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Novel aluminum–BODIPY dyads: intriguing dual-emission *via* photoinduced energy transfer†

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Three novel BODIPY-based heterodinuclear complexes, $[salen(3,5^{-t}Bu)_2Al-(OC_6H_4-BODIPY)]$ (6), $[salen-(3,5^{-t}Bu)_2Al-(OC_6F_2H_2-BODIPY)]$ (7), and $[(mq)_2Al-(OC_6H_4-BODIPY)]$ (8) (salen = N,N'-bis(salicylidene)-ethylenediamine, BODIPY = 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, and mq = methyl-8-quinolinolato) were prepared and characterized by multinuclear NMR spectroscopy. The specific structures of **6–8** were also determined by single crystal X-ray analysis. In particular, the salen-based heterodinuclear complexes **6** and **7** exhibited higher thermal stability ($T_{d5} = 309$ and 306 °C, respectively) than that of the closely related mononuclear aluminum or BODIPY compounds, except for **8**. The UV/vis absorption and PL spectra for **6** and **7** indicated a significant photoinduced energy transfer from the aluminum–salen moiety to the BODIPY group in an intramolecular manner. Theoretical calculations revealed independent transition states of the aluminum–salen moiety or the BODIPY group in the Al^{III}–BODIPY dyads, further supporting these experimental results.

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Introduction

Tetra-coordinate BODIPY (boron dipyrromethane) compounds have received considerable attention in a wide range of chemical applications, such as fluorescent probes for biological/ environmental fields,¹ promising chromophores or fluorophores in optoelectronic materials,² chemical indicators for other molecules,³ due to their outstanding photophysical properties. In order to enhance the inherent character of the BODIPY group, a number of concepts have been developed in conjunction with introduction of various functional groups into the BODIPY moiety.⁴ In addition to tri-coordinate boranebased BODIPY dyads (I in Chart 1)⁵ and triads (II),⁶ BODIPYbased compounds containing various functional groups (III)^{7,8} were shown to expand their application. They exhibited intriguing spectroscopic and photophysical properties originating from significant interactions such as partial energy transfer between individual building units. This feature highly depends on their molecular structures. For example, Thilagar

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Chart 1 Examples of BODIPY-based compounds.

and coworkers recently reported the triarylborane–BODIPY dyad systems, demonstrating multiple emission bands as chemical sensors for fluoride ions.⁹

In an effort to develop novel BODIPY-based dyads with high stability, we were interested in the Al complexes based on the Schiff base salen (*N*,*N*'-bis-(salicylidene)ethylenediamine) and the quinolinate ligand as conjugates. Although the aluminum salen complexes are well-known for various catalytic systems,¹⁰⁻¹² they have widely been investigated as excellent luminophores in optoelectronic materials,¹³⁻¹⁵ owing to their potential photophysical properties. Along with these studies, a



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data of **6-8** in CIF format, NMR spectra, and computational details. CCDC 1400922–1400924. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt05067g

heterodinuclear Al–salen/Ir complex recently reported was shown that it could act as an emitter in organic light-emitting diodes (OLEDs).¹⁶ Nonetheless, to the best of our knowledge, Al(III)–BODIPY heterodinuclear complexes have never been investigated. Bearing this in mind, novel Al–BODIPY dyads could be also considered promising candidates for opto-electronic applications, such as emitting materials in OLEDs.

In this regard, we report the Al–BODIPY dyad systems based on two individual fluorescent luminophores, which are connected with a phenoxy spacer with the emergence of intriguing luminescent properties resulting from the efficient energy transfer between the two moieties. Herein, we describe the detailed synthesis, characterization, thermal stability, and photophysical properties of Al–BODIPY dyads (6–8) along with theoretical considerations.

Results and discussion

Synthesis and characterization

The synthetic procedures of mono-aluminum compounds (4a, 4b and 5), and heterodinuclear compounds 6–8, which were linked between the aluminum and BODIPY groups, are shown in Scheme 1. The aluminum compounds 4 and 5 were produced readily from the reaction of the corresponding aluminum precursor with phenol derivatives, and the aluminum-BODIPY dyads 6–8 were prepared from the selective reaction of the aluminum salen complex (2) with 1a or 1b, and the aluminum quinolinate complex (3) with 1a in toluene, respectively in moderate yield (58% for 6, 42% for 7, and 39% for 8).

The formation of **4–8** was characterized by multinuclear NMR spectroscopy (Fig. S1–S10 \dagger) and elemental analysis. The

¹H NMR and ¹³C NMR spectra of all compounds showed the expected range corresponding to the aluminum moieties and the BODIPY. Additionally, the ¹¹B NMR signals of **6–8** observed at δ 0.27, 0.20, and 0.23 ppm, respectively, were consistent with the presence of four-coordinate boron centers. The ¹¹B nucleus of the BODIPY group is coupled to the F atoms, leading to a sharp triplet (${}^{1}J_{B-F} = 28.2$ Hz for **6** and **7**; ${}^{1}J_{B-F} = 29.5$ Hz for **8**) similar to those found in previously reported BODIPY derivatives.^{5–9} Furthermore, the solid-state structures of **6–8** were determined by a single crystal X-ray diffraction study (Fig. 1, Tables S1 and S2†). Single crystals suitable for X-ray structural analysis were obtained by cooling a solution of saturated CH₂Cl₂/Et₂O at –20 °C. The phenoxy group connects the aluminum centre with a BODIPY moiety indicating that



Fig. 1 X-ray crystal structures of **6–8** (50% thermal ellipsoids). H atoms are omitted for clarity.



Scheme 1 Synthetic routes for mononuclear compounds (4a, 4b, and 5) and heterodinuclear compounds (6-8).

the three complexes 6-8 are heterodinuclear complexes with both a five-coordinate aluminum centre and a boron centre. The Al-O and Al-N bond distances of 6-8 were observed as ca. 1.8 Å and 2.0 Å, respectively, similar to those found in typical pentacoordinate aluminum complexes.^{13,14} The distortion of the coordination around an Al centre was generally determined by geometric analysis such as the trigonality parameter τ (τ = $[\alpha - \beta]/60$, where α and β are the largest and next-largest interligand bond angles).¹⁷ The trigonality parameter τ for the perfectly square-pyramidal (sqp) geometry is 0 and τ for the regularly trigonal-bipyramidal (tbp) geometry is 1. The τ values for 6, 7, and 8 are 0.35, 0.39, and 0.82, respectively, indicating that the geometries around the Al centre of 6 and 7 are sqp, whereas 8 is more in favour of tbp. The meso-carbon atom of BODIPY in 6-8 adopts a perfectly trigonal planar geometry, as judged from the sum of the three C–C_{meso}–C angles ($\sum_{(C-C-C)}$ = 360°, 6: 119.8°, 120.9°, and 119.3°, 7: 120.7°, 120.1°, and 119.2°, 8: 119.4°, 120.1°, and 120.5°, respectively). On the other hand, the BODIPY-centred plane for 6-8 was significantly distorted with respect to the phenoxy group linked to the Al centre, resulting from the dihedral angles of 53.5°, 54.4°, and 41.4°, respectively. Thus, this feature might make it difficult for achieving delocalization of electrons between the bridged phenoxy group and the BODIPY moiety.

Thermal properties

The thermal stabilities of **1a**, **1b**, and **4–8** were investigated by thermogravimetric analysis (TGA) (Fig. 2 and Table 1). While the mono-aluminum precursors **4a**, **4b** and **5** exhibited T_{d5} values of 250, 281, and 263 °C, respectively, the heterodinuclear **6–8** showed T_{d5} values of 309, 306, and 206 °C, respectively, despite stepwise thermal degradation. It is expected that the bond between the aluminum centre and phenoxy group degraded at an early stage at a relatively low temperature. The BODIPY precursors **1a** and **1b** also exhibited T_{d5} values of 251 and 225 °C, respectively, implying that the BODIPY moiety is more thermally unstable than the aluminum moieties. Note that **6** and **7** exhibit significantly enhanced thermal stability as

Fig. 2 TGA curves of mononuclear (1a, 1b, 4a, 4b, and 5) and heterodinuclear complexes (6–8).

Table 1Photophysical and thermal properties of mononuclear (1a, 1b,4a, 4b, and 5) and heterodinuclear compounds (6–8)

Compound	$\lambda_{\rm abs} {}^{a}/{\rm nm}$ $(\varepsilon \times 10^{-3} { m M}^{-1} { m cm}^{-1})$	$\lambda_{\rm em}{}^a/{\rm nm}$	$\Phi_{ m em}{}^b$	$T_{\mathrm{d5}}{}^{c}/^{\mathrm{o}}\mathrm{C}$
1a	$380, 500 (1.30, 5.75)^d$	514	0.09	251
1b	365, 507 (1.29, 5.19)	522	0.02	225
4a	365 (0.81)	480	0.41	250
4b	365 (0.85)	482	0.46	281
5	e	470	0.03	263
6	370, 500 (2.03, 5.46)	481, 514	0.16	309
7	366, 503 (1.71, 5.02)	477, 519	0.10	306
8	377, 500 (1.14, 4.65)	463, 513	0.13	206

^{*a*} Measured using a 1.0×10^{-5} M CHCl₃ solution. ^{*b*} Quinine sulfate as a standard (0.5 M H₂SO₄, Φ = 0.55). ^{*c*} Determined by TGA at 5% weight loss. ^{*d*} Molar absorption coefficient, ε (×10⁻³ M⁻¹ cm⁻¹). ^{*e*} Not observed.

compared to that of each of the mono-aluminum complexes (**4a** and **4b**) or the BODIPY (**1a** and **1b**) precursors, except for **8**. This feature is attributed to both the thermally robust salen–Al bond and the significant bulkiness of **6** and **7**.

Photophysical properties

The optical properties of mononuclear and heterodinuclear compounds were investigated by UV/Vis absorption and photoluminescence (PL) measurements (Fig. 3 and Table 1) at room temperature. The absorption spectra of 6 and 7 in CHCl₃ exhibited two low-energy major absorption bands at ca. 370 nm assignable to both the salen-centred $\pi - \pi^*$ transitions^{13–15} and the BODIPY-centred $S_0 \rightarrow S_2$ (π - π^*) transitions, and at *ca.* 500 nm originating from the $S_0 \rightarrow S_1 (\pi - \pi^*)$ transitions in the BODIPY moiety (Fig. 3a).⁸ Despite a slight change in the position of an absorption maxima below 300 nm, probably indicating minimal electronic communication between the two luminophores in **6** and 7, ^{5*a*} the absorption spectra of aluminum (4a and 4b) and BODIPY (1a and 1b) mononuclear compounds mostly overlapped with those of the corresponding heterodinuclear compounds (6 and 7). The distorted arrangement of the two moieties is probably responsible for this feature.^{8,18} Importantly, these independent absorption features of the two luminophores in 6 and 7 provide a basis for intramolecular energy transfer transitions.

On the other hand, the low-energy absorption band ($\lambda_{abs} = 500 \text{ nm}$) of the heterodinuclear compound **8** is almost identical to that of its closely related mononuclear BODIPY compound (**1a**) due to no significant absorption of the quinolinate-based aluminum compound **5** in the 350–500 nm range. While the high-energy absorption bands of **6** and 7 were slightly broadened by ligand-centered (LC) transitions ascribable to the corresponding mono-aluminum and BODIPY compounds, **8** showed a marginal absorption band in a region ranging from 250 to 300 nm.

The emission spectra of **6** and 7 irradiated at 370 nm displayed dual emission patterns ($\lambda_{em} = 481$ and 514 nm for **6**, $\lambda_{em} = 477$ and 519 nm for 7), which correspond similarly to those of the closely related mononuclear aluminum and



Paper



Fig. 3 (a) UV/Vis absorption and (b) photoluminescence spectra in CHCl₃ (5.0×10^{-5} M) for mononuclear (1a, 1b, 4a, 4b, and 5) and heterodinuclear compounds (6–8) at room temperature.

BODIPY compounds (Fig. 3b and Table 1). The excitation spectra for two emission maxima of 6-8 showed the maximum point around 370 nm, indicating that excitation at 370 nm can effectively reveal the dual emission for the aluminum and BODIPY moieties (Fig. S11-S13[†]). For this reason, we chose 370 nm as the excitation wavelength. A comparison of the emission intensities for 6 and 7 with closely related mononuclear aluminum (4a or 4b) and BODIPY compounds (1a or **1b**) at the same concentration reveals that the intensity of the aluminum moiety decreased and that of BODIPY increased in both 6 and 7 (Fig. 3b). The observation that the emission intensity of each moiety was only changed without any alteration in the emission maxima indicates the involvement of partial energy transfer from the Al-centred fluorophore to the BODIPY-centred chromophore. This feature resulted from the characteristic distorted nonplanar molecular structures of 6 and 7.

Furthermore, the observation of the obvious emission bands attributable to the corresponding mononuclear compounds from the solution of an equimolar mixture (λ_{ex} = 370 nm, Fig. S14 and S15†) demonstrates such intramolecular energy-transfer transition features in **6** and 7.^{8,18,19} Further considerations of significant overlaps between the emission bands of the aluminum–salen compounds (**4a** or **4b**) and the absorption bands of the BODIPY compounds (**1a** or **1b**) also confirm this feature (Fig. S17 and S18†). This result is also in good agreement with the overlapping feature between the corrected excitation spectra recorded for two emissions and the absorption spectrum recorded over the entire spectral range (Fig. S11 and S12†). This feature is clearly verified by the observation that measurement of the fluorescence decay lifetime of the emissions at 470 nm and 520 nm for **6** or 7 in CHCl₃ (5×10^{-5} M) as <4 and >6 ns, respectively, reveals that the former is assignable to the Al-centre fluorescence and the latter to the BODIPY-centre fluorescence (Fig. S19–S22†).

On the other hand, the emission spectrum of **8** showed emission maxima at 463 and 513 nm, which correspond exactly to those of **1a** and **5**, respectively. This result indicates the absence of energy transfer between the two luminophores in **8**, suggesting that each moiety behaves entirely independently within a heterodinuclear molecule. This feature is further confirmed by the observation of the individual emission bands without change originating from the corresponding mononuclear compounds from the solution of an equimolar mixture ($\lambda_{ex} = 370$ nm, Fig. S16†).

Theoretical calculations and molecular orbital analyses

To gain insight into the electronic transitions and the electronic structures of **6–8**, TD-DFT calculations on the ground state (S₀) were performed with the B3LYP functional and 6-31G(d) basis sets (Fig. 4 and Table 2). The geometries of **6–8** for the calculations were optimized from their X-ray structures. To include the solvent effects of CHCl₃, the conductor-like polarizable continuum model (CPCM) was used.²⁰ The calculation results for **6–8** show that the largest contribution (f > 0.4) to lower-energy absorptions below 400 nm is involved with the transition from HOMO–2 to LUMO ($\lambda_{abs} = 416$ nm for **6** and $\lambda_{abs} = 420$ nm for 7) or from HOMO–1 to LUMO ($\lambda_{abs} = 416$ nm for **8**, Table 2). While both the HOMO–2 (for **6** and 7) and the HOMO–1 (for **8**) are predominantly localized on the BODIPY (*ca.* 89%) and the bridged phenyl group (*ca.* 10%) for all of the



Fig. 4 Frontier molecular orbitals for 6-8 at their ground state (S₀) optimized geometries and the lowest-energy electronic transition from TD-DFT calculations (isovalue = 0.04).

Table 2 The major low-energy electronic transition for $6{-}8$ from TD-DFT calculations $^{\rm a}$

	$\lambda_{\rm calc}/{\rm nm}$	$f_{ m calc}$	Assignment
6	416.05	0.4279	HOMO-2 \rightarrow LUMO (95%)
	392.99	0.0328	HOMO \rightarrow LUMO+1 (98%)
	360.37	0.0551	$HOMO-3 \rightarrow LUMO+1 (95\%)$
7	419.90	0.4338	$HOMO-2 \rightarrow LUMO(95\%)$
	388.53	0.0216	HOMO \rightarrow LUMO+1 (98%)
	363.09	0.0690	$HOMO-1 \rightarrow LUMO+1 (97\%)$
8	416.26	0.4319	HOMO-1 \rightarrow LUMO (95%)
	384.33	0.1114	HOMO \rightarrow LUMO+1 (92%)

 a Singlet energies for the vertical transition calculated at the optimized S_0 geometries.

compounds (Tables S3, S5, and S7†). Although the transition to the S1 (f > 0.13, for 6) or S1 and S2 (f > 0.02, for 7) state was slightly observed in the lower-energy absorptions (Tables S3–S6†), the Al moieties and bridged phenyl group very slightly contribute to the major transitions below 400 nm.

However, most electronic transitions (f > 0.02, Fig. 4 and Table 2) to LUMO+1 (>99% for salen ligands (6 and 7) and quinolate moiety (8)) in the range of 300–400 nm are limited to the aluminum ligand moieties and the bridged phenyl groups. The major contributions for 6 in this region are observed from HOMO–3 to LUMO+1 ($\lambda_{abs} = 360$ nm) and from HOMO to LUMO+1 ($\lambda_{abs} = 393$ nm). The HOMO–3 and HOMO correspond to the delocalized electron density of the salen moiety (52% and 93%) and bridged phenyl group (41% and 6%), respectively. Similarly, the significant transitions of 7 in the region are from HOMO–1 to LUMO+1 ($\lambda_{abs} = 363$ nm) and from HOMO to LUMO+1 ($\lambda_{abs} = 389$ nm).

The delocalized electron density of HOMO–1 and HOMO for 7 is distributed over the salen moieties (92% and 96%) and bridged phenyl group (8% and 3%), respectively. On the other

hand, the major transition of **8** in the range of 300–400 nm is only assigned from HOMO to LUMO+1 ($\lambda_{abs} = 384$ nm, Fig. 4). The HOMO is entirely localized on the quinolate ligand (>99%). These findings suggest that the BODIPY has little orbital contribution in the higher-energy region above 400 nm. It is notable that the significant absorptions occur independently of the salen- (**6** and 7) or the quinolinate-centred (**8**) π - π^* transitions and the BODIPY-centred π - π^* transitions (**6**-**8**). Along with the experimental absorption spectra in chloroform solution, these DFT calculation results further confirm that the heterodinuclear complexes **6** and 7 only exhibit partial intramolecular energy transfer from the salen moiety to the BODIPY moiety.

Experimental

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 them through an activated alumina column and stored over activated molecular sieves (5 Å). Spectrophotometric grade CHCl₃ (Aldrich) was used as received. Commercial reagents were used without any further purification after purchasing from Aldrich (salicylaldehyde derivatives, ethylenediamine, 8-hydroxyquinaldine, trimethylaluminum (2.0 M in toluene), phenol derivatives, benzaldehyde derivatives, hexamethylenetetramine, pyrrole, trifluoroacetic acid, DDQ (2,3-dichloro-5,6-dicyano-1,4benzoquinone), triethylamine, $BF_3 \cdot OEt_2$). Compounds 1a,²¹ 2,²² and 4a¹⁴ were analogously prepared according to the reported procedures. Deuterated solvents from Cambridge Isotope Laboratories were used after drying over activated molecular sieves (5 Å). NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for ¹H, 100.62 MHz for

Paper

¹³C, and 128.38 MHz for ¹¹B) at ambient temperature. Chemical shifts are given in ppm, and are referenced against external Me₄Si (¹H, ¹³C), and BF₃·OEt₂ (¹¹B). Elemental analyses were performed on an EA3000 (Eurovector) in the Central Laboratory of Kangwon National University. UV/Vis absorption and PL spectra were recorded on a Jasco V-530 and a Spex Fluorog-3 Luminescence spectrophotometer, respectively. Fluorescence decay lifetimes were measured using a time-correlated singlephoton 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. Thermogravimetric analysis (TGA) was performed under a N2 atmosphere using a TA Instrument Q500 at a heating rate of 20 °C min⁻¹ from 50 °C to 800 °C.

Synthesis of 1b. A 3,5-difluoro-4-hydroxybenzaldehyde (1.58 g, 10 mmol) was dissolved in pyrrole (17.4 mL, 0.25 mol). After stirring for 30 min at ambient temperature, the solution was cooled to 0 °C. To this solution was slowly added trifluoroacetic acid (0.08 mL, 1 mmol) via a syringe and the reaction mixture was allowed to cool slowly to room temperature. After stirring for 2 h, a 0.1 M aqueous solution of NaOH was added and the resulting solution was extracted with ethyl acetate. The combined organic portions were dried over MgSO4 and the solvent was removed under reduced pressure. The residue was redissolved in THF (150 mL) and 2,3-dichloro-5,6-dicyano-1,4benzoquinone (2.27 g, 10 mmol) was added. After stirring for 12 h, triethylamine (13.9 mL, 0.10 mol) and BF3·OEt2 (18.4 mL, 0.15 mol) were added and stirred for 2 h. After the reaction was quenched with a 1 M aqueous solution of NaOH (100 mL), the organic layer was separated, and the aqueous layer was extracted with CH2Cl2 (50 mL). The combined organic portions were dried over MgSO4 and concentrated under reduced pressure. Purification by column chromatography (eluent: CH_2Cl_2/n -hexane, 2:1 v/v) afforded **1b** as a brown solid (0.93 g, 29%). ¹H NMR (CDCl₃): δ 7.94 (s, 2H), 7.18 (m, 2H), 6.94 (d, 2H), 6.56 (d, 2H); 13 C NMR (CDCl₃): δ 152.61, 150.16, 144.46, 135.40, 134.49, 131.20, 124.96, 119.00, 114.28. Anal. Calcd for C15H9BF4N2O: C, 56.29; H, 2.83; N, 8.75. Found: C, 56.13; H, 2.66; N, 8.73.

Synthesis of 3. 8-Hydroxyquinaldine (0.96 g, 6 mmol) was dissolved in toluene (50 mL) and cooled at -78 °C. Trimethylaluminum (2.0 M in toluene, 1.5 mL, 3 mmol) was slowly added *via* a syringe to the 8-hydroxyquinaldine solution. The reaction mixture was then slowly heated at 110 °C for 1 h. After cooling to room temperature, all volatiles were removed at reduced pressure and washed with toluene and *n*-hexane to afford an ivory solid residue 3 (0.90 g, 84%). It was used *in situ* for the next step without any purification. ¹H NMR (CDCl₃, 400.13 MHz, ppm): δ = 8.16 (d, 2H), 7.39 (m, 4H), 7.11 (d, 2H), 7.00 (d, 2H), 3.06 (s, 6H), -0.65 (s, 3H).

Synthesis of 4b. To a solution of 2 (0.80 g, 1.5 mmol) in toluene (20 mL) was slowly added 2,6-difluorophenol (0.20 g, 1.5 mmol) in toluene (20 mL). After stirring for 20 min, the reaction mixture was then heated at 110 $^{\circ}$ C for 4 h. After

cooling to ambient temperature, the solvent was removed under reduced pressure and washed with pentane to afford a yellow solid **4b** (0.84 g, 87%). ¹H NMR (CDCl₃): δ 8.39 (s, 2H), 7.49 (d, 2H), 7.01 (d, 2H), 6.49 (m, 2H), 6.32 (m, 1H), 4.19 (m, 2H), 3.73 (m, 2H), 1.44 (s, 18H), 1.29 (s, 18H). ¹³C NMR (CDCl₃): δ 170.16, 163.31, 156.87, 154.46, 140.95, 138.26, 137.44, 130.87, 127.05, 118.21, 115.00, 110.65, 55.08, 35.52, 33.97, 31.47, 29.61.

Synthesis of 5. To a solution of 3 (0.54 g, 1.5 mmol) in toluene (20 mL) was slowly added phenol (0.14 g, 1.5 mmol) in toluene (20 mL). After stirring for 20 min, the reaction mixture was then heated at 110 °C for 4 h. After cooling to ambient temperature, the solvent was removed under reduced pressure. The residue was washed with *n*-hexane and recrystallization from a mixture of CH₂Cl₂/*n*-hexane afforded 5 as a white solid (0.50 g, 76%). ¹H NMR (CDCl₃): δ 8.19 (d, 2H), 7.45 (t, 2H), 7.33 (d, 2H), 7.19 (d, 2H), 7.09 (d, 2H), 6.83 (t, 2H), 6.51 (t, 2H), 6.35 (d, 2H), 2.98 (s, 6H). ¹³C NMR (CDCl₃): δ 159.50, 157.34, 156.10, 139.47, 139.19, 129.03, 128.93, 126.72, 124.08, 119.05, 117.32, 114.20, 112.84, 22.77. Anal. Calcd for C₂₆H₂₁AlN₂O₃: C, 71.55; H, 4.85; N, 6.42. Found: C, 72.14; H, 4.92; N 6.60.

Synthesis of 6. To a solution of 2 (0.80 g, 1.5 mmol) in toluene (30 mL) was slowly added 1a (0.43 g, 1.5 mmol) in toluene (20 mL). After the solution was heated at reflux for 4 h, it was cooled to ambient temperature, and then the solvent was removed under reduced pressure. The residue was washed with diethyl ether (50 mL) and recrystallization from a mixture of CH_2Cl_2/n -hexane afforded 6 as an orange solid (0.70 g, 58%). Single crystals suitable for X-ray diffraction study were grown from the CH₂Cl₂/Et₂O solution of 6. ¹H NMR (CDCl₃): δ 8.44 (s, 2H), 7.80 (s, 2H), 7.56 (d, 2H), 7.14 (d, 2H), 7.07 (d, 2H), 6.84 (d, 2H), 6.46 (m, 4H), 4.13 (m, 2H), 3.78 (m, 2H), 1.46 (s, 18H), 1.31 (s, 18H). ¹³C NMR (CDCl₃): δ 170.39, 165.02, 163.31, 141.80, 141.06, 138.82, 134.57, 132.68, 131.33, 131.16, 127.16, 123.19, 120.29, 118.32, 117.48, 55.11, 35.60, 34.05, 31.36, 29.66. ¹¹B NMR (CDCl₃): δ 0.27 (t, ¹J_{B-F} = 28.2 Hz). Anal. Calcd for C47H56AlBF2N4O3: C, 70.50; H, 7.05; N, 7.00. Found: C 70.39; H, 7.11; N, 6.96.

Synthesis of 7. This compound was prepared in a manner analogous to the synthesis of **6** using **1b**. A brown solid was obtained (0.53 g, 42%). Single crystals suitable for an X-ray diffraction study were grown from the CH₂Cl₂/Et₂O solution of 7. ¹H NMR (CDCl₃): δ 8.46 (s, 2H), 7.84 (s, 2H), 7.52 (d, 2H), 7.06 (d, 2H), 6.81 (dd, 2H), 6.78 (d, 2H), 6.47 (dd, 2H), 4.24 (m, 2H), 3.81 (m, 2H), 1.42 (s, 18H), 1.29 (s, 2H). ¹³C NMR (CDCl₃): δ 170.53, 163.14, 156.49, 154.06, 146.37, 143.24, 141.36, 140.91, 138.70, 134.46, 131.15, 127.20, 120.81, 118.23, 114.02, 55.22, 35.55, 34.02, 31.35, 29.62. ¹¹B NMR (CDCl₃): δ 0.20 (t, ¹J_{B-F} = 28.2 Hz). Anal. Calcd for C₄₇H₅₄AlBF₄N₄O₃: C, 67.46; H, 6.50; N, 6.70. Found: C, 67.19; H, 6.76; N, 6.82.

Synthesis of 8. This compound was prepared in a manner analogous to the synthesis of 6 using 3 with 1a. A brown solid was obtained (0.37 g, 39%). Single crystals suitable for an X-ray diffraction study were grown from the CH₂Cl₂/Et₂O solution of 8. ¹H NMR (CDCl₃): δ 8.24 (d, 2H), 7.81 (s, 2H), 7.48 (t, 2H), 7.39 (d, 2H), 7.23 (d, 2H), 7.11 (d, 2H), 6.78 (d, 2H), 6.45 (m,

4H), 3.00 (s, 6H). ¹³C NMR (CDCl₃): δ 163.51, 157.34, 155.84, 148.59, 141.22, 139.48, 134.52, 132.78, 131.07, 129.26, 126.75, 124.11, 123.42, 119.30, 117.62, 114.50, 113.11, 53.41, 22.87. ¹¹B NMR (CDCl₃): δ 0.23 (t, ¹ J_{B-F} = 29.5 Hz). Anal. Calcd for C₃₆H₂₈AlBCl₂F₂N₄O₃: C, 60.79; H, 3.97; N, 7.88. Found: C, 60.90; H, 3.86; N, 7.82.

X-ray crystallography

Single crystals of **6–8** were coated with Paratone oil and mounted onto a glass capillary. The crystallographic measurements were performed on a Bruker SMART Apex II CCD area detector diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by the full-matrix least-squares method on F^2 by using the SHELXTL/PC package, resulting in the X-ray crystallographic data of **6–8** in CIF format (CCDC 1400922–1400924). Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The detailed crystallographic data are given in Tables S1 and S2.†

UV/Vis absorption and photoluminescence (PL) measurements

UV/Vis absorption and PL measurements were performed with a 1 cm quartz cuvette. The solution quantum efficiencies were measured with reference to that of quinine sulfate (0.5 M H₂SO₄, $\Phi = 0.55$).²³ Absorption and PL experiments were carried out in a solution of CHCl₃ (5 × 10⁻⁵ M) at room temperature.

Theoretical calculations

The possible structures of **6–8** from their X-ray structures were optimized using the density functional theory (DFT) method with the B3LYP functional²⁴ and 6-31G(d)²⁵ basis sets. Time-dependent density functional theory (TD-DFT)²⁶ measurements using the hybrid B3LYP functional (TD-B3LYP) were used to obtain the electronic transition energies which also included an account of electron correlation. All the calculations for **6–8** were performed in CHCl₃ solution. Solvent effects were evaluated with the conductor-like polarizable continuum model (CPCM).²⁰ All calculations were carried out using the GAUSSIAN 09 program.²⁷ GaussSum 3.0 was used to calculate the percentage contribution of a group in a molecule to each molecular orbital.²⁸

Conclusions

We have synthesized and characterized Al(III)-BODIPY dyads (6-8) from the selective coupling of the mono-aluminum complexes (4a, 4b and 5) and BODIPY compounds (1a and 1b). The structures of the novel three heterodinuclear complexes (6-8) were also investigated by single crystal X-ray diffraction. 6 and 7 exhibited higher thermal stability than that of each mono-

nuclear compound, except for **8**. UV-Vis absorption and emission spectra of **6** and **7** demonstrated obvious partial intramolecular energy transfer from the salen moiety to BODIPY. Theoretical calculations further supported the experimental features. To the best of our knowledge, these dyad systems are the first example of BODIPY-based compounds containing various functional groups. For these reasons, these heterodinuclear complexes can constitute a novel class of luminophores. Relevant studies on modifying the given system to make novel BODIPY-based compounds are in progress.

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References

- (a) L. A. Juárez, A. Barba-Bon, A. M. Costero, R. Martínez-Máñez, F. Sancenón, M. Parra, P. Gaviña, M. C. Terencio and M. J. Alcaraz, *Chem. – Eur. J.*, 2015, 21, 15486–15490;
 (b) T. Kowada, H. Maeda and K. Kikuchi, *Chem. Soc. Rev.*, 2015, 44, 4953–4972.
- 2 (a) G. Duran-Sampedro, A. R. Agarrabeitia, I. Garcia-Moreno, L. Gartzia-Rivero, S. de la Moya, J. Bañuelos, I. López-Arbeloa and M. J. Ortiz, *Chem. Commun.*, 2015, 51, 11382–11385; (b) T. Bura, N. Leclerc, S. Fall, P. Lévêque, T. Heiser, P. Retailleau, S. Rihn, A. Mirloup and R. Ziessel, *J. Am. Chem. Soc.*, 2012, 134, 17404–17407; (c) Z. Kostereli, T. Ozdemir, O. Buyukcakir and E. U. Akkaya, *Org. Lett.*, 2012, 14, 3636–3639.
- 3 N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.*, 2012, 41, 1130–1172 and references cited therein.
- 4 (a) R. Ziessel and A. Harriman, *Chem. Commun.*, 2011, 47, 611–631; (b) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, 47, 1184–1201; (c) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, 107, 4891–4932.
- 5 (a) C. A. Swamy, P. S. Mukherjee and P. Thilagar, *Chem. Commun.*, 2013, 49, 993–995; (b) Z. Yin, A. Y.-Y. Tam, K. M.-C. Wong, C.-H. Tao, B. Li, C.-T. Poon, L. Wu and V. W.-W. Yam, *Dalton Trans.*, 2012, 41, 11340–11350; (c) G.-L. Fu, H. Pan, Y.-H. Zhao and C.-H. Zhao, *Org. Biomol. Chem.*, 2011, 9, 8141–8146; (d) J. O. Huh, Y. Do and M. H. Lee, *Organometallics*, 2008, 27, 1022–1025.
- 6 (a) S. K. Sarkar and P. Thilagar, *Chem. Commun.*, 2013, 49, 8558–8560; (b) J.-S. Lu, S.-B. Ko, N. R. Walters and S. Wang, *Org. Lett.*, 2012, 14, 5660–5663; (c) H. Sun, X. Dong, S. Liu, Q. Zhao, X. Mou, H. Y. Yang and W. Huang, *J. Phys. Chem. C*, 2011, 115, 19947–19954.

- 7 (a) B. Basumatary, A. R. Sekhar, R. V. R. Reddy and J. Sankar, *Inorg. Chem.*, 2015, 54, 4257-4267;
 (b) S. Mukherjee and P. Thilagar, *Chem. Eur. J.*, 2014, 20, 9052–9062; (c) P. Yang, W. Wu, J. Zhao, D. Huang and X. Yi, *J. Mater. Chem.*, 2012, 22, 20273–20283.
- 8 R. Ziessel, C. Goze, G. Ulrich, M. Césario, P. Retailleau, A. Harriman and J. P. Rostron, *Chem. – Eur. J.*, 2005, **11**, 7366–7378.
- 9 C. A. Swamy, P. S. Mukherjee and P. Thilagar, *Inorg. Chem.*, 2014, **53**, 4813–4823.
- 10 (a) T. Baronsky, C. Beattie, R. W. Harrington, R. Irfan, M. North, J. G. Osende and C. Young, ACS Catal., 2013, 3, 790-797; (b) J. Meléndez, M. North, P. Villuendas and C. Young, Dalton Trans., 2011, 40, 3885-3902; (c) W. Clegg, R. W. Harrington, M. North and R. Pasquale, Chem. - Eur. J., 2010, 16, 6828-6843; (d) W. Clegg, R. W. Harrington, M. North and P. Villuendas, J. Org. Chem., 2010, 75, 6201-6207; (e) M. S. Taylor, D. N. Zalatan, A. M. Lerchner and E. N. Jacobsen, J. Am. Chem. Soc., 2005, 127, 1313-1317; (f) J. F. Larrow and E. N. Jacobsen, Top. Organomet. Chem., 2004, 6, 123-152; (g) C. D. Vanderwal and E. N. Jacobsen, J. Am. Chem. Soc., 2004, 126, 14724-14725; (h) M. S. Taylor and E. N. Jacobsen, J. Am. Chem. Soc., 2003, 125, 11204-11205; (i) G. M. Sammis and E. N. Jacobsen, J. Am. Chem. Soc., 2003, 125, 4442–4443; (j) J. K. Myers and E. N. Jacobsen, J. Am. Chem. Soc., 1999, 121, 8959-8960; (k) M. S. Sigman and E. N. Jacobsen, J. Am. Chem. Soc., 1998, 120, 5315-5316.
- (a) T.-T. Wang, Y. Xie and W.-Q. Deng, J. Phys. Chem. A, 2014, 118, 9239–9243; (b) D. Tian, B. Liu, Q. Gan, H. Li and D. J. Darensbourg, ACS Catal., 2012, 2, 2029–2035; (c) D. J. Darensbourg and D. R. Billodeaux, Inorg. Chem., 2005, 44, 1433–1442.
- 12 (a) D. J. Darensbourg, P. Ganguly and W. Choi, *Inorg. Chem.*, 2006, 45, 3831–3833; (b) D. J. Darensbourg, P. Ganguly and D. Billodeaux, *Macromolecules*, 2005, 38, 5406–5410; (c) P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2004, 126, 2688–2689; (d) T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 1999, 121, 4072–4073.
- 13 K. Y. Hwang, H. Kim, Y. S. Lee, M. H. Lee and Y. Do, *Chem. Eur. J.*, 2009, **15**, 6478–6487.
- 14 K. Y. Hwang, M. H. Lee, H. Jang, Y. Sung, J. S. Lee, S. H. Kim and Y. Do, *Dalton Trans.*, 2008, 1818–1820.

- 15 (a) H. Kim and Y. S. Lee, Chem. Phys. Lett., 2013, 585, 143–148; (b) H. J. Bae, K. Y. Hwang, M. H. Lee and Y. Do, Bull. Korean Chem. Soc., 2011, 32, 3290–3294; (c) V. Béreau, V. Jubéra, P. Arnaud, A. Kaiba, P. Guionneau and J.-P. Sutter, Dalton Trans., 2010, 39, 2070–2077; (d) P. G. Cozzi, L. S. Dolci, A. Garelli, M. Montalti, L. Prodi and N. Zaccheroni, New J. Chem., 2003, 27, 692–697.
- 16 J. O. Huh, M. H. Lee, H. Jang, K. Y. Hwang, J. S. Lee, S. H. Kim and Y. Do, *Inorg. Chem.*, 2008, 47, 6566–6568.
- 17 D. A. Atwood and M. J. Harvey, *Chem. Rev.*, 2001, **101**, 37–52.
- 18 (*a*) A. Harriman, J. P. Rostron, M. Cesario, G. Ulrich and R. Ziessel, *J. Phys. Chem. A*, 2006, **110**, 7994–8002;
 (*b*) C.-W. Wan, A. Burghart, J. Chen, F. Bergström, L. B.-Å. Johansson, M. F. Wolford, T. G. Kim, M. R. Topp, R. M. Hochstrasser and K. Burgess, *Chem. – Eur. J.*, 2003, **9**, 4430–4441.
- (a) M. Koepf, A. Trabolsi, M. Elhabiri, J. A. Wytko, D. Paul,
 A. M. Albrecht-Gary and J. Weiss, *Org. Lett.*, 2005, 7, 1279–1282; (b) I. V. Sazanovich, C. Kirmaier, E. Hindin, L. Yu,
 D. F. Bocian, J. S. Lindsey and D. Holten, *J. Am. Chem. Soc.*, 2004, 126, 2664–2665; (c) R. W. Wagner and J. S. Lindsey, *J. Am. Chem. Soc.*, 1994, 116, 9759–9760.
- 20 (a) M. Cossi, N. Rega, G. Scalmani and V. Barone, J. Comput. Chem., 2003, 24, 669–681; (b) V. Barone and M. Cossi, J. Phys. Chem. A, 1998, 102, 1995–2001.
- 21 M. Baruah, W. Qin, N. Basarić, D. Borggraeve and N. Boens, J. Org. Chem., 2005, 70, 4152–4157.
- 22 D. A. Atwood, M. S. Hill, J. A. Jegier and D. Rutherford, Organometallics, 1997, 16, 2659–2664.
- 23 A. M. Brouwer, Pure Appl. Chem., 2011, 83, 2213–2228;
 W. H. Melhuish, J. Phys. Chem., 1961, 65, 229–235.
- 24 (a) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, 98, 11623–11627;
 (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, 37, 785–789.
- 25 J. S. Binkley, J. A. Pople and W. J. Hehre, J. Am. Chem. Soc., 1980, 102, 939–947.
- 26 E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997–1000.
- 27 M. J. Frisch, et al., *Gaussian 09 Revision D.01*, Gaussian Inc., Wallingford, CT, 2013.
- 28 N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, J. Comput. Chem., 2008, 29, 839–845.