Synthesis and photophysical properties of aluminium tris-(4-morpholine-8-hydroxyquinoline)

Walaa A.E. Omar *

Department of Science and Mathematics, Faculty of Petroleum and Mining Engineering, Suez Canal University, Suez 43721, Egypt

Received 20 August 2012; revised 12 September 2012; accepted 20 September 2012

Abstract Aluminium tris(4-morpholinyl-8-hydroxyquinoline) has been synthesized and characterized. The photoluminescence measurements showed that the new derivative is blue shifted and has relative photoluminescence quantum yield two times higher compared to the pristine Al tris(8-hydroxyquinoline). Differential scanning colorimetric studies revealed that the newly synthesized Alq3 derivative in this work is amorphous material with the highest transition glass temperature value among the reported amorphous Alq3 derivatives.

© 2012 Cairo University. Production and hosting by Elsevier B.V. All rights reserved.

Introduction

Aluminium tris(8-hydroxyquinoline) is a widely used material in photovoltaic applications due to its excellent electronic and thermal properties. In organic light emitting diodes (OLEDs), it has been used successfully as electron transporting layer and/or emitting layer [1–6]. Recently, the use of the parent Alq3 and its derivatives in organic solar cells (OSCs) as dopant and/or buffer layer has been reported to increase the efficiency and the life time of the cell [7–11].

Curioni and Andreoni [12] provided a clue for obtaining more efficient Alq3 derivatives with enhanced intrinsic luminescence by attaching specific chemical substitutions on the quinolate ligand. The study stated that the introduction of an electron donating group at 4-position will widen the band gap energy and cause a blue shifted emission maximum compared to the parent Alq3 and the opposite is true for 5-position. Based on this study many research groups focused on the synthesis of new Alq3 derivatives and studying their photoluminescence (PL) and electroluminescence (EL) properties.

In our previous efforts we have designed and prepared Alq3 derivatives with different substitutions at C-4 and C-5 in order to achieve derivatives with better stability, higher efficiency and different emission colors [13,14]. Among the different prepared 4- and 5-substituted Alq3 [13–17], derivatives with nitrogen functionalities at C-4 were proved to be exceptionally efficient emitters in OLEDs in addition to their efficiency in OSC when used as dopant [9,14].

On the other hand amorphous materials have received growing attention as materials for photovoltaic applications. Compared with crystalline materials, amorphous materials tend to form uniform, stable and transparent thin films during the OLED fabrication [18]. Transition glass temperature is a key factor that determines the thermal stability of amorphous material. The best of our knowledge, the blue shifted Alq3

* Tel.: +20 623306300; fax: +20 623360254.
E-mail address: walaa_omar@s-petrol.suez.edu.eg
derivative, Al tris(4-piperidin-1-yl-quinolin-8-ol), was the first reported amorphous Alq3 derivative with high transition glass temperature ($T_g = 196 ^\circ C$), excellent photoluminescence, electroluminescence and thermal properties in addition to its improved solubility in organic solvents compared to the parent Alq3 [14].

Solvent free amination is environmentally friendly synthesis which offers high yield in short reaction time [19,20]. In previous work, we were able to prepare 4-piperidyl-8-hydroxyquinoline and 4-(4-methylpiperazinyl)-8-hydroxyquinoline in high yields (95% and 88%, respectively) by solvent free amination reaction [14]. The current study will focus on the preparation of a new amorphous 4-substituted Alq3 derivative through the synthesis of the new ligand 4-morpholinyl-8-hydroxyquinoline using solvent free amination reaction and complexing it to Al$^{3+}$. The synthesis is followed by spectroscopic and thermal studies in comparison to the parent Alq3 and other Alq3 derivatives.

**Experimental**

**General**

Melting points and $T_g$ were determined using METTLER TOLEDO DSC 821 thermo analyzer. NMR ($^1$H and $^{13}$C) analysis were performed on bruker DPX 200 (200 MHz) spectrometer using DMSO-$d_6$ solution referenced internally to Me$_4$Si, $^1$H NMR values are given in Hz. TLC were performed on dry silica gel plates and developed by using chloroform/methanol mixture as eluent. The starting material 4-chloro-8-tosyloxyquinoline 1 has been prepared from the commercially available xanthurenic acid according to the earlier reported procedures [21].

**Synthesis of 4-morpholinyl-8-hydroxyquinoline (2)**

4-Chloro-8-tosyloxyquinoline 1 (0.5 g, 1.5 mmol) was mixed with morpholine (1.4 mL, 16 mmol) and heated in an oil bath at 140–150 °C for 1 h. After cooling to room temperature, water was added (15 mL). The formed precipitate was filtered, dissolved in hot ethanol (5 mL) and then allowed to cool. The formed colorless crystals was found to be 4-tosylmorpholine 4 (mp 146–7 °C, lit. 147–8 °C [22,23]) which was separated by filtration and the filtrate was concentrated and allowed to cool. Then the title compound was separated as yellowish crystals (mp 131–2 °C, yield 0.31 g, 90%). $^1$H NMR (200 MHz, DMSO-$d_6$) δ 3.18 (s br, 4H), 3.88 (s br, 4H), 7.02–7.07 (m, 2H), 7.35–7.49 (m, 2H), 8.66–8.69 (d, $J = 4.8$ Hz, 1H); $^{13}$C NMR (50 MHz, DMSO-$d_6$) δ 52.5, 66.6, 109.8, 111.1, 114.0, 123.7, 126.7, 140.1, 148.89, 154.2, 156.7. HRMS (M + H)$^+$ calc for C$_{13}$ H$_{15}$N$_2$O$_2$: 231.1134, found: 231.1131.

**Synthesis of Al tris(4-morpholinyl-8-hydroxyquinoline) (3)**

4-Morpholinyl-8-hydroxyquinoline 2 (0.20 g, 0.87 mmol) and Al isopropoxide (0.06 g, 0.29 mmol) were refluxed in dry acetone for 24 h under N$_2$ atmosphere. The reaction mixture was concentrated and petroleum ether was added. The title compound was separated as greenish yellow powder and dried in oven at 60 °C (yield 0.27 g, 87%). $^1$H NMR (200 MHz, DMSO-$d_6$) δ 3.26–3.36 (m, 12H), 3.81 (s br, 12H), 6.62–6.66 (d, $J = 7.6$, 1H), 6.72–7.13 (m, 9H), 7.32–7.42 (m, 3H), 8.34–8.37 (d, $J = 5.3$, 1H), 8.44–8.47 (d, $J = 5.3$, 1H). HRMS (M + H)$^+$ calc for C$_{39}$ H$_{40}$N$_6$O$_6$Al: 715.2825, found: 715.2827.

**DSC measurements**

To detect the overall thermal properties of the new Alq3 derivative, 1 mg of complex 3 was heated from 25 °C to 500 °C by dynamic 20 °C/min heating rate in a standard 40 ml Al cup with 60 ml/min N$_2$ flow. For determination of $T_g$, 5 mg of the new Alq3 derivative was heated from −50 °C to 350 °C with 20 °C/min heating rate and cooled back to −50 °C. The procedure was repeated three times to remove the thermal history.

![Scheme 1](image-url)
Synthesis and properties of a novel Alq3 derivative

4-Morpholinyl-8-hydroxyquinoline 2 has been prepared under solvent free condition by reacting 4-chloro-8-tosyloxyquinoline 1 [21] with morpholine at 140–150 °C. 1H NMR analysis of the product revealed that the product is a mixture of 2 and 4-tosylmorpholine 4. The two products were then separated depending on their relative solubility in ethanol. The formation of the ligand 2 was proved by 1H NMR, 13C NMR spectroscopy and HRMS. The splitting of the tosyl protecting group during the amination reaction of 4-chloro-8-tosyloxyquinoline 1 was also observed during the amination of 1 with pyrrolidine and it was attributed to the high nucleophilicity of the alicyclic mines [21]. The solvent free amination offered fast reaction with a high yield of 2 (90%).

Then ligand 2 was allowed to react with aluminium isopropoxide in refluxing acetone under N2 atmosphere for 24 h. The formed Alq3 derivative 3 was observed to be highly soluble in organic solvents such as alcohols and acetone compared to the parent Alq3. 1H NMR analysis for the new Alq3 derivative 3 proved the formation of the meridional isomer which is more stable than the facial isomer [24]. The overall synthetic route for 3 is described in Scheme 1.

Absorption and photoluminescence properties of complex 3

UV–vis absorption spectrum of the new derivative 3 showed two absorption bands at 299 nm and 375 nm. The morpholinyl substituent at C-4 shortened the absorption wavelength of the new derivative compared to the parent Alq3 Fig. 1. This proves that the morpholinyl substitution at C-4 is powerful enough to change the π-π∗ system effectively and widen the optical band gap.

The photophysical properties of the new Alq3 derivative correlate well with the electronic properties of the morpholinyl group at C-4. The electron donating property of the morpholinyl group (εp = −0.51, calculated from pKa value) caused a blue shift of 33 nm in the emission spectrum of the new derivative compared to the parent Alq3 as shown in Fig. 2. Moreover, the relative fluorescence quantum yield (ΦPL) of the new complex is two times higher than that of the parent Alq3 as shown in Table 1. The optical band gap energy of the new Alq3 derivative is higher than that of the parent Alq3 in agreement with the blue shifted PL emission spectra. In comparison with the efficient emitter Al tris(4-piperidin-1-yl-quinolin-8-ol) (λPL = 477 nm, ΦPL = 2.1)) [14], complex 3 is also blue shifted (489 nm) and has almost similar relative PL quantum yield value ΦPL = 2.02. The UV–vis absorption and PL emission spectra in Figs. 1 and 2 were made in chloroform solution and the results are summarized in Table 1.

DSC measurements

The DSC thermogram of the new Alq3 derivative 3 showed no melting endotherm up to 500 °C. However a glass transition endotherm was clearly observed at 232 °C Fig. 3. The absence of the melting endotherm during the measurement indicates that the complex is amorphous. In addition the higher transition glass temperature of complex 3 than the parent Alq3 (Tg of Alq3 = 174 °C) [26] indicates higher stability of the glass phase which increases device efficiency [18]. In the open literature, only four amorphous Alq3 derivatives have been reported with various Tg values ranging from 142 to 216 °C [14,27].

### Table 1: The photophysical and thermal properties of Alq3 and complex 3.

| Complex | λ_{ol}(nm) | λ_{em}(nm) | Φ_{PL} | Optical band gap (eV) | T_g (°C) |
|---------|------------|------------|--------|------------------------|----------|
| Alq3    | 387 (5.9×10^3) | 522        | 1      | 3.19                   | 174      |
| 3       | 375 (16.9×10^3) | 489        | 2.02   | 3.31                   | 232      |

* a Absorption maximum (nm) and molar absorptivity (Lmol⁻¹ cm⁻¹) in brackets.
* b Photoluminescence emission maximum (nm) of 20 µM of sample in chloroform.
* c Relative photoluminescence quantum yield with respect to Alq3 giving a quantum yield of 1.00 to Alq3 (the absolute quantum yield for Alq3 in chloroform is 0.223 [25]).
* d Estimated from the UV–vis spectra by using E = hC/ν.

Please cite this article in press as: Omar WAE, Synthesis and photophysical properties of aluminium tris-(4-morpholine-8-hydroxyquinoline), J Adv Res (2012), http://dx.doi.org/10.1016/j.jare.2012.09.003
three of those amorphous derivatives have higher relative fluorescence quantum yield than the parent Alq3. It is also worth to mention that all the reported amorphous Alq3 derivatives are amino substituted derivatives at C-4. The newly synthesized Alq3 in this work (complex 3) has the highest $T_g$ value so far ($T_g=232^\circ C$). Generally complex 3 is expected to be the most thermally stable material of the new emerging generation of amorphous Alq3 derivatives due to the absence of melting endotherm along with the highest $T_g$ value.

Conclusions

A new ligand, 4-morpholinyl-8-hydroxyquinoline, could be prepared in a high yield by the reaction of 4-chloro-8-tosyloxyquinoline and morpholine under solvent free condition. The attachment of the saturated cyclic morpholinyl group at C-4 in the newly synthesized Alq3 derivatives improved the thermal and photophysical properties compared to the parent Alq3. The new derivative showed blue shifted emission spectrum, excellent photoluminescence properties and higher relative photoluminescence quantum yield compared to the parent Alq3. DSC measurement revealed that complex 3 is amorphous with high transition glass temperature ($232^\circ C$). The efficient PL properties, high solubility along with the amorphous property and high $T_g$ value indicate that the newly synthesized Alq3 derivative in this work can be employed as a highly efficient emitter in OLED devices.

Acknowledgements

The author thanks Ms. Venla Manninen in Tampere University of Technology for the help with the PL measurements and the Department of Chemistry, University of Oulu for the NMR analysis.

References

[1] Tang CW, Vanslyke SA. Organic electroluminescent diodes. Appl Phys Lett 1987;51:913–5.
[2] Tang CW, Vanslyke SA, Chen CH. Electroluminescence of doped organic thin films. J Appl Phys 1989;65:3610–6.
[3] Vanslyke SA, Chen CH, Tang CW. Organic electroluminescent devices with improved stability. Appl Phys Lett 1996;69:2160–2.
[4] Hughes G, Bryce MR. Electron-transporting materials for organic electroluminescent and electrophosphorescent devices. J Mater Chem 2005;15:94–107.
[5] Kulkarni AP, Tonzola C, Babel A, Jenekhe SA. Electron transport materials for organic light-emitting diodes. Chem Mater 2004;16:4556–73.
[6] Wong KT, Chen YM, Lin YT, Su H, Wu CC. Nonconjugated hybrid of carbazole and fluorene: a novel host material for highly efficient green and red phosphorescent OLEDs. Org Lett 2005;7:5361–4.
[7] Song QL, Li FY, Yang H, Hu HR, Wang X, Zhou W, et al. Small-molecule organic solar cells with improved stability. Chem Phys Lett 2005;416:42–6.
[8] Kao P-C, Chu S-Y, Huang H-H, Tseng Z-L, Chen Y-C. Improved efficiency of organic photovoltaic cells using tris(8-hydroxy-quinoline) aluminum as a doping material. Thin Solid Films 2009;517:5301–4.
[9] Tolkki A, Kaunisto K, Heiskanen JP, Omar WAE, Huttunen K, Lehtimäki S, et al. Organometallic tris(8-hydroxyquinoline) aluminum complexes as buffer layers and dopants in inverted organic solar cells. Thin Solid Films 2012;520:4475–781.
[10] Wang N, Yu J, Zang Y, Huang J, Jiang Y. Effect of buffer layers on the performance of organic photovoltaic cells based on copper phthalocyanine and C60. Sol Energy Mater Sol Cells 2010;94:263–6.
[11] Du H, Deng Z, Lu Z, Chen Z, Zou Y, Yin Y. The effect of small-molecule electron transporting materials on the performance of polymer solar cells. Thin Solid Films 2011;519:4357–60.
[12] Curioni A, Andreoni W. Computer simulation for organic light-emitting diodes. IBM J Res Dev 2001(45):101–13.
[13] Omar WAE, Hormi OEO. Synthesis of 4-(2-arylvinyl)-8-hydroxyquinolines via anhydrous Heck coupling reaction and the PL of their Al complexes. Tetrahedron 2009;65:4422–8.
[14] Omar WAE, Haverinen H, Hormi OEO. New Alq4 derivatives with efficient photoluminescence and electroluminescence properties for organic light-emitting diodes. Tetrahedron 2009;65:9707–12.
[15] Perez-Bolivar C, Takizawa S-Y, Nishimura G, Montes VA, Anzenbacher P. High efficiency tris(8-hydroxyquinoline) aluminum (Alq3) complexes for organic white-light-emitting diodes and solid state lightening. Chem Eur J 2011;17:9076–82.
[16] Montes VA, Pohl R, Shinar J, Anzenbacher P. Effective manipulation of the electronic effects and its influence on the emission of 5-substituted tris(8-quinolate) aluminum (III) complexes. Chem Eur J 2006;12:4523–35.
[17] Heiskanen JP, Hormi OEO. Absorption and photoluminescence properties of 4-substituted Alq3 derivatives and tris(4-hydroxypyridinoanthrene) aluminum. Tetrahedron 2009;65:8244–9.
[18] Shirata YJ. Photo-and electroactive amorphous molecular materials-molecular design, syntheses, reactions, properties, and applications. Mater Chem 2005;15:75–93.
[19] Narayanan S, Seelhammer T, Gawley RE. Microwave assisted solvent free amination of halo-(pyridine or pyrimidine) without transition metal catalyst. Tetrahedron Lett 2004;45:757–9.
[20] Wei Y-J, Ren H, Wang J-X. Solvent- and catalyst-free geminal dialkxylation of carboxylic acid derivatives with allylzinc bromide. Tetrahedron Lett 2008;49:5697–9.
[21] Omar WAE, Heiskanen JP, Hormi OEO. Synthesis of 8-hydroxyquinolines with amino and thioalkyl functionalities at position 4. J Heterocycl Chem 2008;45:593–5.
[22] Amstutz ED. The reaction of β-halogen ethers with metals. Mechanism of the reaction and related processes. J Org Chem 1944;9:310–8.
[23] De Luca L, Giacomelli G. An easy microwave-assisted synthesis of sulfonamides directly from sulfonic acids. J Org Chem 2008;73:3967–9.

[24] Muccini M, Loi MA, Kenevey K, Zamboni R, Masciocchi N, Sironi A. Blue luminescence of facial tris(quinolin-8-olato) aluminum (III) in solution, crystals, and thin films. Adv Mater 2004;16:861–4.

[25] Ravi Kishore VVN, Narasimhan KL, Periasamy N. On the radiative lifetime, quantum yield and fluorescence decay of Alq3 in thin films. Phys Chem Chem Phys 2003(5):1386–91.

[26] Liao SH, Shiu JR, Liu SW, Yeh SJ, Chen YH, Chen CT, et al. Hydroxy naphthyridine-derived group III metal chelates: wide band gap and deep blue analogues of green Alq3 (tris(8-hydroxyquinolate) aluminum) and their versatile applications for organic light-emitting diodes. J Am Chem Soc 2009;131:763–77.

[27] Heiskanen JP, Tolkki AE, Lemmetyinen HJ, Hormi OEO. Fused Alq3 derivatives: syntheses and photophysical characteristics. J Mater Chem 2011;21:14766–75.