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Development of fluorinated benzils and bisbenzils as room-temperature phosphorescent molecules

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Abstract

Pure organic phosphorescent molecules are attractive alternatives to transition metal complexes-based phosphores for biomedical and technological applications owing to their abundance and nontoxicity. This article discloses the design, synthesis, and photophysical property of fluorinated benzil and bisbenzil derivatives as potential pure organic room-temperature phosphorescent molecules. These compounds were separately converted from the corresponding fluorinated bistolanes via PdCl2-catalyzed oxidation by dimethyl sulfoxide, while non-fluorinated bistolane provided the corresponding bisbenzil derivatives exclusively in a similar manner. Intensive
investigation of the photophysical properties of the benzil and bisbenzil derivatives in toluene at 25 °C showed both fluorescence with a photoluminescence (PL) band at a maximum wavelength ($\lambda_{PL}$) of around 400 nm and phosphorescence with a PL band at a $\lambda_{PL}$ of around 560 nm. Interestingly, intersystem crossing effectively caused fluorinated benzils to emit phosphorescence, which may be due to immediate spin-orbit coupling involving the $1(n, \pi) \rightarrow 3(\pi, \pi)$ transition, unlike the case of fluorinated or non-fluorinated bisbenzil analogues. These findings would become useful tool to develop novel pure organic room-temperature phosphorescent materials.

Keywords
alkyne-oxidation; benzils; bistolanes; fluorinated compounds; phosphorescence

Introduction
The development of organic light-emitting molecules is recognized as one of the most important studies because of the broad application of these compounds as fluorescence probes, bio-imaging materials, and bio-sensors in the biomedical field [1–4] and as organic light-emitting diodes in the technological field [5–8]. Among the organic light-emitting molecules developed thus far, extended $\pi$-conjugated compounds (e.g., pyrenes and perylenes) emit fluorescence, which is a radiative deactivation process from the lowest singlet ($S_1$) excited state to the ground ($S_0$) state [9]. Interestingly, for such $\pi$-conjugated molecules, suitable structural modification can switch the radiative $S_1 \rightarrow S_0$ process to another radiative deactivation process from the triplet ($T_1$) excited state to $S_0$ via an $S_1 \rightarrow T_1$ intersystem crossing (ISC), resulting in the emission of phosphorescence [9].
Phosphorescent molecules generate two excitons (i.e., 25% S\textsubscript{1} excitons and 75% T\textsubscript{1} excitons) by application of an electric field, well-known for organic light-emitting diodes. S\textsubscript{1} excitons are converted to T\textsubscript{1} excitons via an ISC, finally achieving an excellent light-emitting efficiency (up to 100%) [10]. Therefore, extensive investigations to develop phosphorescent molecules have been performed thus far [11–13].

It has been established thus far that the construction of transition metal complexes containing a heavy atom that can promote an ISC process by a heavy metal effect (e.g., Ru [14], Ir [15,16], Pt [17], and Au [18–21]) (Figure 1A) is a possible molecular design for phosphorescence emission. However, it is strongly necessary to explore alternatives to rare metals because of the latter’s scarcity and toxicity. Owing to recent considerable efforts, several molecular designs have been proposed as alternatives, particularly the use of pure organic phosphorescent molecules [22].
Figure 1: (A) Transition-metal-containing and (B) pure organic phosphorescent materials reported thus far (bpy: 2,2'-bipyridine, ppy: 2-phenylpyridine, OEP: octaethylporphyrin).

For example, methyl 4-bromobenzoate (Figure 1B) exhibits phosphorescence in crystalline form via nonradiative ISC to the $T_1$ state owing to crystallization-induced restriction of intramolecular motions [23]. Moreover, the crystalline 2,5-dihexyloxy-4-bromobenzaldehyde displays green phosphorescence, which stems from a quick ISC due to the heavy atom effect via halogen bonding (C=O···Br) [24]. Moreover, benzophenone- or benzil-type molecules can achieve long-lived phosphorescence owing to significant acceleration of spin-orbit coupling based on the El-Sayed rule involving the $^1(n, \pi) \rightarrow ^3(\pi, \pi)$ transition [25,26].

Over the past few years, our group has intensively investigated fluorinated 1,4-bis(2-phenylethyn-1-yl)benzenes (1), called bistolanes (Figure 2A), which show
prominent fluorescence not only in dilute solution, but also in the crystalline state [27–31].

Figure 2: (A) Chemical structures of fluorescent bistolane derivatives previously developed by our group and (B) phosphorescent molecular structures intended for this work.

As a powerful tool to develop novel pure organic phosphorescent molecules, we envisioned the structural modification of the carbon-carbon triple (C≡C) bond in fluorinated bistolane 1 via oxidation to form the corresponding benzil (2) and/or bisbenzil (3) derivatives (Figure 2B). A literature review reveals that bisbenzil-type analogues have not received much attention, despite several publications on benzil-type phosphorescent molecules [25,26,32]. In this study, therefore, we examined the synthesis of novel benzil- and bisbenzil-type molecules via oxidation of fluorinated and non-fluorinated bistolane derivatives and evaluated their photophysical properties in detail.
Results and Discussion

Synthesis

Our study was initiated with the synthesis of fluorinated bisbenzil derivatives. According to the reported procedure [33,34], the PdCl₂-catalyzed oxidation of the C≡C bonds in 1 by dimethyl sulfoxide (DMSO) was performed (Scheme 1).

Scheme 1: Synthetic pathway for fluorinated benzil (2) and bisbenzil (3) derivatives.

The methoxy-substituted fluorinated bistolane 1a was prepared from commercially available 4-ethynylanisole in four facile steps. Interestingly, stirring 1a in DMSO solution in the presence of 30 mol% of PdCl₂ at 140 °C for 17 h produces two products (56% yield for the less polar product and 37% yield for the more polar one) after purification with column chromatography. Spectroscopic analyses (i.e., ¹H, ¹⁹F, and ¹³C nuclear magnetic resonance (NMR) spectroscopy, infrared spectroscopy, and high-resolution mass spectrometry) successfully identified the more polar product as the half-oxidized benzil 2a and the less polar one as the fully oxidized bisbenzil 3a. Fluorinated bistolane 1b, bearing a hexyloxy chain, also undergoes PdCl₂-catalyzed C≡C oxidation to give rise to the corresponding benzil 2b and bisbenzil 3b in 28% and 21% yield, respectively. When non-fluorinated bistolane 1c is used as the substrate, the corresponding bisbenzil 3c is obtained in 40% yield as the major product together with an inseparable mixture.
The mechanism of Pd(II)-catalyzed C≡C oxidation is proposed as follows (Scheme 2) [33]: The catalytic cycle starts with the coordination of the electron-rich C≡C bond to the electron-deficient divalent Pd center, forming the corresponding π-complex (Int-A). Int-A smoothly undergoes nucleophilic attack by the oxygen atom in DMSO to construct a cationic vinylpalladium(II) species (Int-B). Further nucleophilic attack of another DMSO against Int-B, followed by elimination of dimethyl sulfide, furnishes a cationic intermediate (Int-C). Finally, immediate elimination of dimethyl sulfide and the Pd(II) catalyst gives rise to the corresponding benzil 2, after which the eliminated Pd(II) catalyst is recycled to provide the oxidation products. The fully oxidized bisbenzil 3 can be yielded by further Pd(II)-catalyzed C≡C oxidation of the half-oxidized benzil 2 via the same catalytic cycle.

Scheme 2: Proposed mechanism of Pd(II)-catalyzed alkyne oxidation by dimethyl sulfoxide (DMSO).

Considering the proposed reaction mechanism, the successful isolation of the half-oxidized benzil derivatives 2a and 2b from the oxidation of fluorinated bistolanes 1a and 1b, respectively, may be due to the decreased reactivity of the C≡C bond.
toward Pd(II)-catalyzed C≡C oxidation caused by the adjacent electron-deficient fluorinated aromatic ring. To confirm the electron-withdrawing effect of this fluorinated aromatic ring, the electronic charge at the adjacent C≡C bond was calculated by density functional theory (DFT) using the Gaussian 16 (Revision B.01) software package [35]. As typical examples, the molecular geometries of 1a and 1c were optimized at the CAM-B3LYP/6-31+G(d) level of theory. The absence of any imaginary frequency in the vibrational analysis proved that the calculated structures are the minima. Figure 3 shows the calculated Mulliken charge distributions of fluorinated 1a and non-fluorinated 1c.

![Mulliken charge distribution](image)

**Figure 3:** Mulliken charge distributions of fluorinated 1a and non-fluorinated 1c obtained from density functional theory calculations [CAM-B3LYP/6-31+G(d) level].

The sp-hybridized carbon adjacent to the fluorinated aromatic ring of 1a has a largely positive Mulliken charge (+0.472), while that adjacent to the non-fluorinated aromatic ring of 1c has the opposite negative charge (−0.304). This clearly indicates that the fluorinated aromatic ring retards the Pd(II)-catalyzed oxidation of the adjacent C≡C bond, thereby allowing the isolation of the half-oxidized benzil derivative 2a. On the basis of this theoretical investigation, the unique reactivities of bistolanes with
fluorinated and non-fluorinated aromatic rings toward oxidation by DMSO can be rationally explained.

**Photophysical behavior**

Our interest was then directed toward the photophysical properties of benzil and bisbenzil derivatives, which were freshly purified by column chromatography (eluent: hexane/EtOAc = 10/1 for benzil and 5/1 for bisbenzil) and subsequently recrystallized from hexane. The sample solution concentrations in toluene were $1.0 \times 10^{-5}$ and $1.0 \times 10^{-3}$ M for the absorption and photoluminescence (PL) measurements, respectively, and the absorption and PL spectra are shown in Figure 4. The photophysical data obtained from these measurements are summarized in Table 1.

![Figure 4](image-url)

**Figure 4:** Absorption and PL spectra of (A) 2a, (B) 2b, (C) 3a, (D) 3b, and (E) 3c in toluene solution. Concentrations: $1.0 \times 10^{-5}$ and $1.0 \times 10^{-3}$ M for absorbance and PL measurements, respectively. Color legend: black: absorption, red: PL as prepared, green: PL under N$_2$ atmosphere, and blue: PL under O$_2$ atmosphere.
Table 1: Photophysical data from ultraviolet (UV)-visible absorption and steady-state photoluminescence (PL) measurements

<table>
<thead>
<tr>
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<th>( \lambda_{\text{abs}} ) [nm] ( (\varepsilon \text{ [M}^{-1} \text{ cm}^{-1}] ) )</th>
<th>( \lambda_{\text{PL}} ) [nm] ( (\Phi_{\text{PL}}) )</th>
<th>( k_{560}/k_{395} )</th>
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<tr>
<td>pristine</td>
<td>N(_2)</td>
<td>O(_2)</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>295 (28700), 315 (36500), 407 (160)</td>
<td>395, 406sh(^d), 507, 563</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.018)</td>
<td></td>
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<tr>
<td>2b</td>
<td>293 (40500), 314 (30400), 407 (180)</td>
<td>395, 406sh, 507, 563</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.015)</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>290 (30500), 405 (180)</td>
<td>393, 406sh, 516, 551</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(&lt;0.01)</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>290 (51200), 405 (212)</td>
<td>396, 412, 517, 554</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(&lt;0.01)</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>290 (29600), 402 (260)</td>
<td>397, 412, 514, 569</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
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<td>(&lt;0.01)</td>
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\(^a\)Toluene solution (concentrations: \( 1.0 \times 10^{-5} \) and \( 1.0 \times 10^{-3} \) M for UV-visible absorption and PL measurements, respectively); \(^b\)Excitation wavelength: 350 nm; \(^c\)Quantum yield measured using a calibrating sphere. Excitation wavelength: 290 nm. \(^d\)Shoulder peak.

The methoxy-substituted fluorinated benzil 2a in toluene absorbs UV light at 315 and 295 nm with molar extinction coefficients \( (\varepsilon) \) of 36500 and 28700 M\(^{-1}\) cm\(^{-1}\), respectively (Figure 4A). Similarly, the toluene solution of the fluorinated benzil with a hexyloxy chain (2b) absorbs UV light at 314 \( (\varepsilon: 30400 \text{ M}^{-1} \text{ cm}^{-1}) \) and 293 nm \( (\varepsilon: 40500 \text{ M}^{-1} \text{ cm}^{-1}) \) (Figure 4B). Both 2a and 2b exhibit weak absorption at around 400 nm \( (\varepsilon: \sim 170 \text{ M}^{-1} \text{ cm}^{-1}) \). As shown in Figures 4C–4E, on the other hand, the bisbenzil derivatives 3a–c show an absorption band at 290 nm \( (\varepsilon: 29600–51200 \text{ M}^{-1} \text{ cm}^{-1}) \) as
the major signal, together with a quite weak absorption band at 402–405 nm ($\varepsilon$: 180–260 M$^{-1}$ cm$^{-1}$). To gain more information about the slight difference between the absorption behaviors of the benzil and bisbenzil derivatives, DFT and time-dependent DFT (TD-DFT) calculations at the CAM-B3LYP/6-31+G(d) level of theory were performed for fluorinated benzil 2a and bisbenzil derivative 3a as representative examples. Figure 5 shows the distributions of molecular orbitals involved in vertical electronic transitions in 2a and 3a.

**Figure 5**: Distributions of molecular orbitals (isosurface value: 0.04 a.u.) involved in vertical electronic transitions in 2a and 3a calculated using density functional theory (DFT) and time-dependent DFT at the CAM-B3LYP/6-31+G(d) level (HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital).
The main electronic transition with a relatively large oscillator strength (f) in both 2a and 3a is the highest occupied molecular orbital (HOMO)→the lowest unoccupied molecular orbital (LUMO) transition. Focusing on the orbital distribution, the HOMO lobe of 2a covers the entire molecule, while the LUMO lobe is localized at the tolane moiety. In case of 3a, the HOMO lobe is localized at the methoxy-substituted benzene ring, while the LUMO lobe is localized at the central benzene ring. Accordingly, it can be concluded that the absorption bands at the short-wavelength region (around 290–315 nm) stems from the π-π* transition. The TD-DFT calculation also reveals that n-π* transitions (e.g., HOMO–2→LUMO for 2a and HOMO–3→LUMO for 3a) have small values of f; thus, the small absorption band at around 400 nm can be safely attributed to a n-π* transition.

Upon irradiation of the toluene solutions of benzil derivatives 2a and 2b with a 350-nm UV light, three PL bands at 395, 507, and 563, along with a shoulder signal at around 406 nm, are observed (Figures 4A and 4B). The bisbenzil derivatives, i.e., 3a–c, also show similar PL behavior to the aforementioned benzil analogues: four PL bands with λ_{PL} of 393–397, 406–412, 514–517, and 551–569 nm are observed. To gain more information about the PL process in benzils and bisbenzils, the PL spectra of the toluene solutions (1.0 × 10^{-3} M) were acquired after bubbling with N_{2} or O_{2} gas for 30 min. In general, an O_{2}-saturated environment strongly deactivates the triplet states of specimens; thus, PL emission stems only from fluorescence. On the other hand, elimination of O_{2} gas from a solution by bubbling with an inert gas (N_{2} or Ar) allows the triplet states to survive for a long lifetime, which leads to an increase in the radiative rate of phosphorescence. Hence, the elimination of O_{2} gas from solutions by N_{2} gas bubbling (or addition of O_{2} gas in solutions) can judge the presence of phosphorescence, as well as the assignment of PL bands. The obtained PL spectra are superimposed on the PL spectra of a pristine sample (Figure 4). Upon bubbling
the solution with N₂ gas for 30 min, a dramatic enhancement of the PL intensities of benzils 2a and 2b at \( \lambda_{PL} = 563 \) nm is observed. The PL intensities of bisbenzils 3a–c at the long-wavelength region between 551 and 569 nm also increase, although the increment rates are not as high as those of 2a and 2b. On the contrary, bubbling the toluene solutions of benzil or bisbenzil derivatives with O₂ gas causes the intensity of the long-wavelength PL band to decrease compared with that of the pristine solution, while the other remaining PL bands in the short-wavelength region do not change. Judging from the PL behavior under N₂ or O₂ flow condition, the PL bands at the short-wavelength region around 395 nm and long-wavelength region around 560 nm can be safely considered fluorescence via radiative deactivation from the S₁ excited state to S₀ state and phosphorescence via electronic transition from the T₁ excited state to S₀ state, respectively. Accordingly, fluorinated benzils and bisbenzils show room-temperature phosphorescence in the solution state.

To understand the effects of structural modification (e.g., benzil structure with tolane moiety vs. bisbenzil structure) and incorporation of fluorine atoms on phosphorescence, the ratio between the peak intensities at \(~395\) and \(~560\) nm \( (I_{560}/I_{395}) \) was quantitatively calculated, and the results are summarized in Table 1. The \( I_{560}/I_{395} \) values of benzils 2a and 2b under N₂ flow condition increase up to sevenfold compared with those of the corresponding pristine solutions. On the other hand, the increase in the \( I_{560}/I_{395} \) values of fluorinated bisbenzil derivatives 3a and 3b is low (only 1.1 times) under N₂ flow condition, although the PL intensity of non-fluorinated 3c increases by approximately three times. Judging from these comprehensive observations, the benzil structure promotes ISC from S₁ to T₁, causing increment phosphorescence, unlike the corresponding bisbenzil scaffold. Moreover, fluorine substituents on the bisbenzil molecules causes significant retardation of ISC, leading to a weak phosphorescence intensity.
Additionally, the quantum yields ($\Phi_{\text{PL}}$) of the PL bands in the range of 350–600 nm were acquired using an absolute quantum yield measurement system with a calibrating sphere. All samples have a low $\Phi_{\text{PL}}$ of less than 0.02 (Table 1), meaning that a vast amount of excited states of all the samples deactivates nonradiatively. At the moment, we cannot determine the cause of the low $\Phi_{\text{PL}}$ in terms of the molecular properties: for instance, the main pathway of the non-radiative deactivation. To understand the photophysical mechanism of these benzil and bisbenzil derivatives, further experimental study of the excited-state dynamics is necessary and ongoing by us.

**Conclusion**

In this article, we described the design and synthesis of benzil- or bisbenzil-based room-temperature phosphorescent molecules via a simple oxidation protocol for fluorescent bistolane derivatives. Non-fluorinated bistolane derivatives exclusively yielded the corresponding products with a bisbenzil scaffold, whereas the use of fluorinated bistolane derivatives as the starting materials provided not only mono-oxidized benzil derivatives bearing a fluorinated tolane scaffold, but also bis-oxidized bisbenzil derivatives. Based on theoretical calculations, the selective formation of the fluorinated analogues stemmed from the slight modulation of the charge distribution at the alkyne moiety of the reactant induced by electron-withdrawing fluorine atoms. Evaluation of the photophysical behaviors of benzils and bisbenzils through several PL measurements under $\text{N}_2$ and $\text{O}_2$ flow conditions probed the successful room-temperature phosphorescence of the compounds in toluene solution. The achievement of our ongoing study of the excited state dynamics of the benzil and
bisbenzil derivatives would provide promising knowledge to develop environmentally benign pure organic phosphorescent materials.

**Supporting Information**

Experimental procedures for the synthesis and characterization of fluorinated benzils 2a and 2b, fluorinated bisbenzils 3a and 3b, and non-fluorinated bisbenzil 3c. $^1$H, $^{13}$C, and $^{19}$F NMR spectra of 2a, 2b, and 3a–c. Cartesian coordinates of the optimized geometries of 1a, 1c, 2a, and 3a obtained from DFT calculations.

Supporting Information File 1:

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**References**


