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## Phosphorescence from a pure organic fluorene derivative in solution at room temperature†

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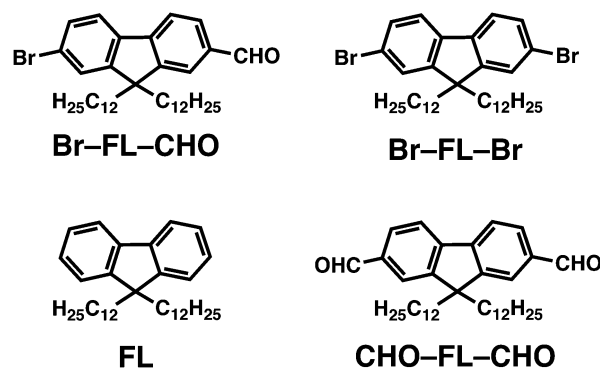
**A fluorene derivative having both bromo and formyl groups exhibited bright phosphorescence emission in common organic solvents at room temperature. The absolute phosphorescence quantum yield reached 5.9% in chloroform at 298 K. When the fluorene derivative was incorporated into a poly(methyl methacrylate) film, the phosphorescence emission was similarly observed even under air at room temperature for over five days.**

Recent advances in luminescent materials using pure organic compounds have provided low-cost, easily-handled, and thermally stable platforms for optoelectronic devices,<sup>1</sup> chemosensors,<sup>2</sup> and photoresponsive switches.<sup>3</sup> Fluorene and its derivatives are some of the most attractive luminescent  $\pi$ -conjugated chromophores exhibiting excellent fluorescent and electrical properties in organic light-emitting diodes and dye-sensitized solar cells.<sup>4,5</sup>

On the other hand, materials that show phosphorescence and delayed fluorescence *via* reverse intersystem crossing from the triplet excited state have attracted much attention, because the electroluminescence efficiency of these materials is 100% in principle, which is four times larger than that of conventional fluorophores (25%).<sup>6,7</sup> Coordination complexes containing late transition metals such as Pt and Ir have so far been extensively investigated for use as phosphorescent materials.<sup>2,6,8</sup> Recently, efforts have also been made to develop pure organic phosphors for practical applications.<sup>9,10</sup> However, in most cases, phosphorescence emission of pure organic compounds is observed under specific conditions (*e.g.*, in crystals and in solid states at 77 K),<sup>10</sup> which hampers the development of prospective phosphorescent materials. In this context, there is still a strong incentive to look for new organic materials which exhibit phosphorescence under ambient conditions such as in solution and doped films at room temperature.

We report herein that a versatile fluorene derivative, 7-bromo-9,9-didodecylfluorene-2-carbaldehyde (Br-FL-CHO), exhibits phosphorescence in conventional organic solvents at room temperature (Scheme 1). It has been very recently reported that bromo and formyl groups enhance spin-orbit coupling to allow phosphorescence emission from crystalline pure organic compounds.<sup>10a,b</sup> We designed the Br-FL-CHO molecule, because the directly-linked bromo and formyl substituents may promote the intersystem crossing from the single excited state to the triplet excited state, and the rigid fluorene framework may suppress the nonradiative process. A series of fluorene derivatives was also prepared (Scheme 1) to compare the effect of substituents on emission properties.<sup>11</sup> We further investigated the emission properties of the fluorene derivatives incorporated in films of poly(methyl methacrylate), PMMA, whose oxygen permeability is relatively low at room temperature.<sup>12</sup>

UV-Vis absorption spectra of Br-FL-CHO and other fluorene derivatives in chloroform (CHCl<sub>3</sub>) are shown in Fig. 1a and Fig. S1, ESI.† The absorption transitions of Br-FL-CHO ( $\lambda_{\text{max}} = 332$  nm) and CHO-FL-CHO ( $\lambda_{\text{max}} = 354$  nm) are red-shifted as compared to those of the other fluorene derivatives, indicating that the formyl groups of Br-FL-CHO and CHO-FL-CHO contribute to absorption transitions. The absorbance of all the fluorene derivatives increased linearly with increasing concentration, and no aggregation behavior was observed.



Scheme 1 Chemical structures of fluorene derivatives.

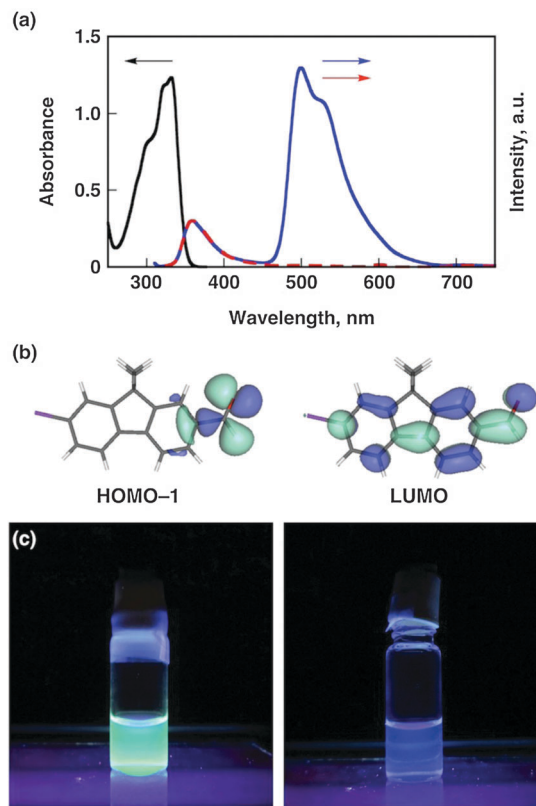
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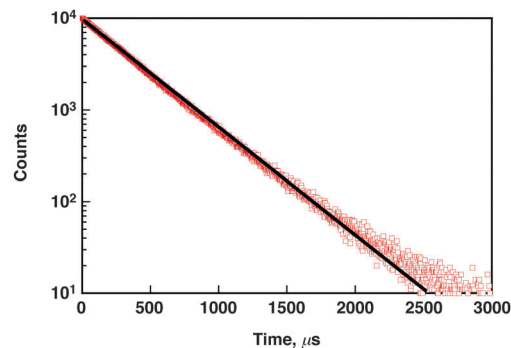
‡ These authors contributed equally to this paper.



**Fig. 1** (a) UV-Vis (black line) and emission spectra of Br-FL-CHO ( $4.0 \times 10^{-5}$  M) under air (red dashed line) and Ar (blue line) in CHCl<sub>3</sub> at 298 K. The excitation wavelength is 300 nm. (b) HOMO-1 $\pi$  and LUMO of Br-FL-CHO calculated by time-dependent density functional theory (TDDFT) with B3LYP/6-31G\*. The calculation reveals that the configuration of S<sub>1</sub> of Br-FL-CHO is dominated by  $n, \pi^*$  (HOMO-1 to LUMO), rather than  $\pi, \pi^*$ . (c) Photographic image of Br-FL-CHO upon UV-light irradiation (365 nm) under Ar (left) and air (right) in CHCl<sub>3</sub> at 298 K.

Emission spectra of Br-FL-CHO were measured in CHCl<sub>3</sub> under air and argon (Ar) atmospheres at 298 K as shown in Fig. 1a. The characteristic emission bands at 358 nm and 500 nm were observed for Br-FL-CHO under Ar (blue line in Fig. 1a). The emission band at 500 nm completely disappeared under air, in the presence of dioxygen (red line in Fig. 1a). In contrast, the emission at 358 nm remained constant under both air and Ar. The appearance and the quenching of the emission at 500 nm can be repeated by bubbling of Ar gas and exposure to air. These results indicate that the emission at 358 nm is attributed to fluorescence, whereas the emission at 500 nm is phosphorescence, which is strongly affected by the presence of dioxygen.<sup>9a</sup> No significant shift of the phosphorescence emission at 500 nm was observed regardless of solvent polarity (Fig. S2, ESI<sup>†</sup>), in contrast to the case of charge-transfer emission.<sup>13</sup> The excitation spectrum of Br-FL-CHO ( $\lambda_{\text{em}} = 500$  nm) is consistent with the UV-Vis spectrum (Fig. S3 in ESI<sup>†</sup>). In addition, the phosphorescence intensity at 500 nm is proportional to the concentration of Br-FL-CHO (Fig. S4a in ESI<sup>†</sup>), indicating that the phosphorescence emission originates from monomeric Br-FL-CHO species.<sup>14</sup>

The emission lifetime of the Br-FL-CHO fluorescence at 358 nm is 1.1 ns as shown in Fig. S5 (ESI<sup>†</sup>), which is in agreement with that observed for other fluorene derivatives.<sup>15</sup> On the other hand, the Br-FL-CHO emission at 500 nm decays



**Fig. 2** Emission lifetime of Br-FL-CHO observed at 500 nm in CHCl<sub>3</sub> at 298 K. The solid line is a fitted line with a mono-exponential function. The excitation wavelength is 300 nm.

with an emission lifetime of 355 μs, as shown in Fig. 2. The long emission lifetime at 500 nm unambiguously shows that the Br-FL-CHO emission at 500 nm is phosphorescence emission.

The emission color of Br-FL-CHO in deaerated CHCl<sub>3</sub> at 298 K is distinctively different from that observed under air (Fig. 1c). Such a color change occurs immediately and is completely reversible (see supplementary movie in ESI<sup>†</sup>). The absolute quantum yield of the phosphorescence emission from Br-FL-CHO in CHCl<sub>3</sub> at 298 K is 5.9%.<sup>16</sup> The phosphorescence emission of Br-FL-CHO was enhanced upon decreasing the temperature due to depression of the nonradiative process from the triplet excited state (T<sub>1</sub>) to the ground state. The absolute quantum yield of the Br-FL-CHO phosphorescence emission reached 35% in deaerated 2-methyl-tetrahydrofuran at 77 K, as shown in Fig. S6, ESI<sup>†</sup>.

In stark contrast to the case of Br-FL-CHO, no characteristic phosphorescence was observed for the other fluorene derivatives (FL, Br-FL-Br, and CHO-FL-CHO), as shown in Fig. S7 (ESI<sup>†</sup>) and Table 1. These results indicate that both of the bromo and the formyl groups in Br-FL-CHO play important roles in the efficient phosphorescent emission.<sup>17</sup> It should be noted that halogen-bonding is not attributed to the phosphorescence emission under the present experimental conditions, unlike the case of 2,5-dihexyloxy-4-bromobenzaldehyde in the crystal.<sup>10a</sup>

The energy diagram and the molecular orbitals of Br-FL-CHO in the ground state and the excited states were investigated by using TDDFT calculation in order to scrutinize the photophysical events of Br-FL-CHO, as shown in Fig. S8 (ESI<sup>†</sup>). The energy levels of S<sub>1</sub> (3.59 eV;  $n, \pi^*$ ) and T<sub>1</sub> (2.67 eV;  $n, \pi^*$ ) are consistent with the values evaluated from the spectroscopic measurements (Table 1). The intersystem crossing (ISC) from S<sub>1</sub> to T<sub>1</sub> is a spin-forbidden process and the energy gap between them is too large to undergo the ISC.

**Table 1** Absorption and luminescence data of the fluorene derivatives in CHCl<sub>3</sub> at 298 K

	Absorption (nm) $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	Emission (nm)	$E(S_1)^b$ (eV)
FL	282 ( $2.0 \times 10^4$ )	314	3.95
Br-FL-CHO	332 ( $4.0 \times 10^4$ )	358, 500 <sup>a</sup>	3.46, 2.48 <sup>c</sup>
Br-FL-Br	282 ( $4.2 \times 10^4$ )	321	3.86
CHO-FL-CHO	354 ( $3.7 \times 10^4$ )	412	3.01

<sup>a</sup> Observed only under an Ar atmosphere. <sup>b</sup> The singlet energy levels of the fluorene derivatives. <sup>c</sup> The triplet (T<sub>1</sub>) energy level of Br-FL-CHO.



On the other hand, the transition from  $S_1$  to  $T_2$  (3.07 eV;  $\pi$ ,  $\pi^*$ ) is symmetrically allowed. Together with the large spin-orbit coupling of Br-FL-CHO due to the bromo and the formyl groups, the ISC from  $S_1$  to  $T_2$  occurs efficiently. Subsequently, the transition from  $T_2$  to  $T_1$  through internal conversion is followed by the radiative decay from  $T_1$  to the ground state ( $S_0$ ).

The fluorene derivatives shown in this study are readily soluble in various common organic solvents, and such soluble phosphorescent organic materials can be embedded in a polymer matrix. Indeed, Br-FL-CHO can be incorporated into poly(methyl methacrylate), PMMA, by solution processing. We chose PMMA because the oxygen permeability of PMMA is relatively low at room temperature.<sup>12</sup> Films of Br-FL-CHO and FL doped in PMMA were fabricated by drop-casting of  $\text{CHCl}_3$  solution containing the corresponding fluorene derivatives and PMMA (5 wt%) onto the surface of quartz cells. The emission spectra and the photographic image of PMMA films of Br-FL-CHO and FL are shown in Fig. S9, ESI†. The emission maximum of the Br-FL-CHO-doped PMMA film at 500 nm is in agreement with that observed in organic solvents. The Br-FL-CHO-doped PMMA film displayed bright green emission upon UV-light irradiation at 254 nm, whereas blue emission was observed for the FL-doped PMMA film under the same experimental conditions. Surprisingly, the phosphorescence emission of the Br-FL-CHO-doped PMMA film was observed for over five days even under air, as shown in Fig. S9a, ESI†. These results indicate that Br-FL-CHO inside the PMMA matrix is molecularly dispersed and shielded from dioxygen to exhibit the phosphorescence emission at 500 nm as well as the fluorescence emission at 358 nm.

In conclusion, we have successfully demonstrated that a pure organic fluorene derivative with bromo and formyl groups, Br-FL-CHO, exhibits phosphorescence emission in versatile organic solvents at room temperature. A Br-FL-CHO-doped PMMA film showed bright phosphorescence emission for several days at room temperature even upon exposure to dioxygen. These results offer a great platform for the development of practical optoelectronic devices and dioxygen-sensors based on purely organic phosphors under ambient conditions.

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§ HOMO–1 means the orbital next to HOMO.

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- The  $^1\text{H}$  NMR charts of Br-FL-CHO at different concentrations are shown in Fig. S4b (ESI†). No change in chemical shifts was observed, again indicating that Br-FL-CHO does not aggregate under the present experimental conditions.
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- It is known that 1,4-dibromonaphthalene exhibits phosphorescence in solution at room temperature (see ref. 9c). However, the phosphorescence quantum yield of 1,4-dibromonaphthalene is lower (4.2%) as compared to that of Br-FL-CHO under the same experimental conditions.
- When the bromine atom of Br-FL-CHO was replaced by an iodine atom, the compound (I-FL-CHO) did not show phosphorescence, probably because the electronic structures of I-FL-CHO are different from those of Br-FL-CHO due to their different electronegativity.