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Synthesis and Dual-Emission Feature of Salen-Al/Triarylborane Dyads

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Supporting Information

ABSTRACT: Novel salen-Al/triarylborane dyad complexes were prepared and characterized with their corresponding mononuclear compounds. The UV–vis and photoluminescence experiments for dyads exhibited photoinduced energy transfer from borane to the salen-Al moiety in an intramolecular manner. Theoretical calculation and fluoride titration results further supported these intramolecular energy-transfer features.

uminescent organometallic-based luminophores have been extensively studied as promising materials in the field of optoelectronic devices such as organic light-emitting diodes and photovoltaics because of their intriguing optical properties.¹ The implementation of these interesting features is mainly generated from the systematic combination of various ligand frameworks and proper functional groups. Such controls can improve their photophysical properties, such as emission color change and high quantum efficiency, thus expanding their applications as optoelectronic materials.² Among them, aluminum-based luminophores have attracted considerable interest because of their outstanding electronic and thermal stabilities.³ In particular, aluminum (Al) complexes with ligands based on the tetradentate Schiff base N,N'-bis(salicylidene)ethylenediamine (salen) have received growing attention as multicolor fluorophores as well as promising electronic materials.^{4,5} The Schiff base derivatives have been extensively utilized as chelating agents to form stable transition-metal complexes,⁶ and, in particular, salen-Al complexes led to extensive chemical applications, such as catalysts for various organic transformations⁷ or polymerization.⁸ In addition, recent reports on luminescent salen-Al complexes have appeared with the introduction of various functional groups to control the optical properties.^{2,4,5} Furthermore, novel dyad systems based on heterodinuclear complexes, such as salen-Al/iridium (Ir)⁹ and salen-Al/boron dipyrromethane (BODIPY),¹⁰ have been reported. These dyads exhibit dual-emission bands via intramolecular energy transfer (IET) from salen-Al to Ir or BODIPY, respectively. Along with these studies, although versatile triarylborane (TAB)-containing transition-metal complexes have received great interest for enhancing the luminescent properties,¹¹ there have been no reported studies on Al/TAB

dyad systems, capable of inducing IET to Al moieties. The incorporation of the TAB group as an efficient anion receptor is advantageous to obtaining attractive photophysical properties. In this perspective, we designed new types of salen-Al/TAB dyad systems [D1 and D2 (CCDC 1498862)] in which two moieties are directly connected by a phenoxy linker to induce IET from borane to salen-Al. Herein, we describe the detailed synthesis and photophysical properties of D1 and D2 based on IET in conjunction with fluoride binding experiments and theoretical considerations.

Novel Al/TAB dyads (D1 and D2) were obtained in moderate yield (67%) by the reaction of the corresponding salen-Al precursors (M1 and M2) with B1 in toluene. While the ¹H and ¹³C NMR spectra (Figures S1–S3 in the Supporting Information, SI) showed the predicted range corresponding to the salen-Al parts and TAB moieties, the ¹¹B NMR signals for the dyads were not observed, despite a prolonged acquisition time. The solid-state structure of D2 was determined by single-crystal X-ray diffraction (Scheme 1, inset, and Tables S1 and S2 in the

Scheme 1. Synthetic Routes for Dyad Compounds (D1 and D2) and Their Fluoride Adducts ($[D1-F]^-$ and $[D2-F]^-$) and the Crystal Structure of D2^{*a*}



^{*a*}The H atoms are omitted for clarity in the crystal structure (50% thermal ellipsoids) of D2.

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SI). The structure clearly revealed the dyad system of D2, in which the Al and B centers are linked through the phenoxy group. The trigonality parameter¹² (τ) for D2 is 0.51, indicating that the geometry around the Al center is in an intermediate form between square pyramidal and trigonal bipyramidal. In addition, the fluoride adducts ([D1-F]⁻ and [D2-F]⁻) of D1 and D2 were produced by the reaction with excess KF in the presence of 18-crown-6 in toluene at ambient temperature (Scheme 1). The ¹¹B and ¹⁹F NMR signals at δ 4.02 and -162, respectively, only observed for [D1-F]⁻ confirmed the formation of four-coordinate triarylfluoroborate, indicating the binding of fluoride to the B atom of the TAB moiety.

The absorption and fluoride-anion-binding properties of D1 and D2 were investigated by UV-vis titration experiments in tetrahydrofuran (THF; Figure 7a in the SI and Table 1). Both

Table 1. Photophysical Data of Mononuclear (A1, A2, andB1) and Heterodinuclear (D1 and D2) Compounds

			τ , ^{<i>a</i>} ns	
compound	λ_{abs} , $\stackrel{a}{}$ nm (ε , $\times 10^{-3}$ M ⁻¹ cm ⁻¹)	$\lambda_{ m em}$, and nm	400 nm	>460 nm
A1	280 (26.9), 357 (10.0)	473 ^b		6.86
A2	271 (26.9), 348 (10.0)	454 ^c		3.88
B1	318 (27.0)	407 ^b , 406 ^c	2.60	
D1	322 (25.7), 357 (14.5)	476 ^b , 478 ^d	4.41	6.52
D2	322 (31.4), 350 (16.9)	430 ^c , 456 ^e	6.29	12.8
^{<i>a</i>} Measured u 310 nm. ${}^{d}\lambda_{e}$	using a 3.0×10^{-5} M THF _x = 362 nm. ${}^{e}\lambda_{ex}$ = 360 nm	S solution. ${}^{b}\lambda_{ex}$ m.	= 314 n	m. $^{c}\lambda_{ex} =$

dyads exhibited a major low-energy absorption band at ca. 322 nm, which can be assigned to the dominant $\pi(Mes)-p_{\pi}(B)$ charge-transfer (CT) transition on the borane moiety (as is clearly observed with B1; Figure S8 in the SI) and a shoulder absorption band in the region of ca. 350 nm, which is assignable to the salen-Al-centered $\pi\pi^*$ transition that is also observed for mononuclear compounds [A1, (3,5-^tBu-salen)Al-OPh; A2, (3-^tBu-5-H-salen)Al-OPh; Figure S8 in the SI] and other salen-Al luminophores.^{4,5} The absorption spectra of D1 and D2 are well matched with the arithmetic sum of the absorption bands for each relevant mononuclear compounds (Figure S8 in the SI). Upon the addition of incremental amounts of fluoride into the THF solution of D1 or D2, the absorption band at around 322 nm for the borane moiety is gradually quenched [the binding constants (*K*) of **D1** and **D2** are 3.2×10^4 M⁻¹ (Figure 7a in the SI, inset) and 3.6×10^4 M⁻¹ (Figure S7b in the SI), respectively, similar to that of B1 $(3.3 \times 10^4 \text{ M}^{-1})$; Figure S9 in the SI)]. Each absorption shape with the addition of Bu_4NF (5.83 × 10^{-5} M) is very similar to that of the fluoride adduct, [D1-F]⁻ or [D2-F]⁻, under the same molar concentration $(3.00 \times 10^{-5} \text{ M})$ as the neutral dyads (Figure S7 in the SI).

The emission spectra of D1 showed dual-emission patterns when irradiated at 314 nm, which is the minimum point of the excitation curve of D1 and very close to the maximum point of the excitation of B1 (Figure S10a in the S1). A comparison of the emission intensities for D1 and its relevant mononuclear compounds, B1 and A1, at the same conditions reveals that the intensity of the borane moiety ($\lambda_{em} = 407$ nm for B1) decreased and that of salen-Al ($\lambda_{em} = 473$ nm for A1) is remarkably enhanced (Figure 1a). The finding that the PL intensity of each part was only changed without significant alteration in the emission wavelength indicates the involvement of partial IET from borane to salen-Al. Furthermore, this feature



Figure 1. PL spectra in THF (3.0×10^{-5} M) for (a) **D1**, **A1**, **B1**, and **A1** + **B1** ($\lambda_{ex} = 314$ nm) and (b) **D2**, **A2**, **B1**, and **A2** + **B1** ($\lambda_{ex} = 310$ nm) at ambient temperature.

is clearly demonstrated by the observation of emission bands for the corresponding mononuclear compounds (A1 and B1) in a solution with an equimolar mixture ($\lambda_{ex} = 314$ nm; Figure 1a). Additionally, the fluorescence decay lifetime study of D1 reveals that the emission at 400 nm assignable to borane-centered fluorescence (4.41 ns) is a little shorter than that of the emission at 480 nm (6.52 ns) attributable to the salen-centered fluorescence (Table 1), further verifying the IET phenomenon. This feature originated from good overlap between the emission band of B1 and the absorption band of A1. On the other hand, in comparison to each relevant mononuclear compound (B1 and A2), the emission spectra of D2 (λ_{ex} = 310 nm) showed that the intensity of the borane moiety was evidently decreased but that of salen-Al was only slightly enhanced (Figure 1b). This result indicates that a less efficient energy transfer between the salen-Al and borane centers occurs in D2 than in D1. This emissive characteristic of D2 can be caused by poor overlap of the emission band of **B1** and the absorption band of **A2** (λ_{abs} = 348 nm; Table 1), which is blue-shifted more than A1 ($\lambda_{abs} = 357$ nm; Table 1). The PL spectra of D1 and D2 in the film state [5 wt % doped in poly(methyl methacrylate)] exhibited the intense emission of salen-Al moieties including a slight emission shoulder of borane parts around 400 nm (Figure S11 in the SI), indicating that IET in a rigid state could be more efficiently evoked than in a solution state.

Furthermore, such an IET feature was clearly confirmed by the PL titration for the dyads (Figure 2 for D1 and Figure S12 in the SI for D2). Upon the addition of fluoride anions, while the PL spectra of D1 excited at 314 nm were remarkably quenched by over ca. 85% of the initial intensity, the emission spectra excited at 362 nm decreased only by ca. 20%. The spectral quenching of the emission band ($\lambda_{ex} = 314$ nm) is strongly thought to be due to



Figure 2. Spectral changes in the PL of **D1** in THF (3.00×10^{-5} M) upon the addition of Bu₄NF ($0-5.83 \times 10^{-5}$ M) and PL spectra of [**D1**-F][18-crown-6·K] (red line). $\lambda_{ex} = (a)$ 314 nm and (b) 362 nm.

the steady decrease of IET from borane to the salen-Al moiety attributable to the emissive decrease of the TAB group by the bound fluoride anions. However, the PL ($\lambda_{ex} = 362$ nm) attributable to luminescence of the salen-Al center is relatively well-maintained despite the addition of the fluoride anion. Accordingly, the results clearly verify the IET feature in **D1**. The end point of the titration was confirmed by a comparison with the PL of [**D1**-F][18-crown-6·K] (Figure 2, red line). Similar to **D1**, the quenched PL spectra of **D2** were also observed upon the addition of fluoride anions ($\lambda_{ex} = 310$ or 360 nm; Figure S12 in the SI). However, the quenched PL intensity was only 42%, which is about half the degree of quenching in comparison with **D1**.

To gain insight into the electronic transitions of D1 and D2, time-dependent density functional theory (TD-DFT) calculations on the ground state (S_0) were performed with the B3LYP functional and 6-31G(d) basis sets (Figure 3). Also, to include



Figure 3. Frontier molecular orbitals for **D1** at their ground-state (S_0)-optimized geometries in THF and the lowest-energy electronic transition from TD-DFT calculations (isovalue = 0.04).

the effects of the THF solvent, the conductor-like polarizable continuum model was used.¹³ The calculated transitions for D1 and D2 show that major contributions (f > 0.05) in the lowenergy absorption regions below 330 nm are associated with the three transitions of HOMO-2 \rightarrow LUMO (95.4%, λ_{abs} = 358 nm for **D1**, and 94.7%, λ_{abs} = 350 nm for **D2**), HOMO \rightarrow LUMO+1 (97.8%, λ_{abs} = 350 nm for **D1**, and 96.6%, λ_{abs} = 346 nm for **D2**), and HOMO-1 \rightarrow LUMO+1 (94.4%, λ_{abs} = 340 nm for D1, and 93.2%, λ_{abs} = 335 nm for **D2**; Figure 3 and Figure S19 and Tables S4 and S6 in the SI). While LUMO and LUMO+1 are predominantly localized on the salen-Al moiety (>97% for D1 and D2), HOMO to HOMO-2 are distributed over the salen-Al moiety (55-76% for D1 and 21-89% for D2) and the bridged phenoxy group (20-35% for D1 and 4-63% for D2). These results indicate that the salen-Al moiety and bridged phenoxy group mainly contribute to the major transitions below 330 nm. Therefore, the absorption below 330 nm of D1 and D2 originates from the salen-Al-centered $\pi\pi^*$ and CT transitions from the phenoxy group to the salen-Al moiety. However, the largest electronic transitions (f > 0.2; Figure 3 and Figure S19 and Tables S4 and S6 in the SI) for D1 and D2 in the region above 330 nm were from HOMO-3 to LUMO+2 (Figure 3 and Figure S19 and Tables S4 and S6 in the SI). While HOMO-3 of the

dyads was predominantly located at the arylborane moiety (95%), LUMO+2 was delocalized over the arylborane moiety (65%; Tables S3 and S5 in the SI) and the bridged phenoxy moiety (31%). DFT calculations for the regions above 330 nm verify that the major transitions are both the borane-centered $\pi\pi^*$ and CT transitions from borane to the phenoxy group. These findings from theoretical calculations firmly support that the significant absorptions independently occur because of salen-Al or TAB-centered $\pi\pi^*$ transitions and partial CT bands via the phenoxy group. Along with the photophysical data, these DFT results further demonstrate that the dyads exhibit IET from borane to salen-Al.

We have synthesized and characterized Al^{III}/TAB dyads (**D1** and **D2**) and their fluoride adducts. The emission spectra of the dyads, especially that for **D1**, demonstrated an obvious IET feature from borane to the salen-Al moiety. PL titrations and DFT calculations further supported the experimental results. We anticipate that these dyads will constitute a novel class of luminophores. Relevant studies on developing novel Al-based heterodinuclear complexes are in progress.

ASSOCIATED CONTENT

S Supporting Information

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NMR spectra and computational details (PDF)

Accession Codes

CCDC 1498862 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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