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Reactivity differences of Si^+MPC^+ ($\text{M} = \text{Al}$ and B): Synthesis of the first metal-substituted dendrimers for K^+ and Na^+

175 YEARS

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Salen–Al/Carbazole Dyad-Based Guest–Host Assembly: Enhancement of Luminescence Efficiency via Intramolecular Energy Transfer

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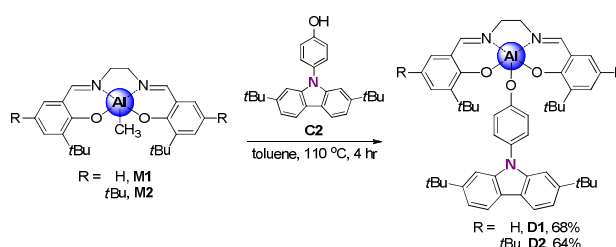
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A novel class of salen–Al/carbazole dyads (**D1** and **D2**) was synthesized and fully identified. The emission spectra of the dyads presented intriguing dual-emission patterns via the intramolecular energy transfer (IET) state in solution. Furthermore, the IET feature of the dyads was clearly observed in the rigid state. Interestingly, the emission efficiency of the dyads was enhanced by the significant IET process from the carbazole group to the salen–Al moiety. Particularly, **D1** exhibited a nearly three-fold enhanced luminescence efficiency compared to the corresponding mononuclear aluminum complexes (**A1**). Such an emission process of these guest–host systems was further supported by theoretical calculation.

Carbazole-based compounds have been widely utilized in prominent optoelectronic applications such as organic light-emitting diodes (OLEDs) and photovoltaic cells, because of their excellent thermal and electronic properties.^{1–5} These intriguing properties are mainly attributed to the rigidity and electron-abundant nature of the carbazole unit,^{6,7} and can be further improved by systematic combination with various functional groups, thus allowing carbazole derivatives to broaden their applicability in optoelectronics.^{8–12}

Recently, a novel class of Pt,^{13–16} Au,^{17,18} Cr,¹⁹ and Ru-based²⁰ organometallic complexes containing carbazole ligand has received much attention because it can provide positive effects altering optical properties such as emission-colour tuning and enhancement of quantum efficiency. Among them, Yam and co-workers developed novel platinum complexes via systematic design between the platinum centre and electron-donating carbazolyl ligands, exhibiting highly efficient multicolour emission derived from the intramolecular charge transfer (ICT) process arising from the donor–acceptor conjugate systems.¹³ Until now, to the best of our knowledge, there have been no reported studies on aluminum–carbazole



Scheme 1 Synthetic routes for salen–Al/carbazole dyads.

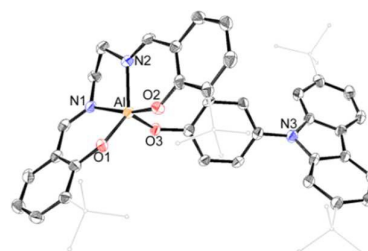


Fig. 1 X-ray crystal structures of **D1** (40% thermal ellipsoids). The H atoms are omitted and t-butyl groups are simply drawn for clarity.

complexes for optical applications, though aluminum-based complexes have been well known as prominent optoelectronic materials. Therefore, we selected salen and carbazole ligands as proper anchoring ligands into aluminum centre for the induction of the desired luminescent properties and the enhancement of emission efficiency via the IET process. Herein, we describe the detailed synthesis and optical properties of novel guest–host dyads (**D1** and **D2**) based on salen–Al complexes with a carbazole unit in conjunction with computational calculations.

The synthetic routes for salen–Al/carbazole dyads (**D1** and **D2**) are shown in Scheme 1. These dyads were prepared by the reaction of the salen–Al precursors (**M1**: (3-*t*Bu-salen)Al–Me and **M2**: (3,5-*t*Bu-salen)Al(CH₃)) with 4-(2,7-di-*t*Bu-9H-carbazol-9-yl)phenol (**C2**) in moderate yield (68% for **D1** and 64% for **D2**). **D1** and **D2** were fully characterized by ¹H and ¹³C NMR spectroscopy (Figs. S1–S4 in the ESI†) and elemental

† Electronic Supplementary Information (ESI) available: X-ray crystallographic data in CIF format (CCDC 1819002), experimental, computational, and spectroscopic data and ¹H, ¹³C NMR Spectra (PDF). For crystallographic data in CIF or other electronic format. See DOI: 10.1039/b000000x/

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analysis. The solid-state molecular structure of **D1** was analysed by the single-crystal X-ray diffraction method (Fig. 1). Single crystals of **D1** suitable for X-ray diffraction studies were obtained from the slow diffusion of MeOH into a THF solution. The structural parameters including selected bond lengths (Å) and angles (°) for **D1** are presented in Tables S1 and S2 of the ESI†. The phenoxy group connects the Al atom with a carbazole group as the key group, indicating that **D1** is an assembly dyad with a five-coordinate aluminum centre. The trigonality parameter^{21,22} (τ) value for **D1** is 0.47, indicating that the geometry around the Al centre of **D1** is an intermediate between trigonal bipyramidal (tbp) and square pyramidal (sp) structures. Furthermore, the carbazole-centred plane is significantly distorted with respect to the phenoxy group linked to the Al centre, owing to the dihedral angle of 54.6°. This structural feature confirms that the delocalization of electron density between the salen–Al moiety and the carbazole group in the assembly dyad cannot occur.

To investigate the photophysical properties of the assembly dyads (**D1** and **D2**), UV–vis absorption (Fig. 2 and Table 1) and photoluminescence (PL) measurements (Fig. 3 and Table 1) were performed in THF at room temperature. **D1** and **D2** exhibited a dominant low-energy absorption band at ca. 346 nm and 358 nm, respectively, which is associated with the major salen–Al-centred π – π^* transition that is also observed for closely related aluminum compounds ($\lambda_{\text{abs}} = 348$ nm for **A1** and 359 nm for **A2**, Table 1) without the carbazole unit. The high-energy absorptions in the region of ca. 288 nm are assignable to the carbazole-centred π – π^* transition that is also present in the absorption spectra of **C2** and other carbazole-

Table 1 Photophysical data of mononuclear (**A1**, **A2**, and **C1**) and dyad compounds (**D1** and **D2**)

Comp.	λ_{abs}^a /nm ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em}^a /nm	Φ_{PL}^b	τ^a /ns	
				380 nm	460 nm
A1	348 (13.8) 280 (31.4)	459 ^c	0.026 ^c	–	3.9 ²³
A2	359 (10.3) 281 (26.4)	478 ^d	0.117 ^d	–	6.9 ²³
C2	326 (4.60) 299 (23.9)	360 ^{c,d}	–	0.38	–
D1	346 (12.8) 288 (37.4)	364 ^c 458 ^c	0.072 ^c	5.0	7.7
D2	358 (9.10) 288 (34.7)	360 ^d 475 ^d	0.244 ^d	6.4	8.2

^a Measured using a 5.0×10^{-5} M THF solution. ^b Absolute PL quantum yield measured in film state (5 wt% doped on PMMA). ^c $\lambda_{\text{ex}} = 310$ nm. ^d $\lambda_{\text{ex}} = 316$ nm.

based compounds.^{13,14,16,18–20}

Hence, the absorption spectra of **D1** and **D2** are quite similar to the arithmetic sum of the absorption bands for the corresponding mononuclear compounds, strongly suggesting that the electronic transitions of these assembly dyads independently occur on the salen–Al moiety and the carbazole group, respectively. The PL spectra of **D1** and **D2** present specific dual-emission patterns when excited at 316 nm and 310 nm, respectively (Fig. 3 and Table 1). These excited values are the minimum points in each excitation graph for dyads, and can only partially excite the carbazole moieties (Fig. S5 in the ESI†). A comparison of the emission intensities of **D1** and **D2** with their relevant mononuclear aluminum (**A1** or **A2**) and carbazole compound (**C2**) at the same condition reveals that the intensity of the carbazole moiety ($\lambda_{\text{em}} = 360$ nm for **C2**) was drastically reduced and simultaneously, the intensity of the salen–Al part ($\lambda_{\text{em}} = 459$ nm for **A1** and 478 nm for **A2**) increased nearly two-fold compared to that of mononuclear Al compound (**A1** or **A2**). Particularly, the fact that the PL intensity of each part changed with no significant alteration in the emission wavelengths shows the relevance of the partial IET from the carbazole group to the salen–Al moiety. These IET

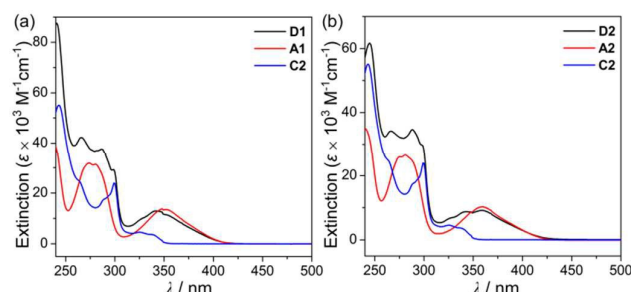


Fig. 2 (a) UV–vis absorption spectra in THF (5.0×10^{-5} M) for (a) **D1**, **A1**, and **C2** and (b) **D2**, **A2**, and **C2**.

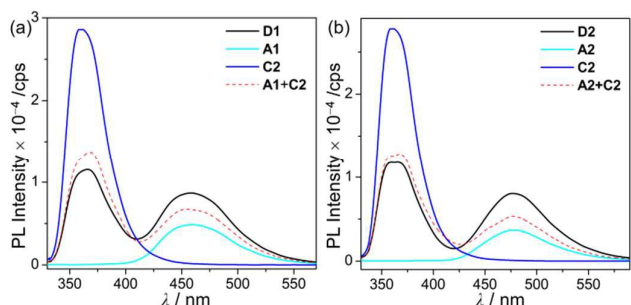


Fig. 3 PL spectra in THF (5.0×10^{-5} M) for (a) **D1**, **A1**, and **C2** ($\lambda_{\text{ex}} = 310$ nm) and (b) **D2**, **A2**, and **C2** ($\lambda_{\text{ex}} = 316$ nm) at room temperature.

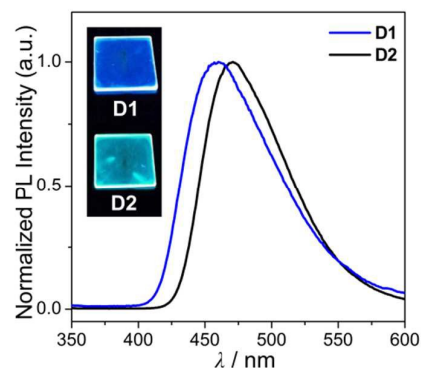


Fig. 4 PL spectra of film (5 wt% doped on PMMA) for **D1** and **D2**. The insets are photographs of film under a handheld UV lamp ($\lambda_{\text{ex}} = 365$ nm).

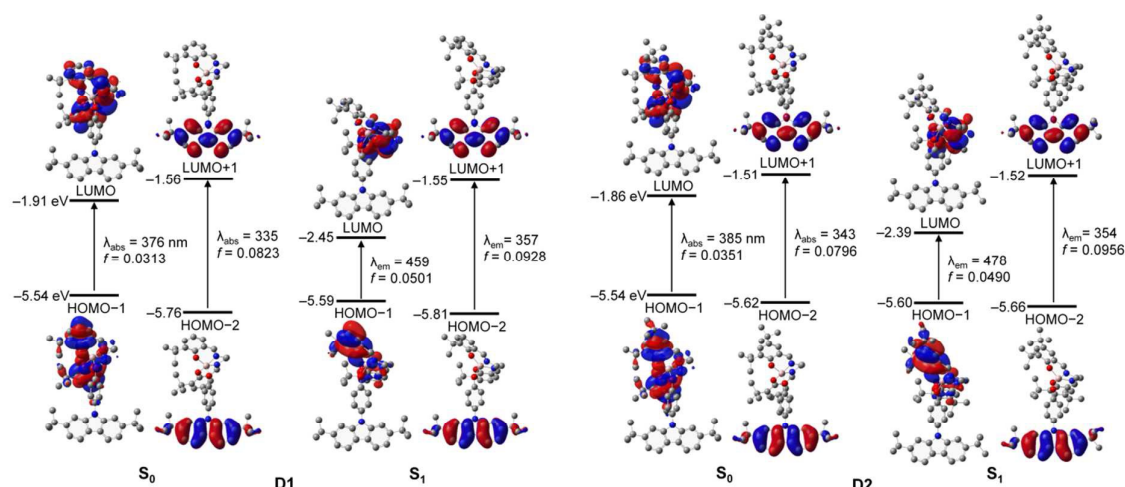


Fig. 5 Frontier molecular orbitals for **D1** and **D2** at their ground (S_0) and first singlet (S_1) state optimized geometries in THF and the major electronic transitions from TD-DFT calculations (isovalue = 0.04).

Table 2 Major low-energy electronic transitions determined for **D1** and **D2** for the ground state (S_0) and first excited singlet state (S_1) using TD-DFT calculations^a

		λ_{calc} /nm	f_{calc}	assignment
D1	S_0	375.71	0.0313	HOMO-1 \rightarrow LUMO (70.6%)
		335.32	0.0823	HOMO-2 \rightarrow LUMO+1 (92.0%)
	S_1	458.81	0.0501	HOMO-1 \rightarrow LUMO (99.9%)
		356.89	0.0928	HOMO-2 \rightarrow LUMO+1 (93.0%)
D2	S_0	384.98	0.0351	HOMO-1 \rightarrow LUMO (97.7%)
		342.97	0.0796	HOMO-2 \rightarrow LUMO+1 (93.2%)
	S_1	477.66	0.0490	HOMO-1 \rightarrow LUMO (98.9%)
		354.08	0.0956	HOMO-2 \rightarrow LUMO+1 (94.8%)

^a Singlet energies for the vertical transition calculated at the optimized S_0 and S_1 geometries.

features are also evident in the emission spectra of the corresponding mononuclear compounds (**A1**+**C2** (λ_{ex} = 310 nm) and **A2**+**C2** (λ_{ex} = 316 nm)) in a solution with an equimolar mixture (Fig. 3). However, the IET characteristics of the mixture systems are not as efficient as those of the guest–host dyads (**D1** and **D2**). Additional considerations of significant overlaps between the emission band of the carbazole compound (**C2**) and the absorption bands of the salen–Al compounds (**A1** or **A2**) also confirm this phenomenon (Fig. S8 in the ESI[†]). Thus, the mechanism of the IET between the carbazole moiety (as the donor) and the salen–Al moieties (as the acceptor) in the dyads (**D1** and **D2**) is the Förster mechanism via through-space interaction. The emission decay lifetime measurements (Figs. S9–S12 in the ESI[†]) of these dyads indicate that the emissions at 380 nm assignable to carbazole-centred fluorescence (5.0 ns for **D1** and 6.4 ns for **D2**) are slightly shorter than those at 460 nm (ca. 8.0 ns). To check the rate constant (k_{IET}) for the IET process in the dyads (**D1** and **D2**) and the equimolar systems (**A1**+**C2** or **A2**+**C2**), we additionally carried out the decay lifetime measurements (at

380 nm and 460 nm) for the equimolar mixtures (Figs. S12 and S13). From the results (6.5 ns for **A1**+**C2**, 8.3 ns for **A2**+**C2**), the k_{IET} values for **A1**+**C2** and **A2**+**C2** at 380 nm, which is the emission region of the energy donor (**C2**), were calculated as $1.5 \times 10^8 \text{ s}^{-1}$ and $1.2 \times 10^8 \text{ s}^{-1}$, respectively, resulting that the values are lower than those of dyad complexes ($2.0 \times 10^8 \text{ s}^{-1}$ for **D1** and $1.6 \times 10^8 \text{ s}^{-1}$ for **D2**). These results clearly indicate that the IET process in the dyad systems is faster and more effective than that of the physically mixed systems,²⁴ further implying the IET from the carbazole group to the salen–Al moiety. Interestingly, such an IET phenomenon of **D1** and **D2** is observed in the rigid state. The only intense emission assigned to the salen–Al moiety appeared in the film state (5 wt% doped in poly(methyl methacrylate) (PMMA)), indicating that the IET feature completely occurs.

In the PMMA film, importantly, the obtained quantum efficiency (Φ_{PL}) of these guest–host dyads (**D1** and **D2**) clearly indicates that the emission efficiency can be tuned by the nature of the IET feature (Table 1). **D1** (Φ_{PL} = 0.072) and **D2** (Φ_{PL} = 0.244) containing a key carbazole group had higher quantum efficiencies than **A1** (Φ_{PL} = 0.026) and **A2** (Φ_{PL} = 0.117), respectively. Notably, the Φ_{PL} of **D1** was enhanced approximately three-fold compared to that of **A1**. Accordingly, both guest–host dyads showed significantly higher luminescence efficiency than their corresponding aluminium complexes without key carbazole groups. These findings highlight the significance of the IET effect of guest–host dyads on Φ_{PL} .

To better elucidate the origin of the electronic transitions of the dyad complexes, time-dependent density functional theory (TD-DFT) calculations on the ground (S_0) and first excited state (S_1) optimized structures for the two guest–host dyads were performed using the B3LYP functional and 6-31G(d) basis sets (Fig. 5, Table 2, and Figs. S14–S17 in the ESI[†]). The computed electronic transitions for the dyads in their S_0 and S_1 states are in good agreement with the experimentally observed absorption and emission bands. The calculation results for the

optimized structures in the S_0 state demonstrate that the major contributions ($f_{\text{calc}} > 0.03$) to the low-energy absorptions below 370 nm are mainly associated with HOMO-1 \rightarrow LUMO transitions ($\lambda_{\text{abs}} = 376$ nm for **D1** and 385 nm for **D2**; Fig. 5 and Table 2). HOMO-1 is dominantly localized on the salen-Al moiety (94.6% for **D1** and 97.7% for **D2**), and LUMO also predominantly occupies the salen-Al parts (99.4% for **D1** and **D2**, Tables S4 and S8 in the ESI[†]), indicating that the absorptions originate from the salen-Al-centred $\pi-\pi^*$ transition. On the other hand, the largest electronic transitions ($f_{\text{calc}} \approx 0.8$) for the absorption regions above 370 nm are mainly attributed to the HOMO-2 \rightarrow LUMO+1 transition. The orbital contribution of HOMO-2 and LUMO+1 is completely localized on the carbazole moiety (> 99%, Tables S4 and S8 in the ESI[†]), due to which the absorption process corresponds to a carbazole-centred $\pi-\pi^*$ transition. Hence, these findings for the calculated absorption transitions clearly indicate that the main absorption processes in **D1** and **D2** occur independently of the salen-Al-centred and carbazole-centred $\pi-\pi^*$ transitions, respectively. The same features are also present in the calculation results for the S_1 -optimized structures of dyads (Fig. 5 and Table 2), which were used to clarify the intrinsic character in emission bands. The main contribution to low-energy emissions below 450 nm is the HOMO-1 \rightarrow LUMO transition, which could be assigned to the salen-Al-centred emission, whereas the high-energy emissions above 350 nm are closely related to the HOMO-2 \rightarrow LUMO+1 transition attributed to the carbazole-centred emission. While the molecular orbital distributions of HOMO-1 and LUMO are concentrated in the salen-Al parts (>99%, Tables S6 and S10 in the ESI[†]), those of HOMO-2 and LUMO+1 are localized on the carbazole parts (>99%, Tables S6 and S10 in the ESI[†]). Consequently, the insights obtained from the computed results for the S_1 -optimized structures of **D1** and **D2** strongly suggest that the experimentally observed dual-emissions in the THF solution resulted from the independently bounded transition in the salen-Al centre and carbazole moieties, respectively. Along with the experimental results, DFT calculations further confirm that the dyads only exhibit partial IET from the carbazole group to the salen-Al moiety.

In summary, novel guest-host systems (**D1** and **D2**) based on salen-Al/carbazole dyads were prepared and fully characterized. These guest-host systems exhibited nearly two-fold enhanced luminescence efficiencies compared to the corresponding aluminum complexes through the significant IET feature from the carbazole group to the salen-Al moiety in PMMA films. The computed calculation results also showed the independently bounded transition on the salen-Al centre and carbazole moieties, respectively, further verifying the experimental results. Thus, it is anticipated that these guest-host systems based on salen-Al/carbazole dyads can constitute a novel class of optoelectronic materials in OLEDs. In particular, the dyads can be used as a promising candidate of guest-host systems in blue-emitting fluorescent OLEDs (FLOLEDs). Furthermore, the present study may provide important insights for the future development of prominent optoelectronic materials using small-molecule

organometallic complexes based on their different desirable electronic features. Relevant studies on expanding novel Al-based guest-host systems are in progress.

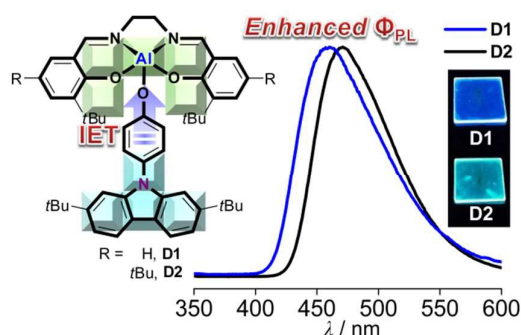
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Graphical and Textual Abstract for TOC



A novel class of salen–Al/carbazole dyads was synthesized and fully identified. The dyads exhibited an over two-fold enhanced luminescence efficiency compared to the corresponding aluminum complexes through the significant intramolecular energy transfer process from the carbazole group to the salen–Al moiety.