

**Supporting information**

**Aluminum-Salen Luminophores as New Hole-Blocking Materials  
for Phosphorescent OLEDs**

Kyu Young Hwang, Min Hyung Lee, Hyosook Jang,  
Yeunjoo Sung, Jong Soon Lee, Se Hun Kim, and Youngkyu Do

Department of Chemistry, School of Molecular Science BK-21 and Center for Molecular Design and  
Synthesis, Korea Advanced Institute of Science and Technology, Daejeon 305–701, Korea.

Fax: 82 42 869 2810

Tel: 82 42 869 2829

E-mail: ykdo@kaist.ac.kr

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**General Considerations.** All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous grade solvents (Aldrich) were dried by passing through an activated alumina column and stored over activated molecular sieves (5Å). Commercial reagents were used without any further purification after purchasing from Aldrich. CDCl<sub>3</sub> from Cambridge Isotope Laboratories was used after drying over activated molecular sieves (5Å). NMR spectra were recorded on a Bruker Spectrospin 400 spectrometer (400.13 MHz for <sup>1</sup>H, 100.62 MHz for <sup>13</sup>C) at ambient temperature. Chemical shifts are given in ppm, and are referenced against external Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C). Elemental analyses were performed on an EA1110 (FISONS Instruments) at KAIST. Thermogravimetric analyses (TGA) were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min with Dupont 9900 Analyzer. UV-vis and PL spectra were recorded on a Jasco V-530 and a Spex Fluorog-3 Luminescence spectrophotometer, respectively. Redox potentials of the complexes were determined by cyclic voltammetry (PAR 273A) in CH<sub>2</sub>Cl<sub>2</sub> relative to the external ferrocene reference at a scan rate of 100 mV/s ([*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] as the electrolyte; ITO as the working electrode; Pt as the counter electrode; AgNO<sub>3</sub>/Ag as the reference electrode).

**Synthesis of [salen(<sup>t</sup>Bu)<sub>4</sub>Al(OC<sub>6</sub>H<sub>5</sub>)] (1):** A toluene solution (10 mL) of phenol (0.19g, 2.00 mmol) was added to a solution of the precursor (1.06 g, 2.00 mmol) in 30 mL of toluene. The reaction mixture was refluxed at 110 °C for 2 h and cooled to an ambient temperature, and then the solvent was removed under reduced pressure to give yellow powder which was washed with *n*-hexane. The resulting solid was dried under vacuum and recrystallized from toluene/*n*-hexane pair as yellow powder. Yield: 79 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.31 (s, 2H), 7.56 (d, 2H), 7.02 (d, 2H), 6.87 (t, 2H), 6.53 (t, 1H), 6.40 (d, 2H), 4.00 (m, 2H), 3.64(m, 2H), 1.53 (s, 18H), 1.32 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 169.97, 163.28, 160.47, 140.96, 138.30, 130.84, 128.60, 127.05, 119.80, 118.31, 116.86, 54.93, 35.57, 33.98, 31.36, 29.69. C<sub>38</sub>H<sub>51</sub>AlN<sub>2</sub>O<sub>3</sub>: calcd. C, 74.72, H 8.42, N 4.59 found C 75.64, H 8.67, N 4.65.

**Synthesis of [salen(<sup>t</sup>Bu)<sub>4</sub>Al(OC<sub>6</sub>H<sub>4</sub>-*p*-OMe)] (2):** This complex was synthesized by an analogous method to **1** but with *p*-methoxy phenol as an ancillary ligand. Yield: 80 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.31 (s, 2H), 7.54 (d, 2H), 7.00 (d, 2H), 6.43 (d, 2H), 6.30 (d, 2H), 3.98 (m, 2H), 3.64(m, 2H), 3.60 (s, 3H), 1.51 (s, 18H), 1.31 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 169.95, 163.30, 154.56, 151.06, 140.94, 138.27, 130.81, 127.03, 119.84, 118.33, 114.02, 55.74, 55.94, 35.57, 33.97, 31.36, 29.69. C<sub>39</sub>H<sub>53</sub>AlN<sub>2</sub>O<sub>4</sub>: calcd. C 73.10, H 8.34, N 4.73; found C 72.66, H 8.55, N 4.38.

**Synthesis of [salen(<sup>t</sup>Bu)<sub>4</sub>Al(OC<sub>6</sub>F<sub>5</sub>)] (3):** This complex was synthesized by an analogous method to **1**

but with pentafluorophenol as an ancillary ligand. Yield: 72 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.42 (s, 2H), 7.51 (d, 2H), 7.03 (d, 2H), 4.17 (m, 2H), 3.77 (m, 2H), 1.43 (s, 18H), 1.29 (s, 18H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  170.53, 163.08, 140.92, 138.77, 131.30, 127.15, 118.10, 55.06, 35.52, 34.00, 31.31, 29.51.  $\text{C}_{39}\text{H}_{53}\text{AlN}_2\text{O}_4$ : calcd. C 65.13, H 6.62, N 3.99; found C 65.17, H 6.79, N 3.99.

**Synthesis of  $[\text{salen}(\text{}^t\text{Bu})_4\text{Al}(\text{OC}_6\text{H}_4\text{-}p\text{-}\text{C}_6\text{H}_5)]$  (**4**):** This complex was synthesized by an analogous method to **1** but with phenylphenol as an ancillary ligand. Yield: 80 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.35 (s, 2H), 7.55 (d, 2H), 7.40 (d, 2H), 7.28 (t, 2H), 7.15 (m, 3H), 7.02 (d, 2H), 6.45 (d, 2H), 4.02 (m, 2H), 3.68 (m, 2H), 1.51 (s, 18H), 1.30 (s, 18H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  170.07, 163.31, 160.40, 141.79, 141.03, 138.40, 130.87, 129.63, 128.40, 127.36, 127.09, 126.22, 125.55, 119.98, 118.32, 54.99, 35.60, 34.01, 31.37, 29.10.  $\text{C}_{39}\text{H}_{53}\text{AlN}_2\text{O}_4$ : calcd. C 76.94, H 8.07, N 4.08; found C 76.96, H 8.01, N 4.16.

**X-ray Crystallography:** Single crystals of **4** suitable for X-ray diffraction studies were obtained by diffusion of *n*-hexane into a toluene solution. Reflection data were collected on a Bruker 1K SMART-CCD area detector diffractometer, with a graphite-monochromated Mo- $\text{K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. The hemisphere of reflection data were collected as  $\omega$  scan frames with a width of  $0.3^\circ/\text{frame}$  and exposure time of 10 s/frame. Cell parameters were determined and refined by SMART program.<sup>[1]</sup> Data reductions were performed using SAINT software,<sup>[2]</sup> which corrects for Lorentz and polarization effects. Empirical absorption corrections were applied with SADABS program.<sup>[3]</sup> The structure was solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

**Fabrication of OLEDs:** OLEDs were fabricated by thermal evaporation under high vacuum ( $10^{-7}$  torr) on pre-cleaned indium tin oxide (ITO)-coated glass. CuPc,  $\alpha$ -NPD, CBP doped Ir(ppy)<sub>3</sub>, complex **4** or BAiq, Alq<sub>3</sub>, LiF, and Al electrode were successively deposited on ITO glass with the deposition rates of about 1 or 2  $\text{\AA}/\text{s}$ . EL spectra were obtained with Ocean Optics USB2000 fiber-optic spectrometer. Current-voltage-luminescence (I-V-L) characteristics were recorded on Keithley 237 and Minolta CS-100A. All EL measurements were carried out at room temperature under an ambient atmosphere.

[1] *SMART, Version 5.0, Data collection software*, Bruker AXS, Inc., Madison, WI, USA, 1998.

[2] *SAINTE, Version 5.0, Data integration software*, Bruker AXS, Inc., Madison, WI, USA, 1998.

Supplementary Material (ESI) for Dalton Transactions

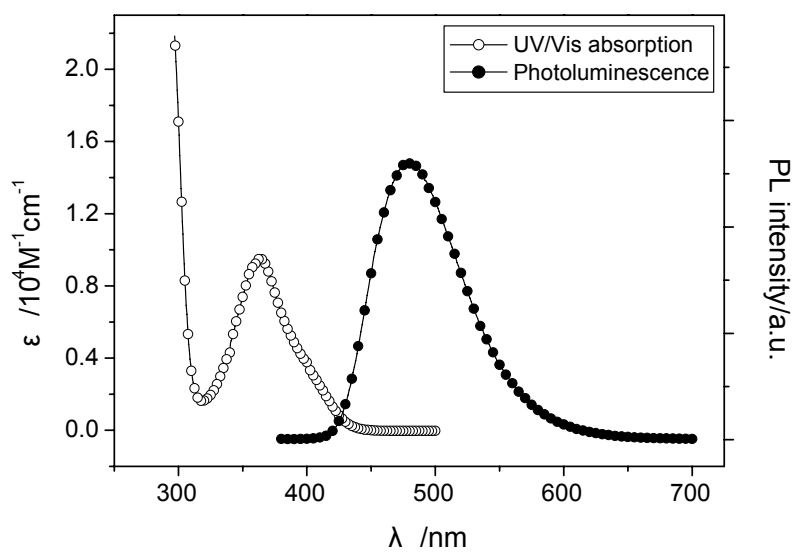
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[3] G. M. Sheldrick, *SADABS, Program for absorption correction with the Bruker SMART system*, Universität Göttingen, Germany, **1996**.

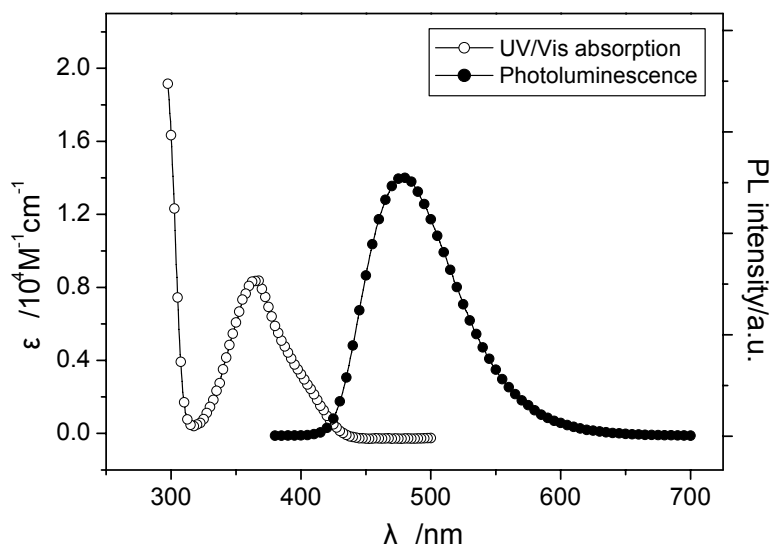
**Table S1.** Crystallographic data for **4**

Compound	<b>4</b>
formula	C <sub>44</sub> H <sub>55</sub> AlN <sub>2</sub> O <sub>3</sub>
formula weight (g/mol)	686.88
crystal system	Monoclinic
space group	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	20.263(8)
<i>b</i> /Å	11.792(4)
<i>c</i> /Å	18.060(9)
<i>α</i> /°	90.00
<i>β</i> /°	114.585(12)
<i>γ</i> /°	90.00
<i>V</i> /Å <sup>3</sup>	3924(3)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.163
$\mu$ (mm <sup>-1</sup> )	0.092
<i>F</i> (000)	1480
<i>T</i> (K)	293(2)
no. of reflections measured	22087
no. of reflections used ( <i>R</i> <sub>int</sub> )	0.0482
<i>R</i> 1 <sup>a</sup> , <i>wR</i> 2 <sup>b</sup> ( <i>I</i> >2σ( <i>I</i> ))	0.0522, 0.1137
goodness of fit on <i>F</i> <sup>2</sup>	1.003
$\rho_{\text{fin}}$ (max/min) (e Å <sup>-3</sup> )	0.316/ -0.257

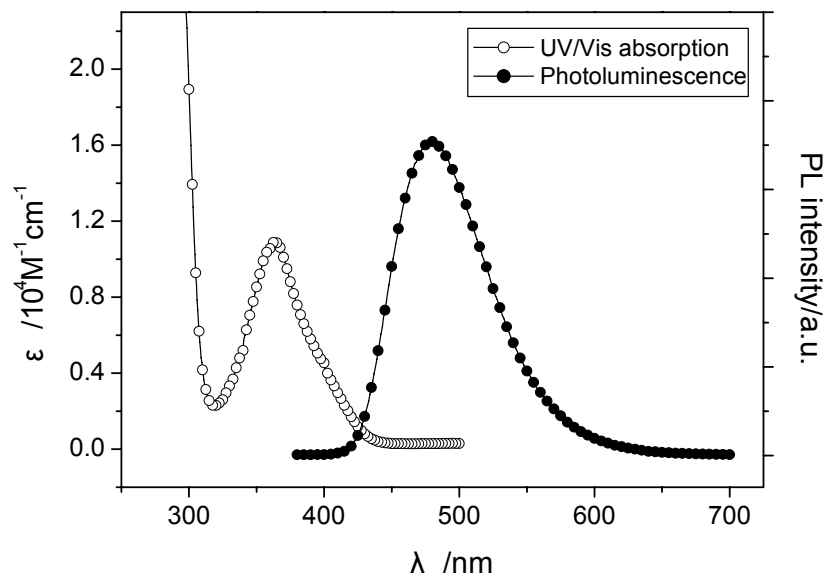
<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$ .



**Figure S1.** UV/Vis absorption and photoluminescence (PL) spectra of **2**.



**Figure S2.** UV/Vis absorption and photoluminescence (PL) spectra of **3**.



**Figure S3.** UV/Vis absorption and photoluminescence (PL) spectra of **4**.

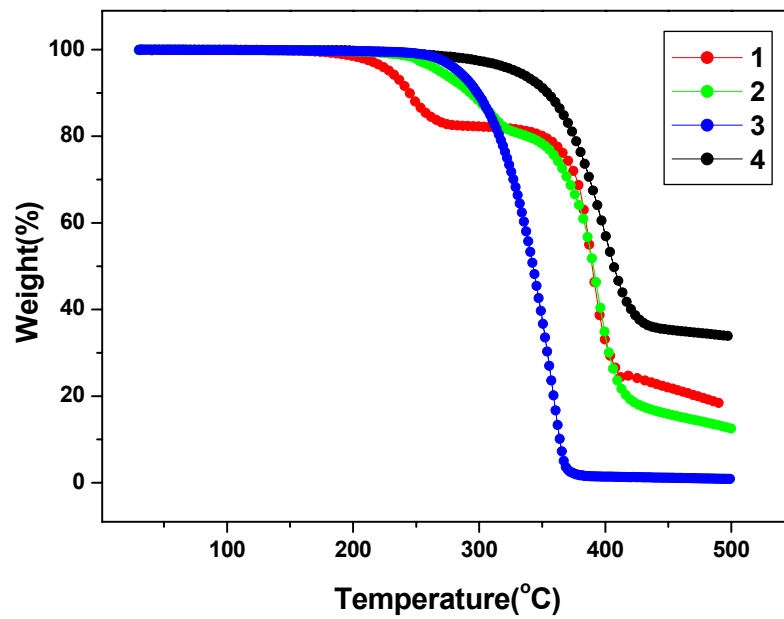


Figure S4. TGA spectra of 1-4.