were acquired for RII. In analogy to green devices RI-III exhibited low efficiency roll-off of 25.8–27.9% at 5000 cd m$^{-2}$. In summary, o-PCzPOXD, o-2MPCzPOXD and o-3MPCzPOXD featured comparable
performance in red and green devices; no negative effects arise from the introduced methyl groups and, with the exception of G2, devices incorporating o-2MPCzPOXD and o-3MPCzPOXD showed slightly higher efficiency values compared to o-PCzPOXD. Most importantly, the power efficiency of devices employing o-2MPCzPOXD and o-3MPCzPOXD is not decreased as result of the slightly higher singlet band gap compared to o-PCzPOXD.

While red and green devices showed similar performance values the results for blue devices (FIrpic as phosphorescent emitter) are distinctly different. Significantly improved efficiencies were achieved in o-2MPCzPOXD and o-3MPCzPOXD based devices revealing an EQE max increase from 9.0% (o-PCzPOXD) to 11.5% (o-3MPCzPOXD) and 13.6% (o-2MPCzPOXD), which corresponds to an efficiency improvement of 27.8% and 51.1%, respectively. These findings are clearly attributed to the increased ET of o-2MPCzPOXD and o-3MPCzPOXD as result of the additional methyl groups and, thus, better confinement of triplet excitons on the phosphorescent emitter. Strikingly, for o-2MPCzPOXD this effect is even more pronounced at high brightness and BII exhibited EQE of 13.6% (+56.3% compared to o-PCzPOXD) at 1000 cd m⁻² and 11.9% (+67.6%) at 5000 cd m⁻². Furthermore, low efficiency roll-off was observed for BII-III. At 1000 cd m⁻² BII featured CE of 28.7 cd A⁻¹ (roll-off: 0.0%) whereas at 5000 cd m⁻² CE was still as high as 25.1 cd A⁻¹ (roll-off: 12.5%). Despite the higher ET of o-3MPCzPOXD BII showed slightly lower efficiencies compared to BII due to the low HOMO level of FIrpic (-5.8 eV). Thus, charge balance should play a dominated role regarding to device performance and the more balanced charge transport properties of o-2MPCzPOXD (Fig. 5) explains the better performance of the BII device (for energy level diagrams see Supplementary Material). Additionally the PE of both BII and BIII were significantly improved compared to BI at high brightness, which is of particular importance regarding the practical applicability of host materials in commercial devices. BII exhibits a CE of 18.8 lm W⁻¹ at 1000 cd m⁻² and 12.3 lm W⁻¹ at 5000 cd m⁻² displaying an improvement of 74.1% and 86.4% compared to o-PCzPOXD, respectively.

Although FIrpic is by far the most frequently used phosphorescent emitter for the characterization of new host materials, FIrpic emits in the sky-blue region. However, for the realization of full-color displays and white lighting with good color rendering index, high quality blue light is indispensable. Recent reports on FIr6 devices based on host materials [58] with relatively low ET compared to blue
emitting Flr6 ($E_g$: 2.72 eV) [59] encouraged us to investigate o-2MPCzPOXD and o-3MPCzPOXD as host materials for that purpose. Thus, devices BIV (o-2MPCzPOXD) and BV (o-3MPCzPOXD) with the architecture of ITO/MoO$_3$/NPB (70 nm)/TCTA (5 nm)/EML (10 nm)/TmPyPB (35 nm)/LiF/Al applying Flr6 as dopant have been fabricated. TmPyPB is applied as electron transporting layer due to its slightly higher $E_g$ (2.78 eV) compared to TPBI (2.74 eV) [7]. Current density–voltage–luminance and current efficiency–luminance–power efficiency curves are depicted in Fig. 7 and the key EL parameters of all devices are summarized in Table 4. Devices BIV and BV exhibited similar performance with CE$_{\text{max}}$ of 15.9 and 16.7 cd A$^{-1}$, PE$_{\text{max}}$ of 13.3 and 14.9 lm W$^{-1}$ and EQE$_{\text{max}}$ of 7.8% and 7.8%, respectively. Although these values are lower than previously reported efficiencies [58] the fabrication of Flr6 based devices BIV and BV demonstrates the broadened applicability of o-2MPCzPOXD and o-3MPCzPOXD as a result of sterically induced torsion.

4. Conclusion

The investigations reveal the strategic objective of tuning the triplet energy virtually independently from the singlet energy for the specific adjustment of material properties accompanied with PHOLED performance of bipolar host materials. The strategy of rational molecular design applying sterically induced torsion to raise triplet energies, which is of particular importance for high-energy emitters, has been demonstrated for carbazole–oxadiazole based o-PCzPOXD. As a result, the triplet energies were affected more pronouncedly compared to the singlet energy values in novel materials o-2MPCzPOXD and o-3MPCzPOXD leading to significantly improved device performances for blue devices while showing similar efficiencies for the green devices. Ongoing research will focus on molecular design concepts to more efficiently separate the tuning of triplet energies from the impact on singlet energy values and the adaptation to further donor–acceptor motives, which is of relevance for the functional organic materials community in general.

Acknowledgement

This work was supported in part by the Swiss National Science Foundation, the Vienna University of Technology research funds and the Austrian Federal Ministry of Science, Research and Economy. The X-ray center of the Vienna University of Technology is acknowledged for providing access to the single-crystal diffractometer. G. Fafilek is acknowledged for support regarding the CV measurements and K. Föttinger for assisting the photo-physical analysis.

Appendix A. Supplementary material

Supplementary data ($^{1}$H,$^{13}$C NMR spectra, TGA/DSC measurements, electro- and photoluminescence spectra and X-ray crystallography) associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.orgel.2014.11.027.

References


[42] C2H9BNO5, M = 383.3, monoclinic, Cc, a = 21.28(2) Å, b = 14.46(2) Å, c = 12.06(1) Å, α = 90.16(1)°, β = 90.37(1)°, γ = 90.07(1)°, R1 = 0.0669, R1 (all data) = 0.0425; CCDC reference number 1008518.

[43] C2H10BNO5, M = 383.3, monoclinic, P21, a = 21.28(2) Å, b = 14.46(2) Å, c = 12.06(1) Å, α = 90.16(1)°, β = 90.37(1)°, γ = 90.07(1)°, R1 = 0.0669, R1 (all data) = 0.0425; CCDC reference number 1008521.

[44] C2H9BNO5, M = 383.3, monoclinic, P21, a = 21.28(2) Å, b = 14.46(2) Å, c = 12.06(1) Å, α = 90.16(1)°, β = 90.37(1)°, γ = 90.07(1)°, R1 = 0.0669, R1 (all data) = 0.0425; CCDC reference number 1008523.

[45] C2H9BNO5, M = 383.3, monoclinic, P21, a = 21.28(2) Å, b = 14.46(2) Å, c = 12.06(1) Å, α = 90.16(1)°, β = 90.37(1)°, γ = 90.07(1)°, R1 = 0.0669, R1 (all data) = 0.0425; CCDC reference number 1008524.

[46] (1) C2H9BNO5, M = 383.3, monoclinic, Cc, a = 21.28(2) Å, b = 14.46(2) Å, c = 12.06(1) Å, α = 90.16(1)°, β = 90.37(1)°, γ = 90.07(1)°, R1 = 0.0669, R1 (all data) = 0.0425; CCDC reference number 1008525.