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COMMUNICATION

Asymmetric dinuclear bis(dipyrrinato)zinc(II) complexes: Broad absorption and unidirectional quantitative exciton transmission

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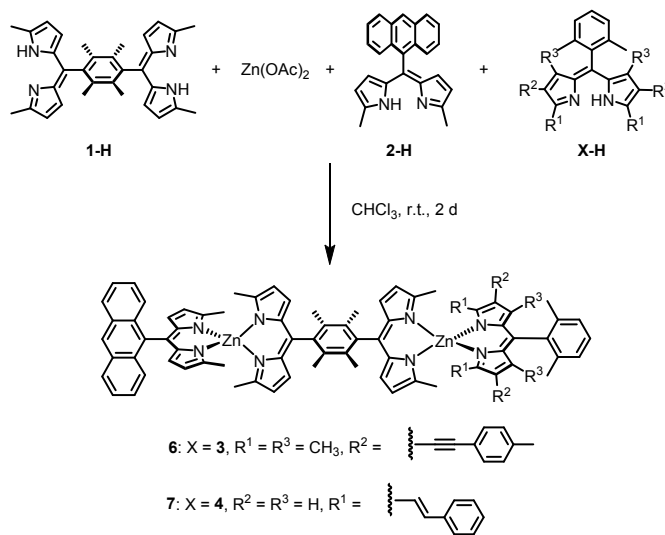
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Asymmetric, heteroleptic dinuclear bis(dipyrrinato)zinc(II) complexes were synthesized and demonstrated to collect a wide range of light across the UV and visible regions (340–655 nm). The complexes also conveyed excitons across their structure from one end to the other, with spectroscopic studies demonstrating quantitative and fast energy transfer.

Natural photosynthetic systems employ light-harvesting antenna pigments that funnel excitons to a single point, the reaction centre. Inspired by such systems, various artificial light-harvesting molecular systems have been proposed.^{1,2} Their development might allow the fabrication of “molecular photonic wires”, a class of nano-sized optic fibres for molecular photonic systems that are similar to the natural photosynthetic antennae.^{3–5} They would enable the transport of excitons over long distances from one end of a molecular system to the other.

Dipyrrin, or dipyromethene, is composed of two pyrrole rings connected to one another at their alpha-positions by a methine bridge.⁶ It may serve as a bidentate ligand to cations. Its boron difluoride complexes (BODIPYs) show strong absorption in the visible region ($\epsilon \sim 10^5 \text{ M}^{-1}\text{cm}^{-1}$), high fluorescence quantum yields, and chemical and photochemical stability, thereby finding many applications as fluorescent dyes.⁷ Bis- and tris(dipyrrinato) metal complexes can be designed to form oligomeric and polymeric structures through the coordination of two and three dipyrrinato ligands, respectively, to one metal centre.^{8,9} This provides an advantage over BODIPYs for supramolecular designs. However, their fluorescence quantum yields are generally inferior to those of

BODIPYs, which has led to dipyrrin metal complexes receiving little



Scheme 1 Synthesis of dinuclear bis(dipyrrinato)zinc(II) complexes **6–8** and ligand molecules used therein.

interest as photoactive materials. We note that multinuclear dipyrrinato-metal complexes, hybrids of boron and zinc complexes, have been reported to date, though none is described to be fluorescent.^{9d–f}

We recently developed heteroleptic bis(dipyrrinato)zinc(II) complexes with high fluorescent quantum yields.^{9b} In the present work, we report the synthesis of asymmetric dinuclear bis(dipyrrinato)zinc(II) complexes **6–8** (Scheme 1) that collect a wide range of light across the UV and visible regions (340–655 nm) and quantitatively convey excitons from one end of the molecular system to the other.

^aDepartment of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan E-mail: sakamoto@chem.s.u-tokyo.ac.jp; nisihara@chem.s.u-tokyo.ac.jp; Fax: (+81) 3-5841-4489; Tel: (+81) 3-5841-4348

^bDepartment of Chemistry, Graduate School of Science, Osaka University, 1-1, Machikaneyama, Toyonaka, Osaka 056-0043, Japan

† Electronic supplementary information (ESI) available: Detailed synthetic and measurement procedures, DFT calculation, fluorescence lifetime decay, and detailed procedures of estimation of rate constants. See DOI: 10.1039/xxxxxxx

Table 1 Spectroscopic properties of **6-8**.

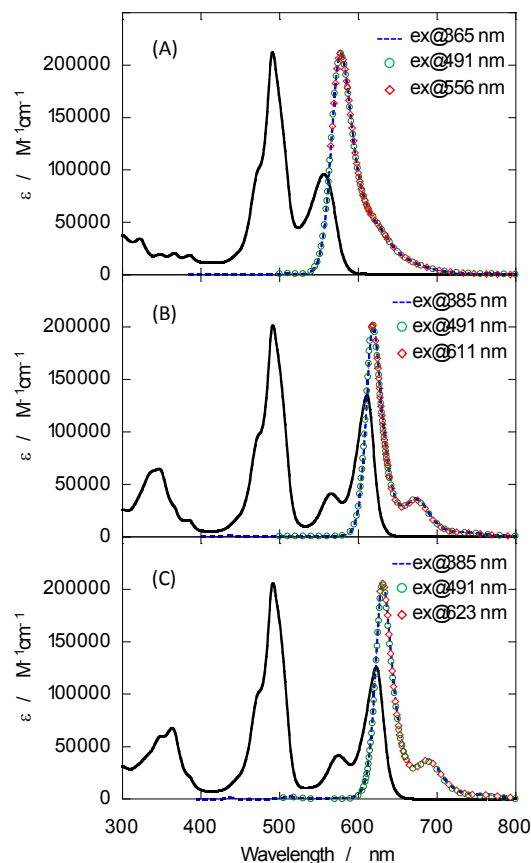
	λ_{abs} (nm) ^a	ϵ_{max} ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$) ^b	λ_{em} (nm) ^c	ϕ^d	τ (ns) ^h
6	366	1.98	578	0.65	2.6 ⁱ
	491	21.1	578	0.68	2.6 ⁱ
	556	9.51	578	0.68	2.6 ^k
7	347	6.49	619	0.74 ^e	3.5 ⁱ
	491	20.1	619	0.78	3.6 ⁱ
	611	13.5	619	0.77 ^f	3.7 ^k
8	363	6.76	631	0.71 ^e	3.4 ⁱ
	491	20.6	631	0.74	3.4 ⁱ
	623	12.6	631	0.78 ^g	3.5 ^k

^aAbsorption maximum wavelength. ^bMaximum molar absorptivity. ^cFluorescence maximum wavelength. ^dFluorescence quantum yield excited at the absorption maximum. ^eExcited at 385 nm. ^fExcited at 600 nm due to a small Stokes shift. ^gExcited at 605 nm due to a small Stokes shift. ^hFluorescence lifetime. ⁱExcited at 365 nm. ^jExcited at 470 nm. ^kExcited at 590 nm.

The complexes **6-8** each contain three types of dipyrinato ligand (Scheme 1, see Scheme S1 in ESI† for their synthesis). Dipyrinato ligand **2-H**¹⁰ comprises anthracene and α,α' -dimethyldipyrin. The former acts as a UV absorbent (340–400 nm); visible light (400–520 nm) is acquired by the latter. Ligand **1-H** is equipped with two α,α' -dimethyldipyrin ligands tethered by a durene linker, which allows it to act as a bridging ligand to form a dinuclear configuration. The variation among the complexes **6-8** arises through the third ligand, with **3-H**¹¹, **4-H**¹², or **5-H**¹² being used as π -extended (β -arylethynyl and α -styryl) dipyrins to absorb wavelengths longer than those absorbed by α,α' -dimethyldipyrin (520–655 nm). Complexes **6-8** were characterized using ¹H and ¹³C NMR, and HR-ESI-MS (ESI†). Additionally, the molecular structures of **6** and **7** were estimated by means of DFT calculation (Fig. S1 and Tables S1 and S2†). This series of complexes can be regarded as a model for molecular photonic wires: photoexcitation of the anthracene moiety corresponds to an optical input, the α,α' -dimethyldipyrin array serves as an exciton transmitter, and the π -extended dipyrins receive excitons, thereby emitting luminescence as an output.

UV-vis absorption spectra of the dinuclear zinc(II) complexes **6-8** are depicted in Fig. 1 and Table 1. Each complex possesses three chief absorption bands; for example, complex **6** shows two strong absorptions with maxima at 490 and 556 nm and a moderate one with a developed vibronic structure spanning 340–380 nm. The two strong absorptions are assignable to the $^1\pi-\pi^*$ transitions of the α,α' -dimethyl^{9b} and β -arylethynyl^{9b} dipyrins, respectively; the other absorption to the anthracene moiety.¹³ The absorption spectrum of **6** corresponds to the sum of its components' spectra, indicating that there is minimal ground state interaction among the pigments. Similar discussion is applicable to **7** and **8**, except that another absorption of α -styryldipyrins **4-H** and **5-H** at around 350 nm overlaps with that of anthracene.

Steady-state fluorospectrometry acquired fluorescence spectra and fluorescence quantum yields (ϕ) (Fig. 1 and Table 1). Each complex was irradiated at three different wavelengths corresponding to its three absorption bands. The fluorescence spectrum exhibits only one emission band, irrespective of the choice of excited absorption band.

**Fig. 1** UV-vis absorption and fluorescence spectra for **6-8**: (A) complex **6**; (B) complex **7**; (C) complex **8**.**Fig. 2** Photographs of toluene solutions of **6-8** under ambient light (left) and under illumination of 365 nm light (right). The fluorescence of **6-8** is substantial even under ambient light, so that the solutions look cloudy (left).

For example, **6** fluoresces exclusively with a maximum at 578 nm, which corresponds to luminescence from β -arylethynylidipyrin **3-H**,^{9b} thus indicating the lack of contribution by emissions from the anthracene and α,α' -dimethyldipyrin moieties, which would be expected at around 400 nm¹³ and 510 nm,^{9b} respectively. Similarly, the luminescence of **7** and **8** (with maxima at 619 nm and 631 nm) is derived from α -styryldipyrins **4-H** and **5-H**, respectively. High ϕ_f values (0.65–0.78) are noted (Photographs of solutions of **6–8** are shown in Fig. 2). What is also important is that ϕ_f is constant regardless of the photoexcitation wavelength (Table 1). This series of results indicates the quantitative migration of excitons from either the anthracene or the α,α' -dimethyldipyrin moiety to the π -extended dipyrin moiety. Fluorescence lifetime studies for the complexes (Table 1 and Fig. S2†) show that each complex exhibits a first-order decay with a lifetime (τ) of a few nanoseconds, which is typical for bis(dipyrinato)zinc(II) complexes.⁹ The lifetime appears independent of the excitation wavelength, suggesting that exciton transfers from the anthracene to the α,α' -dimethyldipyrin and from the α,α' -dimethyldipyrin to the π -extended dipyrin are both very fast processes compared with the radiative processes from the anthracene and the α,α' -dimethyldipyrin moieties. For anthracene, $\phi_f = 0.36$ and $\tau = 5.25$ ns (in cyclohexane)¹³; the respective values for α,α' -dimethyldipyrin are 0.18 and 3.9 ns (in toluene). These values along with the $\phi_f > 0.001$ detection limit of the fluorospectrometer employed here suggest that the rate constant for the exciton transfer from the anthracene moiety to the α,α' -dimethyldipyrin is greater than $7 \times 10^{10} \text{ s}^{-1}$ and that from the α,α' -dimethyldipyrin to the π -extended dipyrin is greater than $5 \times 10^{10} \text{ s}^{-1}$ in **6** (see ESI† for derivation).

In conclusion, asymmetric and dinuclear bis(dipyrinato)zinc(II) complexes **6–8** were demonstrated as potential artificial light-harvesting systems and molecular photonic wires. They collected a broad range of UV and visible light (340–655 nm) and underwent quantitative and unidirectional exciton transfer from one end (the anthracene part) of the molecular system to the other (the π -extended dipyrin unit), resulting in bright emission ($\phi_f = 0.65$ –0.78). Elongation to multinuclear complexes is feasible,¹⁴ with such systems expected also to show efficient unidirectional exciton transfer.

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