

## Elucidation of the Structure of a Highly Efficient Blue Electroluminescent Material

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The shortcomings of today's electronic displays include a lack of brightness, a narrow viewing angle, and a high dependence on power. Therefore, the high demand for displays which are of low-cost, power-efficient, lightweight, bright, flexible, and ultrathin, especially for portable applications, has led to the search for alternatives to conventional technology. Organic light-emitting diodes (OLEDs) have emerged as a promising new technology for the next generation of flat panel displays.<sup>1</sup>

Interest in OLEDs has dramatically increased in the past decade, since the pioneering work of Tang et al.<sup>2a</sup> and Friend et al.<sup>2b</sup> on small-molecule and polymer-based LEDs. In particular, a great deal of effort has been devoted to the development of highly efficient red-, green-, and blue-emitting materials.<sup>3</sup> Despite much progress achieved to date, there is still need to further optimize the color, lifetime, and efficiency of these active components of OLEDs. Furthermore, blue luminescent materials have remained a challenge and most are aluminum and zinc compounds of 8-hydroxyquinoline derivatives.<sup>1f–j</sup> In this report, we describe the elucidation of the structure of a recently published blue electroluminescent material.

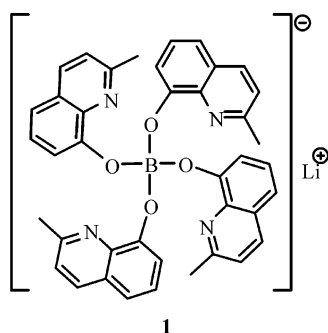
The groups of Tao<sup>4</sup> and Wang<sup>5</sup> have reported a new lithium borate complex (**1**)<sup>6</sup> as a highly efficient blue electroluminescent material. The emission peak at 470 nm is significantly blue-shifted (by about 60 nm) with respect to its aluminum analogue Alq<sub>3</sub> (tris-(8-hydroxyquinolato)aluminum), which was initially reported by Tang and Van Slyke<sup>2a</sup> and since then has become an industry standard in OLED fabrication.<sup>3,7</sup> The blue-shifting was attributed to the lack of interaction between the boron center and the nitrogen atoms of the ligands. The device reported (ITO/PVK:TPD(50 nm)/**1**(60 nm)/Mg:Ag<sup>8</sup>) showed one of the highest blue emissions for such a device configuration (luminance efficiency of 1.3 lm/W and the maximum luminance is 6900 cd/m<sup>2</sup>).<sup>4</sup> Another attractive feature of this compound is its facile synthesis, which involves the reaction of LiBH<sub>4</sub> and 2-methyl-8-hydroxyquinoline (MeqH) in ethanol.

compounds, we were interested in exploring the electroluminescent properties of a diverse set of analogues of this class of materials.

Our initial study included several commercially available 8-hydroxyquinolines and LiBH<sub>4</sub> or NaBH<sub>4</sub> as the boron source.<sup>9</sup> The compounds were synthesized following Tao's procedure.<sup>4a</sup> Surprisingly, however, during the course of our study, characterization of the analogues of **1** did not support the expected structure. For instance, the sodium analogue of **1** (**2**) had a silent <sup>11</sup>B NMR spectrum, and the elemental analysis showed the expected amount of carbon, hydrogen, and nitrogen but showed only 0.02% boron.<sup>9</sup> Similar spectroscopic and elemental analysis data were obtained for the off-white powder (**3**) isolated by reacting NaBH<sub>4</sub> and 5-chloro-8-hydroxyquinoline (ClqH), and the products (**4** and **5**) obtained from the reaction of NaBH<sub>4</sub> or LiBH<sub>4</sub> with 5,7-dichloro-2-methyl-8-hydroxyquinoline (Cl<sub>2</sub>MeqH), respectively.<sup>9</sup>

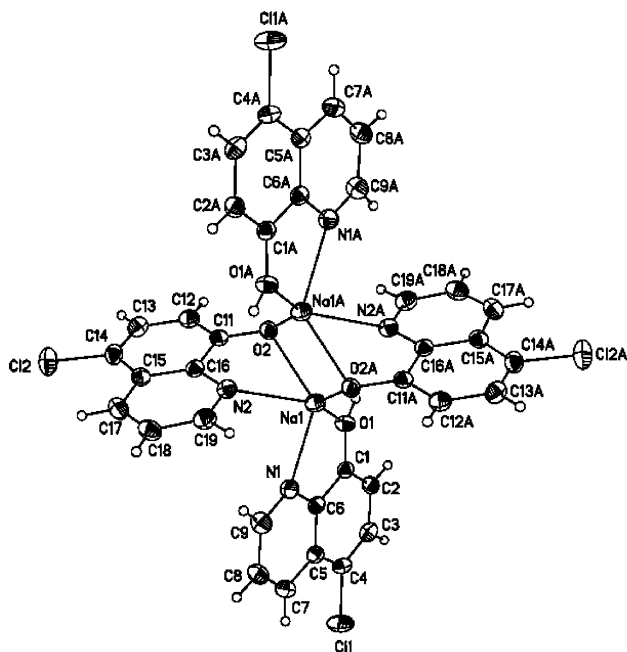
Given these curious results, we repeated the synthesis of **1** and obtained a blue luminescent solid that has the same <sup>1</sup>H NMR and elemental analysis (for carbon, hydrogen, and nitrogen) as previously reported. However, it does not display a <sup>11</sup>B NMR signal, and it only contains 0.07% boron.<sup>10</sup> Furthermore, this compound does not sublime intact, which is not desirable for vapor-deposited OLED devices, which is the deposition method used by Tao.<sup>4</sup> Specifically, the thermogravimetric analysis shows that the blue emitter loses about 44% of its mass at 150 °C, corresponding to the loss of MeqH, as identified by <sup>1</sup>H NMR.<sup>9</sup> The remaining material shows blue photoluminescence, albeit not as bright as before sublimation, without significant mass change up to 300 °C where a relatively abrupt weight loss of about 80% occurs. The mass spectroscopy of this material shows peaks corresponding to the presence of fragments LiMeq (*m/z* = 165) and [LiMeq<sub>2</sub>][Li] (*m/z* = 330).<sup>9</sup> In addition, alkali metal salts of 8-hydroxyquinoline derivatives have recently been shown to be efficient emitters and interface materials in OLEDs.<sup>11</sup> Particular attention focused on Liq and LiMeq complexes as electron injection materials, which are obtained by reacting LiOH with the appropriate 8-hydroxyquinoline derivatives.<sup>11a,c</sup> The spectroscopic and analytical data for LiMeq and its photoluminescence spectrum are similar to those reported for **1**. Therefore, the above results suggest that the reaction between LiBH<sub>4</sub> and MeqH does not yield **1**, as previously reported; rather, the reaction yields the lithium salt of MeqH, [(Meq)(MeqH)Li]<sub>x</sub>.

We have further affirmed this finding by characterizing the structure of **3**<sup>9</sup> using X-ray crystallographic analysis, as a sodium hydroxyquinoline–hydroxyquinolate dimeric complex (see Figure 1), rather than the borate analogue of **1**. The crystal structure of **3** shows that the sodium centers are bridged by two Clq ligands in which each oxygen and nitrogen atom coordinates to two different sodium atoms. The coordination sphere around each sodium is completed by an O,N-coordinated ClqH ligand. To our knowledge, this is the first structurally characterized alkali metal salt of an 8-hydroxyquinoline derivative. The dimeric structure of **3** is similar to that found in the sodium bis(*o*-amino)phenolate **6**.<sup>12a</sup> The Na–O



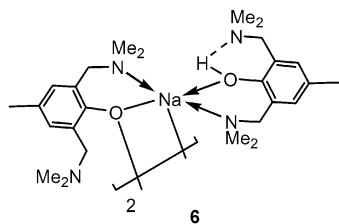
Given the ease of the synthesis of such efficient blue emitters, it's amenability to high-throughput approaches, and the commercial availability of a large number of hydroxyquinoline and borohydride

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**Figure 1.** Structure of  $[(\text{Clq})(\text{ClqH})\text{Na}]_2$  (**3**) with thermal ellipsoids drawn to the 50% probability level.

bond distances for the anionic ligand Clq (range 2.367(15)–2.470(16) Å) are comparable to those previously reported for sodium phenolates,<sup>12b,c</sup> while the Na–N bond (2.662(19) Å) is slightly lengthened with respect to reported sodium phenolates which contain ortho amino substituents.<sup>12a</sup> For the neutral ClqH ligands, both the Na–O and Na–N bond lengths (2.313(16) Å and 2.482(18) Å, respectively) are in the range found in the coordination of the neutral phenol ligand in **6**. The  $\text{Na}_2\text{O}_2$  unit observed in the solid-state structure of **3** is presumably formed due to the presence of excess ClqH ligand (4 equiv were used since we followed the previously reported preparation of **1**).<sup>9</sup> In fact, when performing Tao's procedure, but using equimolar amounts of MeqH and  $\text{LiBH}_4$ , the product isolated is  $\text{LiMeq}(\text{EtOH})_2$  (**7**).<sup>9</sup> This complex was also recently reported by Thelakkat and Kido as the product of the reaction of LiOH with MeqH in ethanol.<sup>11a,d</sup>



In summary, on the basis of the structural characterization of **3** and the spectroscopic and analytical data collected for the products of the reaction of  $\text{MBH}_4$  ( $\text{M} = \text{Li}$  and  $\text{Na}$ ) with several 8-hydroxyquinolines we believe that the reaction of  $\text{LiBH}_4$  with MeqH does not yield **1**, as previously reported; rather, the lithium salt  $[(\text{Meq})-(\text{MeqH})\text{Li}]_x$  is isolated. This lithium complex loses the neutral

MeqH ligand upon thermolysis, rendering a complex with possible structures such as  $[(\text{LiMeq})_x]$  and  $[(\text{Li}(\text{Meq})_2)[\text{Li}]]$ , which are the possible structures of the emitter in the device reported by Tao.<sup>4</sup>

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**Supporting Information Available:** Synthetic and characterization data for compounds **1–5** and **7** (PDF), and X-ray structure details for compound **3** (in CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) Compound **1** is now commercially available from H. W. Sands Corp., Jupiter, FL, <http://www.hwsands.com>, and American Dye Source, Inc., Quebec, Canada, <http://www.adsdyes.com>.
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- (8) Definition of abbreviations: indium tin oxide (ITO), poly(*N*-vinylcarbazole) (PVK), *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD).
- (9) See Supporting Information for experimental details.
- (10) Characterization data for **1**:  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz)  $\delta$  2.46 (s, 3H), 6.48 (d,  $J = 10$  Hz, 1H), 6.56 (d,  $J = 10$  Hz, 1H), 7.09 (t,  $J = 10$  Hz, 1H), 7.16 (d,  $J = 10$  Hz, 1H), 7.95 (d,  $J = 9.5$  Hz, 1H). Anal. Calcd for  $\text{C}_{40}\text{H}_{32}\text{B}_4\text{LiN}_4\text{O}_4$ : C, 73.78; H, 4.92; N, 8.61; B, 1.66. Found: C, 72.77; H, 5.21; N, 8.46; B, 0.07.
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