




## Article

# Synthesis and Photophysical Properties of a Series of Dimeric Indium Quinolinates

Sang Woo Kwak <sup>1,†</sup>, Ju Hyun Hong <sup>2,†</sup>, Sang Hoon Lee <sup>1</sup>, Min Kim <sup>1</sup> , Yongseog Chung <sup>1</sup>, Kang Mun Lee <sup>2,\*</sup> , Youngjo Kim <sup>1,\*</sup> and Myung Hwan Park <sup>3,\*</sup> 

<sup>1</sup> Department of Chemistry, Chungbuk National University, Cheongju 28644, Korea; sangwoo814@hanmail.net (S.W.K.); lsanh94@gmail.com (S.H.L.); minkim@chungbuk.ac.kr (M.K.); yschung@chungbuk.ac.kr (Y.C.)

<sup>2</sup> Department of Chemistry, Institute for Molecular Science and Fusion Technology, Kangwon National University, Chuncheon 24341, Korea; asqm2253@kangwon.ac.kr

<sup>3</sup> Department of Chemistry Education, Chungbuk National University, Cheongju 28644, Korea

\* Correspondence: kangmunlee@kangwon.ac.kr (K.M.L.); ykim@chungbuk.ac.kr (Y.K.); mhpark98@chungbuk.ac.kr (M.H.P.); Tel.: +82-33-250-8499 (K.M.L.); +82-43-261-3395 (Y.K.); +82-43-261-2736 (M.H.P.)

† The first and second authors contributed equally to this work.

**Abstract:** A novel class of quinolinol-based dimeric indium complexes (1–6) was synthesized and characterized using <sup>1</sup>H and <sup>13</sup>C(<sup>1</sup>H) NMR spectroscopy and elemental analysis. Compounds 1–6 exhibited typical low-energy absorption bands assignable to quinolinol-centered  $\pi$ – $\pi^*$  charge transfer (CT) transition. The emission spectra of 1–6 exhibited slight bathochromic shifts with increasing solvent polarity (*p*-xylene < tetrahydrofuran (THF) < dichloromethane (DCM)). The emission bands also showed a gradual redshift, with an increase in the electron-donating effect of substituents at the C5 position of the quinoline groups. The absolute emission quantum yields ( $\Phi_{PL}$ ) of compounds 1 (11.2% in THF and 17.2% in film) and 4 (17.8% in THF and 36.2% in film) with methyl substituents at the C5 position of the quinoline moieties were higher than those of the indium complexes with other substituents.

**Keywords:** indium quinolinates; charge transfer; quantum yield; radiative decay constant; non-radiative constant



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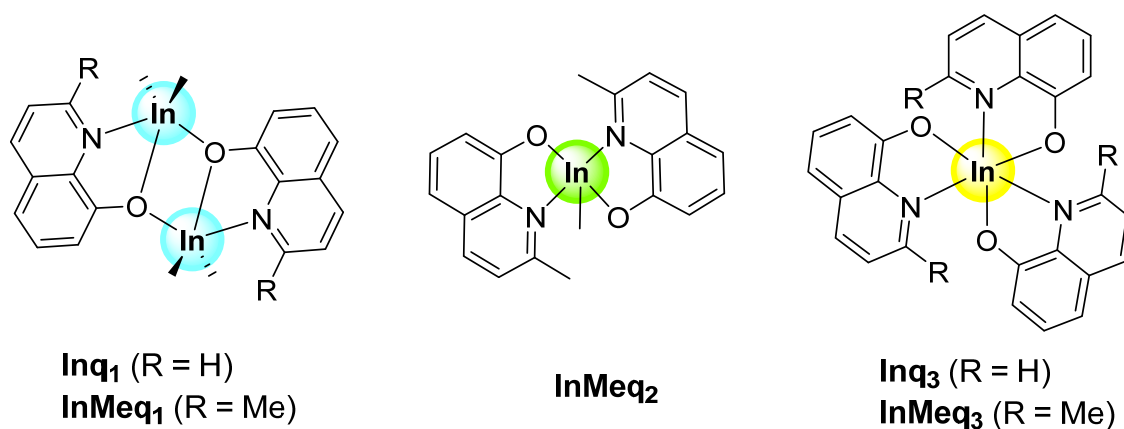
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## 1. Introduction

The creation of tris(8-hydroxyquinolino)aluminum (Alq<sub>3</sub>) by Tang and Van Slyke pioneered a new era of group 13-based organometallic luminescent materials that can be used in versatile optoelectronic fields [1]. Numerous efforts and approaches have been used to modulate the quinolate ligands and expand their applications in organic light-emitting diodes (OLEDs) [2–6]. In this context, particular emphasis has been placed on the development of tris-incorporated metal complexes (Mq<sub>3</sub>). Owing to the ease of introducing various substituents at the C2 and C5 positions of the quinolinolate moiety, studies of various tris-organometallic complexes based on quinolate derivatives have also been conducted [7,8]. These complexes are endowed with photophysical properties that originate from the control of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. Specifically, the systematic variation in the substituents at the C5 position of the quinolinolate groups led to excellent optical properties such as emission-color tuning and enhanced quantum efficiencies [9–18]. However, most of the previous studies primarily focused on tris-complexes.

Recently, our group reported a series of quinolinol-based indium complexes in which the sequential introduction of quinolate ligands to the indium center could control both the emission color and quantum efficiency (Figure 1) [19]. Importantly, the dimeric indium complex (InMeq<sub>1</sub>) with a quinolate ligand exhibited the highest quantum efficiency

( $\Phi_{\text{PL}} = 59\%$  in the poly(methyl methacrylate) (PMMA) film) compared to all the indium luminophores reported to date.



**Figure 1.** Mono-, bis-, and tris-incorporated indium quinolinate complexes.

In this study, we designed a series of dimeric indium quinolates with different substituents (Me, Br, and Ph) at the C5 position of two types of quinolinate ligands (q and Meq) to prove the substitution effects for developing potential indium-based luminescent materials. The detailed synthetic procedures and optical properties of these complexes were investigated.

## 2. Materials and Methods

### 2.1. General Considerations

All manipulations were carried out under an inert N<sub>2</sub> atmosphere using the standard Schlenk and glovebox techniques. All anhydrous-grade solvents (*n*-hexane, diethyl ether, and toluene) were purchased from Alfa Aesar (Ward Hill, MA, USA) and dried by passing them through an activated alumina column and storing them over activated molecular sieves (5 Å). The spectrophotometric-grade solvents (*p*-xylene, tetrahydrofuran (THF), dichloromethane (DCM), and acetonitrile (MeCN)) were used as received from Merck (Darmstadt, Germany). All the commercially available reagents (2-amino-4-bromophenol, 2-amino-4-methylphenol, and 2-amino-4-phenylphenol) were purchased from Alfa Aesar (Ward Hill, MA, USA) and used without any further purification. The trimethylindium (InMe<sub>3</sub>) was analogously prepared according to the literature [19–23]. Because InMe<sub>3</sub> is highly reactive and pyrophoric, it should be stored in a glovebox and used carefully. The quinolinol compounds 5-bromoquinolin-8-ol (**2a**) [24], 5-methylquinolin-8-ol (**3a**) [25], 5-phenylquinolin-8-ol (**5a**) [26], 5-bromo-2-methylquinolin-8-ol (**6a**) [27], 2,5-dimethylquinolin-8-ol (**7a**) [28], and 5-phenyl-2-methylquinolin-8-ol (**8a**) [29] were synthesized using previously reported methods. The deuterated solvent (CDCl<sub>3</sub>) from Cambridge Isotope Laboratories (Tewksbury, MA, USA) was used after drying it over activated molecular sieves (5 Å). The NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for <sup>1</sup>H and 100.62 MHz for <sup>13</sup>C) (Bruker Corporation, Billerica, MA, USA) at the laboratory's ambient temperature. The chemical shifts are given in ppm and are referenced against external Me<sub>4</sub>Si (<sup>1</sup>H and <sup>13</sup>C NMR). The elemental analyses were performed on an EA3000 spectrometer (Eurovector, Pavia, Italy) in the Central Laboratory of Kangwon National University. The UV–vis absorption and PL spectra were recorded on Jasco V-530 (Jasco, Easton, MD, USA) and Fluoromax-4P spectrophotometers (HORIBA, Edison, NJ, USA), respectively. The fluorescence decay lifetimes were measured using an FLS920 time-correlated single-photon-counting spectrometer (Edinburgh Instruments, Livingston, UK) in the Central Laboratory of Kangwon National University, which was equipped with a picosecond pulsed diode laser (EPL 375-ps) pulsed semicon-

ductor diode laser as an excitation source and a microchannel plate photomultiplier tube (200–850 nm) as a detector at 298 K.

### 2.2. Synthesis of [5-methyl-8-quinolinolate In(III)–Me<sub>2</sub>]<sub>2</sub> (1)

A toluene solution (10 mL) of InMe<sub>3</sub> (0.080 g, 0.50 mmol) was added to a toluene solution (20 mL) of **1a** (0.088 g, 0.55 mmol) at room temperature. The reaction mixture was stirred for 12 h, and the insoluble parts were collected by filtration. The remained solid was washed with *n*-hexane (3 × 20 mL) and dried in vacuo to obtain **1** as a pale-yellow solid (0.090 g, 62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.51 (dd, *J* = 1.2 and 4.0 Hz, 2H), 8.34 (m, 2H), 7.47 (m, 2H), 7.26 (dd, *J* = 1.4 and 3.6 Hz, 2H), 6.94 (d, *J* = 6.8 Hz, 2H), 2.55 (s, 6H), −0.13 (s, 12H, In–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 156.43, 143.58, 140.17, 134.97, 129.57, 128.92, 120.86, 119.58, 112.44, 17.62, −5.49. Anal. Calcd for C<sub>24</sub>H<sub>28</sub>In<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 47.56; H, 4.66; N, 4.62. Found: C, 47.38; H, 4.59; N, 4.57.

### 2.3. Synthesis of [5-bromo-8-quinolinolate In(III)–Me<sub>2</sub>]<sub>2</sub> (2)

This compound was prepared in a manner analogous to the synthesis of **1** using **2a** (0.12 g, 0.55 mmol). The desired compound **2** was obtained as a yellow solid (0.12 g, 65%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.58 (dd, *J* = 1.0 and 4.2 Hz, 2H), 8.54 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.56 (m, 2H), 6.91 (d, *J* = 6.8 Hz, 2H), −0.11 (s, 12H, In–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 158.10, 144.60, 140.72, 137.95, 132.82, 128.80, 122.43, 113.72, 104.63, −5.19. Anal. Calcd for C<sub>22</sub>H<sub>22</sub>Br<sub>2</sub>In<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 35.91; H, 3.01; N, 3.81. Found: C, 36.31; H, 3.06; N, 3.74.

### 2.4. Synthesis of [5-phenyl-8-quinolinolate In(III)–Me<sub>2</sub>]<sub>2</sub> (3)

This compound was prepared in a manner analogous to the synthesis of **1** using **3a** (0.12 g, 0.55 mmol). The desired compound **3** was obtained as a yellow solid (0.11 g, 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.23 (d, *J* = 6.4 Hz, 2H), 7.84 (d, *J* = 6.8 Hz, 2H), 7.46–7.42 (m, 6H), 7.40–7.37 (m, 2H), 7.34–7.33 (m, 4H), 7.16 (dd, *J* = 1.2 and 4.2 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 2H), −0.10 (s, 12H, In–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 161.23, 153.28, 147.73, 143.85, 141.08, 135.94, 132.03, 131.93, 125.56, 121.17, 118.04, 116.85, 107.75, −5.06. Anal. Calcd for C<sub>34</sub>H<sub>32</sub>In<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 55.92; H, 4.42; N, 3.84. Found: C, 55.81; H, 4.41; N, 3.74.

### 2.5. Synthesis of [2-methyl-5-methyl-8-quinolinolate In(III)–Me<sub>2</sub>]<sub>2</sub> (4)

A toluene solution (10 mL) of InMe<sub>3</sub> (0.080 g, 0.50 mmol) was added to a toluene solution (20 mL) of **4a** (0.095 g, 0.55 mmol) at room temperature. The reaction mixture was stirred for 12 h, and the insoluble parts were collected by filtration. The remained solid was washed with diethyl ether (3 × 20 mL) and dried in vacuo to obtain **4** as a pale-yellow solid (0.098 g, 62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.56 (dd, *J* = 1.4 and 4.2 Hz, 2H), 7.53 (dd, *J* = 1.2 and 3.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 2.86 (s, 6H), 2.59 (s, 6H), −0.18 (s, 12H, In–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 158.93, 156.78, 140.52, 135.33, 129.93, 129.27, 121.21, 119.94, 112.80, 24.13, 17.97, −5.13. Anal. Calcd for C<sub>26</sub>H<sub>32</sub>In<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 49.24; H, 5.09; N, 4.42. Found: C, 49.20; H, 5.00; N, 4.38.

### 2.6. Synthesis of [2-methyl-5-bromo-8-quinolinolate In(III)–Me<sub>2</sub>]<sub>2</sub> (5)

This compound was prepared in a manner analogous to the synthesis of **4** using **5a** (0.095 g, 0.55 mmol). The desired compound **5** was obtained as a dark yellow solid (0.11 g, 58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.56 (dd, *J* = 1.4 and 4.0 Hz, 2H), 7.52 (m, 2H), 7.33 (dd, *J* = 1.6 and 3.4 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 2.60 (s, 6H), −0.08 (s, 12H, In–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 157.88, 154.39, 140.50, 137.74, 132.60, 128.58, 122.21, 113.51, 104.41, 24.39, −5.40. Anal. Calcd for C<sub>24</sub>H<sub>26</sub>Br<sub>2</sub>In<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 37.73; H, 3.43; N, 3.67. Found: C, 37.68; H, 3.49; N, 3.63.

### 2.7. Synthesis of [2-methyl-5-phenyl-8-quinolinolate In(III)–Me<sub>2</sub>]<sub>2</sub> (6)

This compound was prepared in a manner analogous to the synthesis of **4** using **6a** (0.13 g, 0.55 mmol). The desired compound **6** was obtained as a yellow solid (0.13 g, 67%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.25 (d,  $J = 7.2$  Hz, 2H), 7.46–7.44 (m, 6H), 7.42–7.40 (m, 2H), 7.35 (dd,  $J = 1.4$  and 3.2 Hz, 4H), 7.18–7.17 (m, 2H), 7.10 (d,  $J = 6.8$  Hz, 2H), 2.73 (s, 6H,  $\text{CH}_3$ ),  $-0.07$  (s, 12H,  $\text{In}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  160.94, 158.71, 149.14, 146.74, 142.52, 141.72, 136.40, 132.14, 127.64, 127.22, 121.21, 119.99, 113.69, 25.21,  $-5.16$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{36}\text{In}_2\text{N}_2\text{O}_2$ : C, 57.02; H, 4.79; N, 3.69. Found: C, 56.98; H, 4.66; N, 3.59.

### 2.8. Cyclic Voltammetry

The cyclic voltammetry (CV) measurements were performed in a deoxygenized MeCN (0.5 mM) solution with a three-electrode cell configuration (platinum working and counter electrodes and an  $\text{Ag}/\text{AgNO}_3$  reference electrode (0.1 M in MeCN)) using an AUTO-LAB/PGSTAT12 system at room temperature. Tetra-*n*-butylammonium hexafluorophosphate ( $n\text{-Bu}_4\text{PF}_6$ ) in MeCN (0.1 M) was used as the supporting electrolyte. The redox potentials were investigated at a scan rate of 100 mV/s and determined with respect to the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple.

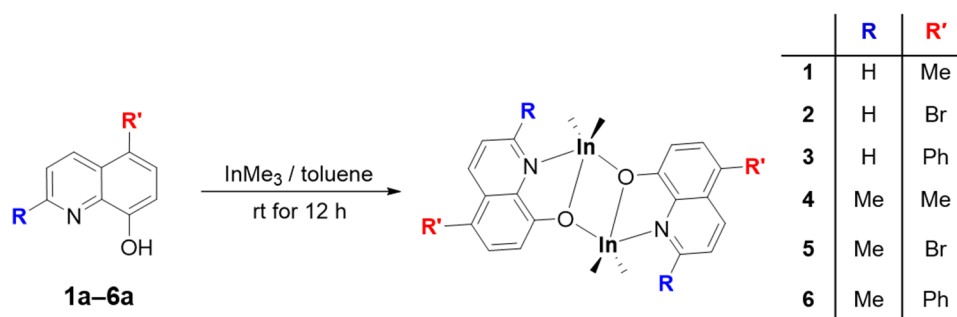
### 2.9. Photophysical Properties

The samples for the UV–vis absorption and photoluminescence (PL) measurements were prepared using degassed solvents (*p*-xylene, THF, and DCM) in 1 cm quartz cuvettes (50  $\mu\text{M}$ ) at 298 K. The absolute PL quantum yields ( $\Phi_{\text{PL}}$ ) of indium complexes 1–6 in THF solution were obtained using a Horiba Fluoromax-4P spectrophotometer equipped with a 3.2 inch integrating sphere (HORIBA, Edison, NJ, USA) at 298 K. The fluorescence decay lifetimes ( $\tau$ ) were measured using a FLS920 fluorescence spectrophotometer (Edinburgh Instruments, Livingston, UK) in time-correlated single-photon-counting (TCSPC) mode with a picosecond pulsed diode laser (EPL 375-ps) as a light source and a microchannel plate photomultiplier tube (MCP-PMT, 200–850 nm) as a detector at room temperature.

## 3. Results and Discussion

### 3.1. Synthesis and Characterization

Scheme 1 shows the routes for the synthesis of dimeric quinoline-based indium complexes 1–6, which were easily produced in moderate yields (58–67%) by the reaction of 1.1 equivalent of the corresponding quinolines (1a–6a) with  $\text{InMe}_3$  in toluene at room temperature. Based on previously reported results, all the complexes were expected to exist as dimeric species in solution [20]. All the complexes were found to possess good solubility in common organic solvents. The formation of 1–6 was confirmed by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy (Figures S1–S6) and elemental analysis. In particular, specific singlet signals assignable to the  $\text{In}-\text{Me}$  bonds were clearly observed in both the  $^1\text{H}$  (ca. 0.1 ppm) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (ca.  $-5.0$  ppm) spectra of all the indium complexes.



**Scheme 1.** The synthetic routes for producing a series of dimeric indium quinolinate complexes.

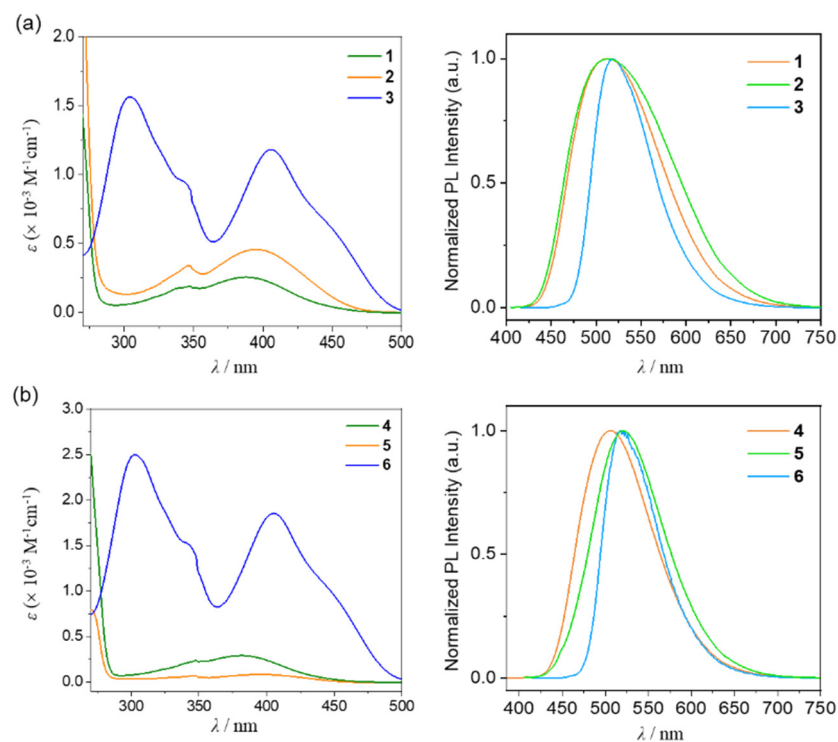
### 3.2. Photophysical and Electrochemical Properties

To examine the photophysical properties of the dimeric indium complexes, UV–vis absorption and PL experiments were performed (Figure 2 and Table 1) in a diluted THF

(50  $\mu\text{M}$ ) solution at 298 K. All the complexes **1–6** exhibited typical low-energy absorption bands in the range of 380 to 406 nm. The absorption bands can be ascribed to the quinolinol-centered  $\pi-\pi^*$  charge transfer (CT) transition. The absorption maximum ( $\lambda_{\text{abs}}$ ) of these complexes gradually redshifted on increasing the electron-donating ability of the substituents at the C5 position of the quinolinolate groups. The emission spectra of **1–6** displayed broad peaks in the range of 507 (green) to 523 (yellow) nm in THF, corresponding to a typical CT transition. The emission bands featured a gradual redshift phenomenon with an increase in the electron-donating effect of the substituents at the C5 position of the quinoline group (Figure 2 and Table 1). These results are not well-matched with the Hammett  $\sigma$  constants [30]. However, the observation indicated that the introduction of substituents with a high electron-donating effect at the C5 position of the quinolinolate group caused an increase in the HOMO energy levels in all the indium complexes. Furthermore, the emission maxima ( $\lambda_{\text{em}}$ ) of **1–6** exhibited slight bathochromic shifts in response to an increase in solvent polarity (*p*-xylene < THF < DCM) (Table 1; Figures S7 and S8). Such emission behavior indicated that all the dimeric indium complexes possessed polarized excited states. The solvatochromic nature of the broad emission bands confirmed that the PL spectra of compounds **1–6** correspond to the quinoline-based intramolecular charge transfer (ICT) transitions. The PL spectra of the compounds in the film (10 wt% doped with PMMA) displayed trends similar to those in the THF solution (Figure S9). The emission lifetime ( $\tau$ ) of **1–6** was measured to be in the range of nanoseconds in both the THF solution and the film state, indicating fluorescence (Table 1; Figures S10–S13).

The absolute emission quantum yields ( $\Phi_{\text{PL}}$ ) of these complexes were investigated in both the THF solution and the film state at room temperature (Table 1). The  $\Phi_{\text{PL}}$  values of **1** (11.2% in THF and 17.2% in film) and **4** (17.8% in THF and 36.2% in film) with Me substituents at the C5 position of the quinoline moiety were determined to be higher than those of the indium complexes with other substituents in both the THF solution and the film state. The  $\Phi_{\text{PL}}$  values gradually decreased as the electron-donating effect of substituents bound to the C5 position of the quinoline group increased (**1**  $\rightarrow$  **2**  $\rightarrow$  **3**: 11.2%  $\rightarrow$  6.6%  $\rightarrow$  0.05% in THF and 17.2%  $\rightarrow$  5.9%  $\rightarrow$  0.4% in film; **4**  $\rightarrow$  **5**  $\rightarrow$  **6**: 17.8%  $\rightarrow$  14.0%  $\rightarrow$  0.05% in THF and 36.2%  $\rightarrow$  18.0%  $\rightarrow$  0.4% in film). These results were elucidated by comparing the radiative decay constant ( $k_{\text{r}}$ ) with the non-radiative decay ( $k_{\text{nr}}$ ) constant for **1–6** in THF solution and the film state. As the electron-donating effect of C5 substituents increased, the  $k_{\text{r}}$  values gradually decreased (**1** ( $1.1 \times 10^7 \text{ s}^{-1}$ ) > **2** ( $0.9 \times 10^7 \text{ s}^{-1}$ ) > **3** ( $0.4 \times 10^7 \text{ s}^{-1}$ ) in THF; **1** ( $1.2 \times 10^7 \text{ s}^{-1}$ ) > **2** ( $0.9 \times 10^7 \text{ s}^{-1}$ ) > **3** ( $0.9 \times 10^7 \text{ s}^{-1}$ ) in film), while the  $k_{\text{nr}}$  values rapidly increased (**1** ( $8.6 \times 10^7 \text{ s}^{-1}$ ) < **2** ( $13.3 \times 10^7 \text{ s}^{-1}$ ) < **3** ( $719.6 \times 10^7 \text{ s}^{-1}$ ) in THF; **1** ( $5.7 \times 10^7 \text{ s}^{-1}$ ) < **2** ( $14.7 \times 10^7 \text{ s}^{-1}$ ) < **3** ( $249.1 \times 10^7 \text{ s}^{-1}$ ) in film). Importantly, the indium complexes **4–6** based on the Meq ligand possessed higher quantum efficiencies than those of the corresponding q ligand-based complexes **1–3**, similar to other dimeric indium quinolinates [20]. This feature is supported by the comparison of the  $k_{\text{r}}$  (**4** ( $1.8 \times 10^7 \text{ s}^{-1}$ ) > **1** ( $1.2 \times 10^7 \text{ s}^{-1}$ ), **5** ( $1.5 \times 10^7 \text{ s}^{-1}$ ) > **2** ( $0.9 \times 10^7 \text{ s}^{-1}$ ), and **6** ( $1.4 \times 10^7 \text{ s}^{-1}$ ) > **3** ( $0.9 \times 10^7 \text{ s}^{-1}$ ) in film) and  $k_{\text{nr}}$  values (**4** ( $3.2 \times 10^7 \text{ s}^{-1}$ ) < **1** ( $5.7 \times 10^7 \text{ s}^{-1}$ ), **5** ( $7.0 \times 10^7 \text{ s}^{-1}$ ) < **2** ( $14.7 \times 10^7 \text{ s}^{-1}$ ), and **6** ( $382.4 \times 10^7 \text{ s}^{-1}$ ) < **3** ( $249.1 \times 10^7 \text{ s}^{-1}$ ) in film) between the corresponding indium complexes in the THF solution and in the film state. These results imply that dimeric indium quinolinates based on the Meq ligand are more efficient luminophores.

Based on the electrochemical data obtained from CV measurements in MeCN, **1–6** showed totally irreversible oxidation processes (Figure 3 and Table 1). The HOMO energy levels and bandgaps ( $E_{\text{g}}$ ) of all the complexes were calculated using the measured onset oxidation potentials with the absorption edges ( $\lambda_{\text{abs,edge}}$ ). Contrary to the expectation, the calculated HOMO levels were found to decrease when the electron-donating effect of substituents at the C5 position of the quinoline groups increased. However, the calculated  $E_{\text{g}}$  values gradually decreased, which is consistent with the photophysical results.



**Figure 2.** UV–vis absorption (left) and PL (right) spectra in THF (50  $\mu\text{M}$ ) of the dimeric indium complexes (a) 1–3 and (b) 4–6.

**Table 1.** Photophysical and electrochemical results of 1–6.

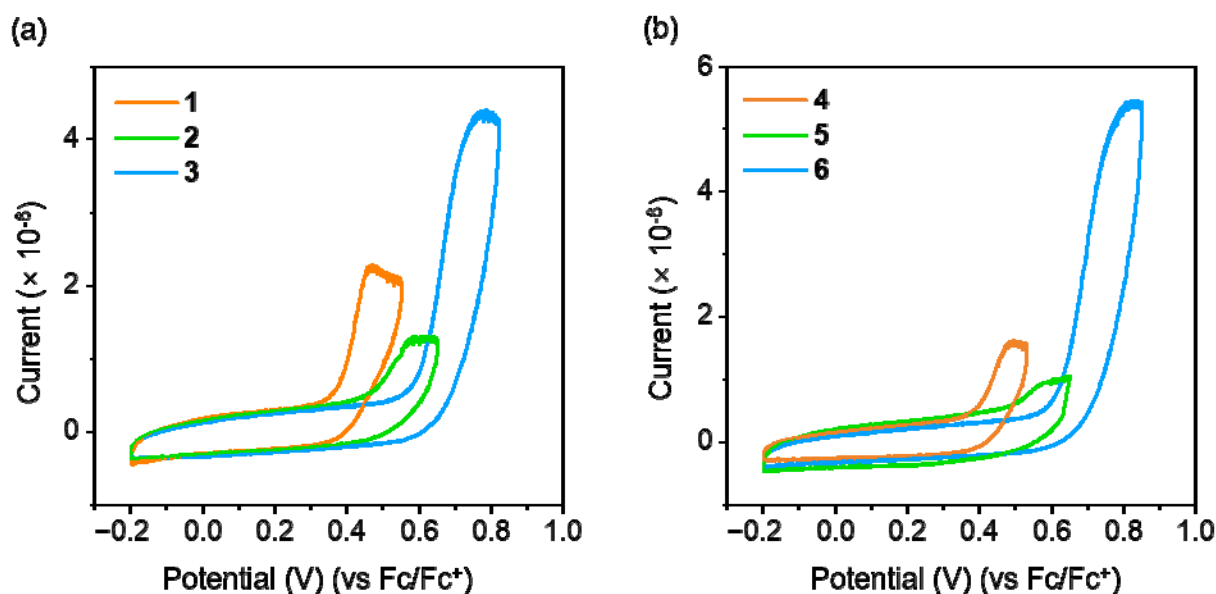
Compd	$\lambda_{\text{abs}}^1/\text{nm}$ ( $\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$				$\Phi_{\text{em}}^4/\%$	
			<i>p</i> -xylene <sup>2</sup>	THF <sup>2</sup>	DCM <sup>2</sup>	film <sup>3</sup>	THF	film
1	388 (5.1)	396	508	515	518	505	11.2	17.2
2	395 (9.1)	395	495	510	503	500	6.6	5.9
3	406 (23.6)	406	519	518	521	515	0.05	0.4
4	380 (5.8)	365	503	507	511	498	17.8	36.2
5	396 (1.7)	396	489	523	502	492	14.0	18.0
6	405 (37.1)	405	522	520	521	519	0.05	0.4

Compd	$\tau/\text{ns}$		$k_{\text{r}}^5/\times 10^7 \text{ s}^{-1}$		$k_{\text{nr}}^6/\times 10^7 \text{ s}^{-1}$		$V_{\text{ox}}^7/\text{V}$	HOMO <sup>8</sup> /eV	$E_{\text{g}}^9/\text{eV}$
	THF <sup>2</sup>	Film <sup>3</sup>	THF <sup>2</sup>	film <sup>2</sup>	THF <sup>2</sup>	film			
1	10.3	14.5	1.1	1.2	8.6	5.7	0.30	−5.10	2.55
2	7.0	6.4	0.9	0.9	13.3	14.7	0.37	−5.17	2.48
3	0.2	0.2	0.4	0.9	719.6	249.1	0.53	−5.33	2.44
4	12.7	20.0	1.4	1.8	6.5	3.2	0.31	−5.11	2.57
5	10.2	11.7	1.4	1.5	8.4	7.0	0.40	−5.20	2.67
6	0.2	0.3	0.2	1.4	479.8	382.4	0.55	−5.35	2.38

<sup>1</sup>  $c = 50 \mu\text{M}$  in THF. <sup>2</sup>  $c = 50 \mu\text{M}$ , observed at 298 K. <sup>3</sup> Measured in the film state (10 wt% doped on poly(methy methacrylate), PMMA) at 298 K. <sup>4</sup> Absolute PL quantum yields. <sup>5</sup>  $k_{\text{r}} = \Phi_{\text{em}}/\tau$ . <sup>6</sup>  $k_{\text{nr}} = k_{\text{r}}(1/\Phi_{\text{em}} - 1)$ . <sup>7</sup> Oxidation onset potentials in DMSO ( $c = 50 \text{ mM}$ , scan rate  $100 \text{ mV s}^{-1}$ ) with reference to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. <sup>8</sup> Highest occupied molecular orbital (HOMO) energy level calculated from  $V_{\text{ox}}$ . <sup>9</sup> Calculated from  $\lambda_{\text{abs,edge}}$ .





**Figure 3.** Cyclic voltammograms of the oxidation of (a) q-based complexes (1–3) and (b) Meq-based complexes (4–6) (0.5 mM in DMSO, scan rate = 100 mV/s for oxidation).

#### 4. Conclusions

In summary, we prepared a new series of quinolinol-based dimeric indium complexes (1–6) that exhibited low-energy absorption bands assignable to quinolinol-centered  $\pi$ – $\pi^*$  CT transition. The emission spectra of 1–6 exhibited a gradual redshift as the electron-donating effect of substituents at the C5 position of the quinoline groups increased. The quantum efficiencies of 1 and 4, which had methyl substituents at the C5 position of the quinoline groups (q or Meq), were higher than those of the indium complexes with other substituents (Br and Ph). Consequently, these results provide a new perspective on the development of quinolinol-based dimeric indium complexes as potential organometallic luminophores. Further studies are underway to develop quinolinol-based indium complexes with improved quantum efficiencies for application as efficient luminescent materials.

**Supplementary Materials:** Figures S1–S6: Multinuclear NMR spectra (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) of a series of dimeric indium quinolinates; Figures S7–S13: photophysical data.

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**Sample Availability:** Samples available from the author.

#### References

1. Tang, C.W.; VanSlyke, S.A. Organic electroluminescent diodes. *Appl. Phys. Lett.* **1987**, *51*, 913. [[CrossRef](#)]
2. Lin, N.; Qiao, J.; Duan, L.; Xue, J.; Wang, L. Rational design of chelated aluminum complexes toward highly efficient and thermally stable electron-transporting materials. *Chem. Mater.* **2014**, *26*, 3693–3700. [[CrossRef](#)]
3. Pérez-Bolívar, C.; Takizawa, S.-Y.; Nishimura, G.; Montes, V.A.; Anzenbacher, P., Jr. High-efficiency tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) complexes for organic white-light-emitting diodes and solid-state lighting. *Chem. Eur. J.* **2011**, *17*, 9076–9082.

4. Liao, S.-H.; Shiu, J.-R.; Liu, S.-W.; Yeh, S.-J.; Chen, Y.-H.; Chen, C.-T.; Chow, T.J.; Wu, C.-I. Hydroxynaphthyridine-derived group III metal chelates: Wide band gap and deep blue analogues of green Alq<sub>3</sub> (tris(8-hydroxyquinolate)aluminum) and their versatile applications for organic light-emitting diodes. *J. Am. Chem. Soc.* **2009**, *131*, 763–777. [[CrossRef](#)] [[PubMed](#)]
5. Pohl, R.; Montes, V.A.; Shinar, J.; Anzenbacher, P., Jr. Red-green-blue emission from tris(5-aryl-8-quinolinolate)Al(III) complexes. *J. Org. Chem.* **2004**, *69*, 1723–1725. [[CrossRef](#)]
6. Pohl, R.; Anzenbacher, P. Emission Color Tuning in AlQ<sub>3</sub> Complexes with Extended Conjugated Chromophores. *Org. Lett.* **2003**, *5*, 2769–2772.
7. Wang, S. Luminescence and electroluminescence of Al(III), B(III), Be(II) and Zn(II) complexes with nitrogen donors. *Coord. Chem. Rev.* **2001**, *215*, 79–98. [[CrossRef](#)]
8. Chen, C.H.; Shi, J. Metal chelates as emitting materials for organic electroluminescence. *Coord. Chem. Rev.* **1998**, *171*, 161–174. [[CrossRef](#)]
9. Zlojutro, V.; Sun, Y.; Hudson, Z.M.; Wang, S. Triarylboronfunctionalized 8-hydroxyquinolines and their aluminium(III) complexes. *Chem. Commun.* **2011**, *47*, 3837–3839. [[CrossRef](#)]
10. Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. Synthesis and Characterization of Organoboron Quinolate Polymers with Tunable Luminescence Properties. *Macromolecules* **2006**, *39*, 9041–9048. [[CrossRef](#)]
11. Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. Luminescence Tuning of Organoboron Quinolates through Substituent Variation at the 5-Position of the Quinolato Moiety. *Org. Lett.* **2006**, *8*, 5227–5230. [[CrossRef](#)] [[PubMed](#)]
12. Montes, V.A.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. Effective manipulation of the electronic effects and its influence on the emission of 5-substituted tris(8-quinolinolate) aluminum(III) complexes. *Chem. Eur. J.* **2006**, *12*, 4523–4535. [[CrossRef](#)] [[PubMed](#)]
13. Shi, Y.-W.; Shi, M.-M.; Huang, J.-C.; Chen, H.-Z.; Wang, M.; Liu, X.-D.; Ma, Y.-G.; Xu, H.; Yang, B. Fluorinated Alq<sub>3</sub> derivatives with tunable optical properties. *Chem. Commun.* **2006**, 1941–1943. [[CrossRef](#)] [[PubMed](#)]
14. Cui, Y.; Liu, Q.-D.; Bai, D.-R.; Jia, W.-L.; Tao, Y.; Wang, S. Organoboron Compounds with an 8-Hydroxyquinolato Chelate and Its Derivatives: Substituent Effects on Structures and Luminescence. *Inorg. Chem.* **2005**, *44*, 601–609. [[CrossRef](#)]
15. Cheng, J.-A.; Chen, C.H.; Liao, C.H. Solution-Processible Small Molecular Organic Light-Emitting Diode Material and Devices Based on the Substituted Aluminum Quinolate. *Chem. Mater.* **2004**, *16*, 2862–2868. [[CrossRef](#)]
16. Montes, V.A.; Li, G.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. Effective Color Tuning in Organic Light-Emitting Diodes Based on Aluminum Tris(5-aryl-8-hydroxyquinoline) Complexes. *Adv. Mater.* **2004**, *16*, 2001–2003. [[CrossRef](#)]
17. Sapochak, L.S.; Padmaperuma, A.; Washton, N.; Endrino, F.; Schmett, G.T.; Marshall, J.; Fogarty, D.; Burrows, P.E.; Forrest, S.R. Effects of Systematic Methyl Substitution of Metal (III) Tris(*n*-Methyl-8-Quinolinolato) Chelates on Material Properties for Optimum Electroluminescence Device Performance. *J. Am. Chem. Soc.* **2001**, *123*, 6300–6307. [[CrossRef](#)]
18. Hopkins, T.A.; Meerholz, K.; Shaheen, S.; Anderson, M.L.; Schmidt, A.; Kippelen, B.; Padias, A.B.; Hall, H.K.; Peyghambarian, N.; Armstrong, N.R. Substituted Aluminum and Zinc Quinolates with Blue-Shifted Absorbance/Luminescence Bands: Synthesis and Spectroscopic, Photoluminescence, and Electroluminescence Characterization. *Chem. Mater.* **1996**, *8*, 344–351. [[CrossRef](#)]
19. Kwak, S.W.; Kim, M.B.; Shin, H.; Lee, J.H.; Hwang, H.; Ryu, J.Y.; Lee, J.; Kim, M.; Chung, Y.; Choe, J.C.; et al. A series of Quinolate-based Indium Luminophores: A Rational Design Approach for Manipulation Photophysical Properties. *Inorg. Chem.* **2019**, *58*, 8056–8063. [[CrossRef](#)]
20. Woo, W.H.; Lee, S.H.; Kwak, S.W.; Kim, M.; Lee, K.M.; Park, M.H.; Kim, Y. Synthesis and Photophysical Properties of (Cl<sub>2</sub>Ph)Salen-based Indium Complexes. *Bull. Korean Chem. Soc.* **2020**, *41*, 748–752. [[CrossRef](#)]
21. Kwak, S.W.; Kwon, H.; Lee, J.H.; Hwang, H.; Kim, M.; Chung, Y.; Kim, Y.; Lee, K.M.; Park, M.H. Salen-indium/triarylborane triads: Synthesis and ratiometric emission-colour changes by fluoride ion binding. *Dalton Trans.* **2018**, *47*, 5310–5317. [[CrossRef](#)] [[PubMed](#)]
22. Lee, S.H.; Shin, N.; Kwak, S.W.; Hyun, K.; Woo, W.H.; Lee, J.H.; Hwang, H.; Kim, M.; Lee, J.; Kim, Y.; et al. Intriguing Indium-salen Complexes as Multicolor Luminophores. *Inorg. Chem.* **2017**, *56*, 2621–2626. [[CrossRef](#)] [[PubMed](#)]
23. Lugo, A.F.; Richards, A.F. Ketimate-Supported LiCl Cages and Group 13 Complexes. *Eur. J. Inorg. Chem.* **2010**, 2025–2035. [[CrossRef](#)]
24. Motati, D.R.; Uredi, D.; Watkins, E.B. A general method for the metal-free, regioselective, remote C–H halogenation of 8-substituted quinolones. *Chem. Sci.* **2018**, *9*, 1782–1788. [[CrossRef](#)]
25. Thinner, C.C.; Tumber, A.; Yapp, C.; Scozzafava, G.; Yeh, T.; Chan, M.C.; Tran, T.A.; Hsu, K.; Tarhonskaya, H.; Walport, L.J.; et al. Betti reaction enables efficient synthesis of 8-hydroxyquinoline inhibitors of 2-oxoglutarate oxygenases. *Chem. Commun.* **2015**, *51*, 15458–15461. [[CrossRef](#)]
26. Heiskanen, J.P.; Hormi, E.O. 4-Aryl-8-hydroxyquinolines from 4-chloro-8-tosyloxyquinoline using a Suzuki–Miyaura cross-coupling approach. *Tetrahedron* **2009**, *65*, 518–524. [[CrossRef](#)]
27. Szala, M.; Nycz, J.E.; Malecki, G.J. New approaches to the synthesis of selected hydroxyquinolines and their hydroxyquinoline carboxylic acid analogues. *J. Mol. Struct.* **2014**, *1071*, 34–40. [[CrossRef](#)]
28. Bakewell, C.; Platel, R.H.; Cary, S.K.; Hubbard, S.M.; Roaf, J.M.; Levine, A.C.; White, A.J.P.; Long, N.J.; Haaf, M.; Williams, C.K. Bis(8-quinolinolato) aluminium ethyl complexes: Iso-selective initiators for *rac*-lactide polymerization. *Organometallics* **2012**, *31*, 4729–4736. [[CrossRef](#)]
29. Xu, H.-B.; Li, J.; Shi, L.-X.; Chen, Z.-N. Sensitized luminescence in dinuclear lanthanide(III) complexes of bridging 8-hydroxyquinoline derivatives with different electronic properties. *Dalton Trans.* **2011**, *40*, 5549–5556. [[CrossRef](#)]
30. Hansch, C.; Leo, A.; Taft, R.W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev.* **1991**, *91*, 165–195. [[CrossRef](#)]