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Synthesis and characterization of tris-(5-amino-8-hydroxyquinoline) aluminum complexes and their use as anode buffer layers in inverted organic solar cells†

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Tris-(8-hydroxyquinoline)aluminum (Alq₃) and its derivatives have been studied as light-emitting materials in organic light emitting diodes (OLEDs) and recently also as buffer layer materials in inverted organic solar cells based on the well-known bulk-heterojunction (BHJ) of poly(3-hexylthiophene) (P3HT) and C₆₁-butyric acid methyl ester (PCBM). Due to the positions of the highest occupied molecular orbital (HOMO) energy levels of P3HT and Alq₃, an extraction barrier for the photogenerated holes to escape the device is created. To reduce the height of the barrier, the position of the Al-complex HOMO level can be elevated by attaching different substituents on the 8-hydroxyquinoline ligand. In this study three new tris-(5-amino-8-hydroxyquinoline)aluminum complexes with electron donating amino substituents were synthesized, characterized and used as anode buffer layers in inverted organic solar cells. Results of the performed spectroscopic and electrochemical studies confirmed that 5-amino substitution of the hydroxyquinoline ligand is directly correlated with the position of HOMO levels in the complexes while lowest unoccupied molecular orbital (LUMO) levels remained unaffected. Although the complexes exhibit extremely low emission properties compared to the parent Alq₃, they performed nicely as charge transporting buffer layers between the photoactive layer and the gold anode in the organic solar cells.

1. Introduction

Alq₃ is an organometallic complex consisting of three 8-hydroxyquinoline ligands coordinated to aluminum. By attaching different electron-withdrawing or -donating substituents on the 8-hydroxyquinoline ligands, the properties of the complex, such as solubility, emission wavelength, and HOMO and LUMO energy levels, can be modified. Therefore, Alq₃ derivatives have become an interesting research target for different organic electronic applications. The parent Alq₃ has been studied as an electron-transporting and light emitting material since Tang and VanSlyke reported¹ for the first time on the use of Alq₃ in organic light emitting diodes (OLEDs). Recently, the possibilities of applying Alq₃ as a buffer layer in organic solar cells have been investigated. As a buffer layer, Alq₃

is believed to obstruct the permeation of oxygen and moisture into the photoactive layer, thus increasing the stability and lifetime of the organic solar cells.² A layered organic solar cell with Alq₃/Au as a cathode showed a 60-fold enhancement in efficiency, from 0.01% to 0.60%, compared to a cell without Alq₃.³

Studies have shown that chemical tailoring of the ligand backbone can produce Alq₃ derivatives, which can exhibit tremendously higher photoluminescence (PL) quantum yields and better electroluminescence properties compared to the parent Alq₃.⁴ In addition, an inverted organic solar cell equipped with the Alq₃ derivative, tris-(4-pyrazolyl-8-hydroxyl-quinoline) aluminum, as an anode buffer layer showed more than 30% improvement in the efficiency compared to that with the parent Alq₃ as a buffer layer.⁵

In the Alq₃ complex, the highest HOMO electron density is allocated on the 5-position of the 8-hydroxyquinoline ligand and the nature of the substituent attached to this position affects the properties of the resulting complex through modification of its HOMO level.⁶ The studied derivatives have electron-donating amino substituents,⁷ which are supposed to ease the oxidation of the complexes and to elevate the HOMO energy levels compared to the parent Alq₃.

In organic solar cells the energy levels of the different materials in the layered solar cell structure determine the open circuit

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voltage (V_{OC}) and have an effect on the fill factor (FF) and short circuit current (I_{sc}). In the used indium tin oxide (ITO)/zinc oxide (ZnO)/P3HT:PCBM/Alq₃/Au inverted solar cell structure, Alq₃ functions as an anode buffer layer between the photoactive P3HT:PCBM BHJ layer and the metal anode. If the HOMO energy level of the P3HT donor lies more than 0.2 eV higher than the HOMO of the buffer layer, an extraction barrier is created at the interface and the FF decreases.⁸ An extraction barrier denotes an energetic barrier for the photogenerated holes in the donor to escape the device. By elevating the HOMO level of the buffer material compared to that of the parent Alq₃, the extraction barrier between P3HT and the buffer material can be reduced, which is supposed to improve the FF. Therefore, 5-amino substituted Alq₃ derivatives are interesting candidates for anode buffer layer materials in organic solar cells.

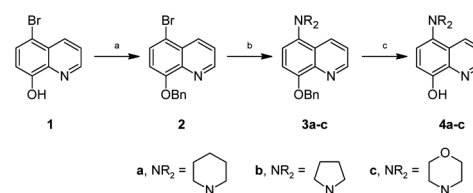
In order to study the properties of 5-amino substituted Alq₃ derivatives and the possibility of applying them in organic solar cells, a synthetic method to produce these target compounds had to be developed. Hartwig–Buchwald (H–B) coupling reaction is currently a widely used method to form arylamines. On the other hand, there are only a few literature references about H–B couplings between quinoline substrates and amines,⁹ even though many aminoquinolines have shown remarkable pharmaceutical properties in the treatment of Alzheimer's disease and further potential as antimalarial agents.^{9f,10} Amination of quinoline rings has turned out to be somewhat problematic and moreover, the catalytic systems vary from one substrate to another and from one amine to another. Such variations in the reaction conditions create a need for more investigation of different catalytic systems with different substrates and amines. Optimization and screening of the reaction conditions become a prerequisite for any type of Pd catalyzed amination reaction.

In this paper, the effect of three commercially available phosphine ligands in the H–B amination of 8-(benzyloxy)-5-bromoquinoline with three secondary amines was studied to prepare 5-amino-8-benzyloxyquinoline derivatives. It was observed that β -hydrogen elimination competes severely with reductive elimination if reaction conditions have not been optimized carefully. The benzyloxy protecting group at the 8-position tolerated the strong basic medium needed in the H–B amination and could be removed smoothly after the reaction by catalytic hydrogenation affording the corresponding 8-hydroxyquinoline derivatives. The synthesized 5-amino-8-hydroxyquinolines were complexed with Al³⁺ to form three new Alq₃ derivatives. The synthetic work was then followed by extensive studies of the photophysical, electrochemical and thermodynamic properties of the new Alq₃ derivatives and their use as anode buffer layers in organic solar cells.

2. Results and discussion

2.1 Synthesis

Three 5-amino substituted Alq₃ derivatives have been prepared in this work in order to study their photophysical characteristics and their behavior as buffer layers in organic solar cells. The preparation of the new Alq₃ derivatives started from commercially available 5-bromo-8-hydroxyquinoline **1** by protecting the hydroxyl group at the 8-position with the benzyloxy group



Scheme 1 Reagents and conditions: (a) BnBr, K₂CO₃, DMF, rt, 1 h; (b) Pd(OAc)₂, ligand **L1**, **L2** or **L3**, NaO-*t*-Bu (1.25 equiv.), amine (1.25 equiv.), toluene, 80–100 °C, 0.5–24 h; (c) Pd–C (10 wt%), H₂, ethanol, reflux, 3 h.

(Scheme 1).¹¹ After that, the Hartwig–Buchwald coupling was carried out between 8-(benzyloxy)-5-bromoquinoline **2** and amine.

For the Hartwig–Buchwald amination, optimization of the reaction conditions was mandatory. Three phosphine ligands were considered in our preliminary tests in the H–B amination along with palladium acetate as the palladium source. Palladium acetate has served as a stable effective palladium source in the Pd catalyzed aminations¹² while electron rich, sterically demanding ligands proved to be active in many H–B aminations.^{9c,12,13} The activities of such ligands are attributed to a combination of steric and electronic factors. Among the active ligands reported in the H–B amination are tri-*tert*-butylphosphine (TTBP) **L1**,¹⁴ di-*tert*-butylneopentylphosphine (DTBNpP)^{13,15} **L2**, and (2-biphenyl)di-*tert*-butylphosphine (Johnphos)^{12a} **L3** (Fig. 1). Ligands **L1** and **L2** were used as their air stable tetrafluoroborate salts. Piperidine was used as a coupling partner and sodium *tert*-butoxide as a base in the preliminary tests. Both *N,N*-dimethylacetamide (DMA) and toluene were tested as solvents in the amination reaction. During the optimization (Table 1), ¹H NMR analysis of the crude reaction mixtures revealed that the main side product of this amination reaction was 8-(benzyloxy)quinoline, which is the reduction product of compound **2**. Hartwig *et al.*¹⁶ stated that the arene *versus* amine ratio is controlled by electronic and steric factors of the intermediate complex and that the formation of the arene along with the amine is attributed to the competitive reductive elimination of the amine and the β -hydrogen elimination from the amido aryl intermediate during the reaction.

Experiments showed considerable difference in reaction outcome between toluene and DMA (Table 1, entries 1 and 2). Clearly, the reduction of the starting material is a more favored process in DMA than in toluene. Among the tested ligands, **L2** was the most effective ligand in the H–B amination of compound **2** with piperidine, producing 8-(benzyloxy)-5-(piperidin-1-yl)quinoline **3a** in a high yield (entry 6). The catalyst ligand ratio 1 : 2 was proved to improve the amine : arene ratio and allowed the complete conversion at lower Pd loading (Table 1, entries 3, 4, and 6). Closely related to the present work, it is interesting to

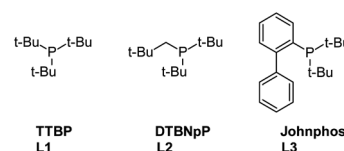


Fig. 1 The ligands used in the optimization of H–B amination reaction of compound **2**.

Table 1 Pd catalyzed amination of 8-(benzyloxy)-5-bromoquinoline **2** with piperidine^a

Entry	Lig.	Pd/Lig.	Pd cont. (mol%)	Solvent	<i>t</i> (h)	Start (%)	Red. prod. (%)	Prod. 3a (%)
1	L1	1/1	5	DMA	4	12	36	52
2	L1	1/1	5	Tol.	24	25	12	63
3	L2	1/1	5	Tol.	24	5	7	88
4	L2	1/1	8	Tol.	24	0	6	94
5	L3	1/1	8	Tol.	24	5	11	84
6	L2	1/2	5	Tol.	24	0	3	97 (84) ^b

^a Reaction conditions: 50–250 mg of 5-bromo-8-benzyloxyquinoline, Pd(OAc)₂, NaO-*t*-Bu (1.25 equiv.), amine (1.25 equiv.), 100 °C, under argon atmosphere. The percentages were analyzed based on ¹H NMR from the crude reaction mixtures after the reaction time mentioned. ^b Isolated yield.

note that Hamann *et al.* observed a very low yield (4%) of 8-methoxy-5-(piperidin-1-yl)quinoline during the amination of 5-bromo-8-methoxyquinoline with piperidine at 120 °C, using the Pd₂(dba)₃/PPFA catalytic system.^{9a} The use of microwave heating improved the yield to a moderate level (46%). Both the methoxy and benzyloxy substituents are electron-donating groups and thus deactivate the quinoline ring and hinder the oxidative addition to palladium, but in our case the used catalyst system is powerful enough to perform the coupling affording the products in high yields and without need for microwave assistance.

During the coupling of compound **2** with pyrrolidine using **L2**, although there was a complete conversion of the starting materials to products, the formation of the reduction product was observed noticeably along with the desired amination product (Table 2, entry 2). Therefore, the effect of **L1** and **L3** was also investigated under same conditions. Similarly to the coupling between compound **2** and piperidine, **L1** did not afford complete conversion and, surprisingly, the reduced product was the main reaction product (Table 2, entry 1). The experiment with ligand **L3** was successful giving a complete conversion and affording the amination product, 8-(benzyloxy)-5-(pyrrolidin-1-yl)quinoline **3b**, in high yield (Table 2, entry 3). Moreover, during the coupling of compound **2** with pyrrolidine, the reaction proceeded faster (30 minutes) and at lower temperature. In contrast to our result, ligand **L3** was previously observed to be ineffective in the H–B amination of halogenated quinoline derivatives.^{9c,f}

In the third amination reaction, morpholine was employed as the amine under the same reaction conditions (Table 3). Both **L1** and **L2** showed incomplete conversion of the starting material to product (Table 3, entries 1 and 2). When **L3** was used under the same reaction conditions, the complete conversion was observed and the coupling product, 4-(8-(benzyloxy)quinolin-5-yl)morpholine **3c**, was formed in a high yield (Table 3, entry 3). The

Table 2 Pd catalysed amination of 8-(benzyloxy)-5-bromoquinoline with pyrrolidine^a

Entry	Lig.	Start (%)	Red. prod. (%)	Prod. 3b (%)
1	L1	44	40	16 ^b
2	L2	0	43	57 ^c
3	L3	0	16	84 ^c (80) ^d

^a Reaction conditions: 50 mg of **2**, Pd(OAc)₂ (5 mol%), ligand (10 mol%), NaO-*t*-Bu (1.25 equiv.), amine (1.25 equiv.), toluene, 80 °C. The resulting percentages were analyzed based on ¹H NMR from crude reaction after the reaction time. ^b Reaction time was 3 h under argon. ^c Reaction time 30 min. ^d Isolated yield.

Table 3 Pd catalyzed amination of 8-(benzyloxy)-5-bromoquinoline with morpholine^a

Entry	Lig.	Start (%)	Red. prod. (%)	Prod. 3c (%)
1	L1	56	9	35
2	L2	35	10	55
3	L3	0	14	86 (84) ^b

^a Reaction conditions: 50 mg of compound **2**, Pd(OAc)₂ (5 mol%), ligand (10 mol%), NaO-*t*-Bu (1.25 equiv.), amine (1.25 equiv.), toluene, 80 °C for 3 h under argon. The resulting percentages were analyzed based on ¹H NMR from crude reaction after the reaction time. ^b Isolated yield.

amination with morpholine took place at 100 °C and lasted for 3 hours.

Hill *et al.*¹³ stated that the optimal cone angle for the effective ligand in the H–B reactions falls between 190° and 200°. This suggestion can explain the low activity observed for **L1** with all the amine substrates used in our reactions, as **L1** has the lowest cone angle among the ligands used ($\theta = 182^\circ$). Replacement of one *tert*-butyl group with a biphenyl group in **L3** increases the cone angle significantly ($\theta = 246^\circ$)¹⁷ which is clearly out of the suggested range. However, ligand **L3** gave high conversion of compound **2** to the desired product in all cases. Actually, this criterion stated by Hill *et al.* worked only with ligand **L2** ($\theta = 198^\circ$)¹⁷ in the coupling between compound **2** and piperidine. Obviously, a larger ligand size facilitates the formation of active PdL species from the coordinatively saturated PdL₂ by the ligand dissociation and thus promotes the oxidative addition to the quinoline substrate. Moreover, it could be observed during the amination of compound **2** with secondary amines, piperidine, pyrrolidine, and morpholine, that the different ligands employed, gave different conversion percentages from the starting materials to products and different arene/arylamine ratios. This can be attributed to the different steric requirements for each amine and to the ease of the β -hydrogen elimination from the intermediate complex. Pyrrolidine seems to be the most sensitive to the ligand size variation, in which case the amount of β -hydrogen elimination product decreases with the increasing ligand size.

After the optimization of the reaction conditions for each amine substrate, the reaction mixtures of the 5-amino-8-benzyloxyquinolines **3a–c** prepared under the optimal conditions were obtained in a pure form by column chromatography using the proper eluent. The purified compounds **3a–c** were deprotected by using the palladium catalyzed hydrogenation. The deprotection took 1–3 hours and gave the resulting deprotected 5-amino-8-hydroxyquinolines **4a–c** in high yields after work up.

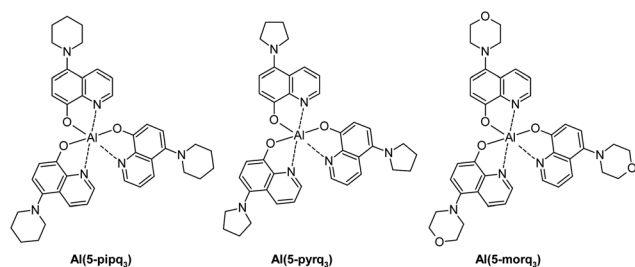


Fig. 2 The chemical structures of the 5-amino substituted Alq₃ derivatives.

The aluminum complexes Al(5-pipq)₃, Al(5-pyrq)₃ and Al(5-morq)₃ (Fig. 2) were prepared by complexing the ligands **4a–c** with aluminum isopropoxide in absolute ethanol for 24 hours under argon atmosphere.

2.2 Thermal analysis

Differential scanning calorimetry (DSC) measurements were carried out to investigate the solid state properties of the Alq₃ derivatives. Although, the parent Alq₃ has a clear melting peak at 417 °C, none of the derivatives exhibited any clear endothermic signal of melting. Around 400 °C all the derivatives showed broad exothermic peaks, which might be caused by the degradation of the complexes. Clear glass transition temperatures (*T_g*) could be observed at 208 °C, 213 °C, and 224 °C for Al(5-pyrq)₃, Al(5-pipq)₃, and Al(5-morq)₃ respectively, as shown in Fig. 3. *T_g* values of the derivatives are clearly higher than that of the parent Alq₃, which undergoes the glass transition at 162 °C (ref. 4b). In consequence of the higher *T_g* values compared to the parent Alq₃, the derivatives would have better stability in photovoltaic applications. The absence of melting peaks and the appearance of clear glass transitions indicate that the prepared Alq₃ derivatives are amorphous. Altogether, the derivatives seem to have very identical thermodynamic properties in a solid state according to the DSC measurements. Based on this result, the derivatives are assumed to have similar morphological properties in solid films as well.

2.3 Electrochemical analysis

The differential pulse voltammetry (DPV) measurements were carried out to determine the HOMO and LUMO levels of the Alq₃ derivatives. DPV curves in Fig. 4 exhibit reversible

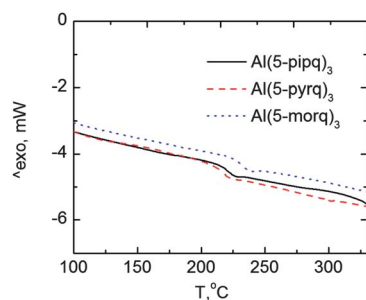


Fig. 3 Third DSC heating scan for Al(5-pipq)₃, Al(5-pyrq)₃ and Al(5-morq)₃.

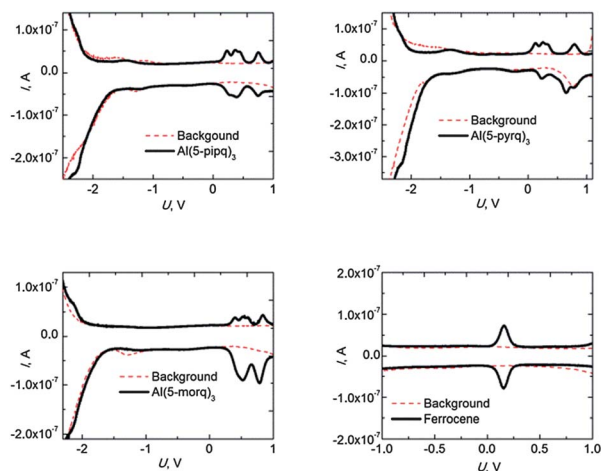


Fig. 4 DPV curves of Al(5-pipq)₃, Al(5-pyrq)₃, Al(5-morq)₃ and the ferrocene reference.

oxidation and reduction for all the derivatives. The ferrocene reference oxidation peak appears at 0.16 V. The HOMO and LUMO energy levels and the band gap energy for the derivatives were calculated based on the sample redox potentials referenced to the ferrocene oxidation potential. The results are presented in Table 4 and the HOMO and LUMO levels are illustrated in Fig. 5.

The absolute values of the electrochemical band gaps (E_g^{ec}) calculated based on the HOMO and LUMO levels differ slightly from the optical band gap (E_g^{opt}) values, which are calculated from the absorption maxima of the compounds in CHCl₃ solution (Fig. 6). However, the values have relative correspondence as Al(5-morq)₃ has the highest and Al(5-pyrq)₃ has the lowest calculated band gap in both methods.

The different electron donating properties of the 5-amino substituents on the 8-hydroxyquinoline ligand are supposed to ease the oxidation and raise the HOMO levels of the complexes with respect to the parent Alq₃. As can be seen in Fig. 5, the LUMO levels of the derivatives remained virtually unaffected, while the HOMO levels lie remarkably higher relative to the parent Alq₃.

2.4 Photophysical studies

Both steady state and time resolved spectroscopies were applied to investigate photophysical properties of the derivatives. Absorption spectra of the derivatives and the parent Alq₃ in CHCl₃ solution and in vacuum evaporated solid films are presented in Fig. 6 and 7. Steady state absorption and emission

Table 4 Electrochemical properties of the 5-amino substituted Alq₃ derivatives^a

Derivative	HOMO [eV]	LUMO [eV]	E_g^{ec} [eV]	E_g^{opt} [eV]
Al(5-pipq) ₃	−4.87	−2.33	2.54	2.89
Al(5-pyrq) ₃	−4.77	−2.46	2.31	2.82
Al(5-morq) ₃	−5.04	−2.48	2.56	2.96

^a E_g^{opt} calculated from the absorption maxima in CHCl₃ solution at 430 nm for Al(5-pipq)₃, at 439 nm for Al(5-pyrq)₃ and at 419 nm for Al(5-morq)₃.

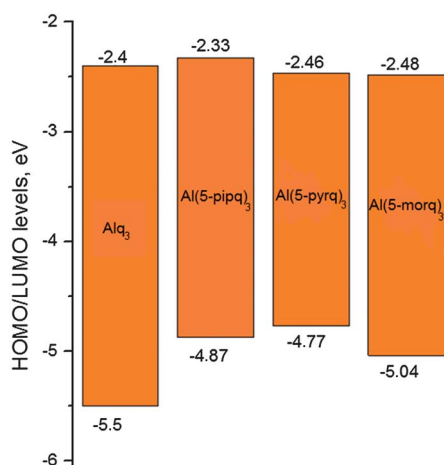


Fig. 5 HOMO and LUMO levels of Alq₃ (ref. 5), Al(5-pipq)₃, Al(5-pyrq)₃ and Al(5-morq)₃.

properties are summarized in Table 5. The most significant difference between the emission properties of the derivatives and the parent Alq₃ is that the fluorescence emissions of the derivatives appear to be remarkably weak. The relative fluorescence emission quantum yields of Al(5-pipq)₃ and Al(5-pyrq)₃ are extremely low, 0.004 and 0.001 respectively, relative to Alq₃. However, Al(5-morq)₃ has a slightly higher relative quantum yield, 0.017, with respect to the parent Alq₃.

All the derivatives have narrow emission bands, as shown in Fig. 8, between 375 and 425 nm, with excitation of the second absorption band at 320 nm. The excitation at the Soret band, 405 nm, provides the fluorescence emission in the range of 525–700 nm in the case of Al(5-morq)₃ and 450–650 nm in the case of Al(5-pyrq)₃ (Fig. 9). Al(5-pipq)₃ has a broadened emission covering the wavelengths between 450 and 750 nm, the largest Stokes shift and the emission decay is multiexponential, as can be seen in the decay curves measured by time correlated single photon counting (TCSPC) in Fig. 10. Although Al(5-morq)₃ has higher fluorescence quantum yield than the other derivatives, the emission decay occurs fastest and is the most clearly two-exponential.

The fluorescence emission lifetimes were calculated based on two-exponential global fittings of the TCSPC measurements and are presented in Table 6. Decay associated spectra (DAS) are presented in Fig. 11. The intensities of the spectra are the product

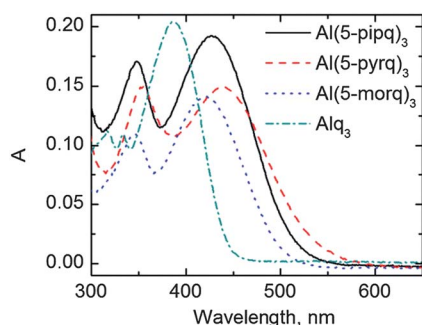


Fig. 6 Absorption spectra of the parent Alq₃ and the derivatives in CHCl₃ solution (60 μM).

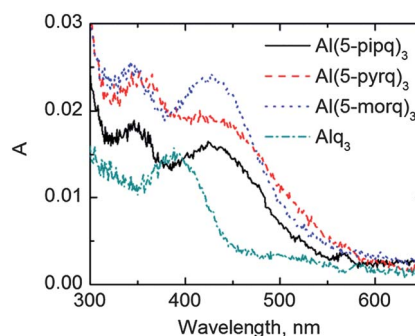


Fig. 7 Absorption spectra of the parent Alq₃ and the derivatives in solid films. The film thicknesses are 7.6 nm, 14.7 nm, 13.5 nm and 5.4 nm for Al(5-pipq)₃, Al(5-pyrq)₃, Al(5-morq)₃ and Alq₃ respectively.

of the amplitude and lifetime at each wavelength, corrected according to the detector wavelength sensitivity. Al(5-pipq)₃ and Al(5-pyrq)₃ both have an intense long living, 3.54 ns and 4.83 ns respectively, decay component around 500 nm. However, the DAS of Al(5-morq)₃ exhibits an intense short living, 0.50 ns (94%), component at 570 nm, whereas a longer living, 5.83 ns, component at 500 nm is faint (6%).

2.5 Alq₃ derivatives as buffer layers in inverted organic solar cells

The synthesized Alq₃ derivatives were tested as anode buffer layers in ITO|ZnO|P3HT:PCBM|Buffer|Au organic solar cells, the schematic structure of which is presented in Fig. 12. The parent Alq₃ was used as a reference buffer layer material. The solution-processed ZnO interlayer between ITO and the photoactive layer efficiently collects the electrons from the active layer to the ITO direction. This provides an inverted solar cell structure,¹⁸ *i.e.* the electrons flow to the ITO cathode as shown in the energy level diagram in Fig. 13a.

The solar cells are illuminated through the glass substrate. The illuminated light passes through the transparent glass, ITO and ZnO layers and most of the light is absorbed by the *ca.* 100 nm thick photoactive P3HT:PCBM layer. The absorption of the *ca.* 5 nm buffer layer behind the photoactive layer is faint. Thus the contribution of the photophysical properties of the buffer layer to the function of the solar cell will be discussed together with the results of the solar cell experiments.

Table 5 Steady state absorption and emission properties of the derivatives and the parent Alq₃

Complex	λ_{sol}^a (nm)	λ_{film}^b (nm)	α^c (μm^{-1})	$\lambda_{\text{PL, sol}}^d$ (nm)	Stokes shift ^e (nm)	ϕ_{PL}^f
Al(5-pipq) ₃	430	426	1.4	617	187	0.004
Al(5-pyrq) ₃	439	429	1.3	511	72	0.001
Al(5-morq) ₃	419	427	1.8	575	156	0.017
Alq ₃	385	385	2.1 (ref. 5)	513	128	1

^a Absorption maximum in CHCl₃ solution. ^b Absorption maximum in a solid film. ^c Absorption coefficient in a solid film at 430 nm for the derivatives and at 398 nm for Alq₃. ^d Fluorescence emission maximum in CHCl₃ solution. ^e $\lambda_{\text{PL, sol}} - \lambda_{\text{sol}}$. ^f Relative fluorescence quantum yield with respect to the parent Alq₃ (the absolute fluorescence quantum yield for Alq₃ in CHCl₃ is 0.171 (ref. 6b)).

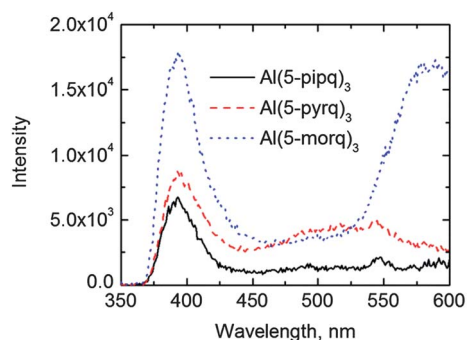


Fig. 8 Fluorescence emission spectra of the derivatives ($\lambda_{\text{ex}} = 320$ nm).

The photovoltaic parameters of the solar cell devices with the derivatives as buffer layers measured one day after preparation are presented in Table 7. The efficiency of the solar cell varies with the different buffer materials. The solar cell with Al(5-morq)₃ as a buffer layer gives the highest power conversion efficiency (η), 2.63%, which is higher than that (2.36%) of the reference device with Alq₃ as a buffer layer. Morphological properties in the solid buffer layers are assumed to be similar for the derivatives, because the DSC measurements showed uniform thermodynamic behavior. Morphological factors, whether crystalline or amorphous, of the buffer material seem not to cause the differences in the performance of the buffer layers because both crystalline Alq₃ and amorphous derivatives seem to work well as buffer layers.

Absorption spectra and I - V curves of the solar cell devices measured one day after preparation are shown in Fig. 14 and 15. The absorption spectra of the solar cells with different buffer layers do not differ between 350 nm and 450 nm, where the absorption of the buffer materials takes place. Some differences in the absorption spectra can be seen around 500 nm, where the P3HT absorption peaks, showing small variation in the photoactive layer thicknesses of the solar cell samples. The cell absorptions are between 0.7 and 0.8, while the maximum absorption of ~ 5 nm buffer layer according to Fig. 7 in the case of Alq₃ is only about 0.015, which is negligible compared to the cell absorption. Also the absorption coefficients of the derivatives and parent Alq₃ are small. Previous studies⁵ about Alq₃ derivatives as buffer layers proposed that due to minor absorption of the buffer compared to the cell absorption, the buffer layer acts as a transparent spacer and charge transporting layer between the photoactive region and the metal anode.

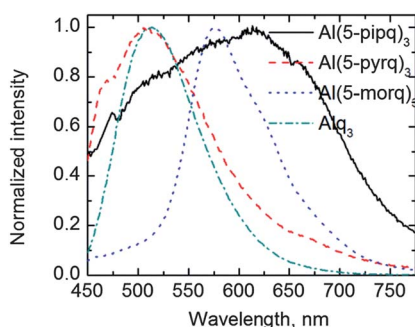


Fig. 9 Normalized fluorescence emission spectra of the derivatives and the parent Alq₃, $\lambda_{\text{ex}} = 405$ nm.

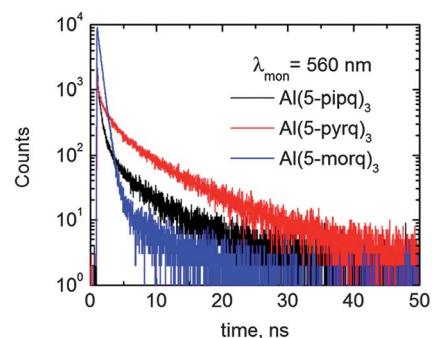


Fig. 10 Fluorescence emission decay ($\lambda_{\text{ex}} = 405$ nm) curves of the derivatives at a monitoring wavelength of 560 nm.

Table 6 Fluorescence emission lifetimes of the two-exponential fit for the derivatives (one-exponential for Alq₃) and the average lifetimes

Complex	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)
Al(5-pipq) ₃	3.54 (56%)	0.15 (44%)	2.05
Al(5-pyrq) ₃	4.83 (87%)	0.51 (13%)	4.27
Al(5-morq) ₃	0.50 (94%)	5.83 (6%)	0.82
Alq ₃	16.62 (ref. 5)	—	16.6

To further validate the assumption, that the photophysical properties of the weakly absorbing buffer layer do not affect the cell efficiency, the fluorescence properties of different buffer layer materials can be compared together with the cell efficiencies. The fluorescence lifetimes and quantum yields of all the 5-substituted derivatives are remarkably smaller than those of the parent Alq₃. This means that the average existence of the excited state of Alq₃ is much longer compared to that of the derivatives. However, the cell efficiency seems not to depend on either quantum yield or lifetime. The cell with Al(5-morq)₃, which has both very low ϕ_{PL} and the shortest τ_{avg} (Table 6) of all the derivatives, has better η than the cell with highly fluorescent Alq₃ as a buffer layer measured one day after the device preparation. According to this result, the contribution of the buffer layer to the cell efficiency seems not to be influenced by the excited state of the buffer layer material. Thus the ground state properties, such as conductivity

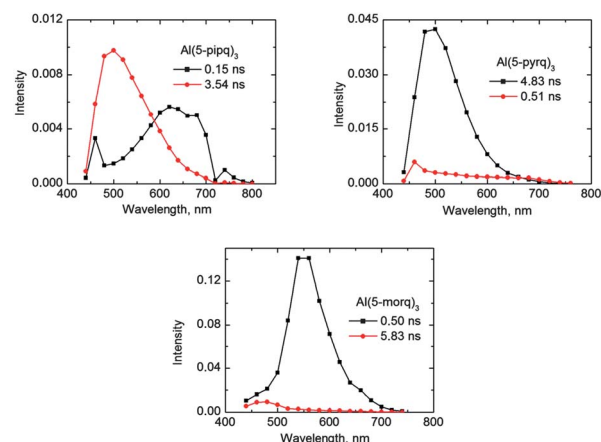


Fig. 11 Decay associated spectra of Al(5-pipq)₃, Al(5-pyrq)₃ and Al(5-morq)₃.

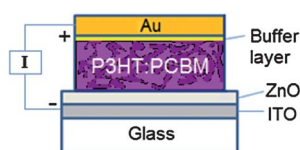


Fig. 12 Schematic structure of the inverted organic solar cell.

or contact with both the metal anode and the photoactive layer, seem to define the function of the buffer layer in the inverted organic solar cells.

Conductivity of both types of carriers inside the buffer layer is necessary, as the holes ejected from the photoactive layer recombine with the electrons produced by the photoexcitation and inserted into the cell from an external circuit *via* the gold anode. The electron to hole mobility ratio (μ_e/μ_h) primarily controls the charge recombination and the mobility of holes in the parent Alq₃ is generally two orders of magnitude less than that of electrons.²⁰ Therefore major attention will be drawn to the transport of slower charge carriers, holes, at the P3HT/buffer interface. The transport of holes, from P3HT to the gold anode modified by the buffer layer, is controlled by the HOMO energy

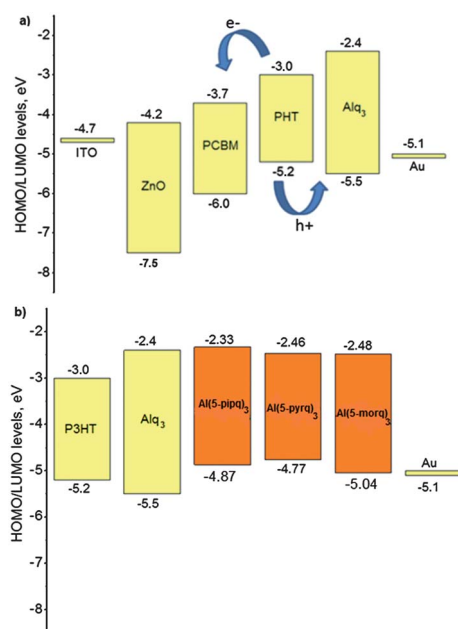


Fig. 13 (a) Energy levels of the inverted organic solar cell device. Measured values for the derivatives and the literature values for ITO,³ ZnO,¹⁹ PHT,¹⁹ PCBM,¹⁹ Alq₃,⁵ and Au;¹⁹ (b) energy levels of the derivatives and the parent Alq₃ positioned between the gold electrode and P3HT in the cell structure.

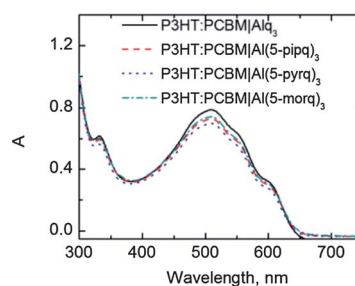


Fig. 14 Absorption spectra of the solar cells with Alq₃ and the derivatives as buffer layers.

levels of P3HT and the used buffer material. Thus the results of solar cell experiments are justified in terms of the energy levels in the following.

The difference between HOMO of P3HT and that of the buffer layer affects the cell V_{OC} . An injection barrier for holes is formed if the HOMO of the buffer layer lies higher than that of P3HT. The current through the P3HT:PCBM blend is driven by the electrons, which recombine with holes at the buffer/blend interface. The extraction force for the photogenerated charge carriers decreases due to the diminished built-in field caused by the injection barrier and V_{OC} is decreased.⁸ The device with Alq₃ as an anode buffer layer produced the highest V_{OC} , 0.51 V. The HOMO level of Alq₃ at -5.5 eV lies lower than the HOMO of P3HT and no injection barrier exists (Fig. 13b). HOMO levels of all the 5-amino substituted derivatives lie higher than that of P3HT and therefore injection barriers are created. However, the HOMO level of Al(5-morq)₃, at -5.04 eV, lies lower than the HOMO levels of Al(5-pipq)₃, at -4.87 eV, and Al(5-pyrq)₃, at -4.77 eV. Thus the device with Al(5-morq)₃ as an anode buffer layer produced low injection barrier, 0.16 eV, and nice V_{OC} , 0.48 V. The devices with Al(5-pipq)₃ and Al(5-pyrq)₃, which have higher injection barriers than Al(5-morq)₃, 0.33 eV and 0.43 eV respectively, produced smaller V_{OC} , 0.45 V.

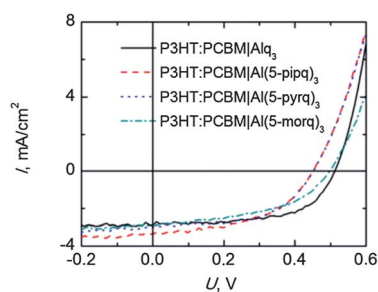


Fig. 15 I - V curves of the solar cells with Alq₃ and the derivatives as buffer layers measured 1 day after preparation.

Table 7 Photovoltaic parameters of the solar cells with Alq₃ and the derivatives as buffer layers measured one day after the cell preparation

Used buffer layer (thickness, nm)	I_{SC} (mA cm ⁻²)	V_{OC} (V)	FF (%)	η (%)	R_s (Ω cm ⁻²)	R_{sh} (Ω cm ⁻²)
Alq ₃ (4.30)	-2.91	0.51	60	2.36	17.94	1797
Al(5-pipq) ₃ (4.00)	-3.33	0.45	50	2.02	19.65	600
Al(5-pyrq) ₃ (3.60)	-3.01	0.45	55	1.99	20.04	820
Al(5-morq) ₃ (3.66)	-3.20	0.48	64	2.63	25.72	564

Table 8 Photovoltaic parameters of the solar cells with Alq₃ and the derivatives as buffer layers measured 5 months after the cell preparation

Used buffer layer	I_{SC} (mA cm ⁻²)	V_{OC} (V)	FF (%)	η (%)	R_s (Ω cm ⁻²)	R_{sh} (Ω cm ⁻²)
Alq ₃	-2.89	0.55	62	2.62	28.03	2824
Al(5-pipq) ₃	-3.52	0.53	56	2.76	30.67	1031
Al(5-pyrq) ₃	-3.46	0.52	54	2.59	24.72	752
Al(5-morq) ₃	-3.56	0.53	56	2.80	28.70	1161

The highest FF, 64%, was also produced by the device with Al(5-morq)₃ as a buffer layer. The high FF is due to the small energy difference, 0.16 eV, between the HOMO levels of P3HT and Al(5-morq)₃. FF decreases as soon as the HOMO mismatch is more than 0.2 eV.⁸ The parent Alq₃ has an extraction barrier, 0.3 eV, and therefore FF is slightly lower, 60%. The difference between HOMO levels of Al(5-pipq)₃ and Al(5-pyrq)₃ compared to the HOMO of P3HT is 0.33 eV and 0.43 eV respectively. The cells with Al(5-pipq)₃ and Al(5-pyrq)₃ had FF values of 50% and 55% respectively, which are clearly lower than that of the cell with Al(5-morq)₃ as a buffer layer.

Long-term stability measurements of the solar cells were carried out 5 months after the device preparation and storage in ambient air in darkness. The photovoltaic parameters measured 5 months after the device preparation are given in Table 8 and the corresponding I - V curves of the solar cells are shown in Fig. 16. The devices with Alq₃ and 5-amino substituted derivatives as buffer layers had better performance (Table 7) after the 5-month storage than one day after the preparation. The highest percentage increase, 36.6%, in η was achieved by the device with the Al(5-pipq)₃ buffer layer. Despite a rather small, 6.5%, increase in η , the device with the Al(5-morq)₃ buffer layer had the highest η , 2.80%, also after the 5-month storage.

Especially, V_{OC} of the cells had increased significantly during the storage. The values followed the same order as measured one day before preparation. The cell with Alq₃ had the highest and the cell with Al(5-pyrq)₃ had the lowest V_{OC} . However, the distinction of the V_{OC} values between the cells with different buffer layers was not as substantial as before.

The FF values of the cells had also changed during the storage. FF of the cell with Al(5-pipq) as the buffer layer had increased from 50% to 56%. FF values of the cells with Alq₃ and Al(5-pyrq)₃ had not changed significantly. The most drastic change, from 64% to 56%, took place in the cell with Al(5-morq)₃ as the buffer layer. Due to the changes during the storage the FF values

are not consistent with the measurements carried out one day after preparation. To explain the differences in FF values and further compare the results of measurements carried out one day and five months after preparation, the serial resistances and shunt resistances (R_s and R_{sh} , Tables 7 and 8) of the solar cells were calculated based on the I - V curves as explained in the literature.²¹

During the storage both R_s and R_{sh} values of the reference cell with the Alq₃ buffer layer increased by a factor of 1.56. The R_s of the cell with Al(5-pipq)₃ also increased by a factor of 1.56, in which case the effective current change caused by the ageing of the cell is of the same order as in the case of Alq₃. However R_{sh} of the cell with Al(5-pipq)₃ increased by a factor of 1.72. R_{sh} is correlated with the amount of recombinations and leakage current²¹ in the cell. The cell with Al(5-pipq)₃ has relatively higher R_{sh} after the storage than the cell with Alq₃, which means lower recombination rate in the cell with Al(5-pipq)₃. This together with the remarkably increased V_{OC} improved the FF and the cell with Al(5-pipq)₃ experienced the largest increase in η and the absolute value, 2.76%, is even bigger than that, 2.62%, of the reference device with Alq₃.

R_s of the cell with Al(5-pyrq)₃ increased by a factor of 1.23 during the storage and therefore the cell has the biggest increase in I_{SC} . Although R_{sh} had decreased during the storage the increased V_{OC} and I_{SC} resulted in improved η . However the absolute η , 2.59%, is slightly smaller than that of the reference device.

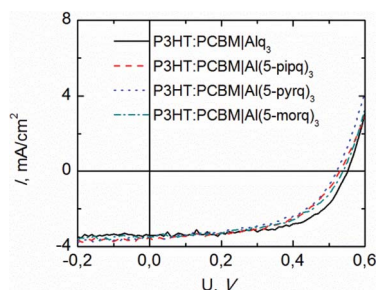
The device with the Al(5-morq)₃ buffer layer had the smallest relative and absolute increase in R_s , which means that the current in the cell is nearly the same before and after the storage. In addition the current losses are diminished efficiently as R_{sh} was improved by the highest factor, 2.06. These together resulted in the best η , 2.80%.

In conclusion, the energy levels of Al(5-morq)₃ seem to lie in advantageous positions in terms of charge transfer in the inverted solar cell structure. The HOMO level of Al(5-morq)₃, positioned close to both HOMO of P3HT and work function of Au, guarantees efficient hole transportation to the anode. Moreover, the LUMO level of Al(5-morq)₃ is high enough to prevent any electron flow to the anode direction. These together result in a I_{SC} of 3.20 mA cm⁻², V_{OC} of 0.48 V and a high FF of 64%, and therefore the device with Al(5-morq)₃ gives the highest η one day after the preparation. The device with Al(5-morq)₃ performed best also after 5-month storage due to smallest increase in R_s and highest relative increase in R_{sh} .

3. Experimental section

3.1 Materials used in the electrochemical measurements and preparation of the solar cell devices

The solvents, TBAPF₆ supporting electrolyte and parent Alq₃ (99.995%) were purchased from Sigma-Aldrich and used without further purification. The solar cell samples were prepared on indium tin oxide (ITO) coated glass substrates (1.2 cm × 3.5 cm) purchased from Solems. The zinc-acetate (Zn(O-COCH₃)₂·2H₂O) for ZnO layer preparation was from Sigma-Aldrich and the active layer compounds P3HT and PCBM from Rieke Metals Inc. (4002-E) and Nano-C, respectively.

**Fig. 16** I - V curves of the solar cells with Alq₃ and the derivatives as buffer layers measured 5 months after preparation.

3.2 DSC measurements

A Mettler Toledo DSC821 thermo analyzer was used for differential scanning calorimetry measurements. To observe the thermodynamic properties of the Alq_3 derivatives, 1 mg of each complex was heated from 25 °C to 500 °C by dynamic 20 °C min^{-1} heating rate in a standard 40 μg Al cup with 60 mL min^{-1} N_2 flow. For determination of T_g , 5 mg of each derivative was heated from -70 °C to 350 °C with 20 K min^{-1} heating rate and cooled back to -70 °C with 60 mL min^{-1} N_2 flow. The same procedure was repeated three times for each sample to first remove the thermal history and then observe the ongoing thermodynamic processes. T_g s are reported as on-set values.

3.3 DPV measurements and determination of HOMO and LUMO levels

DPV measurements were carried out by employing an Iviumstat (Compactstat IEC 61326 Standard) potentiostat and a three-electrode cell configuration to determine HOMO and LUMO energy levels for the derivatives. Measurements were carried out using 0.1 M TBAPF₆ in dichloromethane (DCM) as the supporting electrolyte, glass platinum electrode as the working electrode, graphite rod as the counter electrode and platinum wire as the pseudo reference electrode. For each sample, the background was measured for 2.5 mL of the electrolyte solution after 20 min deoxygenation by purging with N_2 . 100 μL of 0.5 mM sample in DCM was inserted and the system was stabilized again purging with N_2 . Each sample was measured between -2.5 V and 1.5 V scanning in both directions with 2.5 mV steps. Ferrocene (Acros Organics, 98%) was used as the internal standard reference to scale the measured potentials against the vacuum level.²² HOMO and LUMO level calculations were based on the formal oxidation and reduction potentials observed in the DPV curves according to the following equations:

$$E_{\text{HOMO}} = -(4.8 + E_{\text{dif,ox}}) \text{ eV}$$

$$E_{\text{LUMO}} = (-E_{\text{dif,red}} + 4.8) \text{ eV}$$

where 4.8 eV is the oxidation energy of ferrocene. $E_{\text{dif,ox}}$ is the difference in volts between the formal oxidation potentials of ferrocene and the measured sample. $E_{\text{dif,red}}$ is the difference in volts between the formal oxidation potential of ferrocene and the formal reduction potential of the sample.

3.4 Solid film thickness measurements with the profilometer and determination of α value

To determine the film thickness of the derivatives in a solid state, carefully cleaned quartz plates with a narrow strip of tape crossing in the middle of the plate were placed inside an Edwards Auto 306 evaporator. Test films of 5, 10 and 15 nm of each derivative were vacuum ($\sim 10^{-6}$ mbar) evaporated on the quartz plates. Prior to the measurements with a WYKO NT-1100 profilometer the tape was removed, leaving the bare glass stripe in the middle of the evaporated film, and producing a sharp step of the solid film on the edges of the bare glass stripe. The step was analyzed by the profilometer using phase shift interferometry

(PSI) mode and profilometer data were recorded from the area of $230 \times 300 \mu\text{m}^2$. The vertical resolution of this method is close to 1 Å according to the instrument manual and the horizontal resolution of the objective (20 $\times$ magnification) is 0.75 μm . The determination of film thicknesses and absorption coefficients (α) was done according to a literature process²³ and is presented in the ESI.†

3.5 Spectroscopic measurements

The steady state absorption and fluorescence measurements were done employing a UV-3600 Shimadzu UV-VIS-NIR spectrophotometer and a Jobin Yvon-SPEX fluorolog. The fluorescence lifetimes were determined with a time correlated single photon counting (TCSPC) system equipped with a PicoHarp 300 controller and a PDL 800-B driver for excitation and a micro-channel plate photomultiplier (Hamamatsu R3809U-50) for detection in 90° configuration. The excitation wavelength was 405 nm and the pulse frequency was 2.5 MHz. The experimental set-up of the measuring instrumentation was similar for all the derivatives.

3.6 Preparation of the solar cell devices

Solar cells were constructed on commercial ITO covered glass substrates. The ITO layer was taped and polished for *aqua regia* etching to achieve a patterned ITO. After 30 min sonication in acetone, CHCl_3 , SDS (sodium dodecyl sulfate) solution, H_2O and 2-propanol and a 10 min N_2 plasma cleaning procedure (Harrick Plasma Cleaner PDG-236), the 20 nm ZnO layer was deposited by 1 min spin-coating in a WS-400B-6NPP/LITE spin-coater from Laurell Technologies from 50 g L^{-1} zinc-acetate in 96% 2-methoxyethanol and 4% ethanolamine solution following the literature process.¹⁸

The photoactive layer compounds P3HT and PCBM were dissolved separately in 1,2-dichlorobenzene and stirred (250 rpm) for 4 hours at 50 °C. Thereafter the solutions were combined and stirred (500 rpm) at 70 °C for one hour and at 50 °C (250 rpm) overnight. The temperature was raised to 70 °C for 30 min prior to spin-coating the ~ 100 nm thick photoactive layer from the 32 g L^{-1} P3HT:PCBM (mass ratio 1 : 0.8) blend for 5 minutes (600 rpm) under N_2 flow. The spin-coated films were annealed in vacuum at 110 °C for 10 min. The buffer layer and Au anode were evaporated in the vacuum evaporator under $\sim 3 \times 10^{-6}$ mbar pressure. The evaporation rate and film thickness were controlled by evaporator crystals to deposit a ~ 5 nm thick buffer layer and 50 nm thick gold anode layer on top of the buffer. The devices were stored in ambient air for 24 hours in the dark before measurements and analysis.

The photovoltaic parameters were obtained and calculated from current–voltage (I – V) curves, which were measured under simulated AM 1.5 sunlight illumination (50 mW cm^{-2}) using an Agilent E5272A source/monitor unit. A voltage between -0.2 and 0.6 V was applied in 10 mV steps and the measurements were carried out in air at room temperature without encapsulation of the devices. The illumination was produced by a filtered Xe-lamp (Oriel Corporation & Lasertek) in the Zuzchem LZC-SSL solar simulator. The illumination power density was measured using a Coherent Fieldmax II LM10 power meter. Because a certified

measuring system could not be employed, the absolute efficiency values are not directly comparable with the other published results. However, the reported efficiencies and the relative efficiency changes are comparable within the presented devices.

3.7 General considerations about syntheses

All reactions were carried out under argon atmosphere except the palladium catalyzed deprotection of the benzyloxy group in 8-(benzyloxy)-5-bromoquinoline **2** which was carried out under hydrogen atmosphere. Solvents were dried by molecular sieves of the proper size. 5-Bromo-8-hydroxyquinoline was purchased from Tokyo Chemical Industry Co. (TCI). 8-(Benzyloxy)-5-bromoquinoline was synthesized according to previously published procedures.¹¹ Ligands (**L**₁–**L**₃) were purchased from Aldrich Chemical company. Palladium acetate was purchased from Fluka Chemical Company. Melting points were determined using a METTLER TOLEDO DSC821 at a heating rate of 10 °C min⁻¹. NMR analyses (¹H and ¹³C) were performed using Bruker DPX 200 (200 MHz) and Varian Mercury 300 MHz (Varian Inc.) spectrometers. TLC was performed on dry silica gel plates using a chloroform–methanol mixture as the eluent.

3.8 General procedure for the synthesis of 8-(benzyloxy)-5-aminoquinoline derivatives **3(a–c)** via Hartwig–Buchwald amination reaction

In an oven dried vessel with a magnetic stirring bar, toluene was added and bubbled with argon for 10 min. Compound **2**, Pd(OAc)₂ (5 mol%), ligand of choice after optimization (10 mol %), sodium *tert*-butoxide (1.25 equiv.) and amine (1.25 equiv.) were added and the reaction mixture stirred under argon at appropriate temperature. The reaction mixture was then allowed to cool to room temperature, filtered through a thin pad of silica gel and the solvent was evaporated under vacuum. The product was purified by flash chromatography using acetone–*n*-hexane (1 : 1) as the eluent.

8-(Benzyloxy)-5-(piperidin-1-yl)quinoline (3a). The title compound was prepared by following the general procedure. The specific amounts of chemicals used: compound **2** (250 mg, 0.796 mmol), Pd(OAc)₂ (9.0 mg, 0.040 mmol), ligand **L**₂ (24.3 mg, 0.080 mmol), sodium *tert*-butoxide (96.8 mg, 1.01 mmol) and piperidine (0.10 mL, 1.01 mmol). The reaction was stirred for 24 h at 100 °C. The procedure gave the title compound **3a** as an off-white powder (213 mg, 84%). Mp 113–114 °C. ¹H NMR (300 MHz; DMSO-*d*₆; Me₄Si) 1.59 (2H, br s), 1.75 (4H, q, *J* = 5.4), 2.89 (4H, br s), 5.26 (2H, s), 7.09 (1H, d, *J* = 8.1), 7.18 (1H, d, *J* = 8.4), 7.32–7.45 (3H, m), 7.52–7.58 (3H, m), 8.46 (1H, dd, *J* = 8.6, 1.7), 8.85 (1H, dd, *J* = 4.0, 1.6). ¹³C NMR (75 MHz; DMSO-*d*₆; Me₄Si) 24.0 (CH₂), 26.2 (2C, CH₂), 54.4 (2C, CH₂), 70.1 (CH₂), 110.0, 115.1, 121.1, 124.6, 127.8 (3C), 128.4 (2C), 131.7, 137.3, 140.7, 143.6, 148.8, 150.2. HRMS: calcd for C₂₁H₂₃N₂O ([M + H]⁺) 319.1810, found 319.1822.

8-(Benzyloxy)-5-(pyrrolidin-1-yl)quinoline (3b). The title compound was prepared by following the general procedure. The specific amounts of chemicals used: compound **2** (500 mg, 1.59 mmol), Pd(OAc)₂ (5 mol%, 17.86 mg, 0.080 mmol), ligand **L**₃

(49.05 mg, 0.16 mmol), sodium *tert*-butoxide (191.17 mg, 2 mmol) and pyrrolidine (0.16 mL, 2 mmol). The reaction temperature was adjusted to 80 °C and the reaction completed in 30 minutes. The procedure gave the title compound **3b** as yellow crystals (0.38 g, 80%). Mp 102–103 °C. ¹H NMR (200 MHz; DMSO-*d*₆; Me₄Si) 1.90 (4H, br s), 3.14 (4H, br s), 5.23 (2H, s, CH₂), 6.93 (1H, d, *J* = 8.3), 7.10 (1H, d, *J* = 8.7), 7.32–7.54 (6H, m), 8.47 (1H, d, *J* = 8.7), 8.83 (1H, d, *J* = 2.6). ¹³C NMR (50 MHz; DMSO-*d*₆; Me₄Si) 24.9 (2C), 53.4 (2C), 71.1 (CH₂), 111.5, 112.9, 121.2, 124.8, 128.6 (3C), 129.2 (2C), 133.5, 138.4, 141.5, 141.6, 149.5, 150.0. HRMS: calcd for C₂₀H₂₁N₂O ([M + H]⁺) 305.1654, found 305.1659.

8-(Benzyloxy)-5-morpholin-1-yl)quinoline (3c). The title compound was prepared by following the general procedure. The specific amounts of chemicals used: compound **2** (500 mg, 1.59 mmol), Pd(OAc)₂ (5 mol%, 17.86 mg, 0.080 mmol), ligand **L**₃ (49.05 mg, 0.16 mmol), sodium *tert*-butoxide (191.17 mg, 2 mmol) and morpholine (0.17 mL, 2 mmol). The reaction temperature was adjusted to 100 °C and the reaction time was 3 hours. The procedure gave the title compound **3c** as yellowish crystals (0.43 g, 84%). Mp 119–120 °C. ¹H NMR (200 MHz; DMSO-*d*₆; Me₄Si) 2.53 (4H, t, *J* = 4.2), 3.83 (4H, t, *J* = 3.9), 5.29 (2H, s, CH₂), 7.17–7.24 (2H, m), 7.36–7.61 (6H, m), 8.53 (1H, dd, *J* = 8.8, 1.7), 8.88 (1H, dd, *J* = 4.1, 1.5). ¹³C NMR (50 MHz; DMSO-*d*₆; Me₄Si) 53.9 (2C), 67.0 (2C), 70.5, 110.1, 115.9, 121.7, 124.8, 128.2 (3C), 128.9 (2C), 132.1, 137.7, 141.2, 142.6, 149.4, 151.1. HRMS: calcd for C₂₀H₂₁N₂O₂ ([M + H]⁺) 321.1603, found 321.1571.

3.9 General procedure for the synthesis of 5-amino-8-hydroxyquinolines **4(a–c)**

In a dry two-necked round bottom flask, 150 mg of 5-amino-8-benzyloxyquinoline (**3a–c**) and 30 mg Pd–C (10 wt%) were stirred and refluxed in ethanol under hydrogen atmosphere for 3 hours. The reaction mixture was then filtered through a thin pad of silica gel. The solvent was evaporated under vacuum and the residue was recrystallized from the appropriate solvent.

5-Piperidinyl-8-hydroxyquinoline (4a). Compound **4a** was prepared according to the general procedure, dissolved in ethanol, filtered through a 0.20 μm syringe filter and the filtrate was evaporated to dryness. The precipitate was boiled in water, cooled to rt, filtered and washed with water. These procedures gave the product as a greenish powder (102 mg, 94%). Mp 115–116 °C. ¹H NMR (300 MHz; DMSO-*d*₆; Me₄Si) 1.58 (2H, br s), 1.74 (4H, q, *J* = 5.4), 2.88 (4H, br s), 6.98 (1H, d, *J* = 8.1), 7.07 (1H, d, *J* = 8.1), 7.56 (1H, dd, *J* = 8.6, 4.2), 8.46 (1H, dd, *J* = 8.6, 1.4), 8.83 (1H, dd, *J* = 4.0, 1.2), 9.38 (1H, br s). ¹³C NMR (75 MHz; DMSO-*d*₆; Me₄Si) 24.0 (CH₂), 26.2 (2C, CH₂), 54.5 (2C, CH₂), 110.4, 116.2, 121.1, 124.2, 132.0, 139.1, 141.9, 147.9, 149.1. HRMS: calcd for C₁₄H₁₇N₂O ([M + H]⁺) 229.1341, found 229.1348.

5-Pyrrolidinyl-8-hydroxyquinoline (4b). Compound **4b** was prepared according to the general procedure and recrystallized from methanol to give yellow crystals (72 mg, 68%). Mp 83–84 °C. ¹H NMR (200 MHz; DMSO-*d*₆; Me₄Si) 1.92 (4H, br s),

3.13 (4H, br s), 6.97 (2H, s), 7.47–7.54 (1H, m), 8.49 (1H, d, $J = 8.6$), 8.81 (1H, d, $J = 3.1$), 9.21 (1H, OH). ^{13}C NMR (50 MHz; DMSO- d_6 ; Me_4Si) 24.5 (2C), 53.1 (2C), 111.0, 114, 120.9, 124.2, 133.5, 139.2, 139.4, 148.2, 148.5. HRMS: calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}$ ($[\text{M} + \text{H}]^+$) 215.1184, found 215.1180.

5-Morpholinyl-8-hydroxyquinoline (4c). Compound **4c** was prepared according to the general procedure and recrystallized from ethanol to give yellow crystals (85 mg, 79%). Mp 160–161 °C. ^1H NMR (200 MHz; DMSO- d_6 ; Me_4Si) 2.94 (4H, t, $J = 4.4$), 3.85 (4H, t, $J = 4.2$), 7.01 (1H, d, $J = 8.6$), 7.13 (1H, d, $J = 8.4$) 7.55–7.62 (1H, m), 8.54 (1H, dd, $J = 8.5, 1.1$), 8.87 (1H, dd, $J = 4.0, 1.2$), 9.50 (1H, OH). ^{13}C NMR (50 MHz; DMSO- d_6 ; Me_4Si) 54.0 (2C), 67.1 (2C), 110.9, 117.0, 121.7, 124.6, 132.5, 139.6, 140.9, 148.5, 150.1. HRMS: calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_2$ ($[\text{M} + \text{H}]^+$) 231.1134, found 231.1131.

3.10 General procedures for the synthesis of tris(5-amino-8-hydroxyquinoline)aluminum derivatives

Compound **4** (3 equiv.) and aluminium isopropoxide (1 equiv.) were refluxed in ethanol for 21 hours under argon atmosphere. The Alq_3 derivatives were obtained after reaction work up.

Tris-(5-piperidinyl-8-hydroxyquinoline)aluminum (Al(5-pipq) $_3$). Compound **4a** (100 mg, 0.44 mmol) and aluminium isopropoxide (29.8 mg, 0.15 mmol) were refluxed in ethanol (10 mL) for 21 h under argon atmosphere. The reaction mixture was filtered and the filtrate was evaporated to dryness. The precipitate was dissolved in acetone (1.5 mL) and the resulting solution was added dropwise in *n*-hexane (12 mL). The precipitated product was filtered and washed with solvent mixture. The procedure gave the product as a greenish yellow powder (47.1 mg, 46%). ^1H NMR (300 MHz; DMSO- d_6 ; Me_4Si) 1.56 (6H, br s), 1.72 (12H, br s), 2.87 (12H, br s), 6.63 (1H, d, $J = 8.1$), 6.78 (2H, dd, $J = 8.1, 2.2$), 7.13–7.19 (3H, m), 7.28 (1H, d, $J = 4.0$), 7.45 (1H, dd, $J = 8.1, 5.0$), 7.60 (1H, dd, $J = 7.9, 4.8$), 7.69 (1H, dd, $J = 8.6, 4.8$), 8.56–8.64 (4H, m), 8.76 (1H, d, $J = 5.0$). HRMS: calcd for $\text{C}_{42}\text{H}_{45}\text{N}_6\text{O}_3\text{Al}$ (M^+) 708.3369, found 708.3373.

Tris-(5-pyrrolidinyl-8-hydroxyquinoline)aluminum (Al(5-pyrq) $_3$). Compound **4b** (180 mg, 0.84 mmol) and aluminium isopropoxide (57.2 mg, 0.28 mmol) were refluxed in ethanol (10 mL) for 21 h. The reaction mixture was then concentrated under vacuum and light petrol was added. The precipitate formed was filtered and washed with petroleum ether (10 mL, three portions, boiling range 80–110 °C). The procedure gave the product as a reddish brown powder (175.5 mg, 94%). ^1H NMR (200 MHz; DMSO- d_6 ; Me_4Si) 1.93 (12H, br s), 3.04 (12H, br s), 6.62 (1H, d, $J = 8.5$), 6.78 (2H, d, $J = 8.5$), 7.07–7.17 (3H, m), 7.30–7.67 (4H, m), 8.62–8.80 (5H, m). HRMS: calcd for $\text{C}_{39}\text{H}_{40}\text{N}_6\text{O}_3\text{Al}$ ($[\text{M} + \text{H}]^+$) 667.2977, found 667.3007.

Tris-(5-morpholinyl-8-hydroxyquinoline)aluminum (Al(5-morq) $_3$). Compound **4c** (82 mg, 0.36 mmol) and aluminium isopropoxide (24 mg, 0.12 mmol) were refluxed in ethanol 8 mL for 24 h. The reaction mixture was then concentrated and treated with petroleum ether. The precipitate formed was filtered and washed with petroleum ether. The procedure gave the product as an orange

powder (64.0 mg, 75%). ^1H NMR (200 MHz; DMSO- d_6 ; Me_4Si) 2.81 (12H, br s), 3.82 (12H, br s), 6.79 (1H, d, $J = 8.3$), 6.80 (2H, d, $J = 8.1$), 7.20–7.76 (3H, m), 8.64–8.81 (5H, m). HRMS: calcd for $\text{C}_{39}\text{H}_{40}\text{N}_6\text{O}_6\text{Al}$ ($[\text{M} + \text{H}]^+$) 715.2825, found 715.2827.

4. Conclusions

The Hartwig–Buchwald coupling could be applied efficiently in the preparation of 5-amino-8-hydroxyquinolines from 8-(benzyloxy)-5-bromoquinoline. Three phosphine ligands (**L1**–**L3**) were employed during the amination reaction optimization, and only the ligands with a cone angle higher than 182° were proved to achieve the amination successfully. The relative reactivity of **L2** and **L3** depends on the amine steric requirements. The primary side product formed during the amination reaction was the reduction product, 8-benzyloxyquinoline. The amount of the reduction product could be controlled by optimization of the reaction conditions and appropriate choice of the ligand. The benzyloxy group at the 8-position of 8-(benzyloxy)-5-bromoquinoline tolerated the amination reaction conditions and could be removed after the amination reaction by catalytic hydrogenation affording the 5-amino-8-hydroxyquinolines in high purity.

The three 5-amino substituted Alq_3 derivatives were characterized and applied as anode buffer layer materials in inverted organic solar cells. All the derivatives exhibited similar amorphous properties in DSC measurements. Due to higher glass transition temperatures compared to the parent Alq_3 , the derivatives possess better thermodynamic stability than Alq_3 . According to the DPV measurements, the electron-donating 5-amino substituents of the Alq_3 derivatives affected notably HOMO levels of the complexes, which lie remarkably higher compared to those of the parent Alq_3 . LUMO levels of the derivatives remained virtually unaffected. Although the steady state and time resolved spectroscopic measurements showed lower quantum yield and shorter lifetime for all the derivatives compared to Alq_3 , Al(5-morq)_3 performed better than the parent Alq_3 or the other derivatives as anode buffer layer materials in organic solar cells. The cell with Al(5-morq)_3 as a buffer layer had a clearly improved fill factor and showed the highest power conversion efficiency due to suitable HOMO and LUMO levels of the buffer layer relative to the energy levels of the inverted organic solar cell structure.

Note added after first publication

This article replaces the version published on 13th September 2012, which contained errors in the last sentence of Section 2.5.

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