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Luminescent Heteroleptic Tris(dipyrrinato)indium(III) Complexes

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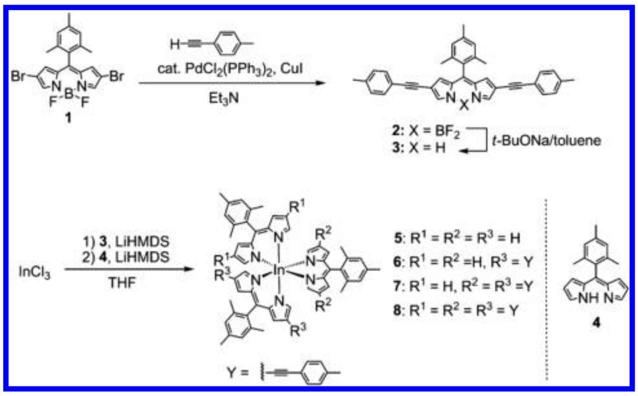
Supporting Information

ABSTRACT: To provide an improvement over the low fluorescence efficiencies often shown by homoleptic tris(dipyrrinato)indium(III) complexes, luminescent heteroleptic tris(dipyrrinato)indium(III) complexes bearing two types of dipyrrinato ligands are designed here by theoretical calculation and then synthesized. They possess frontier orbitals linked to suppression of the nonemissive charge-separated states; one shows a high fluorescence quantum yield (0.41) in toluene, which exceeds that of the corresponding BF_2 complex.

Metal complexes are becoming increasingly important in photochemistry. A particular group of metal complexes, photofunctional metal−organic frameworks (MOFs), is being developed as, for example, luminescent materials,[1] photocatalysts,[2] and sensors.[3] The spontaneous coordination of dipyrrins with metal ions makes them useful in supramolecular systems[4] such as MOFs.[5] Dipyrrin and its complexes are promising photofunctional dyes because of their strong and sharp absorption bands.[6] Some dipyrrin complexes show notable luminescence,[7] particularly the BF_2 complexes (4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacenes, or BODIPYs).[8] However, metal complexes of dipyrrins have remained relatively neglected because of their low emission efficiencies. We recently developed a heteroleptic bis(dipyrrinato)zinc(II) complex that showed a unprecedentedly high fluorescence quantum yield.[9] Improvement was gained through suppression of the formation of nonemissive charge-separated states between the two dipyrrinato ligands that compete with the emissive $^1\pi{-}\pi^*$ state (Figures S1−S3 in the Supporting Information, SI). Cohen and co-workers reported the first homoleptic tris(dipyrrinato)metal complexes with group 13 metals [gallium(III) and indium(III)]; however, the complexes showed poor quantum efficiencies (e.g., **5** in Scheme 1).[10] Here we report the development of brightly luminescent tris(dipyrrinato)indium(III) complexes by using the same strategy that we employed to find the previous zinc(II) complex. The result is the design and syntheses of heteroleptic indium(III) complexes bearing two types of dipyrrinato ligand (**6** and **7** in Scheme 1).

Scheme 1. Synthesis of Tris(dipyrrinato)indium(III) Complexes (LiHMDS = Lithium Hexamethyldisilazide)



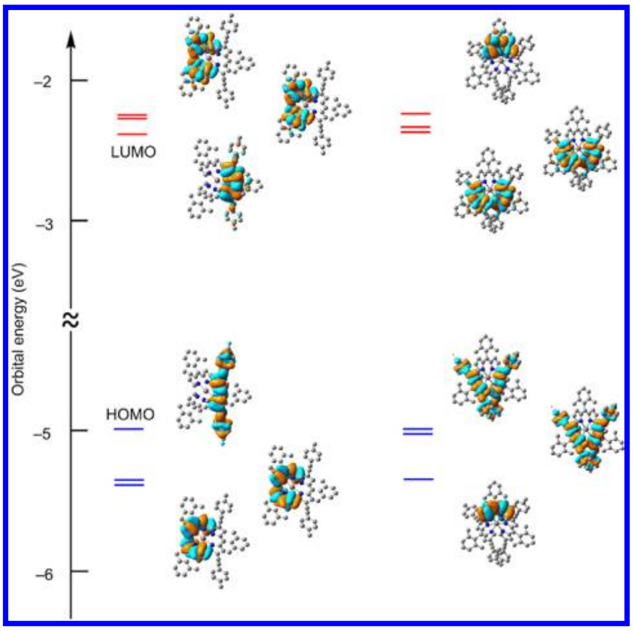


Figure 1. Frontier orbitals of heteroleptic complexes **6** and **7** estimated by DFT calculations at the B3LYP/(LanL2DZ for indium and 6-31G* for carbon, hydrogen, and nitrogen) level.

Theoretical calculations were conducted for complexes **6** and **7** (Figure 1) and **8** (Figure S4 in the SI). Frontier orbitals are composed of π or π^* orbitals on dipyrrinato ligands and contain negligible contributions from the indium(III) center. No remarkable energy differences were found among the frontier orbitals composed of the same ligand (Table S1 in the SI). The localization of both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) on ligand **3** was considered particularly important. The resulting electronic structures of **6** and **7** were expected to suppress photoinduced charge transfer between ligands **3** and **4** (Figure S5 in the SI). Only hydrogen was considered to be a suitable substituent on the α position of the dipyrrinato ligand; larger species would induce large steric repulsion that would

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significantly destabilize the coordination sphere. Complexes incorporating α-methylated dipyrrinato ligands, in fact, dissociated quickly in solution (data not shown).

Our previously reported deborylation method[9] allowed free base dipyrrin **3** to be synthesized from BODIPY **1**.[11] Heteroleptic complexes **6** and **7** and reference homoleptic complex **8** were synthesized by the treatment of $InCl_3$ with the corresponding equivalents of the lithium salts of dipyrrins **3** and **4**. Neither silica nor alumina chromatography could effectively isolate **6** and **7** because of decomposition, but the complexes were isolated by gel permeation chromatography (GPC). Note that the gallium(III) analogues of **6** and **7** could also be similarly synthesized using $GaCl_3$. Their formation was detected by mass spectrometry, but their decomposition prevented their isolation, even by GPC. The smaller atomic radius of gallium(III) (0.62 nm) in comparison with that of indium(III) (0.81 nm) may have resulted in greater steric interference among the ligands.

Heteroleptic complexes **6** and **7** were identified by NMR spectroscopy and elemental analysis. Their ^1H NMR spectra showed very different peak patterns, indicating no dissociation or disproportionation of the dipyrrin ligands in solution (Figure S6 in the SI). The single-crystal X-ray diffraction of **7** demonstrated its heteroleptic nature (Figure 2 and Table S2 in the SI). It showed a coordination sphere with a slightly distorted octahedral geometry, and Δ and Λ isomers coexisted as a racemic mixture. The In−N distances were 2.194(2)−2.242(3) Å, and the N−In−N angles ranged from 83.78(10)° to 95.02(10)°; these values are comparable to those of homoleptic complex **5**.[10]

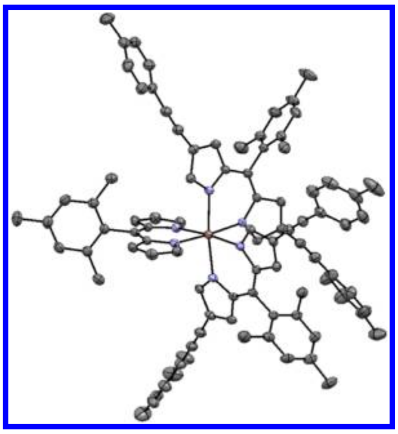

Figure 2. Crystal structure of complex **7**·toluene (thermal ellipsoid plot at 50% probability). Color code: gray, carbon; blue, nitrogen; brown, indium). Hydrogen atoms and toluene molecules are omitted for clarity. R1 = 0.0427; wR2 = 0.1075.

The optical properties of the series of indium(III) complexes were disclosed in UV−vis absorption and emission spectroscopy (Figure 3). Each heteroleptic complex showed two absorption bands, corresponding to the $^1\pi-\pi^*$ transitions of the two types of dipyrrinato ligands: π-extended dipyrrinato ligand **3** featured the red-shifted $^1\pi-\pi^*$ band.

Complexes **6** and **7** show differently shaped peaks and different absorption maxima because of exciton coupling.[12] Heteroleptic complex **6** underwent exciton coupling between its two dipyrrnato ligands **4**, which resulted in the sub-band at 500 nm. Similarly, heteroleptic complex **7** showed an absorption band (with its maximum at 564 nm) with a shoulder, which resulted from exciton coupling between the two dipyrrinato ligands **3**. Homoleptic **8** underwent more significant excition coupling among its three dipyrrinato ligands **3**, such that the single $\pi-\pi^*$ absorption band broadened and split into two bands.

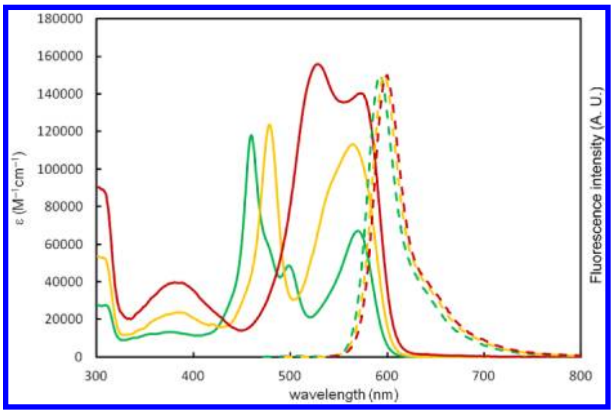

Figure 3. Absorption (solid line) and emission (broken line) spectra for complexes **6** (green), **7** (yellow), and **8** (red) in toluene. Excitation wavelengths: **6**, 459 nm; **7**, 480 nm; **8**, 530 nm.

The emission spectra of complexes **6**−**8** each showed a single peak at around 600 nm, whose wavelength position was unaffected by which absorption band was photoexcited. This indicates that the emission was derived exclusively from the $^1\pi-\pi^*$ excited state of the dipyrrinato ligand **3** and that quantitative energy transfer occurred from the dipyrrinato ligand **4** to ligand **3**. Among the three complexes, the highest quantum yield was provided by **6** (0.41 in toluene); the efficiency decreased with increasing number of dipyrrinato ligands **3** (0.34 for **7** and 0.28 for **8**). The quantum yield of heteroleptic complex **6** was much greater than that previously reported for homoleptic complex **5** (0.074 in hexane).[10] Complex **6** surprisingly also showed a greater fluorescence quantum yield in toluene than did the corresponding BODIPY **2** (0.35). This counters the preconception that BODIPYs emit more brightly than do dipyrrinato metal complexes. The authors also describe solid-state luminescence briefly. Complexes **7** and **8** exhibited red emission (Figure 4), whereas complex **6** was hardly fluorescent. The absence of fluorescence in **6** might stem from intermolecular interaction or bimolecular quenching, although the authors cannot give a precise explanation because of the lack of crystal structure. Solid-state fluorescence tends to be more sensitive to crystal packing than to the molecular nature of the fluorophore itself.

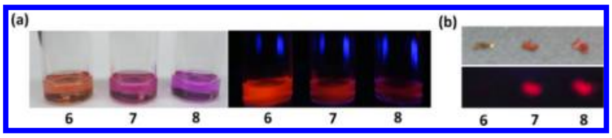

Figure 4. (a) Photographs of dichloromethane solutions of **6**−**8** under ambient light (left) and 365 nm UV light (right). The absorbance of each solution at 365 nm is normalized. (b) Photographs of solids of **6**−**8** under ambient light (top) and 365 nm UV light (bottom).

Our previously synthesized heteroleptic bis(dipyrrinato)zinc(II) complexes recovered their fluorescence quantum yields by suppressing nonemissive charge-separated states competing with emissive singlet $\pi-\pi^*$ excited states (Figures S1−S3 in the SI).[9] A similar mechanism is proposed here (Figure S5 in the SI). Heteroleptic complex **6** with one emissive dipyrrinato ligand **3** avoided nonemissive charge-separated states. In contrast,

Table 1. Optical Properties of Dipyrrin Complexes

	$10^{-4}\varepsilon$ (M^{-1} cm^{-1})	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	ϕ_F[c] (in toluene)	ϕ_F (in CH_2Cl_2)	τ[d] (ns, in toluene)	τ[d] (ns, in CH_2Cl_2)
2	6.11	604	650	0.35	0.18	2.53	1.52
5[e]	6.01	496	522	0.074		1.93	
6	11.8, 6.73	459, 570	592	0.41	0.053	2.44	1.29
7	12.4, 9.24 (sh[f]), 11.3	478, 542 (sh), 564	596	0.34	0.021	2.53	1.42
8	15.6, 14.0	528, 572	600	0.28	0.015	2.49	1.48

[a] Absorption wavelength. [b] Emission wavelength. [c] Fluorescence quantum yields. [d] Mean fluorescence lifetimes. For details, please refer to the SI. [e] From ref 10, where all data are in a hexane solution. [f] Shoulder.

complexes **7** and **8** underwent charge separation among their multiple dipyrrinato ligands **3**, with greater charge separation shown by **8**, reflecting its greater number of dipyrrinato ligands **3**. Optical data in dichloromethane were also acquired. The fluorescence quantum yields of **6**−**8** were respectively 13%, 6.2%, and 5.4% of the values recorded in toluene. The smaller drop shown by **6** may reflect its effective suppression of charge-separated states, which is more effective in polar solvents such as dichloromethane. Fluorescence lifetime studies were also conducted to assess the photophysical properties of the complexes. The emission lifetimes of the complexes in toluene ranged from 2.4 to 2.5 ns (Table 1), consistent with the singlet nature of their luminescence. Each decay curve was fitted using one main and two minor exponential decays (Figures S7−S9 and Tables S3−S5 in the SI). The fluorescence lifetimes decreased to 1.3−1.5 ns in dichloromethane, reflecting fluorescence quenching. In this medium, the fastest decay component gained population (Figures S10−S12 and Tables S6−S8 in the SI). These findings may also be associated with the existence of the quenching charge-separated state.[13]

In conclusion, we synthesized the first heteroleptic tris(dipyrrinato)indium(III) complexes using a combination of plain (**4**) and π-extended (**3**) dipyrrin ligands. Heteroleptic complexes **6** and **7** exhibited higher fluorescence quantum yields than homoleptic complexes **5** and **8**, and the finding was attributed to suppression of the nonemissive charge separated states. This work establishes tris(dipyrrinato)indium(III) complexes as potentially useful in, for example, optically active supramolecular and MOF systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, schematic explanations for charge separation in dipyrrin metal complexes, DFT calculation for **8** and frontier orbital energies for **6**−**8**, ^1H NMR of **6** and **7**, crystallographic data for **7**·toluene, details for a fluorescence lifetime study, and a CIF file for **7**·toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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