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Systematic design of indium-based luminophores with color-tunable emission via combined manipulation of HOMO and LUMO levels

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ABSTRACT

A series of indium complexes with salen ligands bridged by aryl groups such as $[\mathrm{Ar}\text{-}\{\mathrm{N{=}CH(C_6H_2\text{-}3\text{-}{}^tBu\text{-}5\text{-}R)}\}_2]\mathrm{In\text{-}Me}$ (Ar = 4,5-dimethyl-1,2-phenylene, 1,2-phenylene, and 3,4-naphthylene; R = H, Br, ^{t}Bu, Me, OMe, NMe_2, and $NMe_3{}^+$) were prepared and fully identified by NMR spectroscopy and elemental analysis. All indium complexes are highly stable in air and aqueous solutions. Among these complexes, the structurally characterized complexes [(4,5-dimethylphenylene)bis(3-*tert*-butyl-5-methylsalicylideneiminato)-κ*N*,*N′*,*O*,*O′*]methylindium (III) and [(2,3-naphthanlene)bis(3-*tert*-butyl-5-methylsalicylideneiminato)-κ*N*,*N′*,*O*,*O′*]methylindium(III) have slightly distorted square-pyramidal geometries around the central indium atoms. The UV/Vis absorption and emission spectra of all indium complexes exhibited significant intramolecular charge transfer (ICT) transitions assigned to the aryl salen-centered π-π* transitions, which displayed a gradual bathochromic shift, resulting from the electronic alteration of the substituent at the C5 position of phenoxy ring. Furthermore, the emission bands also gradually red-shifted as the electron-donating effect of bridging aryl groups decreased. In particular, the emission spectra of the indium complexes were observed in the visible region ranging from green (ca. 500 nm) to deep red (ca. 700 nm). The colors were obtained by manipulating the HOMO and LUMO energy levels, which was further supported by both electrochemical data and theoretical calculations.

1. Introduction

Group 13-based luminescent materials have received great attention as promising luminophores because of their outstanding optical properties [1–4]. In particular, aluminum-based organometallic complexes have attracted considerable interest in the field of optoelectronic materials [5–13]. Among these complexes, various Al luminophores with tetradentate salen derivatives have been developed [14–18]. Salen compounds, as chelating platforms for transition-metal complexes, can be easily modulated by the introduction of functional groups. Such approaches have led to desirable photophysics, such as emission-color fine tuning and quantum efficiency enhancements [19–21]. In the viewpoint of the foregoing studies, we recently reported novel salen-indium luminophores as heavier congeners for luminescent salen-aluminum complexes (Fig. 1) [22].

The salen-indium complexes exhibited multicolor emission features covering the entire visible region. Recent reports on salen-based aluminum [20–23] or indium [22] luminophores have mainly focused on controlling the highest occupied molecular orbital (HOMO) energy levels via the introduction of different substituents with electronic nature in phenyl ring of salen ligand.

Although the lowest unoccupied molecular orbitals (LUMOs) of the salen-based luminophores are closely associated with the bridging backbones of the salen units [20–23], varying the luminescent properties through controlling the LUMO of the salen moiety has been rarely investigated [23,24]. In this regard, to elucidate the effects of the rigid backbones and functionalities, we systematically prepared a series of indium complexes with three types of salen ligands bridged by 4,5-dimethyl-1,2-phenylene, 1,2-phenylene, and 3,4-naphthylene.

The design of such indium luminophores is attributed to the strategy to fine-tune the HOMO and LUMO energy levels. This strategy can give rise to further insight into the nature of salen-based luminescent

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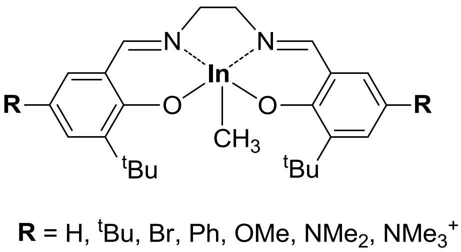

Fig. 1. Luminescent salen-indium complexes.

materials, in particular, salen-indium complexes. Herein, we describe the detailed synthesis, characterizations, and photophysical properties with theoretical calculations.

2. Experimental section

2.1. General considerations

All manipulations were performed under an inert N_2 atmosphere using standard Schlenk and glove box techniques [31,32] All solvents were dried by passing them through an activated alumina column and stored over activated molecular sieves (5 Å). Spectrophotometric grade solvents were used as received. All commercial reagents were used without any further purification after purchasing from Aldrich and Alfa Aesar. All deuterated solvents ($CDCl_3$ and CD_3CN) from Cambridge Isotope Laboratories were used after drying over activated molecular sieves (5 Å). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer at ambient temperature. All chemical shifts are given in ppm (δ) units with reference to the residual $CDCl_3$ (δ 7.24 for ^1H NMR; δ 77.00 for ^{13}C NMR) and CD_3CN (δ 1.94 for ^1H NMR; δ 1.32 and 118.26 for ^{13}C NMR). Elemental analyses and high resolution mass data measurements were performed with an EA 1110-FISONS analyzer and maxis 4G (Hybrid LC/Q-TOF system), respectively. UV/Vis absorption and PL spectra were recorded on a Jasco V-530 and a Fluoromax-4P (HORIBA) spectrophotometer, respectively. Fluorescence decay lifetimes were measured using a time-correlated single-photon counting (TCSPC) spectrometer (FLS920–EDINBURGH Instruments in the Central Laboratory of Kangwon National University) equipped with a EPL-375ps pulsed semiconductor diode laser as an excitation source and a microchannel plate photomultiplier tube (MCP-PMT, 200–850 nm) as a detector at 298 K. Cyclic voltammetry measurements (AUTOLAB/PGSTAT12 system) were carried out with a three-electrode cell configuration consisting of platinum working and counter electrodes and a $Ag/AgNO_3$ (0.1 M in acetonitrile) reference electrode at room temperature (solvent, dimethyl sulfoxide; supporting electrolyte, tetrabutylammonium hexafluorophosphate (0.1 M). The oxidation potentials were recorded at a scan rate of 100 mV/s and reported with reference to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

2.2. Synthesis

Compounds *N,N'*-(4,5-dimethylphenylene)bis(3,5-di-*tert*-butylsalicylideneimine) (**SD3**) [33], *N,N′*-phenylenebis(3-*tert*-butylsalicylideneimine) (**SP1**) [34], *N,N′*-phenylenebis(3-*tert*-butyl-5-bromosalicylideneimine) (**SP2**) [35], *N,N′*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine) (**SP3**) [36], and *N,N′*-phenylenebis(3-*tert*-butyl-5-methoxysalicylideneimine) (**SP5**) [37] were prepared by previously published procedures; 2-hydroxy-3-*tert*-butyl-5-R-benzaldehyde (10 mmol, R = *tert*-butyl for **SD3** and **SP3**, R = H for **SP1**, R = Br for **SP2** and R = methoxy for **SP5**) was treated with corresponding diamines (5.0 mmol, 4,5-dimethylbenzene-1,2-diamine for **SD3** and 1,2-phenylenediamine for **SP1**, **SP2**, **SP3** and **SP5**) in methanol (20 mL) at 75 °C. The reaction mixture was stirred for 12 h, and then cooled to ambient temperature, after which the mixture was filtered. Washing with methanol followed by drying in vacuo afforded the **SD3**, **SP1**, **SP2**, **SP3** or **SP5**.

General synthesis of Ar-{N=CH(C_6H_2-3-^{t}Bu-5-R)}$_2$ (SD, SP, and SN series).

2-hydroxy-3-*tert*-butyl-5-R-benzaldehyde (10 mmol) was treated with corresponding diamines (4,5-dimethylbenzene-1,2-diamine for **SD**, 1,2-phenylenediamine for **SP** and 2,3-diaminonaphthalene for **SN** derivatives, 5.0 mmol, 0.5 equiv.) in methanol (20 mL) at 75 °C. The reaction mixture was stirred for 12 h, and then cooled to ambient temperature, after which the mixture was filtered. Washing with methanol followed by drying in vacuo afforded the precursor ligands (**SD1–SD6**, **SP1–SP6**, and **SN1–SN6**).

Data for *N,N'*-(4,5-dimethylphenylene)bis(3-*tert*-butylsalicylideneimine) (**SD1**): Orange solid (1.64 g, 72%). ^1H NMR ($CDCl_3$): δ 13.83 (br, 2H, O*H*), 8.64 (s, 2H, N=C*H*), 7.36 (dd, J_1 = 7.7 and J_2 = 1.7 Hz, 2H, Ar), 7.23 (dd, J_1 = 7.7 and J_2 = 1.7 Hz, 2H, Ar), 6.87 (t, J = 7.7 Hz, 2H, Ar), 2.32 (s, 6H), 1.42 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 163.55 (N=*C*H), 160.88, 140.16, 137.93, 136.29, 130.70, 130.34, 120.84, 119.41, 118.17, 35.08, 29.52, 19.71. HRMS *m/z* Calcd. for $C_{30}H_{37}N_2O_2$ $[M + H]^+$: 456.2850. Found: 456.2850.

Data for *N,N'*-(4,5-dimethylphenylene)bis(3-*tert*-butyl-5-bromosalicylideneimine) (**SD2**): Orange solid (2.30 g, 75%). ^1H NMR ($CDCl_3$): δ 13.87 (br, 2H, O*H*), 8.56 (s, 2H, N=C*H*), 7.41 (d, J = 2.4 Hz, 2H, Ar), 7.35 (d, J = 2.4 Hz, 2H, Ar), 7.03 (s, 2H, Ar), 2.32 (s, 6H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 162.22 (N=*C*H), 159.87, 140.61, 139.57, 136.94, 133.22, 132.40, 120.82, 120.61, 110.17, 35.32, 29.27, 19.76. HRMS *m/z* Calcd. for $C_{30}H_{35}Br_2N_2O_2$ $[M + H]^+$: 613.1065. Found: 613.1060.

Data for *N,N'*-(4,5-dimethylphenylene)bis(3,5-di-*tert*-butylsalicylideneimine) (**SD3**) [30]: Yellow solid (1.99 g, 70%). ^1H NMR ($CDCl_3$): δ 13.61 (br, 2H, O*H*), 8.64 (s, 2H, N=C*H*), 7.40 (d, J = 2.5 Hz, 2H, Ar), 7.19 (d, J = 2.5 Hz, 4H, Ar), 7.02 (s, 2H, Ar), 2.31 (s, 6H), 1.42 (s, 18H), 1.30 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 163.95 (N=*C*H), 158.65, 140.32, 137.23, 135.99, 127.99, 126.78, 121.00, 118.60, 35.25, 34.30, 31.63, 29.59, 19.68.

Data for *N,N'*-(4,5-dimethylphenylene)bis(3-*tert*-butyl-5-methylsalicylideneimine) (**SD4**): Yellow solid (1.72 g, 71%). ^1H NMR ($CDCl_3$): δ 13.59 (br, 2H, O*H*), 8.60 (s, 2H, N=C*H*), 7.15 (m, 2H, Ar), 7.01 (m, 4H, Ar), 2.30 (s, 6H), 2.27 (s, 6H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 163.70 (N=*C*H), 158.65, 140.05, 137.63, 136.08, 131.49, 130.49, 126.88, 121.21, 119.07, 34.95, 29.52, 20.79, 19.69. HRMS *m/z* Calcd. for $C_{32}H_{41}N_2O_2$ $[M + H]^+$: 485.3163. Found: 485.3163.

Data for *N,N'*-(4,5-dimethylphenylene)bis(3-*tert*-butyl-5-methoxysalicylideneimine) (**SD5**): Orange solid (2.01 g, 78%). ^1H NMR ($CDCl_3$): δ 13.48 (br, 2H, O*H*), 8.61 (s, 2H, N=C*H*), 7.03 (s, 2H, Ar), 7.01 (d, J = 3.0 Hz, 2H, Ar), 6.70 (d, J = 3.0 Hz, 2H, Ar), 3.77 (s, 6H), 2.31 (s, 6H), 1.41 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 163.28 (N=*C*H), 155.61, 151.45, 140.03, 139.61, 136.24, 120.98, 119.51, 118.62, 111.87, 55.93, 35.21, 29.40, 19.70. HRMS *m/z* Calcd. for $C_{32}H_{41}N_2O_4$ $[M + H]^+$: 517.3061. Found: 517.3061.

Data for *N,N'*-(4,5-dimethylphenylene)bis(3-*tert*-butyl-5-dimethylaminosalicylideneimine) (**SD6**): Red solid (1.17 g, 43%). ^1H NMR ($CDCl_3$): δ 13.31 (br, 2H, O*H*), 8.62 (s, 2H, N=C*H*), 7.01 (m, 4H, Ar), 6.64 (s, 2H, Ar), 2.83 (s, 12H), 2.30 (s, 6H), 1.41 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 163.28 (N=*C*H), 155.61, 151.45, 140.03, 139.61, 136.24, 120.98, 119.51, 118.62, 111.87, 55.93, 35.21, 29.40, 19.70. HRMS *m/z* Calcd. for $C_{30}H_{47}N_4O_2$ $[M + H]^+$: 543.3694. Found: 543.3694.

Data for *N,N′*-phenylenebis(3-*tert*-butylsalicylideneimine) (**SP1**) [31]: Yellow solid (1.54 g, 72%). ^1H NMR ($CDCl_3$): δ 13.72 (br, 2H, O*H*), 8.65 (s, 2H, N=C*H*), 7.38 (dd, 2H, J_1 = 7.5 and J_2 = 2.5 Hz, Ar), 7.33 (m, 2H, Ar), 7.23 (m, 2H, Ar), 6.85 (t, 2H, J = 7.5 Hz, Ar), 1.43 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 171.41 (N=*C*H), 164.80, 143.41, 139.37, 134.13, 132.77, 128.34, 119.74, 116.89, 115.11, 35.55, 29.62.

Data for *N,N′*-phenylenebis(3-*tert*-butyl-5-bromosalicylideneimine) (**SP2**) [32]: Orange solid (2.19 g, 75%). ^1H NMR ($CDCl_3$): δ 13.71 (br, 2H, O*H*), 8.56 (s, 2H, N=C*H*), 7.42 (d, 2H, J = 5 Hz, Ar), 7.36 (m, 4H,