8-2003

Emission Color Tuning In Alq(3) Complexes With Extended Conjugated Chromophores

Radek Pohl

Pavel Anzenbacher Jr.
Bowling Green State University, pavel@bgsu.edu

Repository Citation

Pohl, Radek and Anzenbacher, Pavel Jr., "Emission Color Tuning In Alq(3) Complexes With Extended Conjugated Chromophores" (2003). *Chemistry Faculty Publications*. 158.
https://scholarworks.bgsu.edu/chem_pub/158

ORGANIC LETTERS

2003
Vol. 5, No. 16
2769−2772

Emission Color Tuning in AlQ$_3$ Complexes with Extended Conjugated Chromophores

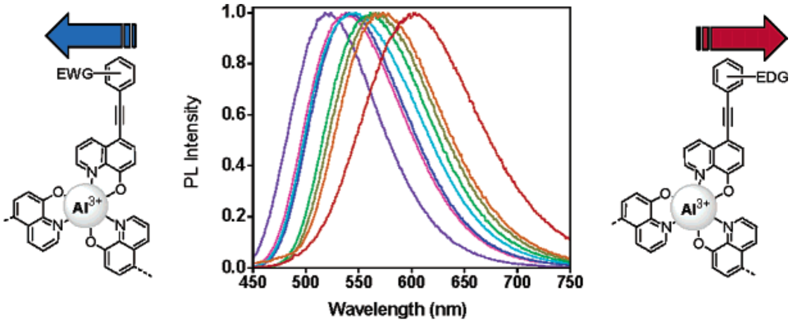
Radek Pohl and Pavel Anzenbacher, Jr.*

Center for Photochemical Sciences and Department of Chemistry,
Bowling Green State University, Bowling Green, Ohio 43403

pavel@bgnet.bgsu.edu

Received April 25, 2003

ABSTRACT



A new method for the synthesis of 5-arylethynyl-8-hydroxyquinoline ligands using Sonogashira–Hagihara coupling was developed. The electronic nature of arylethynyl substituents affects the emission color and quantum yield of the resulting Al(III) complex. Photophysical properties of the metallocomplexes correspond to the electron-withdrawing/-donating character of the arylethynyl substituents. Optical properties of such Al(III) complexes correlate with the Hammett constant values of the respective substituents. This strategy offers a powerful tool for the preparation of electroluminophores with predictable photophysical properties.

Emission properties of metallocomplexes are in general controlled by a number of factors, including electronic properties of the ligand and metal ion, coordination bond lengths and angles that affect the energy mixing, and splitting of electronic states involved in the emission. The design of novel emissive materials with improved photonic properties is predicated upon detailed understanding of the relationship between the structure of a ligand and photonic properties of the resulting metallocomplexes.

Among the luminescent metallocomplexes, tris(8-quinolinolate)Al(III) (AlQ$_3$) plays an important role as an electroluminophore and the most stable electron-transporting compound currently used in organic light-emitting diodes (OLEDs).[1,2] AlQ$_3$-type complexes display ligand-centered excited states.[3] Light emission of the AlQ$_3$ complexes originates from the electronic $\pi-\pi^*$ transitions in the quinolinolate ligands.[4,5] The HOMO-orbitals are located on the phenoxide side of the ligand, while the LUMO-orbitals are located on the pyridyl side.[2b] This suggests that substituents attached to the quinolinolate ligand may be used as a handle for tuning of the complex emission. The literature, however, provides spotty evidence supporting the correlation of the substituent properties with the photophysical properties of quinolinolate chromophores. In general, electron-donating groups (EDGs) such as methyl attached to the pyridine ring

---

(1) Kelly, S. M. *Flat Panel Displays: Advanced Organic Materials*; Connor, J. A., Series Ed.; The Royal Society of Chemistry: Cambridge, 2000.

(2) (a) Wang, S. *Coord. Chem. Rev.* **2001**, *215*, 79−98. (b) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161−174. (c) *Organic Electroluminescent Materials and Devices*; Miyata, S., Nalwa, H. S., Eds.; Gordon and Breach Publishers: Amsterdam, 1997.

(3) Vogler, A.; Kunkely, H. Luminescent Metal Complexes: Diversity of Excited States. In *Topics in Current Chemistry, Vol. 213: Transition Metal and Rare Earth Compounds: Excited States, Transitions, Interactions I*; Yersin, H., Ed.; Springer-Verlag: Berlin, 2001.

10.1021/ol034693a CCC: $25.00

cause a blue shift in the complex emission[1,6] (~510 nm) compared to the emission of the parent AlQ$_3$ (526 nm), while introduction of alkyls to the benzene ring causes a red shift (≥530 nnm).[1,2b,7] The presence of electron-withdrawing groups (EWGs) such as fluoro-, chloro-,[8a,4] and cyano[8b] groups in the 5- or 7-position of the benzene ring results in almost negligible emission shifts (520−530 nm), while strong EWGs such as sulfonamide ($-SO_2NR_2$) result in significantly blue-shifted emission (~480 nm).[8c]

In an effort to explore the magnitude of the substituent effect and its possible use in the emission color tuning in AlQ$_3$ complexes, we decided to synthesize a series of 8-hydroxyquinoline ligands (Q) with various aryl substituents (Ar) connected together via an ethynylene spacer (E). The inclusion of the ethynylene spacer was also motivated by a high degree of electronic communication between the ligand and the substituted aryl moiety as well as avoiding a potential interaction of *ortho*-substituents on Ar with the Q-moiety in the case of directly attached aryl moieties (Q-Ar). Structures of the complexes prepared in this study are shown in Figure 1.

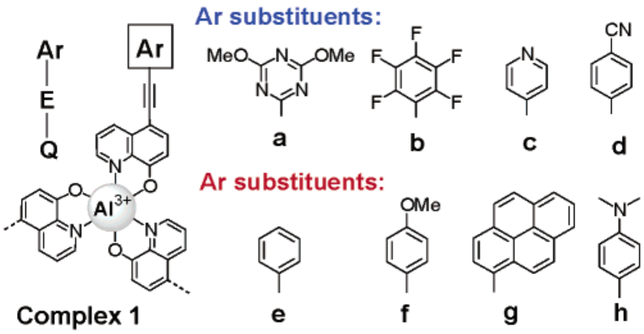
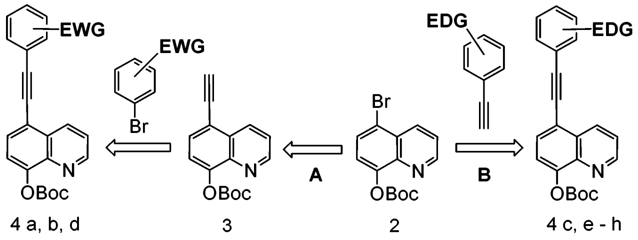


Figure 1. Structures of tris(5-arylethynyl-8-quinolinolate)Al(III) complexes **1a**−**h**.

The strategy for the synthesis of the ligands utilized in complexes **1a**−**h** is depicted in Scheme 1. Pathway A was used for the attachment of electron-deficient arenes, while pathway B was used for the synthesis of electron-rich ligands **4a**,**b**,**d**. The only exception was the synthesis of the 2-(4-pyridyl)ethynyl compound **4c**, which was synthesized using pathway B.

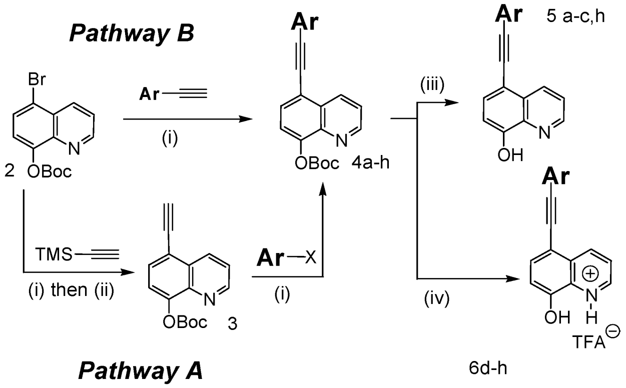
Scheme 1. Strategy for Synthesis of Protected Quinolate Ligands



The synthesis of complexes **1a**−**h** departs from 5-bromoquinoline-8-hydroxyquinoline,[9] which was converted to the corresponding Boc-derivative **2** by reaction with di-*tert*-butyl dicarbonate. The Boc group was selected over the published methyl,[10] benzyl,[11] and TBDMS[12] groups because of its easy deprotection compared to Bn/Me protection and the crystallinity of the TBDMS derivatives.

According to pathway A, compound **2** underwent Sonogashira−Hagihara coupling[13] with TMS-acetylene followed by KF-mediated deprotection of the TMS group to give 5-ethynyl-5-BocO-quinoline **3** in 69% overall yield (Scheme 2).

Scheme 2. Synthesis of Quinolinolate Ligands[a]



[a] Reaction conditions: (i) Pd(TPP)$_4$ (5%), CuI (5%), DIPEA, THF; (ii) KF (2 equiv), MeOH; (iii) piperidine (3 equiv), CH$_2$Cl$_2$; (iv) TFA (5 equiv), CH$_2$Cl$_2$.

Electron-deficient arenes such as 2-chloro-4,6-dimethoxy-1,3,5-triazine,[14] pentafluoroiodobenzene, and *p*-bromoben-

---

(4) Jang, H.; Do, L.-M.; Kim, Y.; Kim, J. G.; Zyung, T.; Do, Y. *Synth. Met.* **2001**, *121*, 1669−1670.

(5) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1986**, *25*, 3858−3865.

(6) (a) Yu, J.; Chen, Z.; Sakuratani, Y.; Suzuki, H.; Tokita, M.; Miyata, S. *Jpn. J. Appl. Phys.* **1999**, *38*, 6762−6763. (b) Kido, J.; Iizumi, Y. *Chem. Lett.* **1997**, 963−964.

(7) Hamada, Y.; Sano, T.; Fujita, M.; Fujii, T.; Nishio, Y.; Shibata, K. *Jpn. J. Appl. Phys.* **1993**, *32*, 514−515.

(8) (a) Matsumura, M.; Akai, T. *Jpn. J. Appl. Phys.* **1996**, *35*, 5357−5360. (b) Burrows, P. E.; Shen, Z.; Bulovic, V.; McCarty, D. M.; Forrest, S. R.; Cronin, J. A.; Thompson, M. E. *J. Appl. Phys.* **1996**, *79*, 7991−8006. (c) Hopkins, T. A.; Meerholz, K.; Shaheen, S.; Anderson, M. L.; Schmidt, A.; Kippelen, B.; Padias, A. B.; Hall, H. K., Jr.; Peyghambarian, N.; Armstrong, N. R. *Chem. Mater.* **1996**, *8*, 344−351.

(9) Prasad, R.; Coffer, H. L. D.; Fernando, Q.; Freiser, H. *J. Org. Chem.* **1965**, *30*, 1251.

(10) (a) Trecourt, F.; Mongin, F.; Mallet, M.; Queguiner, G. *J. Heterocycl. Chem.* **1995**, *32*, 1261−1267. (b) Albrecht, M.; Blau, O.; Röttele, H. *New J. Chem.* **2000**, *24*, 619−622.

(11) Nakano, Y.; Imai, D. *Synthesis* **1997**, 1425−1428.

(12) Jotterand, N.; Pearce, D. A.; Imperiali, B. *J. Org. Chem.* **2001**, *66*, 3224−3228.

(13) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467−4470. (b) Sonogashira, K. in *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, 1998.

(14) Cronin, J. S.; Ginah, F. O.; Murray, A. R.; Copp, J. D. *Synth. Commun.* **1996**, *26*, 3491−3494.

zonitrile were then attached using standard conditions for Sonogashira–Hagihara coupling to give **4a** (83%), **4b** (62%), and **4d** (97%), respectively. The same method was also used for the reaction with *p*-bromonitrobenzene and *p*-bromopyridine-*N*-oxide.[15]

Synthetic pathway B utilizes electron-rich ethynylarenes such as ethynylbenzene, *p*-ethynylmethoxybenzene, 1-ethynylpyrene, and *p*-ethynyldimethylaminobenzene to yield ligands of general structures **4e**–**h** in 69, 65, 76, and 59% yields, respectively. The same approach was used to prepare 8-BocO-5-[(pyridin-4-yl)ethynyl]quinoline **4c** from commercially available *p*-ethynylpyridine hydrochloride, albeit the yield was lower (49%). All Boc-protected ligands were purified by flash chromatography and recrystallization (acetone–hexane). This method also yielded monocrystals of **4g**. X-ray analysis of **4g** (Figure 2) suggests effective conjugation in the extended chromophore ligand.

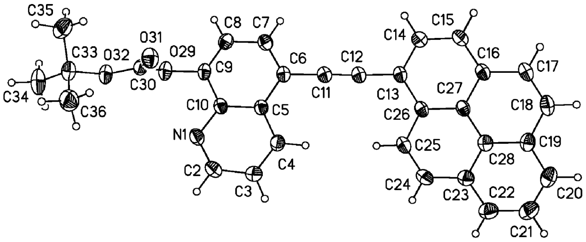


Figure 2. X-ray structure of the protected ligand **4g**. Thermal ellipsoids are scaled to the 30% probability level.

Deprotection of the Boc group may be achieved in several ways, including TFA- or piperidine-mediated deprotection. For example, the dimethylamino derivative **4h** was deprotected by both TFA and piperidine to give after crystallization essentially the same yields of 71% (**5h**) and 73% (**6h**), respectively. Piperidine deprotection yielded ligands **5a**–**c**,**h** in 79, 79, 90, and 73% yields, respectively. Deprotection using TFA gave trifluoroacetate salts of ligands **6d**–**h** in 99, 67, 79, 94, and 71% yields. Ligands **5a**–**c**,**h** and **6d**–**h** were converted to the corresponding complexes **1a**–**h** by reaction of ethanolic solutions of ligands with aqueous $AlCl_3$ followed by neutralization with triethylamine and crystallization from ethanol and dichloromethane–hexane. All complexes **1a**–**h** are soluble in a variety of solvents, including dichloromethane, THF, and DMSO and less soluble in alcohols.

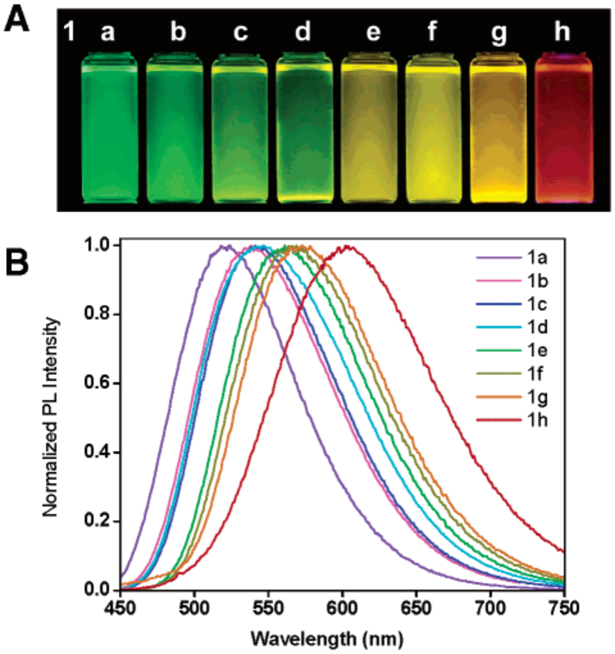


Figure 3. Panel A: Emission of complexes **1a**–**h** upon illumination with black light (365 nm). Panel B: Emission spectra of complexes **1a**–**h**.

Table 1. Optical Properties of Complexes **1a**–**h**[a]

compound	A_{max} (ϵ)[b]	λ_F [nm]	Φ_F[c]	τ [ns]
1a	407 (3.5 × 10^4)	520	0.317	11.85
b	410 (2.7 × 10^4)	538	0.228	8.67
c	414 (2.4 × 10^4)	541	0.235	8.95
d	414 (8.4 × 10^4)	545	0.203	6.61
e	421 (2.2 × 10^4)	561	0.088	3.56
f	421 (1.8 × 10^4)	569	0.047	1.86
g	385 (6.8 × 10^4)	573	0.036	1.28
h	425 (3.9 × 10^4)	600	0.009	0.89
AlQ$_3$	388 (7.0 × 10^3)	526	0.171	15.38

[a] Used 30 μM solutions in dichloromethane. [b] Units = mol^{-1} cm^{-1}. [c] Determined using quinine sulfate as a standard.

Successful emission color tuning in the complexes mediated by the substituents may be observed by naked eye examination of the solutions of the complexes and fluorescence spectroscopy. Complexes **1a**–**h** show bright photoluminescence upon excitation of the dichloromethane solution with black light (365 nm). As expected, the emission shifts from green-blue to yellow and red depending on the electronic nature of the aryl (Figure 3).

Table 1 summarizes the optical properties of complexes **1a**–**h** determined from UV–vis and fluorescence measurements.

One can see that the emission maxima of complexes **1a**–**h** span ~100 nm between 520 and 610 nm, and the emission profiles at ca. 50% of the peaks intensity cover a significant portion of the visible light spectrum (485–670 nm). Complexes **1a**–**d** also display reasonably high fluorescence quantum yields, which makes them potentially useful as electroluminophores. Because the emission of light by the quinolinolate complexes originates from ligand-centered excited states,[3] we were intrigued by the possibility of correlation of the photophysical properties with the Hammett

---

(15) Same method was also used for reaction with *p*-bromonitrobenzene (76%) and *p*-bromopyridine-*N*-oxide (78%); however, these materials after piperidine-mediated deprotection (97 and 73% yields, respectively) did not yield complexes with appreciable luminescence properties and therefore are not discussed in this communication.

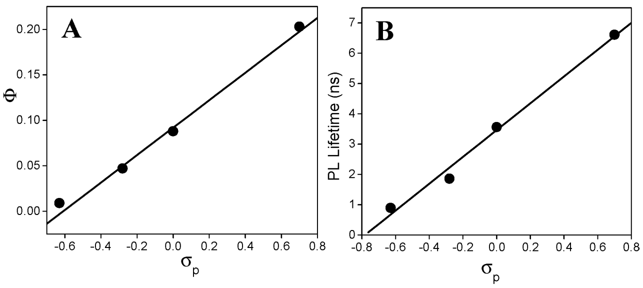


Figure 4. Fluorescence quantum yield correlation with the Hammett constant for complexes **1d−f**,**h** with correlation coefficients $R^2 = 0.9923$ (panel A) and $R^2 = 0.9899$ (panel B).

constants to predict the emission of the complexes before their synthesis is performed. Although the pool of compounds **1a−h** bearing substituents with a known Hammett constant (σ_p)[16] is limited, one can clearly see that the photophysical properties, namely, the fluorescence quantum yield and lifetime, show excellent correlation (Figure 4A,B).

Additionally, photochemical properties of the prepared complexes were investigated in terms of the energy gap law,[17] which describes the exponential energy gap dependence of the nonradiative decay processes in the chromophore. As the energy gap between the lowest excited state and ground state increased, the photoluminescence lifetime and quantum yield increased. Because the energy-gap law correlation is based on recorded fluorescence lifetime, quantum yield, and emission maxima recorded for each compound, the successful correlation for compounds **1a−h** (Figure 5) attests to the high photonic quality of the prepared materials.

We were concerned with the stability of compounds **1a−h** regarding their potential use in OLEDs given the potential sensitivity of the acetylene units to the electron injection. Simple OLEDs were fabricated using ITO-modified glass (anode), Baytron-P (hole-transport layer), a complex spin-coated from CH_2Cl_2, and In−Ga (cathode). Although the performance of these simple OLEDs was somewhat inconsistent, our preliminary results indicate that compounds **1a−h** are potential electroluminophores. The OLEDs fabricated using compounds prepared in this study showed turn-on voltages at 6−7 V.

In conclusion, a new class of electroluminescent compounds based on tris(8-quinolinolate)Al(III) with arylethynyl substituents was synthesized using a Sonogashira−Hagihara coupling procedure. We have shown that the electronic nature of the arylethynyl substituent affects the emission color and fluorescence quantum yield of the resulting Al(III) complex. The optical properties of the resulting Al(III) complexes correlate with the values of the Hammett constant of the respective substituents. This strategy offers a powerful tool for the preparation of electroluminophores with predictable photophysical properties. Efforts toward investigation of solid-state luminescence, fabrication, and evaluation of OLEDs utilizing compounds **1a−h** are currently under way.

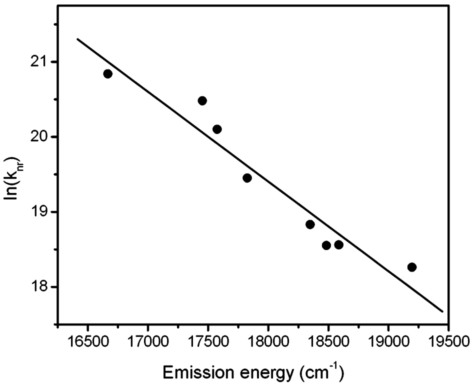


Figure 5. Energy gap correlation performed for complexes **1a−h**. Correlation coefficient $R^2 = 0.9320$.

Acknowledgment. Financial support from Bowling Green State University, the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 38110-G4 to P.A.), and NSF (Grant DMR-0306117 to P.A.) is gratefully acknowledged. We are grateful to Dr. Vince M. Lynch of the University of Texas at Austin for solving the X-ray structure of **4g** and Drs. Kamil Lang and Pavel Kubat of the Czech Academy of Sciences for their help with recording the photophysical properties of **1a-h**.

Supporting Information Available: Experimental procedures and spectroscopic data for complexes **1a−h**, protected ligands **4a−h**, deprotected ligands **5a−c**,**h** and **6d−h**, and crystallographic data for **4g** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OL034693A

---

[16] Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley-Interscience: New York, 2001.

[17] Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444−2453.